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TRACE CONTAMINANTS IN THE ENVIRONMENT

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Proceedings of the Second Annual
NSF-RANN Trace Contaminants Conference
Asilomar, Pacific Grove, California
29 - 31 August 1974

Lawrence Berkeley Laboratory, University of California, Berkeley, California

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Conference Chairman: T. Novakov
Energy and Environment Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

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Preface

The second annual NSF-RANN Trace Contaminants Conference was held at the Asilomar Conference Grounds, Pacific Grove, California, August 29 to 31, 1974. This volume consists of papers presented at the Conference.

The purpose of the Conference was to provide a forum for the review of research performed by the NSF-RANN Trace Contaminants Program grantees. Although the Conference was organized to serve the needs of NSF-RANN supported research groups, it was attended by a number of representatives from governmental agencies and from industries which are present or potential users of the Trace Contaminants Program research.

The technical program was organized in such a way as to reflect the research on trace contaminants in Air, Water, Soil, and Biota. The Conference consisted of two plenary sessions and three parallel sessions devoted to Air, Water and Soil, and Biological Systems. The first plenary session was devoted to the presentation of invited papers describing the state of the art in the problem areas discussed at the Conference. The second plenary session, which was held the last day of the Conference, was for the most part devoted to three summary reports reviewing the presentations and the discussions in parallel sessions. The rapporteurs, H. W. Edwards, W. Fulkerson, and R. I. Van Hook, deserve special thanks for their efforts which resulted in a complete sacrifice of their free time.

Responsibility for the technical program rested with the Program Committee, whose members were: R. A. Carrigan, H. W. Edwards, W. Fulkerson, T. Novakov, J. N. Pitts, Jr., and P. F. Pratt. The dedicated work of the session chairmen contributed immensely to the success of the conference. P. J. Bekowies, D. D. Huff, J. C. Jennett, W. R. Lower, M. R. Patterson, J. L. Sprung, B. Weiss, A. M. Winer, and K. J. Yost served as session chairmen.

Mr. T. S. Kirksey served very effectively as the Conference manager, who handled most of the preconference arrangements. Very special thanks are due to Mr. C. Pezzotti who did magnificent work in coordinating the various tasks and activities at the Conference and who served with great skill and expertise as the technical editor of this volume. Mr. A. Reuss and his colleagues did a superb job with the audio-visual equipment at the Conference. Mrs. K. Thompson and Mrs. L. R. Lewis handled the registration with great dedication and skill.

Special thanks are due Dr. P. J. Bekowies who in a most dedicated way took care of innumerable tasks before, during, and after the Conference.

The Conference was organized by the Energy and Environment Division of the Lawrence Berkeley Laboratory. The help and encouragement of Dr. J. M. Hollander, Head of the Energy and Environment Division, is gratefully acknowledged. The Conference was entirely sponsored by the National Science Foundation - Research Applied to National Needs, Trace Contaminant Program. Special thanks are due to the Trace Contaminants Program Managers Dr. R. A. Carrigan, Dr. R. S. Goor, and Dr. R. Rabin for their help and advice in the organization of the Conference.

T. Novakov

Berkeley, California
December 1974

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WELCOMING REMARKS
SECOND ANNUAL CONFERENCE ON TRACE CONTAMINANTS

Jack M. Hollander
Lawrence Berkeley Laboratory
Berkeley, California

It is a real pleasure for me to represent the host institution to this conference, the Lawrence Berkeley Laboratory, in extending to all of you a cordial welcome to this Second Annual Conference on Trace Contaminants, sponsored by the RANN program of the National Science Foundation. This meeting is significant, of course, because of the importance of the subject matter that we shall be discussing: the state of our knowledge of trace contaminants in the environment. That significance will escape no one.

But I want to focus for a moment on another significance that I believe it is fitting for us to acknowledge: the significance of the NSF-RANN program. There is a lot of history in that acronym, RANN--Research Applied to National Needs. Toward the end of the last decade, when the full impact and seriousness of environmental degradation was beginning to register in the scientific community, the will to devote some of our collective energy to the study of these problems developed quickly. But many of us found that there was an impediment to doing so - the problems we wished to pursue could not receive funding from our usual sources. They were either too interdisciplinary, or too applied, or in the wrong subject area, or in no subject area. Or, in some cases, we were physicists or chemists, and not ecologists. Or, we had no prior experience in these areas. The fact that there was a real national need for the work did not seem to matter--for a while. But then, the National Science Foundation, alert to these new needs for research, begat IRRPOS, a program devoted to interdisciplinary research; and IRRPOS thereupon begat RANN: and RANN thereupon begat most of the research activity that we shall hear about during the next two days at this conference.

The philosophy of RANN, written into its charter, has been a prime component of its success: flexibility has been the keynote. It has been flexible with respect to institutions, private or public. It has been flexible with regard to researchers. RANN has never been hung up on credentials or on union cards: if you knew what needed to be done and you wanted to do it, and if you could make a convincing case that would pass the critical peer review of the Foundation, then RANN was interested. The word "relevance" is implied in RANN's name, and on this RANN has been firm: its research should not be done in a social vacuum. To qualify for RANN support, a project must have a customer: someone must have, and be willing to express, a need for the information, or the method, or the device. It is better still, if the customer will help pay for the research, or take it over completely after it has become established.

So, the RANN program was a friend in need to the country and to the scientific community, when the need developed to broaden our research into new areas relevant to societal problems. It was certainly so for my own laboratory. RANN has worked well, and this conference, as well as its predecessor, is a tribute to that success.

The Conference itself, as you can see from the program, is structured in three parts. First, this morning we have four invited papers whose subjects span the entire range of the Conference agenda; second, we have sessions in Air, Water & Soil, and Biological Systems that run in parallel through today and tomorrow (though you should note the difference in that today the evening is free, while tomorrow the afternoon is free); third, we have the plenary and concluding session on Saturday morning.

I am supposed to welcome you here. But really the best welcome that can be given to Asilomar is given by the place itself, for nowhere, I think, will one find a milieu more conducive to the kinds of interactions that lift a conference out of the ordinary and make of it a memorable experience. The misty, moody, August-morning fog, giving way to crisp sunny afternoon-all this adds to the experience of Asilomar. So--have a productive meeting, and even more, an enjoyable stay in this lovely place.

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IV. BIOLOGICAL SYSTEMS

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I. INVITED PAPERS

ACHIEVING PRAGMATIC SOLUTIONS TO NATIONAL PROBLEMS THROUGH RESEARCH

Keynote Address
by

Dr. Herbert L. Wiser
Deputy Assistant Administrator
For Environmental Sciences
Office of Research and Development
U. S. Environmental Protection Agency

August 29, 1974

Good Morning Colleagues:

I extend the regrets of Mr. Russell E. Train, Administrator, U. S. Environmental Protection Agency, for not being able to personally address you as planned, and his good wishes. I have the double pleasure of acting as his surrogate this morning and, because of my interests in the RANN program and my friendships and associations with many of you, of being the keynote speaker at this important RANN conference.

The Research Applied to National Needs Program was established within the National Science Foundation for the purpose of applying our nation's research efforts and the expertise of its scientists more productively to fulfill national needs. The requirements of my Agency are similar--its research and development program must be quite pragmatic.

In these difficult times it is important that we, as scientists and science managers, address questions that not only interest us professionally, but also--and particularly--those that must be answered for our Nation's high priority problems to be resolved.

The solutions we achieve must be translatable into practical and usable form. An abstract theoretician, to use an extreme example, may produce a formula not obviously recognizable as practical. Such creativity is very valuable, but its germination into applicability requires interpretation and transformation by applied theoreticians and experimenters.

I know that among this exceptionally experienced group are scientists who know how to obtain answers to virtually any specifically directed question in their discipline. But complex problems require a coordinated interdisciplinary attack. The correct and entire question must first be identified and then answered. A less than total solution may mislead us into taking erroneous actions. An overworked research effort is wasteful.

Each of you, in accordance with your own expertise and professional disciplines, can solve those parts of the problem you are best qualified to solve. As a group, however, aiming with a common group purpose to unravel and resolve complex issues, the probability of success will be higher and results achieved more effectively and perhaps more quickly.

The energy shortage is our nation's principal technological problem. The nation is depending on us also for relief--for national self-sufficiency.

Many government departments and agencies worked together all spring and summer to develop an Environmental Science Research & Development Program whose purpose is to minimize the effects on health and environment of new and expanded energy processes. The energy processes considered were oil, oil shale, coal, synthetic fuels, nuclear, geothermal and solar energy and conservation.

We identified, as best we could, with assistance from the process developers, potential pollutants or pollutant types and, from extraction to conversion to use to waste disposal, developed an Environmental Science Research & Development Program, covering all media, for health effects, ecological processes and effects, monitoring and measurement methodology, and integrated assessment (socio-economics). Specific objectives and milestones were established and prioritized as to the need and importance of the knowledge to be obtained for fulfilling that objective. The milestone schedules were set in order for the research outputs to be useful in a timely manner by the energy process development and control technologists. A research output would have doubtful value if it were provided after plants and processes were in full production. Management provisions were identified for the continuous flow of information between the environmental sciences, energy process developers, and control technologists.

Scientists are inventive. Assume that a new or improved energy source or process for the abundant production of energy is developed. It is important that we then consider the overall effectiveness of this finding. It is not sufficient that the process merely be workable. It must not be dependent on a fuel, raw material or natural resource that is rare, that will be difficult to obtain. The process must also be efficient and economical, and the product deliverable to the users. These illustrate some of the things to which scientists, as a group, should give more consideration.

Second, the environmental impact of that process, source, and usage should be considered. Does the process do more good than harm? Consideration of the energy which is needed must be balanced against adverse effects produced. The nation's problem is to minimize effects while maximizing energy production and strike an acceptable balance.

Non-pollutant environmental problems related to energy needs also are to be recognized, such as the oil shale process expected to utilize much of the Rocky Mountain snow pack, thereby affecting the quality of Colorado River water and, potentially, agricultural production. Will construction of deep ports for supertankers destroy an ecosystem? I propose that marine and estuarine scientists participate in the design of such ports, specifying site allowances and limitations.

Waste disposal management problems, be they on land or in the oceans, require new ideas. Waste disposal could become this nation's largest problem.

Let me cite another problem of equal importance to the nation as the energy crisis: the effect of pollutants upon the health and welfare of our people, including the environment.

A question often asked of EPA is, "To what extent will pollutant X affect the balance of an ecosystem?" And a simple answer is expected. We researchers understand that this seemingly simple question must be expanded into many, sometimes more difficult to postulate, frequently more difficult to answer. And when we believe we have obtained the meaningful answer to the many facets of ecosystem dynamics or of the human life system, some interactions and questions not previously considered are bound to arise. Eventually, if we persevere, we should get to know the players, the forces, and the resulting dynamics.

Permit me to restate the qeustion: To what extent will pollutant X affect the balance of an ecosystem? Let's assume researchers determine the ecosystem's many processes and effects with and without pollutant X. Then I pose the following questions: If an entire species is decimated or eliminated, how important is the effect to the total ecosystem? What will happen to biota, both above and below the affected species, in the food web because of its obliteration? Viewing the ecosystem matrix from another direction, how important is the resulting effect, if, say, 25% of every specie in the ecosystem were affected? Is the effect self-reparable in both situations and at what pollutant level? Biological indices are needed to quantitatively state the net effect. Answers to these research questions will enable us to know to what level a pollutant in the environment can be tolerated or should be abated or controlled. Does total environment protection imply the zero discharge level? Many substances considered pollutants are produced naturally in the environment. Furthermore, it is impractical or impossible with our present technology to achieve zero discharge of most pollutants.

The relationship between pollutant exposure and effects to humans is especially difficult to answer. We are exposed simultaneously to a multitude of pollutants (via air, food, water, soil). We know, when high pollution episodes occur in various places in the world, or in various occupations when the exposures are normally or accidentally high, that illnesses and deaths increase. Sometimes, this is how we first learn that a pollutant is toxic. With research at intermediate exposures we try to extrapolate down to low levels to determine a threshold. That is difficult. The bio-index in the case of the 25% decrease could be 0.75, assuming unity represents a normal ecosystem. But in the case where a single species is eliminated, what is the number? What should be the method or formula for determining the bio-index for an ecosystem?

Part of the problem is: How do we define "adverse effects"; and correlate what effects to what levels of exposure? And adverse effects to whom?

At extremely low or virtually non-existent pollutant levels, there is usually no effect--but not necessarily where some toxic substances are concerned. The body organs and tissues may accumulate the pollutant, yet there may be no known clinical or visible signs, damage or discomfort. At higher levels, a person may feel uncomfortable. We all experience this in the form of eye irritations or unpleasant odors. These may or may not cause harm beyond the discomfort experienced. At still higher levels, illness occurs. At much higher levels, there is mortality.

How do we relate the health impact to the costs of preventing that pollutant from reaching man or the ecosystem in harmful quantities? Again, I return to the dose-response curve and ask, "What level is to be defined 'harmful'"?

All life systems, being complex, respond to pollutants and diseases in varying degrees and manners. Certain groups of people, such as the newborn, the unborn, the aged, the asthmatic, the rheumatic, the cardiac patient and those with other illnesses, seem to suffer more at lower levels of pollution and with certain types of pollutants than do normal healthy persons. The variation is dependent, of course, upon how we define "normal, healthy persons."

It is not sufficient to know only effects to protect man or environment, one must be able to control the pollutant. I shall present a real problem to illustrate a need for interdisciplinary cooperation. We believe that sulfur oxides are harmful to people. This nation has an ambient air quality standard for sulfur oxides established by EPA, specifically SO_2. We have begun to learn that the agent harmful to humans is not necessarily or solely SO_2, but most likely SO_4, whether it is in the form of acid mist or suspended sulfates or particulates or soluble sulfates. It really doesn't matter in what form the sulfur oxide is, it is harmful and it should be controlled.

To make a point, let us assume that SO_4, and not SO_2, causes harmful effects and that SO_4 must be controlled. But SO_4 is only a very small fraction of SO emitted by power plants, for example. Therefore, it is important that atmospheric scientists trace the SO_4 in a reverse manner through transformations along its pathways back to its source, because the source is where we may be able to control it. In the water medium perhaps, we may be able to intercept it at some place along its pathway. But in the atmosphere we must control it at the source. An untenable alternative is to intercept it at each human being. Therefore, to handle the problem, we must understand the chemistry and physics of the transformations and transport of sulfur oxides in all forms through the atmosphere.

Another problem contributing to uncertainties in our knowledge of pollution is in the measurement of pollutant levels in the environment and the exposures of people and other living things to them.

An early warning system for pollutants would provide a valuable service. Ambient conditions monitored continuously and with sufficient resolution and sensitivity can provide early warning on the development of elevated pollutant levels before a critical level is attained. Such a monitoring network is expensive even for one pollutant in one city. It would be prohibitive for many pollutants and many cities or regions.

What this country needs are good inexpensive instruments and automated networks.

Where a presently utilized instrument has the required performance is it wise to spend research dollars for the development of a better instrument that will cost no less to purchase, operate and maintain? Even converting a delicate laboratory instrument to a ruggedized field version may not always be worth the effort if the field instrument still will cost many tens of thousands of dollars and require a Ph.D. to operate it. Local, state and federal governments cannot afford such costs.

It may be wiser to attempt to fill instrumentation needs by developing simpler, less accurate, but adequately accurate, instruments or measurement methods costing about $100 in mass production quantities. If semiconduction chip calculators can sell for $30 or $40 each, inexpensive automated measurement systems should not be unattainable.

I have discussed energy, and the environment--now I would like to pose, not discuss but pose, a third important problem that this nation faces today: inflation. What can scientists, that is, scientists who are not economists, do, especially those of you working under RANN? In these times of inflation, economists, so I read, say there are two key ways to curb and abate inflation. One is to decrease the flow of money--cut down on spending. Research has been seriously feeling this for several years already. I do not recommend it as a cure. A second way is to be more productive. We can do our part by using our limited resources (dollars and personnel) more effectively and with greater emphasis toward the objective of solving high priority research problems.

In closing, I would like to commend you on the assemblage of this conference. It brings together a multitude of scientists from many universities and research laboratories and in many disciplines. I hope that the physical and biological scientists will listen to one another and read one another's reports, and that those who are experts in air pollution, water pollution and soil pollution will do likewise. Acquire a feeling for the problems which are of concern to your colleagues in their disciplines, for perhaps their problem is one that your experiences may cause to be more readily answered. Togetherness--integration--of researchers with different disciplines to solve a national problem really works. GET INVOLVED!

I thank you for the opportunity to speak to you today. I wish you success.

AIR POLLUTION CONTROL: MONITORING, MECHANISMS, AND MODELS*

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Abstract

The complex trade-offs between environmental quality and the present crises in food and energy production greatly complicate the formulation and administration of sound, cost-effective programs for the control of trace contaminants. A generally attractive approach to assessing such interactions between energy, economics, and the environment involves generation and validation of various types of computer models. In a broad sense, these relate emissions, transport, and chemical, physical, and biological transformations to ambient concentrations. When dealing with either air or water pollution, it is essential to recognize that adequate refinement and ultimate validation of most models require the development of far broader, more accurate, and, indeed, a more detailed data base than is currently available. This general problem is well illustrated by considering some contemporary aspects of air pollution control and the technical data base and overall knowledge upon which present control programs are founded.

Badly needed information includes (1) complete and detailed emission inventories, (2) an adequate, practical definition of hydrocarbon reactivity, (3) more accurate and consistent monitoring, including calibration techniques for toxic air pollutants for which Federal air quality standards have been promulgated, (4) identification and accurate measurement of a large number of organic and inorganic atmospheric contaminants whose presence in polluted ambient air may be only suspected, or whose levels may have been only "guesstimated," and (5) the development of a comprehensive body of chemical and physical knowledge about atmospheric transformations, including measurement in the laboratory and in precisely characterized smog chambers of the rates of formation, products, and stoichiometries of all reactions which significantly affect the formation of photochemical smog. As this data base is developed, increasing refinement and more precise validation of models will permit their use with confidence to develop sound control strategies for air pollution control which neither overcontrol pollutant emissions at great economic expense nor pose a serious threat to human health due to undercontrol.

Today, decisions involving the complex interactions between energy, economics, and the environment are being made that will cost billions of dollars and directly affect the quality of our lives. Unfortunately, many legislative and administrative actions currently must be based on a meager--and sometimes even unreliable--scientific, technical, medical, and socioeconomic data base. As a result, choices must often be made between differing <u>opinions</u> rather than by selection of the most cost-effective and technically sound <u>options</u>. Rapid and efficient development of information about an exceptionally wide range of questions is required if sound, cost-effective strategies for the control of environmental contaminants are to be devised and implemented.

The many papers presented at this conference amply illustrate how research can be applied to one national need--the development of data needed to solve the problems posed by environmental pollution. In this paper, some current problems in air pollution control will be used, first to illustrate the complexity of this particular environmental problem and, second, to indicate some of the types of data needed to permit sound formulation and implementation of air pollution control programs.

Health, Economics, and Air Pollution: Some Trade-offs

The development and implementation of air pollution control programs and the evaluation of the effects of proposed energy policies on such programs constitute two particularly complicated environmental problems. Choosing the proper degree of control of pollutant emissions provides an appropriate example. Exceptionally stringent control of pollutant emissions is usually costly, while undercontrol, although less expensive, can produce health effects which are wholly unacceptable.

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*Work supported by the National Science Foundation--Research Applied to National Needs, Grant No. GI-41051.

The first point is illustrated by Figure 1, which shows that estimated costs for the control of vehicular emissions increase very steeply once 80 to 90% of the emissions have been controlled.[1] Clearly, reductions in the last 10 to 20% of vehicular emissions will be expensive. Thus, unnecessary overcontrol should be avoided, and other more cost-effective measures should be implemented (e.g., vapor recovery from filling gasoline tanks, etc.).

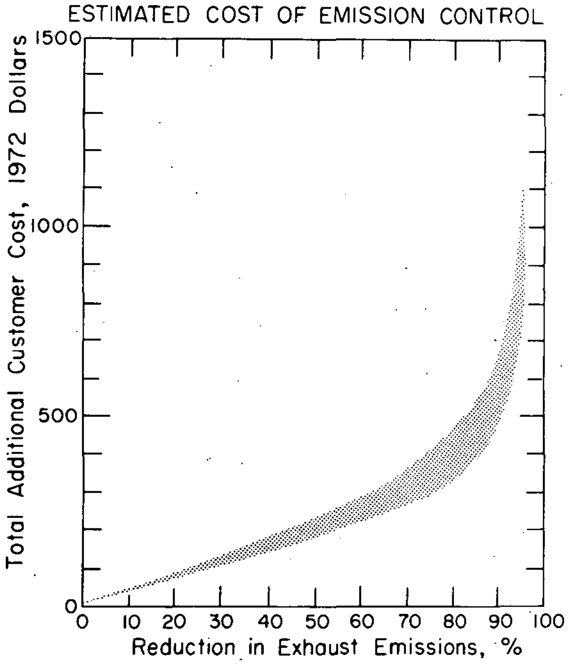


FIG. 1. Plot of cost to the U. S. consumer vs. percent reduction in vehicular exhaust emissions.

Conversely, the threat to human health that could result from undercontrol of air pollution is well illustrated by the tragic London smog episode of 1952. As a result of exposure for only several days to elevated levels of sulfates, sulfuric acid aerosol, and carbonaceous particulates, over 4,000 excess deaths were recorded over a brief priod of time. With the discovery of photochemical smog, formed by the interaction of solar ultraviolet radiation on mixtures of hydrocarbons and oxides of nitrogen, around 1950, additional concern over this new threat to public health arose. The eminent toxicologist, Dr. H. Stokinger, stated in 1969[2] in a summary of environmental pollutants:

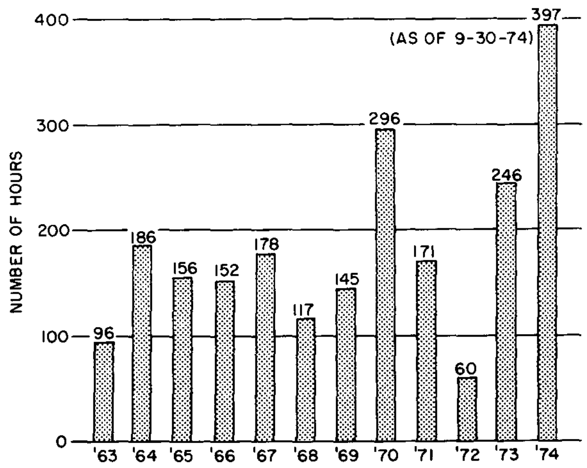
> Airborne pollutants are potentially responsible for more of our ills than are water- and food-borne contaminants together. ... Many of the conditions attributed to exposure to environmental pollutants are either accelerations of the aging process or are associated with aging. This is particularly true of the air pollutants; ozone and photochemical oxidants merely add to and hasten the oxidative destruction of the lung and other tissue sites; respiratory irritants hasten the onset of emphysema and bronchitis and would appear to promote cancer of the respiratory tract.

Unfortunately, during the last 10 years, despite substantial local, state, and federal control programs, population growth and increased use of energy and automobiles have resulted in little or no improvement in photochemical smog in a number of heavily populated metropolitan regions. Furthermore, to add to the general concern, recent studies have confirmed the toxic effects of ozone at levels often experienced in ambient air in southern California. Finally, the United States, among other developed nations, is now experiencing an energy crisis which, understandably, enhances the often-expressed desire, and indeed the need, to more fully utilize our supplies of high-sulfur fuels, such as coal and oil shale. Some recent findings "relevant" to such environment-energy-health trade-offs are cited below.

Photochemical Smog

Two recent reports, one a detailed study of the health effects of ozone and the other a newspaper story, illustrate the pressing need to control photochemical air pollution more effectively. Thus, a thorough and detailed study of the effects of ozone on adult males[3] showed that measurable effects of exposure to ozone occurred at levels beginning at 0.37 parts per million (ppm). This is a level nearly identical to the California second-stage episode level. The report noted that "Some subjects thus exposed not only developed measurable physiological and biochemical changes, but felt physically ill and were unable to perform their normal jobs during exposure and for several hours afterward."

These findings are particularly significant in view of the unusually severe levels of oxidant which have been experienced throughout California's South Coast Air Basin during the most recent smog season. For example, Figure 2 --taken from a story in the San Bernardino Sun Telegram,[4] headlined "Smog Season Worst on Record"--shows that oxidant levels in San Bernardino are not improving. If anything, they appear to be getting worse, although this could be partly the result of adverse meteorological conditions during recent years.



SAN BERNARDINO: 397 HOURS ABOVE FIRST-STAGE SMOG ALERT LEVELS THIS YEAR

...Chart based on statistics gathered by County Air Pollution Control District

FIG. 2.

Energy and Air Pollution: Health Implications

It is important to recognize that relaxation of SO_2 emission standards in areas plagued by photochemical smog could have significant chemical and medical effects. For example, over a decade ago, it was observed[5] that the photooxidation of sulfur dioxide was significantly enhanced and aerosol production, probably sulfate particulate, was greatly increased when SO_2 was irradiated in the presence of ppm concentrations of olefins and NO_x--that is, conditions typical of photochemical smog. More recently, enhanced thermal oxidation of SO_2 was found to occur in the presence of ozone and olefins.[6]

Thus, atmospheric levels of SO_2 are not only of concern to health per se, but also because oxidation of SO_2 ultimately leads to sulfate aerosol which is toxic[7] and which produces substantial degradation of visibility.

Furthermore, last year, Bates and Hazucha[8] reported that exposure of healthy adults to a mixture of 0.37 ppm of both ozone and SO_2 had a significantly greater effect on maximal expiratory flow rate than exposure to either pollutant alone.

In short, combinations of sulfurous and photochemical smog can cause enhanced conversion of SO_2 to visibility-degrading and toxic particulate sulfate and may also promote synergistic health effects not observed for either type of smog alone. Clearly, proposals to ease the energy shortage in major urban areas suffering from photochemical smog, by permitting power plants and major industrial facilities to use high-sulfur fuel oil or high-sulfur coal, have serious implications for public health, particularly on days with adverse meteorological conditions.

Agriculture and Air Pollution

One largely unpredicted and most serious effect of the energy crisis has been a fertilizer shortage which, in combination with unfavorable weather, has produced worldwide shortages of food. Because many crop yields are significantly decreased by exposure to a variety of pollutants, the effects upon agriculture from present levels of smog, as well as from the increased pollution which might result from the development and use of alternative energy sources, should be recognized and assessed.

For example, while the dramatic effects of photochemical oxidant on plants and trees, such as the Ponderosa pine shown in Figure 3, are well known, it is not generally recognized that the invisible effects of smog may be as costly as its visible effects. Thus, photochemical oxidant not only discolors leaves, but it also inhibits photosynthesis by destruction of chloroplasts,[9,10] which substantially reduces both plant growth and crop yields.

FIG. 3. Healthy Ponderosa pine tree in San Bernardino mountains in 1961 and smog-damaged appearance in 1970.

Figure 4 shows the yield of grapes from two vines of equal size, one exposed to ambient air and the other to ambient air filtered to remove photochemical oxidant. At a time of worldwide shortages of food, the decrease in yield (about 50%)[11] is sobering, indeed.

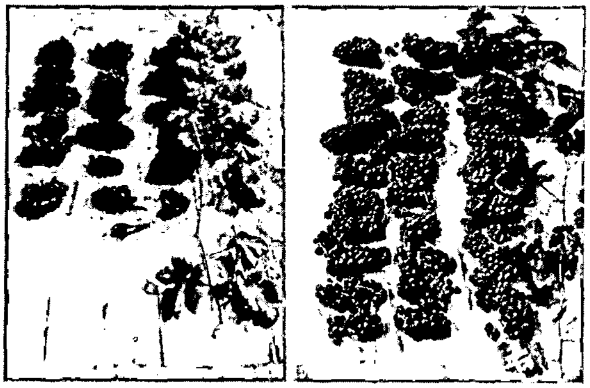
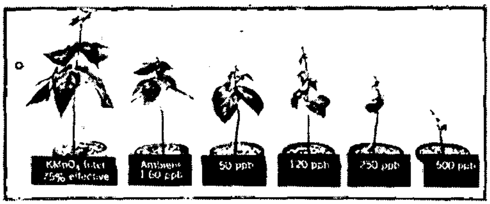


FIG. 4. Comparison of yield from grapes grown in ambient polluted air and in filtered air.

Not only does photochemical oxidant affect many agricultural crop yields, but ethylene--a major olefinic component of auto exhaust, an important industrial chemical, and the most abundant olefin in ambient air--also supresses growth.[12] Figure 5 shows the dramatic effects[13] of air containing up to 500 ppb of ethylene on the growth rate of bean plants and on their yields of beans.



Ethylene Effects on Red Kidney Beans: 75 days growth

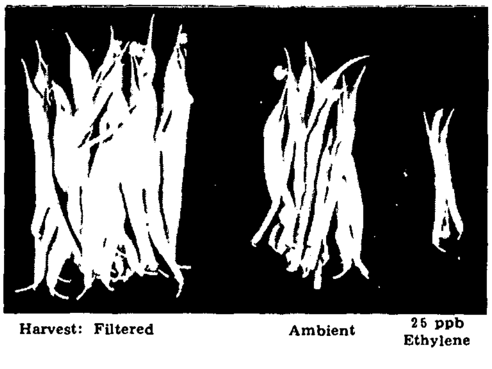


FIG. 5. Comparison of growth and yield of red kidney beans upon exposure to ethylene.

Clearly, complex trade-offs are involved between air pollution control costs and the benefits to be derived from increased crop production due to improved air quality.

Emissions vs. Air Quality

Crucial to the development of strategies for the solution of air pollution problems, such as those cited above, is the determination of the relationships between emissions and air quality. Such relationships can be relatively straightforward for some pollutants--for example, carbon monoxide, a primary pollutant that for modeling purposes can be treated as chemically "inert" (which it really is not) and which is emitted in some locations almost exclusively by motor vehicles. Thus, Figure 6 shows that ambient CO levels in several U. S. cities are linearly dependent on average auto CO emission rates.[1]

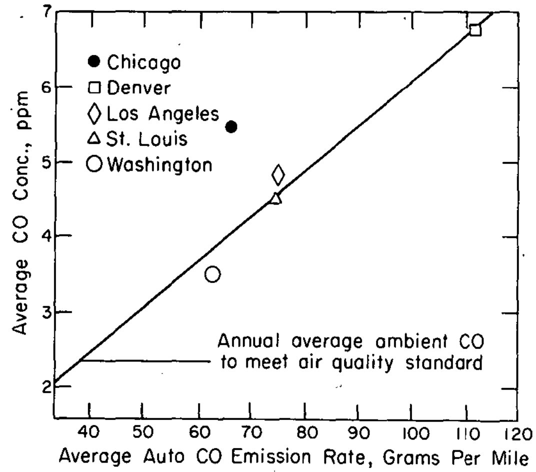


FIG. 6. Relationship between ambient CO levels and automotive CO emissions.[1]

However, the relationship between ambient levels of ozone, a secondary pollutant, and the absolute emission levels of its precursors, hydrocarbons and oxides of nitrogen, is complex, nonlinear, and only qualitatively defined.[14] The uncertainties are shown schematically by the curves in Figure 7, which depict a number of possible relationships between oxidant levels in ambient air and the degree of control of vehicular emissions of hydrocarbons (HC).

Because in 1971 no quantitative relationship between ozone and its precursors was available, the EPA formulated its control strategies for photochemical oxidant by assuming a linear relationship between ambient oxidant and reactive hydrocarbons.[15] While at that time this seemed to be the most reasonable approach, it is now generally recognized by scientists and control officials that this too-simple dependence is a most inadequate foundation upon which to base control strategies costing billions of dollars and having an economic impact not only on the U. S., but on all countries exporting motor vehicles into this country. Currently, major steps are being taken by the EPA to clarify the situation. Indeed, several NSF-RANN research programs, including our own, are focused to a significant extent upon this problem.

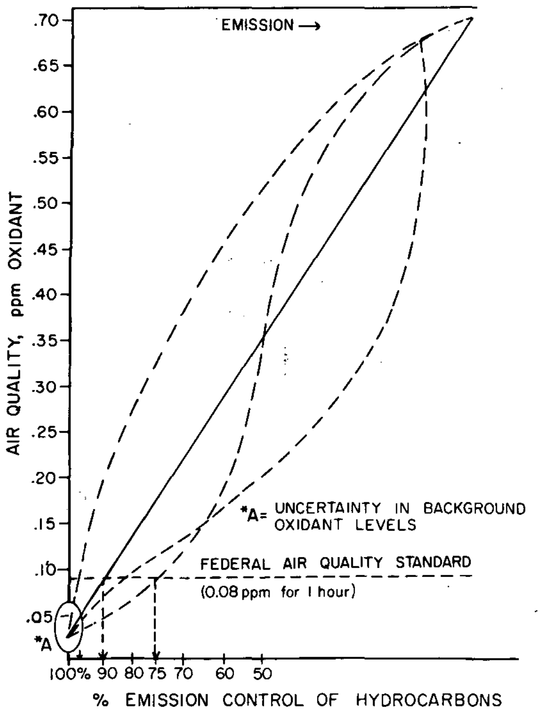


FIG. 7. Possible forms of the relationship between air quality and emissions and percentage of emission control.

Air Pollution Models

A common approach to the problem of relating emissions to air quality and thus to the development of a health-warning alert system capable of predicting pollutant levels well in advance of a serious smog attack is the formulation of models of the formation of smog in an urban airshed. For the sake of convenience, one can categorize such models into three general types--empirical, semiempirical, and ab initio, largely theoretical, models.

An empirical or adapredictive model relates observed levels of pollutants in a specific air basin to meteorological events and is valid only for that basin. In its simplest form, such a model does not require a detailed emission inventory. However, in some cases, such models contain factors which correct for variations of emission levels with day of the week and with the intensity of solar radiation by month of the year.

One of the earliest examples of an adapredictive model is that employed by Professor J. Firket, of the University of Liege, who investigated a smog disaster which occurred in the Meuse Valley in Belgium in December 1930. Sixty people died from sulfurous smog, trapped under a low inversion layer. In 1936, in the Transactions of the Faraday Society, he made the following observation:[16]

> Public opinion was deeply moved, not only in Belgium, but also in neighboring countries. Wherever fogs of several days' duration are frequent, public authorities were anxious to know the cause of this catastrophe and several delegates were sent to the spot. This apprehension was quite justified, when we think that proportionally the public service of London, e.g., might be faced with the responsibility of 3,200 sudden deaths if such a phenomenon occurred there.

As we noted above, in 1952, 4,000 excess deaths did occur in London during the most disastrous smog episode on record. This disaster fulfilled Professor Firket's remarkably accurate prophecy and instigated an air pollution control program that has effectively reduced sulfurous smog in the Clean Air Zones of London.

Another example of an empirical approach to the modeling of smog is the EPA control strategy for oxidant, initially employed by the EPA,[15] which involves (as was noted earlier) a linear rollback of reactive hydrocarbons and is based on the assumption that a direct proportionality exists between observed ambient levels of ozone and emissions of reactive hydrocarbons.

Most semiempirical models substitute a true emission inventory for emission factors based on the day of week and on the season. Many include mathematical descriptions derived from theory of diffusive and convective mixing during transport. However, few semiempirical models attempt to calculate atmospheric chemical transformations solely from fundamental chemical knowledge. Instead, most used a much-compressed and over-simplified reaction mechanism which is validated against air quality data for the basin being modeled. Thus, semiempirical models mix theoretical prediction with empirical correlations.

Finally, ab initio, largely theoretical, models attempt to describe chemical and physical phenomena in polluted atmospheres by appropriate combination of our knowledge of chemical and physical transformations in the gas phase, though not necessarily homogeneous, systems. These extremely complex models have three major submodels: (1) a detailed temporal and spatial emission inventory; (2) a theoretical meteorology package which uses morning weather data to predict stability and movement of air masses and diffusive and convective mixing within those air masses; and (3) a chemical reaction mechanism, possibly using some lumped parameters, but still wholly faithful to a complete set of elementary reactions realistically mimicking the formation of photochemical smog, both in smog chambers and in ambient air.

All of these models have two things in common--they can be no more accurate than the data upon which they are based, and they must be validated against air quality data for the basin to which they are applied. Let us now briefly consider some of the problems posed by these two requirements.

Emission Inventories

It is well worth reemphasizing the point implied above, that fundamental to the formulation of any air pollution control strategy is the development of a consistent and accurate emission inventory. A crucial input to such an inventory is a valid reactivity classification for hydrocarbons and related organics which are important precursors to the formation of photochemical oxidant. A consistent system is clearly necessary, since no control plan or urban airshed model can produce results more reliable than the input data.

While this statement is axiomatic, it is sobering to examine the data in Table I, which illustrate the vastly different emission inventory values obtained for the Los Angeles Basin when one uses different reactivity classifications! Clearly, the generation of a more useful, consistent, and reliable definition of hydrocarbon reactivity and a detailed reassessment of the relative reactivities of common hydrocarbons and other organics, such as commercial solvents, is an essential task and indeed one currently under way in our SAPRC-NSF-RANN program.

TABLE I. Comparison of reactive hydrocarbon inventory levels in the Los Angeles Basin for fixed sources under alternative reactivity assumptions[17]

Control	Reactive hydrocarbons (tons/day)		
	Consistent EPA	ARB/ LAAPCD	Rand Corp.
1970	876.0	228.3	636.3
1975 Nominal	427.2	102.2	239.9
1975 Maximal	290.6	57.7	129.9

The need for accurate measurements of emissions, rather than estimates or "guesstimates," based on "common technical knowledge" is exemplified by the following case in which a seemingly "obvious" control strategy, while proposed with the best of intentions, turned out to be wholly erroneous in concept. Thus, for years it has been an accepted "fact" that "large cars pollute more than small cars." Indeed, several years ago, in order to discourage the sale of "highly polluting" large cars, a bill was proposed for action by the State of California Legislature that would have instituted a new automobile tax which would have increased with engine size and displacement. Subsequently, when the EPA actually measured the exhaust emissions from all U. S. and foreign cars--in the absolute, although rather peculiar, units of grams-per-mile driven--it was discovered that, on the average, small cars pollute as much as large cars![18,19,20] The range of variability of hydrocarbon emissions with engine displacement of 1973 model U. S. and foreign cars is shown in Figure 8.[21,22] This plot, and similar ones for CO and

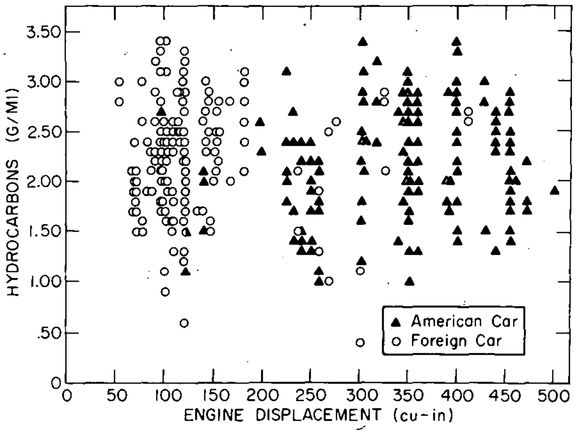


FIG. 8. Plot of hydrocarbon emissions (gm/mi) vs. engine displacement (cu. in.).

oxides of nitrogen (NO_x), clearly demonstrates that there is no direct correlation between exhaust emissions and engine size for currently available automobiles.[18,21,22] Certainly, cars with small engines do save fuel and generally their emissions are technically easier to control than are emissions from cars with large engines. However, it is sobering to realize that a proposed tax law, which almost passed, was technically most unsound.

Ambient Air Monitoring

Equally crucial to the development of any reliable control strategy or health-warning alert systems is the acquisition of ambient air quality data by consistent and reliable monitoring procedures. Thus, the recent joint statement by the California Air Resources Board (ARB) and the Los Angeles Air Pollution Control District (LAAPCD) that different methods of calibration of oxidant monitoring instruments cause oxidant measurements made by the LAAPCD to be "one-quarter to one-third" lower than ARB measurements made at the same time and place came as a surprise to scientists and the lay public alike.[23] Since the calibration method of the ARB has been stated[24,25] to be essentially equivalent to the method used by the U. S. Environmental Protection Agency (EPA), this discrepancy has national and even international ramifications.

If the ARB and EPA methods of calibrating ozone monitors are seriously in error, then these methods and all data referenced to them will have to be changed. This is true, not only throughout the United States, but also throughout most of the rest of the world, which has largely adopted the EPA methods for monitoring air pollutants.

This measurement problem also provides an example of the technical, medical, and socio-economic problems generated by the use in different portions of the same air basin of oxidant monitoring techniques calibrated by non-equivalent methods. Figure 9 shows the oxidant dosage in ppm-hr above the Federal oxidant air quality standard of 0.08 ppm at six South Coast Air Basin monitoring stations for the year 1973. Clearly, the data as reported do indeed suggest an inland buildup of oxidant. However, when all the air monitoring data are placed on the same scale, either the ARB scale or the LAAPCD scale, the corrected data show that, in 1973, cities such as Pasadena, Azusa, and Pomona actually had significantly higher oxidant dosages than did Riverside and San Bernardino. This reversal of the relative oxidant dosages in the western and eastern portions of the basin upsets current views of the oxidant problem in the basin and suggests that all basinwide control programs and models for air pollution control need to be reassessed.

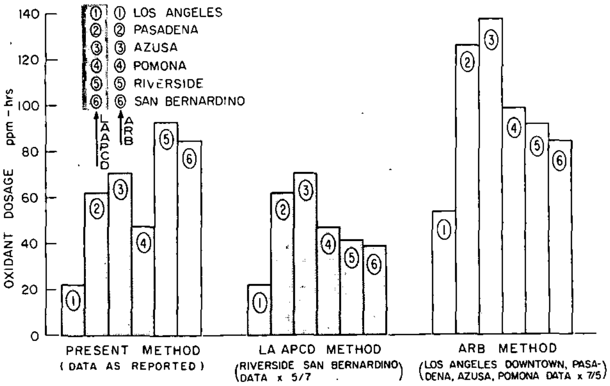


FIG. 9. Oxidant dosage in ppm-hr above the Federal oxidant air quality standard of 0.08 ppm at six South Coast Air Basin monitoring stations; (a) as reported, (b) LAAPCD scale, and (c) ARB scale.

Not only do serious problems exist in monitoring accurately, and in a consistent manner, such major pollutants as ozone and nitrogen dioxide, but ambient air measurements of minor (but potentially important) pollutants--such as hydrogen peroxide, acrolein, formic acid, and nitric and nitrous acids--are also urgently required. Thus, for example, a recent long-path infrared study of ambient air, performed by the EPA in Pasadena on a very smoggy day (July 25, 1973), reported that formic acid was the major hydrocarbon oxygenate observed and that, contrary to expectations, no formaldehyde was observed![26]

Clearly, much more information is needed about the ambient concentrations of important trace smog species. Under our NSF-RANN research program, a detailed analysis of ambient Riverside air is being carried out, using both a Fourier infrared interferometer interfaced to a long-path optical system and a combined gas chromatograph-mass spectrometer. The power of the Fourier infrared interferometry is shown in Figure 10, which presents the spectra that led to the identification of ketene as a product of the reaction of ozone with propylene and cis-2-butene, but not with ethylene. For the reaction of ozone with ethylene, the well-resolved 2143 cm^{-1} band of CO was observed (Figure 10a), while for propylene (Figure 10b) and cis-2-butene (Figure 10c,d), the ketene band centered at 2150 cm^{-1} was observed superimposed on the CO fundamental.[27]

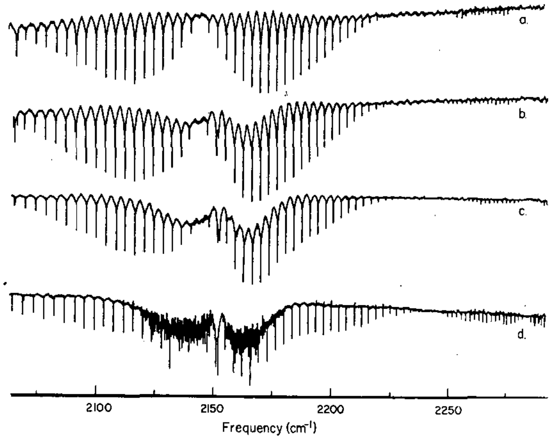


FIG. 10. Product spectra from reaction of O_3 with (a) ethylene, 1 atm air, (b) propylene, 1 atm air, (c) cis-2-butene, 1 atm air, and (d) cis-2-butene, 2 torr O_2.

Models of the Kinetics and Mechanism of Photochemical Smog

Semiempirical and ab initio urban airshed models for photochemical smog frequently include, along with an emission inventory and a meteorology package, a model describing the chemical transformations occurring during transport. Models of chemical transformation may be of the lumped parameter type[28] or may be wholly specific, containing as many as 200 elementary reactions.[29] Although both types of reaction mechanisms are derived principally from experimental data, the specific mechanism does not contain any simplified reaction sequences, while the lumped parameter model does.

Successful formulation of a computer model of photochemical smog requires a broad data base drawn from three related areas. First, laboratory studies must develop the rate and product data necessary to define those reaction sequences which should be included in the model. Thus, for example, much valuable information has been derived from smog chamber studies in the ppm-ppb concentration range, including rates of photooxidation of hydrocarbons, identification of minor but mechanistically significant reaction products, and, in conjunction with laboratory studies in the torr pressure range, evidence for the importance of a number of key reactive intermediates, such as O atoms, ozone, OH and HO_2 radicals. Unfortunately, various chambers yield data which are quantitatively different.[29] More research is necessary to reconcile existing information and to produce new data which will be photochemically and kinetically reliable.

Second, while kinetic-computer modeling continues to provide insight into the extremely complex chemical transformations occurring in photochemical air pollution, crucial input required for further refinement of such computer models are accurate values for absolute rate constants, the chemical nature of all products and intermediates for every step, and accurate concentration time profiles. Problems arise in model validation efforts, because, to date, most models have been applied only to relatively simple systems in smog chambers and because most existing chamber data are subject to substantial experimental uncertainties.

Third, kinetic computer model predictions and chamber results must be carefully compared to ambient air data in order to verify that significant species predicted by the model or detected in chamber experiments are also formed in polluted urban atmospheres.

Conclusion

What is required now is the generation of a great deal of additional reliable monitoring, mechanistic, and kinetic-computer information and its integration into one package--an experimentally validated model of chemical and physical transformations in photochemical air pollution. Concurrently, in light of the energy crisis, modifications to this model must also be developed which will take into account the chemical and physical implications of introducing SO_x chemistry, including both intermediates and stable products, into the highly oxidizing atmosphere of photochemical smog.

This model, along with emission inventories--meteorological, topographical, and demographical input--constitutes a major element of a total urban airshed model directly applicable to the control of photochemical air pollution, both strategically and in a "real time," day-to-day sense. Information used in the development of this airshed model is coming from a number of scientists involved in a wide variety of research programs, many of which are being sponsored by NSF-RANN and which will be discussed at this conference.

Acknowledgments

Review of this manuscript by Dr. J. L. Sprung is much appreciated. The financial support of the National Science Foundation through its RANN program (Grant GI-41051), the Environmental Protection Agency (Grant R-800649), the National Science Foundation (Grants GP-34524 and GP-38053X), and the California Air Resources Board (Grants PCA-122, ARB 2-377, ARB 3-017, and ARB 4-214) is gratefully acknowledged. The contents do not necessarily reflect the views and policies of the supporting agencies, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

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CURRENT RESEARCH IN HEAVY METALS IN SOIL, SEDIMENT AND WATER: JANUARY 1973-OCTOBER 1974

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This review covers a selection of published and unpublished administrative reports on Cd, Cu, Hg, Mn, Pb and Zn in relation to analytical techniques, sources of contamination, flow through the ecosystem, accumulation in soils and sediments, uptake by plants, abatement and other literature reviews. The first, or general, section of this paper is devoted to discussions which pertain to groups of heavy metals, and which cannot be identified with any one individual heavy metal. Where possible, the basic structure of this general section has been maintained throughout the other sections. For Cd, Hg and Pb, this paper is an updating of earlier information (Lagerwerff, 1972).

GENERAL

Analysis

Even where heavy metals occur in excessive amounts, their concentrations usually are sufficiently low to require that efforts be continued at improving analytical techniques. For isolation and concentration prior to analysis, a 5% solution of the quaternary amine Aliquat 336-S in xylene was recommended. Thus it was possible to extract quantitatively from water samples, after their enrichment with an overdose of KI for intermediate complex formation, Hg at pH from 1 to 12.5, Cd at $pH > 7$, and Zn at $pH < 5$. The Aliquat complexes formed were more stable than corresponding iodides in the order $Hg > Cd > Zn$. The Aliquat complex thus was broken down easiest for Zn, bringing it back in the inorganic phase, and separating it thereby from Cd. Several Na salts, as well as EDTA, qualified for this operation (McDonald and Rhodes, 1974).

For subsequent analysis, atomic absorption spectrophotometry, with or without a carbon furnace, presently is the most used method as applied to a variety of substances (Van Loon and Lichwa, 1973). These authors stress the interference of many metals with Ni. Spark source spectrometry has been revived as an accurate method for coal analysis (Guidoboni, 1973). Coal has also been analyzed by X-ray fluorescence, in particular because of the limited necessity of sample preparation. A monochromatic beam exciting the elements, gave a low background. In combination with a Si-Li solid state detector, and a single crystal analyzer isolating the fluorescent radiation of interest, void of all scatter, applicability of this method has been considerably improved (Sparks and Ogle, 1974; Sparks et al., 1974).

Finally, anodic stripping voltammetry and pulse polarography, both modernized versions of "classic" polarography, are rapidly gaining in popularity as accurate and sensitive methods for the determination of a wide array of heavy metals in many different kinds of material, e.g., Lewin and Rowell (1973), and Miguel and Yankowski (1974).

Sources

The idea was confirmed that food and water, rather than air, are the major direct sources of heavy metals found in man. In percent of the total amount of metals entering the digestive system, food and water would contribute at least 58% of the Hg, 68% of the Pb, 95.6% of the Cd, 98.3% of the Cu, 99.6% of the Ni, and 99.7% of the Co (Woolrich, 1973). This information does not consider the fractions absorbed into the bloodstream through the intestinal wall.

Through burning of coal for power generation, depending on precipitator efficiency, heavy metals are released for the most part as aerosols and as fly ash. A minor fraction escapes in effluents (Toca et al., 1973). Studies on the Allen Steam Plant, Mo., indicated that except for Cd and Hg, most elements were ejected in the fly ash (Bolton et al., 1974). Also, smelter ore dust spilling from transport vehicles may cause contamination, but of a more local nature (Dorn et al., 1974).

Effluents from sewage treatment plants have caused increasing environmental concern (Mytelka et al., 1973). The sludge resulting from the treatment is another heavy metal source. Comparing the contents of heavy metals in raw, incoming sewage (in mg/l) with that in digested sewage sludge (in mg/kg dry weight), the average values are 0.007 and 31.3 for Cd, 0.43 and 1,380 for Cu,

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(1) Invited lecture, Second Annual NSF-RANN Trace Contaminants Conference, Asilomar, Calif., August 29-31, 1974. Contribution from the Agricultural Environmental Quality Institute, Agricultural Research Service, U. S. Dept. of Agriculture, Beltsville, Md.

and 0.63 and 2,260 for Pb (Lewin and Rowell, 1973). The impact of metal content of sewage on sludge activating microorganisms has been studied (Poon and Bhayani, 1973). The effect of 2.5 mg Hg per liter had but little effect, but 5 mg Hg per liter inhibited aerobic processes (Ghosh and Zugger, 1973). In this light, the metal content of sewage sludge could prevent effective microbial breakdown of the sludge. A similar situation arises where heavy metals in leaf litter inhibit complete decomposition of that litter (Ruhling and Tyler, 1973).

Mining and smelting at times have caused contamination of the environment. Thus, in Tasmania contamination of a river with Cd, Cu, Mn, Pb, Sn and Zn from mines caused death of fish and injury to pasture grasses irrigated with the water (Tyler and Buckney, 1973). The concentrations of Cd, Cu, Pb and Zn in soils and plants decreased with increasing distance from a smelter near Galena, Ka., indicating it to be a source of contamination. From the analysis of the soil profile a negative relationship was established between metal concentration and depth, pointing to the aerial nature of the contamination. Average ratios between the metal concentrations in the 0 - 20 cm layers of contaminated and uncontaminated soil were 7.0 for Cd, 2.9 for Cu, 2.0 for Mn, 2.3 for Pb and 4.8 for Zn. Coupled with acid soil conditions, these values indicate a deterioration of the soil in a region already high in native metal concentrations (Lagerwerff et al., 1973).

Elsewhere (Kronfield and Navrot, 1974), metal effluents from industrial and sewage treatment facilities containing Cd, Co, Cu, Cr, Ni, Pb and Zn were responsible for the contamination of an entire river system, which was checked only by a high pH resulting from the same contamination. Surprisingly, dredging the bottom and liming the water were the means suggested for abatement. Dredging is usually considered a hazard because of resuspension of contaminants, and liming a river does not seem to be economically feasible in the long run.

Flow

Heavy metals in the environment are carried through a cycle that may take them from the rocks and minerals from which they are released through a wide variety of pathways to the sensitive areas of life, and from there eventually to the oceans and in deposits from which rocks and minerals may be reformed at some time in the geologic future. The release mechanisms partly are natural, and partly triggered by man. The resulting impact may be additive. The natural release mechanisms, responsible for environmental background concentrations, have recently been a topic of interdisciplinary discussion (Natl. Res. Council 1973 a). The heavy metals released by either mechanism arrive in rivers and streams most often adsorbed to specific, suspended particles (Leland et al., 1973).

The distribution downstream from any source depends on many factors (Williams et al., 1973). The mean concentrations of metals adsorbed on suspended particulate matter, and of those dissolved in ambient water in upstate New York were, in ppm, 15.6 and 0.54×10^{-3} for Cd, 21.6 and 0.60×10^{-3} for Cu, 7.9 and 0.12×10^{-3} for Pb, and 79.9 and 2.7×10^{-3} for Zn (Kubota et al., 1974). The adsorbing particles may be of various kind, such as clay, organic matter or Fe oxides (Leland et al., 1973). Several studies have been reported on the distribution of heavy metals in lacustrine (Forstner et al., 1974; Maxfield et al., 1974a and 1974b), and in-shore marine (Jones, 1973) deposits.

Hydrous oxides of Fe and Mn are active scavengers for a number of heavy metals in soils and waters. Adsorption has been observed to take place in the order Pb > Zn > Cd, reversible with respect to H^+ and other cations. Especially Pb, but also Cd, were subject to specific adsorption on these hydroxides (Gadde and Laitinen, 1974).

Soils and Plants

Regarding ore smelting, research in Australia indicated soil accumulation of Cd, Cu, Pb and Zn within 1 km of an urban smelter complex by factors of at least 3, 65, 21 and 30, respectively, relative to rural areas (Beavington, 1973). Whether from fallout or sewage sludge application, heavy metals upon reaching the soil are slowly incorporated due to biological, chemical or physical action. They may eventually enter into several associations. Most frequently reported are reactions with P and with organic matter.

Applying phosphate fertilizer to acid red sandy loam caused the availability of Cu to decrease by up to 61%, of Mn by up to 26%, and of Zn by up to 38% (Badanur and Venkata, 1973). Hydrolysis of polyphosphates which, in unhydrolized form, often chelate heavy metals into soluble compounds, caused heavy metal uptake by young corn plants to decrease (Hashimoto and Wakefield, 1974). With tree seedlings growing in acid soils limed to pH 4.3, P interfered in root-to-shoot translocation of Cu, Fe and Al, but not of Mn and Zn

(Smilde, 1973). This would indicate that the precipitating effect of P internal to the plants prevailed over that external to the roots.

Heavy metal chemistry in organic soils is characterized by strong bonds, raising more often the question of sufficiency than of toxicity in plant production (Tyler et al., 1973). Applying municipal compost in quantities of 143 tons per ha to sorghum, 80 tons per ha to Bermuda grass, and 112 tons per ha to corn, evoked positive responses surpassed only by applying 180 kg N per ha, supplemented with P and K (Mays et al., 1973). The negative effects of trace elements on cabbage, lettuce and beans grown on soils amended with sewage sludge in one report were emphasized with regard only to B, and not Zn or Cu (Purves and Mackenzie, 1973).

The impact of heavy metals on the environment may be of longer duration where closed plant communities prevent runoff and wind erosion (Roberts and Goodman, 1974). Thus, downwind from a smelter in the Missouri New Lead Belt, plantings of lettuce, radish and green beans accumulated no less than 1,324, 518 and 136 μg Pb, and 34.5, 13.7 and 8.5 μg Cd, respectively, per g dry weight of the edible plant parts (Hemphill et al., 1973).

Abatement

With regard to smelters and coal burning plants, scrubber-precipitator technology has advanced to the point that nearly all airborne elements, except Hg and Se, can be collected before stack emission (Kaakinen and Jorden, 1974). The problem thus would become one of proper disposal of scrubber and ash pond water (Bolton et al., 1973). Alternatively, attention has been directed towards prior removal of heavy metals from coal by a beneficiation process based on oil agglomeration involving slurries of finely ground coal (Capes et al., 1974). The economics of this process were not divulged.

Various techniques have been attempted to rid public waters from excessive amounts of heavy metals: adsorption, exchange, chemical precipitation, electro-precipitation, and extraction (Cadman and Dellinger, 1974). Thus, the cation resin Chelex-100(2) removes heavy metals from waters in the pH range of from 5 to 6 in the following order: Cu>Pb>Cr>Ni>Zn>Co>Cd, the position of Cd to be especially noted. Because of their cost, resins have little practical significance for the decontamination of large bodies of water. Chemical precipitation with either lime or alum, or reverse osmosis, have been suggested for removing inorganic heavy metal salts (Lanouett, 1973). For removing organic heavy metal complexes, available means are adsorption on activated carbons or synthetic resins. Alternative methods are based on electrolysis, chemical oxidation (H_2O_2, $NaClO_4$), and ozonization.

Reviews

In an expert review covering 131 references (Kothny, 1973a), information is presented on Pb, Va, Hg, Se and B, the latter element specifically in relation to soil and water, the other elements more in association with air. Covering 234 references, the epidemiology of Cd, Cu, Hg, Pb and Zn has been reviewed by Bremner (1974), emphasizing physiological aspects. Leland et al. (1974) published a review, covering 259 references, in which are discussed trace element sources, trace elements in natural waters and sediments, biochemical transformations, and toxic effects in aquatic flora and fauna as related to human health. Heavy metals in relation to agriculture were discussed in a review, covering 68 references, by Huisingh (1974). Heavy metals in relation to aqueous systems were considered in part of a newly published book by Rubin (1974).

Organic matter interactions with heavy metals in natural waters have been reviewed by Singer (1974). Water pollution control treatments were discussed in a recent issue of the Journal of Environmental Science and Technology (October 1974) by a slate of distinguished workers. Problems associated with heavy metals in sewage sludge have been reviewed from the viewpoint of land application (Chaney, 1973a), and from that of food chain protection (Chaney, 1973b). The flow of heavy metals issuing from sewage sludge through soil with plants has been very thoroughly reviewed by Page (1973) covering 107 references. The relations of a number of trace elements, among which Cd, Pb, Zn, and Cu, to health and disease have been examined as functions of their presence in rocks, soil, water, plants, animals and man in a number of papers that appeared in the proceedings of a recent workshop (National Academy of Sciences, 1973a). Atomic absorption procedures for heavy metal analysis in waters have recently been reviewed in a book by Burrell (1974).

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(2) Bio-Rad Laboratories, Richmond, Calif. The mention of firm names and/or trade products does not imply endorsement or recommendation by the Dept. of Agriculture over other firms or similar products not mentioned.

CADMIUM

Analysis

Application of the carbon furnace associated with flameless atomic absorption has now become also operational for Cd (Ross and Gonzalex, 1974). So have several types of activation analysis (Jervis et al., 1974). Use of a deuterium continuum source and of the standard addition method to correct for background signal interference in atomic absorption spectrophotometry compared favorably (Yamasaki, 1973). The long half-life of Cd-109 has been useful in tracing Cd cycling through the environment (Van Hook et al.,1973).

Preparatory isolation of Cd, when the metal is present in very low concentrations, by liquid-liquid extraction may suffer from interference. Thus, extraction of Cd chelated by methyl isobutylketone with Na-diethyl dithiocarbamate ran into interference by Al. This was avoided by adding NaK-tartrate (Kaminski, 1974). An alternative would be the use of the quaternary amine, Aliquat 336-S, which preferentially chelated Cd as the iodide over a wide pH range (McDonald and Moore, 1973). Another chelating extractant is 2-mercapto-benzo-thiazole in n-butylacetate with systems buffered at pH 10. Addition of a large amount of Zn to water samples allowed for the quantitative removal of Cd with 2-mercapto-benzo-thiazol even if present at concentrations as low as 0.02 ppb (Doolan and Smythe, 1973). Still another method to pre-concentrate and isolate Cd prior to atomic absorption analysis is by using Na-H-Chelex 100 resin(3) at pH 7 (Baetz and Kenner, 1974).

Losses of Cd from aqueous solutions during storage in glass containers ran as high as 75% in 16 hours if Cd were present at concentrations smaller than 25 ppb (King et al., 1974). Borosilicate glass markedly absorbed Cd, while plastic materials did so to a smaller extent.

Sources

One of the most common sources of Cd contamination in soils and, perhaps, waters are phosphatic fertilizers. The Cd content of a great number of New South Wales (Australia) fertilizers ranged from 18 to 91 ppm, and that of superphosphate from 38 to 48 ppm. This Cd was as soluble as that from $CdCl_2$. Uptake by plants, especially subterranean clover, ranged to up to 7% of the available (0.1N HCl extractable) Cd present (Williams and David, 1973). In one experiment carried out by these authors, the percentages of added Cd recovered in the edible portions of beans, tomatoes, peas, cabbage and radish were 0.2, 0.2, 0.3, 2.5 and 2.9%, respectively. With rice and wheat, increasing the orthophosphate application to soil increased the yield by alleviating Cd toxicity without diminishing the Cd content (Koshino, 1973). This would point to a process of detoxification internal to the plant. Pyrophosphate, on the other hand, suppressed Cd uptake, while the uptake of P from this salt was too slow to decrease Cd toxicity internally. Results of studies with rye grass suggested that it was the tissue concentration of Cd <u>per se</u> that determined toxicity (Dijkshoorn et al., 1974).

Another well-known source of Cd for soils, plants and waters is sewage sludge. In Sweden, phosphatic fertilizers cause a greater Cd hazard than sewage sludge. The total amount of phosphatic fertilizers consumed in Sweden in 1971/1972 contributed about 10,000 kg Cd, but the total amount of sewage sludge about 1,300 kg Cd to that nation's soils (Stenström and Vahter, 1974). On the other hand, the fraction of total Cd present in the grain increased as the sludge application increased (Stenström and Lönsjö, 1974). The availability of Cd from sewage sludge increased with the length of the period of incorporation in the soil, and with other time-dependent factors. Also, at lower pH a much higher uptake of Cd from sewage sludge by wheat was observed than at higher pH (Linnman et al., 1973). The uptake of Cd by various crops from soils amended with sewage sludge enriched with $Cd\,Cl_2$ was studied by Bingham et al. (1973). It may be noted that the matrix of the Cd present in this sludge may have been different from that of the "native" Cd in the sludge. With particular reference to the Cd problem, annual sludge application in Sweden per hectare is limited to the equivalent of 1,000 kg of sludge containing 15 mg Cd per kg dry matter. In this light, the content of no less than 18 ppm Cd in soybean plants, of which 1 ppm was in their seeds when the plants were grown on a soil amended with 144,000 kg sewage sludge per ha, should be reason for concern (Jones et al., 1973b).

A more local, and often more serious source of Cd contamination than those mentioned above are zinc mines and smelters. The situation may be of particular concern if the smelters are located in the heart of a densely populated metropolitan area (Van Loon et al., 1973). In a series of papers from the Fukui Agricultural Experiment Station, Japan, the cycling of Cd was examined from

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(3) See footnote (2).

Zn mine drainage into a river from which water was drawn for the irrigation of rice. The resulting total Cd content in the soil ranged from 0.2 to 10 ppm in the 0 - 15 cm layer, while that of the rice was 0.02 to 1.8 ppm, without any apparent relation between the 2 factors (Takijima and Katsumi, 1973a). While Zn in soil showed a positive correlation, soil pH and Ca in soil showed a negative correlation with Cd uptake by rice. The Cd seemed to derive from CdS present in mine waste ores (Takijima et al., 1973a). Incubation of these ores in soil under submerged conditions increased Cd, Zn, Cu and Pb, especially in the presence of rice straw (Takijima et al., 1973b).

The Cd uptake by rice was suppressed by incorporating, in order of decreasing efficacity, Ca-silicate, Ca-phosphate or lime into the soil. A decrease in Cd solubility from soil in 0.1N HCl was noticed upon incubation especially of Ca-silicate (Takijima and Katsumi, 1973b). The removal of heavy metals from this soil by washing with 0.1N HCl proceeded in the order $Cd > Cu > Zn \gg Pb$. Liming reduced Cd uptake by 22% in the straw, and by 7% in the grain of rice. The Cd concentration in the unpolished grain diminished from 0.33 to 0.06 ppm when the soil was treated with Mg phosphate and Ca silicate (Takijima et al., 1973c). Near a lead smelter in Missouri, lettuce, radish and greenbeans were found to contain 34.5, 13.7 and 8.5 ppm Cd in the edible parts. In the same area, due to careless transport of ore by truck to the smelters, the maximum Cd level in roadside forage grass samples was found to be 4.3 ppm (Hemphill et al., 1973).

A general environmental source of contaminant Cd is coal. The Cd concentration in Illinois coal ranged from 0.3 to 28 ppm (Gluskoter and Lindahl, 1973). Precipitators were at least 90% efficient in preventing Cd from being aerially emitted from a coal firing power plant (Klein and Russell, 1973). Concentrations of Cd in coal, fly ash, residual fuel, oil and premium gasoline were measured to range from 0.7 to < 30, from 2 to < 100, from 0.003 to 1, and from 0.001 to < 20 ppm, respectively (Von Lehmden et al., 1974).

Drinking water has been named as a direct dietary source of Cd. A highly significant correlation was found between 15 municipal water constituents, of which 12 were metals including especially Cd, and a number of diseases, especially arteriosclerotic heart disease (Schroeder and Kraemer, 1974). Corroding house pipes and joints generally are the source of Cd in tap water. In one study with rats, no hypertension could be produced by providing Cd-enriched drinking water (Porter et al., 1974). On the other hand, the relations between hard water and hypertension, and between Cd and hypertension, may now have been linked together by an observed relationship between Cd and hard water (Perry and Perry, 1974). The hypertension - Cd issue remains a controversial one.

Other, more personal, sources of Cd intake that have come to be recognized are cigarettes (Elia et al., 1973), and coffee and tea (Horwitz and Vanderlint, 1974). These matters have been discussed in some detail in an excellent review dealing mostly with the medical aspects of Cd (Nordberg, 1974). The report emphasizes that the FAO/WHO recommendation of a daily intake not exceeding 70 μg Cd in order to avoid kidney disorders already implies the need of restricting certain foods in certain countries, even ignoring tobacco smoking.

Flow

Continuing studies on a Zn smelter in Australia involved modeling all the possible Cd flow paths from source to sink, thereby tracing the amounts of Cd deposited at the various nodes in the system (Triplett et al., 1974). The environmental flow of Cd in the Gary-East Chicago area of Northern Indiana is subject to a continuing, multi-disciplinary study yielding important data of benefit both to the cooperating steel and electroplating industries, and to quality preservation of air, water, soils and crops (Yost et al., 1974a and b). Industrial contamination with Cd may result in amazingly elevated substrate concentrations. This is shown in a sediment study near a Cd-Ni battery plant. In its proximity, the Cd concentration was as high as 32,000 ppm, mostly as $CdCO_3$, while 100 m away it still was 780 ppm in an organic milieu (Bondietti et al., 1974). In an excavation near Gary, Indiana, subject to both industrial and automotive inputs, Cd concentrations ranged from 0.32 to 3.4 ppm (Peyton and McIntosh, 1974). In Australia, the Cd concentration of a river near a smelter outlet amounted to 1.75 ppm, as against a background (uncontaminated) concentration of 0.00009 ppm (Doolan and Smythe, 1973b).

Contrary to most heavy metals, notably Zn, the mobility of Cd in soils and sediments is rather independent of pH, even at pH > 8, because of the absence or minor role of hydrolysis. For an aqueous environment theory predicted that the species $Cd(OH)^+$ would start appearing at pH > 7 (cresting at pH 10), while neutral, soluble $Cd(OH)_2$ would start being formed at pH > 8 (Hahne and Kroontje, 1973). This may partly explain the amazing mobility of Cd in the environment, even in nonacid soils, except in the presence of sulfide (Minagawa and Kamada, 1973). Studying 3 columned soils under conditions of saturated flow, Jurinak and Santillan-Medrano (1974) observed Cd to move faster than Pb. They developed a transport model, taking into consideration ion-pair formation, precipitation and acetate chelation. Once steady state had been reached, theoretical predictions following from the model agreed well with the results of measurements.

Although soil organic matter chelation has a relatively minor effect on the flow of native Cd in mineral soils (Haghiri, 1974), it may be of more importance in organic soil amendments like sewage sludge. Using a specific ion electrode to determine stability constants for Cd with humic acid, Cd ranked third after Pb and Cu. At pH 7, Cd could be displaced from humic acid by Ni > Zn ≐ Co>Sr (Bondietti and Sweeton, 1973). In a study dealing strictly with inorganic systems, the Cd-Ca exchange coefficients for aqueous suspensions of clay saturated with these cations amounted to 1.04, 1.01 and 0.89 for montmorillonite, illite and kaolinite (Bittell and Miller, 1974). Comparing the toxicity of a number of metals relative to corn grown either in an organic (11.4% C, pH 6.8), or in a mineral (0.6% C, pH 6.8) soil, root growth in the mineral soil was inhibited by the metals in the order Cd>Co>Ni>Cu>Pb, and in the organic soil in the order Cd>Co>Ni>Cu>Pb (Minami et al., 1973). Thus organic matter chelation of Cd, if it occurred, did not greatly alter the order of toxicity.

Accumulation

Biological magnification was evident with the waterplant Najas-Guadalupensis concentrating Cd by a factor of about 1000 relative to ambient water, where the Cd concentration was either 7, 90 or 830 ppb. While at the lower exposure levels the plant itself did not suffer, it then already had become toxic to sunfish and water fowl (Cearley and Coleman, 1973).

Studies on phytoplankton in Montery Bay, California, indicated that of all the heavy metals studied the concentration only of Cd decreased in water during peak production of plankton, even though the metal was much more concentrated in the Bay than farther out in the ocean (Knauer and Martin, 1973). Effect of dredging operations on concentrations of dissolved Cd have been studied in conjunction with tidal effects. Critical Cd levels for the species Chlamydonomas and Euglena were found to be as high as 0.1 and 10 ppm, respectively, while maximum Cd concentrations from the dredged (i.e., higher Cd) areas were only 0.002 and 0.040 ppm (Kneip et al., 1973). Elsewhere (Kerfoot and Jacobs, 1974), Cd levels in water safe with respect to shellfish for human consumption were estimated to vary from 0.2 to 1.5 ppb Hg, depending on the species.

With regard to uptake of Cd by plants from soils, a background value off < 0.3 ppm for Cd in wheat and perennial grasses in the Eastern US has been proposed on the basis of a large number of analyses (Huffman and Hodgson, 1973). No regional pattern seemed to pertain to these Cd values, or to their corresponding Zn/Cd ratio values. In a study involving different crops, species differentiation with regard to Cd uptake showed the other lettuce>radish tops>celery stalk>celery leaves≫green pepper>radish roots (Haghiri, 1973). Uptake of Cd by oats decreased as the cation exchange capacity of the soil increased, while organic matter chelation was considered a minor factor (Haghiri, 1974). Haghiri also showed that when the concentration of Cd at high levels was raised further, the uptake and translocation not only of Cd, but also of Zn by soybeans increased. Koshino (1973a) found that Zn added in high concentrations to soil boosted not only the uptake of Zn, but also that of Cd by rice. Francis and Rush (1974) observed that more Cd was taken up by bushbeans from solutions containing 5, then from those containing 1 ppm Zn, without apparent Zn toxicity. This reviewer, working with solution cultures of radish, generally agrees with the above observations (Lagerwerff, 1972). He noted a slight cracking of the root cortex, suggesting the possibility of rather unimpeded inflow of Cd and Zn under conditions where either one was present in high concentration i.e., 100 ppb with Cd, and 400 ppb with Zn. Perhaps the formation of phosphates of Cd and Zn in the phospholipid layers of cell membranes results in a physical decay of these traditional barriers to ion influx, allowing their increased rate of entry. At any rate, and contrary to experience with animals and humans, Zn seems to be a poor counteractant with regard to the uptake of Cd by plants.

Solution culture studies with bush beans showed that raising the levels of Ca and N resulted in a decrease in Cd uptake (Francis and Rush, 1974). Also, Cd uptake was many times greater from nutrient solutions containing an Fe chelate, such as Fe DTPA, at pH 4.6 than at pH 6.5. In the presence of the Fe chelate, the translocation rate from roots to tops was higher at the higher than at lower pH. Equal translocation rates prevailed at the 2 pH's in the absence of Fe DTPA. In soil cultures with Japanese millet, the same authors found a strong suppression of Cd uptake from both $CdCl_2$ and CdO in acid soils after liming. When corn was grown on a sandy soil amended with either Cd or Ni in equal concentrations and limed in its earlier stages to pH 6.8, it suffered much more severe retardation from Cd than from Ni (Traynor and Knezek, 1974). In all likelihood, at the prevailing pH Cd was not, but Ni was precipitated. This is because, at equal concentrations, Ni would have been the more toxic metal.

In comparing the effects of the chlorides of Cd, Co, Cu and Zn added to soil cultures in concentrations ranging from 15 to as high as 195 ppm, on nodulation of 6-week old red clover, the order of toxicity was found to be Cd>Co>Cu>Zn (McIlveen and Cole, 1974). In solution culture studies with corn, Cd was found to be toxic even at 1 ppm (Koeppe et al., 1974). Koeppe et al. found evidence of a decrease in chlorophyll content and abnormalization of mitochondria, resulting in inhibitions of substate oxidation and in uncoupling of phosphorylation. Regarding the affinity of Cd to mitochondrial membranes, these authors found the following order: Cd = Zn>Ni>Mn>Co. Elsewhere (Czuba and Ormrod, 1974), ozone-induced phytotoxicity of lettuce and water cress was increased by Cd, and more so with Cd absorbed through the roots than through the leaves.

Working with a soil spiked with Cd to the rather unusual levels of 40 and 200 ppm, the metal was found to accumulate in the roots of carrots>peas>lettuce>cauliflower (John, 1973). The 2 soil levels of Cd caused Cd levels in carrots of 1,738 and 6,122 ppm, which makes one wonder about this crop's toxicological stamina. The presence of Cd in soil even at a concentration of 1 ppm appeared not to affect nitrification (Tyler et al., 1974).

Reviews

An expert overall discussion of the Cd problem has been presented by Fleisher et al., (1974) in a contribution that appeared as the last paper in an issue entirely devoted to a conference on low level Pb toxicity. The 70-page article, covering 261 references, contains sections on rock, coal, oil, air, aerial emissions, soil, water, plants, and animals, on the flow of Cd due to plating, and due to mining, smelting and metallurgy of Zn, on the relationship of Cd to incineration and combustion of waste, and to application of sewage sludge to land, and on analytical techniques. An equally high-quality overview deals with the Cd issue as a societal problem, devoting 15 of the 473 pages to Cd in soil, plants and animals, water and sediments (Fulkerson and Goeller, 1973). A recent draft report (Sanjour, 1974), while predominantly directed towards furnishing basic data to be used in formulating regulatory policy, offers good sections on average intakes, threshold toxic dose, contamination of air, soil, water and crops, and, especially, sewage sludge. Research suggestions are offered. Among the invaluable annotated bibliographies currently issuing from the Toxic Materials Information Center of the Oak Ridge National Laboratory, the one on Cd is of great help to heavy metal devotees (Copenhaver et al., 1973). It contains 938 abstracted citations in all areas of environmental Cd research.

COPPER

Analysis

Analyzing aqueous systems, Cu selective electrodes were of use in the 10^{-6} to 10^{-9} M concentration range (Blaedel and Dinwiddie, 1974). While the response was slow, the interference due to the presence of even 100-fold excesses of H, Ca, Zn, Al and Fe caused errors that did not exceed a factor of 2. Of 3 soil extracting agents viz., 0.4 N HNO_3, 0.05 M EDTA and 0.1 N HCl, only the latter was found to correlate with Cu absorbed during 4 days by Aspergillus niger (Schlichting, 1973).

Sources

The growing demand for Cu has increased surface mining of this metal. This is contributing to existing environmental contamination at mining sites predominantly caused by strip mining techniques (Disraeli, 1973). The spreading of swine manure, rich in dietary Cu supplemented because of antihelminthic effects, is a notable means of regional contamination of agricultural land. This Cu normally is chelated, as most Cu in the presence of organic matter is, and the rate of uptake of the chelate depends strongly on soil conditions and plant species (Hedges et al., 1973).

Smelting activities often constitute a more widespread source of contamination of soil and water with Cu than mining. The industry, aware of this fact, is considering steps to abate Cu emissions (Gobel, 1974). It does not seem quite clear why the toxic effect of Cu on several grass species grown on Cu mine tailings could be partially offset by the application of small amounts of Al (Erbisch, 1974). The stabilization of Cu mine tailings with giant Bermuda grass did not require such an amendment (Day and Ludeke, 1973).

Fallout from power plants constitutes a source of Cu contamination comparable to that from Cu smelters. Modern precipitators are 90% effective for Cu and many other metals (Klein and Russell, 1973). Concentrations of Cu in coal, fly ash, residual fuel oil and premium gasoline were found to range, in ppm, from < 0.4 to 10, from 33 to 300, from 0.2 to 1, and from 0.005 to 3.8, respectively (Von Lehmden et al., 1974).

Older types of high tension voltage wires are a rather infrequent source of Cu contamination (Hemkes and Hartmans, 1973).

Soil

Firm bonding of Cu to soil organic matter largely determines the soil chemistry of this metal. Apparent stability constants determined with specific ion electrodes, describing the bonding of Cu, Pb and Cd by humic acids, are of the same general magnitude as those involving citric and oxalic acids, with the order Cu>Pb>Cd (Bondietti and Sweeton, 1973). Elsewhere (Stevenson et al., 1973), the formation constants between Cu and humic and fulvic acids, as determined by a modification of the Bjerrum potentiometric method, was comparable to those observed for synthetic polycarboxylic acids. The overall formation constants for the 2-step process ranged from 2.5×10^{-4} to 7.9×10^{-3}. After addition of Cu as the natural polyflavonoid complex to surface samples of nine Wisconsin soils, the extractable contents of both Cu and Mn increased, while that of Zn decreased (Dolar and Keeney, 1974).

Attempts at fractionating soil Cu in terms of bonding strength were strictly empirical: soil solution Cu and exchangeable Cu by extraction with 0.05M $CaCl_2$; Cu weakly bound to specific inorganic adsorption sites by extraction with 2.5% acetic acid; organically bound Cu by extraction with M $Na_4P_2O_7$; Cu occluded by oxides with acid (pH 3.3) oxalates; and residual, e.g. clay-lattice occluded, Cu by treatment with HF (McLaren and Crawford, 1973a).

Free oxides of Mn are important scavengers for Cu. Comparing individual soil constituents (McLaren and Crawford, 1973b), the adsorption maximum for Cu followed the order: Mn oxides>organic matter> Fe oxides>clay minerals. Adsorption of Cu by whole soil was of the Langmuir type, with a maximum at pH 5.5 varying between 340 and 5,780 μg per g, mostly due to Mn oxides and organic matter. Where the Cu concentration in the equilibrium solution was < 0.4 μg per ml, specific adsorption prevailed over non-specific adsorption. Between 2 and 21% of total Cu in 24 soils exchanged isotopically. Most of the organically bound Cu was not isotopically exchangeable (McLaren and Crawford, 1974).

Strong retention of Cu occurred with certain clay mineral species, especially vermiculite, as measured by extraction with N NaCl. Kaolinite and montmorillonite showed easy release of Cu using the same extractant (Kishk and Hassan, 1973). In an excellent paper (Steger, 1973), the adsorption has been described of Cu, mostly as Cu^{2+} and $Cu(OH)^{+}$ in the pH range of from 4.3 to 5.9, in terms of an empirical Langmuir-type equation. Two kinds of adsorption sites were recognized, viz., lattice hydroxyl groups located at defective crystal sites and edges, and organic matter associated sites. It is speculated that bentonite loaded with organic matter may be best to adsorb Cu and other undesirable metals from waste waters. Results of a study in marine sediments and clay minerals coated with organic matter points in the same direction (Meyers and Quinn, 1974). Using solutions in which were suspended semipermeable bags with mineral and amorphous inorganic materials coated with Co and Cu, the release of these metals by desorption decreased in the order: Fe-Al hydroxides>bentonite>soil clay fraction>biotite>kaolinite. This was monitored by their uptake by clover from the solution ambient to the bags (Kabata-Pendias, 1973).

Plants

While one reference (Horne and Goldman, 1974) mentioned that blue-green algae in a California lake showed suppressed N fixation due to the presence of 3 μg Cu per liter, other reporters (Manahan and Smith, 1973) held that 30 to 40 μg Cu per liter provided optimum growth with Oocystis and Chlorella algae, respectively. In a solution containing 64 mg Cu per liter, photosynthesis of Chlorella was more impaired than respiration, while chlorophyll and sulfhydryl contents were reduced (Cedenoma and Swader, 1974). Algae species isolated from Cu contaminated lakes in Canada proved to be more tolerant than similar species cultivated in vitro (Stokes et al., 1973).

As with the chemistry of Cu in soil, so the uptake of Cu from soil strongly depends on organic matter complex formation. Uptake of Cu by tomato from organometallic complexes formed by fermentation of alfalfa was higher than from equivalent amounts of $CuSO_4$ added to soil (Piotrowska, 1973). Similar results with bush beans grown on a calcareous Hacienda loam were found when using EDTA (Wallace and Mueller, 1973).

The presence of 5 ppm Cu as CuEDTA caused more accumulation of Cu in leaves of the beans than did 50 ppm Cu as $CuSO_4$. On the other hand, the mineral content of forage plants growing on organically rich tundra soil was inadequate for reindeer (Scotter and Miltimore, 1973). This may have been due to a deficient level of total Cu, viz., 1.5 μg per g of soil.

Workers in Russia found N fertilizers to increase, but P fertilizers to decrease Cu response by pasture grasses, irrespective of whether the Cu concentration of the soil was high or low (Morugina and Chuikov, 1973). Again, the availability of Cu in a sandy loam was found to decrease upon the addition of phosphate fertilizer (Badanur and Venkata, 1973). Internal tolerance of plants to Cu, promoted by P, played a more important role than exclusion of Cu in pot experiments with tree seedlings (Smilde, 1973). In the latter study, P appeared to interfere with root-to-shoot translocation of Cu, Fe and Al, but not of Zn and Mn. Low levels of Cu strongly increased P uptake, because Cu stimulated the activity of phosphatases and glycolytic enzymes participating in P absorption and translocation (Stasauskaite and Navaitiene, 1973).

Scotch pine, white pine and red maple were found to take up Cu through the roots as well as through the foliage. Concentrations of Cu in the trunks were found to be as high as 1,100 ppm with contaminated specimens, as compared to 15 ppm with uncontaminated controls (Weidensaul, 1974).

Fertilization of unlimed soils with Cu significantly increased Ca uptake by lupine and broad-beans (Zhiznevskaya and Borodenko, 1973). The stimulating effects here noted may perhaps simply be ascribed to alleviation of a Cu deficiency. Indications that supplying N would influence the uptake of Cu by oats and barley (Thiel and Finck, 1973) might be a matter of pH lowering due to fertilizers. Interaction between Fe and Cu is well known. In studies with tropical foliar crops, the Cu content decreased in 3 out of 4 cases where Fe was added at the 1 ppm level to nutrient solutions used to irrigate sand cultures (Schmidt et al., 1973). Studying macroscopic and microscopic effects on legumes of high doses of B (30 - 90 ppm), Cu (5 - 10 ppm), Mn (50 - 150 ppm) and Zn (50 - 150 ppm), only Cu appeared to be related to Fe deficiency chlorosis (Vogel, 1973). Studying the interactive effect of Cu on Fe from Fe EDTA or Fe tartrate on beans, it was found that high Cu induced chlorosis by precipitation of Fe as $Fe_3(PO_4)_2$ in the roots (Daniels et al., 1973).

In an organic soil contaminated by Cu and Zn from a brass factory, highly significant negative correlation coefficients existed between Cu plus Zn concentrations on the one hand, and respiration, urease activity and acid phosphatase activity on the other hand (Tyler, 1974).

Reviews

In a review paper covering 66 references, it was pointed out that the use of Cu containing fungicides or swine manure may increase the concentration of Cu in pasture grasses to 30 ppm. This is the limit for sheep, a Cu sensitive animal. Annual soil applications of 7 kg Cu per ha was deemed a practice not to be continued longer than 5 to 10 years (Baker, 1974). Coppenet (1974) reviewed the agronomic consequencies of the application of liquid pig manure to soil.

LEAD

Analysis

Interference by Fe in the atomic absorption spectrophotometry of Pb could be prevented by prior isolation of Fe with acetylacetone and chloroform (Balraadjsing, 1974). In wet ashing of foodstuffs followed by atomic absorption spectrophotometry, certain matrix elements may interfere in the determination of Pb. A procedure is described in which Ag is added to the strong acids assay, followed by perfusion with H_2S. Lead, coprecipitating as the sulfide, is then removed from the assay by redissolution prior to analysis (Boppel, 1974). The determination of naturally occurring variations in stable Pb isotope abundances have been used as a fingerprint technique to identify sources of contamination. Thus, in the New Lead Belt, Missouri, the stable Pb isotope composition in dust and topsoils near Pb smelters showed a set of values comparable to one describing the ore but distinctly different from another such set characterizing gasolines, traffic fumes and roadside soils (Rabinowitz and Wetherill, 1972). Using the same technique, a similar distinction was possible with a smelter near Benicia, California. In general, controversies have arisen around the applicability of this method. Another "fingerprint" technique is based on the separation and pre-concentration of Pb compounds in soil without compound conversion, followed by their analysis (Skogerboe and Olsen, 1974). Finally, cathodic stripping has been developed as a sensitive polarographic approach to the analysis of Pb after its earlier deposition as a monolayer of PbO_2 (Kinard and Propst, 1974). As the method is applicable only to metals that deposit as sparingly soluble oxides, it is relatively free from interferences.

Source

Combustion products of leaded gasoline are now being viewed as the most general cause of environmental Pb contamination in Europe (Sapetti and Arduino, 1973; Pertoldi et al., 1973; Horak and Huber, 1974; Bini, 1973a) and in Australia (Wylie and Bell, 1973). In this connection, concern for public water quality has prompted some studies on urban street runoff (Nightingale, 1974). In one such study, runoff from the edge of a roadbed averaged 5.5 mg Pb per liter (Newton et al., 1974). In comparing the Pb concentration gradient with distance from traffic in wooded land and in cropped land, it was apparent that a lesser gradient existed in the latter case (Rolfe, 1973a). This supports the hypothesis that woodland border strips are effective barriers to Pb dispersal from highways.

In a study involving roadside trees, needles of conifers exposed to 24,000 cars passing by per day contained up to 700 ppm Pb (Bini, 1973b). In another such study (Ward et al., 1974), sharp differences occurred between specimens upwind and downwind from traffic, and between inner and outer bark. The latter observation would suggest that most traffic Pb entered trees through the roots. A study by these workers of the Pb content of year rings showed an increase of from 50 ppm in 1910 to >1,000 ppm in 1970 with plane, chestnut and ash, but less so with oak and, especially, elm. Shoulders of roads used for transportation of metal-rich ores may be exposed to additional heavy metal input if the ore is inadequately containered (Hemphill et al., 1974). An additional roadside input of heavy metals would occur where crushed, worked ore is used for road hardening.

Emissions from metal ore smelters are the next most important cause of environmental Pb. Occasional high rates of Pb fallout around two urban lead smelters in Toronto, Canada, resulted from large-particulate emissions from fugitive sources rather than from stack emissions (Roberts, 1974). In this instance, Pb in dustfall, and, therefore, in soil, vegatation and outdoor dust, decreased exponentially with distance from the 2 smelters. Fallout from smelters in the Missouri New Lead Belt resulted in elevated Pb and Zn concentrations in the A_0 litter layer and in the top one-inch layer of soil. The majority of Pb, however, was present on the surface of leaf fall (Bolter et al., 1973).

Flow

The environmental flow of Pb as a result of contamination caused an increase of Pb in the food chain even in high-altitude ecosystems (Hirao and Patterson, 1974). In central England, dry fallout rather than wet fallout was judged to be the major source of environmental Pb. Within the same area, heavy metal composition of rain was different from that of fly ash (Hallsworth and Adams, 1973).

Aerial fallout of Pb at various latitides in the Atlantic ocean showed a distinct increase with increasing distance from the equator (Chester and Stoner, 1973). As the same has also been observed to take place over continental areas, the consequences of this trend in terms of environmental exposure of humans and animals in arctic and subarctic areas is a matter that no longer can be ignored. With aerial contaminants funneling into these regions, and depositing on tundra grasses with a high moisture content maturing over a long growth period, the effect on the metal burden of the heavily meat dependent population has acquired analytical detectability.

The aquatic environment is a major vehicle for the present and potential flow of heavy metals from watersheds (Rolfe and Edgington, 1973), such as those in which are located the mines and mills of the Missouri New Lead Belt. The transport is mainly in terms of finely ground particles which may escape reservoirs for flotation and tailing, especially during periods of turbulence. In addition, mill effluents sometimes contain nutrients encouraging algal growth, which in turn may cause accumulation of Pb in significant quantities, especially near the source. Dissolved metals per se do not constitute a problem (Gale et al., 1973).

In comparing total Pb output from a watershed with total Pb input, only 2 to 3 percent appeared to be left in the water. This would indicate a large build-up of Pb in the ecosystem under study (Edgington and Wolfe, 1973).

The annual rates of increase of Pb in sea bottom sediments of the Santa Monica, San Pedro, and Santa Barbara, California, basins were 0.9, 1.7 and 2.1 µg per cm^2, as compared with 0.24, 0.26 and 1.0 µg per cm^2 representing background, i.e., pre-contamination era rates (Chow et al., 1973). The concentration of Pb in sediment layers cored down to 50 cm increased 20-fold over the past 100 years due mostly to gasoline combustion (Crecelius and Piper, 1973). As with Cd, the flow of Pb into the human system by way of drinking water has now been related to its hardness (Crawford and Clayton, 1973).

Soil

A study in soil development in Wales revealed a chronological relationship between 19th century Pb contamination and known mining activities in that period (Davies and Lewin, 1974). The authors concluded that "the fact that alluvial materials do incorporate pollutants in this way must mean that they are available for release to rivers and subsequent distribution by them as banks are eroded. A 'pollution pulse' is succeeded by continued pollution at a decreasing level over a considerable period of time." With regard to heavy metal uptake by agricultural crops, the same argument applies when the soils on which they grow during some period in the recent past had been contaminated.

The exchange behavior of Pb present in low concentrations in kaolinitic, montmorillonitic, and illitic soils pretreated with either Al or Ca, and kept at a number of salt levels, agreed with mass-action law principles. The mean values of the Gapon exchange coefficient describing the distribution of ions between the adsorbed solution phases of the three soil types were 0.31, 0.11 and 0.24 for Pb-Al systems, and 4.13, 4.97 and 11.1 for Pb-Ca systems (Lagerwerff and Brower, 1973). A study on equilibrium relationships in soil of various Pb compounds included Pb, PbO, Pb_3O_4, PbO_2, $PbSO_4$, $Pb_3(SO_4)_2$, $PbO{\cdot}PbSO_4$ and $PbCO_3$. Not included were organic matter complexes of Pb (Lindsay, 1973). The importance of the latter was pointed out in relation to certain isolated humic acids (Hildebrand and Blum, 1974). As Pb ages in soil, such complexes may gain in importance.

Applying aerobically composted domestic refuge, experimentally marketed as "Cyclelite TM humus 9" (pH 6.8-7.2), to a silt loam at rates of from 5 to 50% by volume, growth of corn, soybean, ryegrass and snapbean decreased by as much as 50% because of immobilization of inorganic N and P. Whether the humus was freshly produced or had been incubated for 6 months, no increase occurred in Pb uptake by any of the 4 crop species, although the humus contained 300 ppm Pb (Liebhardt and Koske, 1974). Besides organic matter, another strong Pb adsorbent in soil is ferric hydrous oxide. As much as 0.28 moles of Pb per mole of Fe in such a form was found to be sorbed from solutions at pH 6. The adsorption, strongly dependent on pH, is believed to be specific (Gadde and Laitinen, 1973a).

Plants

Growth and Pb uptake by corn and alfalfa were measured on Chester silt loam at 2 soil pH levels and 4 soil Pb levels in the course of a greenhouse study. A double Pb contamination hazard existed, viz., proximity of heavy traffic and fallout of particles of leaded paint. Control treatments were also executed outside, i.e., in the absence of leaded paint. While the fallout of Pb was almost 3 times heavier inside than outside, the aerosol Pb concentration was almost twice as large outside than inside. The latter was reflected by the tassels of corn, apparently the only plant organs capable of monitoring aerosol movement. All other plant parts, especially in the upper plant section, reflected the heavier Pb fallout inside than outside, while the lower plant parts also reflected increases in soil Pb content. Because more Pb was removed by washing alfalfa leaves as more Pb was taken up from the soil by these plants, translocation of Pb seemed to occur from roots to tops (Lagerwerff et al., 1973). Russian work would indicate that increasing the Pb content of a micro-nutrients containing fertilizer from 0.3% to 2% had no adverse affect on corn and wheat grown on calcareous soil, although the Pb content of the plants was high (Mokriyevich et al., 1973).

Between 70 and 96% of Pb taken up by perennial ryegrass from Pb enriched soil was retained in the roots, and did not reach the shoot (Jones et al., 1973a). With S added to the soil, the Pb retaining capability of ryegrass roots was greater than without S added, pointing to an interaction between Pb and S taking place inside the roots (Jones et al., 1973c). Herbage, harvested annually since 1920 at Rothamstead, did not show any noticeable increase in Pb content (Williams, 1974). On the other hand, when the content of native Pb in a soil, i.e. 65 ppm, was boosted by adding $PbCl_2$ to 695 ppm Pb, the Pb content of whole beet plants increased by a factor of more than 3, and of whole lettuce plants by a factor of 6. Boosting the soil Pb content from 65 to 6,680 ppm resulted in a 20-fold increase in the Pb content of whole potato and carrot plants (Crudgington et al., 1973). Studies in Germany with barley growing in a silt loam (pH 5.4) enriched with 40 ppm Pb from $Pb(NO_3)_2$ also showed a strong response, viz., from 8 to 578 ppm (Wagner and Siddiqi, 1973).

An unusual strong response was noted with crops in Nova Scotia (MacLean and Langille, 1973). With Pb concentrations in the soil varying from 8 to 352 ppm, those in the vegetation ranged from 0.8 to 185 ppm. Uptake of Pb by 2-year old seedlings from 3 selected tree species grown on 3 soil types adjusted to 5 soil Pb levels (0-600 ppm) indicated a reduction of Pb uptake by up to 50% when phosphate was added in amounts of up to 340 kg per ha (Rolfe, 1973b).

Studies on young corn plants exposed to Pb in hydroponic solutions showed that in the roots Pb crystals accumulated in that part of the cell wall that was adjacent to the plasmalemma. Similar deposits were observed in stems and leaves (Malone et al., 1974). In a strikingly similar manner, bacterial cells took up substantial quantities of Pb which was retained by the cell membrane, very little of it reaching the cytoplasm. Also, the lipid content of Pb treated bacterial cells was much lower than that of the controls (Tornabene and Edwards, 1974). Leakage of intracellular materials from Pb treated cells pointed to irregularities in the cytoplasmic membrane, perhaps due to the formation of Pb phosphate at the expense of phospholipids. Corn roots were observed to exudate material that could complex Pb and so absorb it (Gadde and Laitinen, 1973b).

Behavioral patterns in response to Pb may differ between plant species. At lower Pb levels, i.e. < 20 µg Pb per plant, corn was more sensitive than soybean, but at higher levels, i.e., > 100 µg Pb per plant, soybean was more sensitive than corn. At 250 µg Pb per plant, photosynthesis was down to 10% with soybeans, and to 47% with corn. As a similar trend was observed with transpiration, the inhibitions may have been partly related to an increase in stomatal resistance (Bazzaz et al., 1974).

Turning to smaller species of plants, a 50% growth reduction was observed with 3 different algae when cultured in nutrient solutions containing from 15 to 18 ppm Pb (Malanchuk and Gruendling, 1973). Such concentrations, however, are at least 50 times higher than those found in soil solutions even of contaminated soils. Examining the uptake from solutions by lichen of various heavy metals, Pb was absorbed at a rate exceeded only by that of Fe: $Fe \gg Pb > Cu > Ni \approx Zn > Co$. The observed sequence was in accord with cation uptake mechanisms involving ion exchange modified by metal complex formation (Puckett et al., 1973). In moss leaves with 50 ppm Pb as a result of uptake, Pb was bound in the nuclear membranes as a diffusible complex (Skaar et al., 1973). It is perhaps due to this mechanism that the cytoplasmic concentration of Pb can be kept below a level otherwise injurious to mitochondrial and other Pb-sensitive cytoplasmic functions. Studies on rat liver indicated that mitochondria accumulate Pb like they do Ca. In the mitochondria, Pb prevented ATP synthesis by hydrolyzing it. Also, Pb interfered with trans-membrane transport of ions, formed complexes with SH-group containing mitochondrial enzymes, and reacted with phosphates, thus causing cell walls to collapse (Walton, 1973). Chlorophyll functions also were impaired by Pb (Bazzaz and Govindjee, 1974; Fiussello, 1974).

Reviews

Good literature reviews on Pb came into print. One deals with the soil-plant system (Zimdahl and Arvik, 1973), while another one briefly details the ecological flow of Pb from source to sink (Chow, 1973). The latter report covers aerial pathways and human impact of Pb. An equally recommendable review deals with toxicity, sources, and atmospheric, hydrospheric, and lithospheric aspects of Pb (Shukla and Leland, 1973). The literature is covered through 1971 by 118 references.

MANGANESE

Analysis

The atomic absorption spectrophotometry of Mn was recently discussed in conjunction with that of other metals (Aoba and Sekiya, 1973). This method is only moderately sensitive.

Sources

Although Mn toxicity, like Al toxicity, often is an acid soil problem, the literature is presently pre-occupied with steam sterilization of greenhouse soils and waterlogging of agricultural land as causes of the occurrence of excess Mn. Steam-sterilization induced increase in Mn concentration was found to be toxic to carnations. As usual, the trouble could be overcome by raising the pH (Ishida and Masui, 1973). Similar events have been reported with regard to lettuce in Ohio (Bauerle, 1973). Using isotope dilution techniques, flooding was found to increase the availability of Mn and Zn to rice because of reduction of the corresponding oxides (Tiller and Wasserman, 1974). In dune slacks rich in organic matter, the availability of Mn and Fe increased when flooding occurred, i.e. in winter, spring and early summer (Jones, 1973b).

Soil

Because of the polyvalent nature of Mn, the availability of Mn is well known to be linked to changes in Eh and pH of the soil (Yamane, 1973; Gotoh, 1973). Flooding of 6 Manitoba soils caused the occurrence of a Mn_2O_3-MnO_2 redox system for Mn, but organic matter chelation for Fe, the chelate carrying a negative electric charge (Olomu et al., 1973). Upon reclaiming such soils, Fe-Mn oxide concretions were formed, mostly in the B horizon of the arable soil and in the A horizon of the forest soil (Orel'skaya, 1974). Extracts of leaf and needle litter deposited on the forest bottom of teak, bamboo, Eucalyptus and wild curry stands caused downward movement of Mn in light soils, but Mn retention in columns of heavier soil (Hadimani et al., 1974). Humic, not fulvic acid, was believed to retain Mn in certain high organic matter soils.

In the presence of organic matter, Fe and sulfidic compounds, the true setting for a swamp, the effect of the Eh - pH relationship in soil on Mn availability becomes even more complicated (Macleod, 1973). Moreover, microorganisms are active soil factors, especially at elevated temperatures (T'Engh, 1973). Even Mn-EDTA added to solution cultures of barley is broken down by microorganisms near or at the root surface, resulting in increased uptake of Mn (Barber and Lee, 1974). Liming still is the best known prevention of Mn reduction (Gupta et al., 1973).

It is possible that P is sometimes implicated. Soil cultures of 2 desert shrub species, upon sterilization, were P deficient and dropped in yield, possibly because symbiotic mycorrhizae necessary for P absorption were killed off. Alternatively, as both Mn and Fe increased in concentration due to the steaming, P may have been precipitated as an Fe or Mn salt. This did not occur with noncalcareous soil supplied with P (Wallace et al., 1973b).

Plants

Genetic factors representing Al and Mn tolerances in plants often are related. Sometimes, Mn and Al toxicity symptoms, such as marginal chlorosis (Vlamis and Williams, 1973), and purple discoloration of leaf tissue, respectively, develop in one and the same species grown on an acid ($pH < 5.5$) soil (Foy, 1973). Species differences may occur. Thus, Atlas 66 wheat from North Carolina was more tolerant to Al than was Monon wheat from Indiana, but for Mn, tolerances were reversed (Foy et al., 1973). Differences in response to excess Mn were also observed with oats (Brown and Jones, 1974).

With cotton, toxic levels of Mn caused increased activities of peroxidase and polyphenoloxidase, and decreased those of catalase, ascorbic acid oxidase and cytochrome c oxidase, while suppressing respiration and ATP production (Sirkar and Amin, 1974). Lucerne suffered from Mn toxicity when grown not only in waterlogged soils, but also in soils subjected to extended hot and dry spells. In both cases, liming corrected these limitations (Siman et al., 1974).

Interaction of Fe and Mn may result in Mn deficiency, as has been noted with peach trees (Rogers, 1973 and 1974). The situation was remedied by spraying the foliage with Mn ethylenediamine hydroxyphenyl acetate.

Reviews

Covering 555 references through 1971, a recent review deals with Mn in the ecosystem, plants and soil, air and man. Epidemiological, physiological and biochemical effects of Mn also were discussed (National Academy of Sciences, 1973). Iron-Mn interactions in alkaline soils with regard to fruit trees have been reviewed by Gilger (1974).

MERCURY

Analysis

Quantitative determination of Hg is difficult. This is due partly to the many forms in which the metal may occur, each requiring a specialized analytical approach, partly to the relative ease of both biological and nonbiological interconversion of these forms, and partly to the volatility of all but a few compounds of Hg.

Loss of Hg from dilute solutions during storage in glass containers could be prevented for periods up to 5 months by dissolving the Hg salt in a solution consisting of 0.01% $K_2Cr_2O_7$ in 5% KNO_3, and not in solutions of either one of these compounds alone, or in a H_2SO_4 solution of $KMnO_4$ (Feldman, 1973). Studying the volatility of Hg from different solutions, the following order was noted: aqueous>0.1n H_2SO_4>0.1N HNO_3>mM KI>0.1N KCl>mN cysteine, no Hg loss occurring from the last solution because of precipitation (Dokiya et al., 1974).

The quantitative recovery of Hg from HgS was attempted by treatment with aqua regia (Jacobs and Keeney, 1974a). This is somewhat surprising because of the known volatility of $HgCl_2$ formed if HCl is used as a digesting agent. The determination of Hg in meat and soil (Deitz et al., 1973), and in plant material and water (Kiekens et al., 1973) was attempted with concentrated HNO_3 and H_2SO_4, and V_2O_5 as a catalyst, without using condensors. The temperature was carefully monitored. The temperature must exceed about 140°C after the addition of H_2SO_4 in order to break the alkyl-Hg bond. This is necessary for the subsequent reduction of Hg^{2+} to Hg° with $SnCl_2$ or $SnSO_4$ to take place. A temperature of 150° C is the limit above which volatilization may occur. Fluorometry was another method applied to determine Hg (Holzbecher and Ryan, 1973). The method suffers from interferences.

Two attempts were aimed at increasing the sensitivity of the determination of inorganic Hg. Both are based on the collection of Hg released from, or present in an intermediate step prior to the final reduction. In one method (Harsanyi et al., 1973), the Hg released as Hg° vapor upon reduction by $SnCl_2$ of large volumes of sample was trapped in a small volume of a solution of $KMnO_4$ in dilute H_2SO_4. This, in turn, was reduced in a subsequent step. In the other method, (Olafsson, 1974), Hg° vapor obtained as before was amalgamated by Au, and subsequently released by programmed heating.

Various new methods are under development to determine monomethyl Hg. Application of pulse polarography resulted in a 2-step process, indicating, first, formation of the CH_3Hg^+ radical on the electrode surface, and, second, its reduction to Hg° and CH_4. The first polarographic wave so caused has analytical capability (Heaton and Laitinen, 1974). Methyl-Hg determination was also attempted by gas/liquid chromatography (Jacobs and Keeney, 1974b) and by flameless atomic absorption (FAA). The latter was performed by first isolating it in benzene, from there in a cysteine-acetate solution, which in turn was reduced by hydroxyl amine hydrochloric acid prior to routine Hg° vapor development with $SnCl_2$ (Bisogni and Lawrence, 1974). Still another way to determine CH_3Hg^+ salts was by the microwave-plasma emission method, as used in an outstanding study involving examination of the edible portions of vegatables grown in 3 soils treated with either $HgCl_2$, CH_3HgCl, phenyl-hg acetate or CH_3Hg dicyandiamide. Little volatilization occurred from the soil, and the plants methylated only little Hg in accumulating it (Bache et al., 1973).

The determination of total Hg by volatilization using the carbon rod atomizer technique has been further refined by instantaneous collection of the Hg vapor on the inner surface of a porous, gold plated atomizer tube. It is heated in the subsequent step of determining Hg by FAA (Siemer and Woodriff, 1974). Considering the many different approaches presently being tried out, a round-robbin to cross-check results obtained with the use of Hg203 proved to be valuable (Heinonen and Suschny, 1974).

Sources

Five sources of environmental contamination with Hg have recently been emphasized. First, natural contamination from geothermal sources in New Zealand, small but continuous, seemed to have caused inland waters to contain enough Hg so that trout contained 0.5 mg Hg per kg fresh weight, which is considered to be the limit for market fish (Weisburg and Zobel, 1973). Second, the purification of Au bearing ore by amalgamation of Au with Hg has caused Hg containing effluents to reach natural waters (Walter et al., 1973). It has caused concern about the acceptability for human consumption of locally caught fish.

Third, even in remote areas of the Great Smoky Mountains National Park, burning of coal appeared to be an important pollution source. The elimination rate from periphyton was twice as long for Hg as CH_3Hg^+ than for Hg as $Hg(NO_3)_2$, but five to six times faster than for Hg from snails and fish (Huckabee and Blaylock, 1973). Oil also contains Hg. Neutron activation analysis of 46 samples of crude representing Illinois' major oil pools and oil bearing strata all contained less than 40 ppb (Mast and Ruch, 1973). This is well below average, which is of the order of 1,000 ppb. A round-robbin indicated the following ranges of Hg concentration, in ppm, in the materials mentioned: coal, 0.02 - 2; fly ash, 0.1 -< 18 residual fuel oil, 0.002 - 0.4; premium gasoline, 0.008 - < 0.02 (Von Lehmden et al., 1974). Nearly all Hg escapes as vapor in the power generation process, and there are no known means to prevent this (Klein and Russell, 1973).

Fourth, the use of Hg in seeddressing of cereal grains is sometimes considered a source of environmental Hg contamination. It has been calculated that for West Germany contamination due to such Hg would increase the Hg content of the soil to not more than would be caused by an annual precipitation of 500 mm, or, from 1% to 10% of the Hg naturally present in the top 20 cm of soil (Lyre, 1974).

Fifth, sewage sludge normally contains Hg, and its application to agricultural land may be the cause of Hg uptake by plants grown thereon. Thus, in the metropolitan area of Toronto, Canada, sewage sludge from 4 different treatment plants varied from 8 to 26 ppm. Due to industrial emission, urban Toronto soils already contain 600 ppb Hg, as compared to 200 ppb and 50 ppb in suburban and rural sections, respectively (Van Loon, 1973). Experiments with barley, tomato, beans, carrot and lettuce grown on fresh sewage sludge treated soil showed the availability to plants of Hg from this substrate (Van Loon, 1974).

Flow

New data suggest that Hg in the Greenland ice sheet is homogeneously distributed, rather than increases in concentration with proximity to the surface. It is also suggested that winds carrying volcanic, Hg-bearing ash from Iceland, rather than emissions from more remote industrial areas, are responsible for the Hg in Greenland ice (Carr and Wilkniss, 1973).

Examination of Hg in the sediments of an English lake revealed the possibility of Hg diffusion in the top 3-cm layer due to methylation. This may have resulted in an upward mobility of Hg, which would have added to the increase in Hg due to sedimentation. Sewage sludge accounted for most of the recent Hg in the top 25 cm of the lake sediment (Aston et al., 1973).

A linear, eight component model (including fish) was developed to describe the dynamic distribution of CH_3Hg^+ in a pond ecosystem. By means of Hg203 introduced in a small pond, validation of this model was attempted. Direct uptake of CH_3Hg^+ appeared to be proportional to the size of the organisms, and biomass turned out to be an important factor (Huckabee and Goldstein, 1974).

Studies on transformations of Hg have concentrated on both enzymatically and non-enzymatically mediated conversions, with emphasis on oxidation of Hg sulfides, and volatilization of Hg^{2+} either as Hg° or alkyl Hg. The kinetics of Hg very much depends on the form and on environmental conditions. Thus, Hg^{2+} conversion to Hg° strongly depends on the presence of organic materials and aerobic conditions. It occurs readily in sewage treatment plant effluents, and may be proportional to the growth of microorganisms therein. In one study, suspended solids reduced volatilization of Hg^{2+}, probably by adsorption or complex formation. Volatilization was also reduced in anaerobic systems where the potential of complex formation was high (Parks et al., 1973).

Flow of Hg in water was studied on the basis of the kinetics of some key chemical and photochemical reactions. Theory indicated that loss of Hg° vapor or dimethyl Hg at the air-water interface can be important, and that S-bonded CH_3Hg^+ species prevail in natural waters, although they are readily decomposed by sunlight to inorganic Hg (Baughman et al., 1973).

The capability of microorganisms to methylate Hg has been linked to the presence of methylcobalamincoenzyme, resulting in both the mono- and dimethyl forms of Hg. Formation of the dimethyl form is considered decontamination, at least of waters, as it leaves the aqueous phase as a vapor. The required association between Hg and 2 methyl groups, sometimes referred to as "symmetrisation," is promoted by the presence of large nucleophiles, such as cyanide, iodide, or certain sulfur compounds. Among these, sulfides and biosulfites occur in nature. The presence of materials with surface OH groups, such as certain clay minerals and Mg hydrous oxide, also may trigger symmetrisation (Cross, 1973).

Soils and Sediments

With regard to Hg accumulation in sediments, results of neutron activation analysis and flameless atomic absorption agree in that the Hg concentration in sediment cores collected in the Santa Barbara basin increased towards the surface, i.e. with time, viz., in mg per kg dry weight: 0.07 in 1820-29, 0.10 in 1880-89, 0.12 in 1950-59, and 0.17 in 1960-69 (Young et al., 1973). The observed rate of increase compares well with those measured earlier in Greenland ice, and in a number of North American lakes. In sediments of lake Windermere, England, the increase of Hg with decreasing depth was related to the time of deposition, as follows: From 50-73 cm: 122 ppb (1269-520 AD); from 30-44 cm: 286 ppb (1800-1400 AD); from 20-26 cm: 608 ppb (1845-1870 AD); from 0-15 cm: 1,026 ppb (1915-present) (Aston et al., 1973).

Analysis of core samples taken in the Everglades, Fla., and in Mobile Bay, Ala., revealed correlations between organic matter contents of sediments and sedimental Hg concentrations, and also between Hg concentrations in interstitial H_2O and dissolved C (Lindberg and Harris, 1974). The amount of Hg present as CH_3Hg^+ in the areas indicated never exceeded 0.07% of the total Hg present, or from 80 to 600 ng Hg per g dry weight of material. Probably on account of sulfide complex formation, the concentration of Hg dissolved in sediment pore water exceeded that in the overlying estuarine water by a factor of 30. This type of release of Hg in interstitial water, followed by diffusion and sediment mixing, rather than methylation and volatilization, constituted the natural detoxification mechanism in the areas mentioned (Andren and Harriss, 1973).

In the Bellingham Bay area of Washington, where operations of a local chlor-alkali plant have been discontinued, the rate of decrease of Hg in the sediments is described by a half-life of 1.3 years. Sediment studies indicated that the natural decontamination mechanism, besides the reduction mechanisms mentioned, included the upward bubbling of gases such as CH_4, wave induced currents, and assimilation by benthic organisms (Bothner and Carpenter, 1974). In another study covering the same problem area (Bothner, 1973), the Hg content was observed to be high and uniform in the surface sediment, suggesting mixing of the top 5 cm by biological organisms or tidal currents. A sharp decrease to background levels occurred at greater depths. Also, in contrast to Hg, the concentration of C was uniform with depth in the cores, hinting at a source of C that was not always the same as that of Hg.

With regard to soils, some Rhine river bottom lands in the Netherlands which are periodically subject to flooding, appeared to have accumulated Hg to concentrations of from 3.4 to 10.4 ppm, as compared to a general regional background concentration of 0.09 ppm (Poelstra et al., 1973). This compares with Hg values of from 0.050 to 0.100 ppm in the Eastern U. S., regardless of cropping system or soil type (Wiersma and Tai, 1974).

Soil accumulation of Hg generally is effected by precipitation or adsorption. Besides clay, oxides especially of Mn, function as Hg scavenging soil components. In the pH range from 3 to 11, MnO_2 appeared to adsorb uncharged $Hg(OH)_2$. In the pH interval from 6 to 8, the adsorption was of the Freundlich type (Lockwood and Chen, 1973). Theoretically, this adsorption could be prevented up to pH 10 if the concentration of Cl were kept at the level of that in sea water. In solutions, the presence of Cl at concentrations of 1.4 ppm at pH 3.7, 3.5 ppm at pH 4, and 14 ppm at pH 5 would suffice for all Hg^{2+} present to be in the form $HgCl_2^{\circ}$. At higher pH, partial to complete remobilization of Hg is possible, depending on the concentrations of Cl^- and Hg^{2+} (Hahne and Kroontje, 1974). Interpolation of these data to soil or sediment systems is difficult mainly because their adsorption and complex formation prevail.

Although in one instance annual application of 2.1 kg per ha of various Hg containing salts over a period of 15 years led to a concentration of no less than 455 μg Hg per kg of soil, without affecting the growth of bentgrass (Estes et al., 1973), accumulation usually is much less on account of volatilization. Thus, from 44 to 56% of total Hg added as a surface application of the fungicide Calocor (60% H_2Cl_2 - 30% $HgCl_2$) to turfgrass was lost in 57 days (Gilmour and Miller, 1973). It was shown to be due to reduction in the soil of Hg to Hg° , followed by volatilization.

Plants

Reduction of Hg^{2+} to Hg° can be performed by fungi as well as bacteria (Vonk and Sypeste, 1973). Thus, it has been observed to occur with a yeast (Brunker and Bott, 1974). Degradation of CH_3Hg compounds was carried out by 73 out of 207 different bacterial cultures (Spangler et al., 1973). Of the 73 cultures, 30 were aerobic, 22 facultative anaerobic, and 21 anaerobic, producing CH_4 in all cases. The production of CH_4 indicates an inability of the microorganisms to use the substrate as an energy source, although they do modify it enzymatically ("cometabolism"). Using bacterial cultures derived from river sediments, the dimethylating efficiency was observed to be of the same order of magnitude at Eh - 100 mV, pH 7.4, as it was at Eh - 250 mV, pH 8.0 (Billen et al., 1974).

It stands to reason that fungi and bacteria involved in these conversions must themselves be rather immune to CH_3Hg compounds. With yeasts, this immunity has been related to either complex formation or volatilization of Hg by a precursor of methionine (Singh and Sherman, 1974). In the same vein, bacteria have been observed to deactivate phenyl mercuric acetate (PMA). The deactivation mechanism, shown by both live and dead bacteria, involved binding of PMA ions by bacterial proteins and amino acids having free SH groups (Balicka et al., 1973). Selected cultures of Hg resistant bacteria degraded PMA, producing Hg° vapor and benzene. Others, not volatilizing Hg°, may have used PMA metabolically, possibly neutralizing Hg by mercaptide formation with sulfhydryl compounds (Nelson et al., 1973). The toxic effect on bacteria of PMA appeared to be greater than that of $HgCl_2$. In general, Hg concentrations is soil due to moderate use of Hg containing pesticides appeared not to disturb breakdown or organic matter, or N mineralization (Van Faassen, 1973).

Growing a variety of crops on soils containing an average of 60 ppb Hg, most Hg was retrieved in plant parts other than the seeds. From the consumer's viewpoint, this reflected favorably on wheat, but unfavorably on flax and rape (Gracey and Stewart, 1974). Release of Hg through the stomata of a number of vascular plant species (Siegel et al., 1974) was indicative of an internal reduction process also noted by Kothny (1973b). Fish and chicks share the same capability.

Alleviation or reversal of Hg toxicity by Se, common with animals, man and fish, has not been observed so far with plants.

Abatement

Methods for the removal of Hg from contaminated waters are often based on the well known affinity between Hg and various organic materials, such as can be temporarily floated in water (Swanson et al., 1973). Thus, Hg was adsorbed quantitatively from solutions by polyethylenimine treated wool fibers (Freeland et al., 1974), and by aminodeoxycellulose type cotton fibers (Snyder and Vigo, 1974). More physical, but not very efficient means included dredging, and covering with an inert layer (Jernelöv and Lann, 1973).

Reviews

The health hazard of agriculturally common forms of Hg has been emphasized in a paper covering 61 references (Vostal and Clarkson, 1973). In this connection, reference should be made to the growing recognition that, like Cd, Hg may cause hypertension. This would follow from experiments in which low dosages of Cd were administered to rats over extended periods of time (Perry and Erlanger, 1974). A great service has been rendered by Jenne and Sanders (1973) by making available English translations of 280 reports, many not originally in English, that were cited in 5 major review articles appearing during the "great mercury boom" in 1970 and 1971. Analytical methods for determining Hg have been reviewed in a recent book issue (Hartung and Dinman, 1974).

ZINC

Analysis

Use of radiofrequency energy for, first, the induction heating of sample containing graphite crucibles flushed with He, and, second, excitation of metal vapors in the He plasma discharging over the mouth of the crucibles, has been developed into a rapid atomic absorption method for Zn as well as Cd (Talmi, 1974). Applied to soil, fly ash and animal tissue samples, this approach, while not as sensitive as certain other flameless techniques, is relatively free from interferences, and allows for the introduction of large samples.

Sources

Near Canberra, Australia, pollution of a fresh water system with Zn occurred on account of slow dissolution of Zn from mining residues containing much pyrite. The latter is chemically oxidized to $FeSO_4$, and from there to $Fe_2(SO_4)_3$ by Thiobacillus ferroxidans. The latter salt oxidizes ZnS to $ZnSO_4$, which is the major contaminant in this area (Weatherly and Dawson, 1973).

Soils

In pot experiments involving rice grown on several soils, flooding doubled the amount of available Zn. The uptake of Zn, however, increased only by a fraction of this factor (Tiller and Wasserman, 1973). When Zn was applied as $ZnSO_4$ in a mixed fertilizer, the latter's granulation was an important factor in the rate of Zn in the soil (Koshino, 1973b). The fixation of Zn and Mn by clay minerals was the subject of a recent dissertation (Reddy, 1974). Using Zn65, the fixation "capacity" was found to follow the order vermiculite > montmorillonite >kaolinite (El Kadi et al., 1972).

In a study involving 2 soils from Texas, the diffusion of Zn65, in $cm^2/sec \times 10^{-11}$, decreased from 19.9 to 5.35 as the pH in a silt loam was raised from 6.0 to 7.2, and from 11.7 to 8.6 as the P content of a loam (pH 8.2) was increased from 0 to 240 ppm. The effect of pH, therefore, was considered greater than that of applied P on the mobility of Zn in soil (Melton et al., 1973).

Zinc can be chelated by organic matter of various types. In a study involving 4 tree species, the water soluble and the washable, though insoluble, deposits collected from the foliage contained relatively large amounts of Zn. Leaching of leaves due to a rainstorm decreased the foliar contents of Zn in oak and willow from 4,000 to 1,600 and from 6,000 to 1,700 ppm, respectively. Of the non-washable fraction, the larger part is actually incorporated in the cuticle and cell walls. Other agents binding Zn are soluble chelates present in cell sap (Little, 1973). Ellagic acid, with a lactone ring and ortho substituted OH groups, was identified as the Zn chelating compound in fresh leaf sap of barley (Gomah and Davies, 1974). Amino acids were also found to have chelating ability.

Resorting to soil extraction and radioisotope equilibration, the "labile" pool Zn and other Zn in soil were determined and related to Zn uptake by plants (Rule, 1973).

Plants

In general agreement with earlier work in Japan, but here specifically referring to results obtained on alkaline soils, Zn added in excess was found to cause chlorosis and reduction in yield of rice (Wells et al., 1973).

Populations of the well known cover crop Agrostis tenuis that were tolerant with respect to Zn contained less Zn than nontolerant populations. Nevertheless, the concentrations of Zn in cell wall and vacuole were higher with the tolerant than with the nontolerant species

(Mathys, 1973).

Studies on the interactive effect of P and Zn on plants generally agree. With solution cultures of soybeans, where the Zn supply was low, an increase in P supply resulted in Zn deficiency. Where the supply was adequate, however, an increase in P supply induced Zn toxicity (Wallace et al., 1973a). With solution cultures of bush beans, an increase in P supply decreased Zn uptake where Zn was present in low concentrations. Meanwhile, the concentration ratio of Zn in roots to Zn in leaves increased, pointing to diminished translocation. An increase in P supply where Zn was ample resulted in increased Zn uptake, without changing the Zn ratio mentioned (Wallace et al., 1974).

Similarly, from a study on corn grown on substrates low in Zn it appeared that Zn became deficient where P was applied in heavy dosages, especially if the pH was raised also (Trier and Bergmann, 1974). Under these conditions, mobility of Zn inside plants was strongly impaired. The uptake of Zn by rice from a silt loam (pH 5.3) increased only when P was added as normal superphosphate, and not when it was added either as concentrated superphosphate, monoammonium phosphate, or diammonium phosphate (Sedberry et al., 1973). In Neubauer type pot experiments, uptake of Zn65 by barley was counteracted by addition of P (Motsura, 1973). Application of 780 kg P per ha over a period of 15 years decreased the content of available Zn from 1.2 ppm to a trace, causing corn to become Zn deficient (Yaravoi et al., 1973). Another soil culture study involving tomato, cotton, corn, sudan grass, beans and lettuce yielded results in general agreement with the foregoing (Koukoulakis, 1973).

Reviews

There are no recent literature reviews on Zn.

CONCLUDING REMARKS

The following thoughts, which are offered to this audience of senior NSF grantees for their consideration, follow from a general acquaintance with the literature in combination with this reviewer's limited personal experience in heavy metal research. They do not issue logically or directly from the foregoing review.

1. Each case of environmental contamination is unique, requiring a specific research design. The approach to be taken with any contaminated pasture system, metropolitan area or river estuary has to be freshly considered in the light of evidence gathered, history examined, and resources mobilized. There is no standard approach, although there may be standard techniques applicable to the approach eventually decided upon.

2. It is unwise to examine tolerance of plants or exchange behavior of soil with regard to heavy metals under conditions in which these metals have been adjusted to high concentrations beyond all known reality. This is because the exposure of soil or plants to such high concentrations triggers responses which not only may differ in degree, but also in kind, from responses triggered at lower concentration levels such as occur in real life. Whereas it may be analytically convenient to operate at concentration levels high enough to obviate certain cumbersome pretreatments necessary with lower concentrations, within the overall costs of an average environmental research project the fraction of funds thus saved is usually insignificant, while the type of information eventually put forth may be short of worthless.

3. Even where one operates at heavy metal concentration levels which, though unusually high, are not altogether out of touch with reality, it is well to remember that while acute, overwhelming contaminations are spectacular on account of both the damage they cause and the type of reporting to which they lend themselves, it is the chronic low-level type of "creeping" contamination that ultimately may turn out to be the more pernicious one. While low-level type contamination as a research object may consume our time and test our patience and ingenuity to extents far greater than more spectacular events would, the long term benefits that flow forth from such efforts in terms of human health protection, while not precisely assessable in the early research phases, may eventually astound even the timid among us.

4. We should realize that a chain reaction may well be instigated under the impact of any one element or compound present in excess. A proper understanding of the imbalance thus brought about compels one to consider also elements or compounds other than the ones believed to be in excess. One can properly say that single element toxicities as such do not exist because of the interlocking multi-element nature of enzyme systems and catalytic processes at the cellular level. This creates problems, but also opens up a wider array of alternatives for abatement. In matters of understanding the functions and dysfunctions of biological systems, cutting corners by ignoring this broader aspect is, at the least, synonymous to taking speculative risks.

5. The increasing awareness that the organic matrix in which heavy metals frequently occur in nature determines their impact on biological systems, should not tempt one to study exclusively simulation type systems in which those natural organic compounds have been replaced by unrelated synthetic compounds not occurring in nature. Analytically convenient and academically interesting as such compounds of known structure may be, such a policy would leave unexamined the dynamic impact of heavy metals on, first, the synthesis of the natural compounds, and second, their biodegradability. From the latter may depend the (re)mineralization of heavy metals into pathologically active agents. This hysteresis type of contamination may either be the cause of the chronic, low level effects referred to above, or add to contamination of more recent date and push matters over the threshold characterizing an acute hazard.

6. The heavy metal problems one faces in environmental quality preservation are highly complex. Their study often pertains to processes in which the slow passing of time is an essential factor. There is no true substitute for this factor. In the long run, this time input should be allowed for in full measure, especially where efforts are directed towards improving the long term future of the human milieu. Therefore, in the customary haste to get out rapid, but not necessarily unimportant, information on presence and impact of heavy metals in any new situation, one must not neglect, for the sake of a more basic understanding of the problem, to initiate also long-term experiments in which "true time" occurs as a prime variable.

7. Finally, with but few exceptions, analytical progress in heavy metal research is strongly dependent on advances in instrumental technology. While the pace in this field has been truly impressive, the resulting information explosion testifying to an upsurge in awareness of chemicals in our environment should not be abused by arousing public apprehensions as a means to generate funds. By the same token, this new understanding should not be ignored to serve vested interests, nor minimized below a level dictated by a balanced interpretation of factual measurements that must include control (background) data. To a considerable extent, the choice between options of this kind is a matter nothing short of professional ethics.

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II. AIR

DEVELOPMENT OF EXPERIMENTALLY VALIDATED MODELS OF PHOTOCHEMICAL AIR POLLUTION[*]

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Abstract

If computer models of chemical transformations in smog are to have real utility in formulating control strategies for U.S. urban atmospheres, they must be validated against an experimental data base which is as accurate and comprehensive as possible. In this paper we describe data obtained at our environmental-chamber, solar-simulator facility, and our preliminary efforts to model these data. Precise concentration/time profiles for O_3, NO, NO_2, HCHO, PAN, aldehydes, ketones and other hydrocarbon oxygenates have been obtained for the photolysis of propylene or n-butane with oxides of nitrogen (NO_x) in air, at ambient conditions and concentrations. In these studies conventional air monitoring instrumentation has been supplemented (1) by a high resolution Fourier infrared interferometer interfaced to a 120 meter multiple reflection system in the evacuable chamber, and (2) by analysis of chamber product mixtures using a combined gas chromatograph-mass spectrometer (GC-MS). Use of the Fourier interferometer has permitted the detection and monitoring, with good time resolution, of a number of important smog species difficult to monitor routinely by other methods, including formic acid, nitric and nitrous acid and alkyl nitrates. GC-MS analysis has led to the detection of propionaldehyde and propylene epoxide in the propylene-NO_x photooxidations. Computer runs directed toward modeling these data using published reaction mechanisms and the best rate constants currently available have shown that additional rate and product data are required for further refinement of the models.

The increasing demand for urban airshed models of real applicability to the air pollution problems afflicting U.S. urban centers arises from the fact that use of such models could represent an extremely cost effecive input to emission control strategy decisions, land-use planning decisions, environmental impact assessments and the development of predictive health warning systems. In general, a practical airshed model consists of (1) an emission inventory, (2) a meteorology model, and (3) a kinetic mechanism describing the photochemistry of polluted atmospheres. This paper focuses on the development of experimentally validated mechanisms (or models) of photochemical smog.

The development of computer kinetic mechanisms[1-4] has been furthered in recent years, first by the determination of accurate rate constants for an ever larger number of important reactions, and secondly by the recognition of the importance of reactive intermediates other than O and O_3, for example, the OH and HO_2 radicals and of photoinitiators other than NO_2 such as HONO and HCHO.[5-7] Unfortunately, the progress made in recent years in the evolution of increasingly sophisticated kinetic descriptions, as well as of more powerful computing methods, has in large measure been neutralized by the lack of a substantial body of appropriate experimental data against which such models could be validated.[1-4,8]

The data base required for mechanism validation consists of comprehensive sets of concentration-time profiles for product and reactant species in hydrocarbon/oxides of nitrogen (HC/NO_x) systems photolyzed at ambient concentrations (ppb to ppm) under carefully controlled and well-characterized conditions. Photolysis experiments in large smog chambers have traditionally been the source of the required type of data.[9-10] However, according to all major modeling groups[2-4,8] and in our own judgment, a situation has developed within the past two years in which the data obtained in previous chamber studies no longer provides an adequate basis for *further* refinement and improvement in computer kinetic models of photochemical air pollution.

Perhaps the best current example of the limitations of presently available chamber data for model validation purposes is provided by the results presented in a recent photochemistry modeling paper by Hecht, Seinfeld and Dodge.[3] In this study they validated a generalized 39-step kinetic mechanism for photochemical smog by comparison of the model predictions with concentration-time profiles obtained in chamber experiments conducted seven years ago.[11] Although good qualitative and semi-quantitative agreement was obtained for three HC/NO_x systems, the possibilities for critical-

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ly testing the adequacy of the mechanism were limited by three factors: (1) substantial uncertainties in the magnitude of light intensity (and hence photolysis rates); (2) lack of precision in the measured concentrations of NO, NO_2, O_3 and hydrocarbons; (3) lack of measurement of all of the other important species which appear in the mechanism.

Recommendations for improving the usefulness of data obtained in chamber studies have been made by several modeling groups[2-4,8] and some of the most important are: (1) employing very pure matrix air; (2) precise control and measurement of temperature and relative humidity; (3) a practical method of cleaning the chamber; (4) accurate characterization of light intensity and spectral distribution, and (5) unambiguous and accurate analytical methods including in-situ real time analysis for highly reactive species.

A new evacuable environmental chamber-solar simulator and air purification facility[12-14] (Figure 1) which addresses these experimental criteria has been established at the Statewide Air Pollution Research Center (SAPRC). The evacuable chamber is a 205-cubic-foot, thermostated, cylindrical vessel constructed of FEP Teflon-lined aluminum with quartz end windows.[13] A 20-KW solar simulator was designed specifically for use with this chamber and provides a highly collimated beam with a spectral distribution that very closely matches that of sunlight.[12] Supporting analytical methods are as shown in Figure 1.

This facility is being employed in a highly synergistic relationship between the chamber and modeling staffs at SAPRC to generate a data base with which a sophisticated kinetic mechanism for photochemical air pollution can be validated. One approach to obtaining chamber data suitable for model refinement and validation has been a study of HC/NO_x systems in which a representative olefin, paraffin or aromatic compound is used to study first single HC/NO_x mixtures and then binary and tertiary mixtures. HC and NO_x concentrations are varied using a factorial design approach such that a wide range of concentrations may be studied with a minimum number of runs. Results for a typical propene/NO_x run are shown in Figure 2 (propene deleted for clarity). Such results are representative of both the precision and density of data obtained in our chamber studies. An additional level of complexity may be introduced by the addition of an aldehyde to the reaction mixture permitting investigation of the role of aldehydes as photoinitiators in the mechanism. The effect of 0.13 ppm of HCHO on a butane/NO_x (2.0 and 0.5 ppm, respectively) reaction is shown in Figure 3.

Even a brief examination of any of the current kinetic models[2-4] indicates that modelers require more than just accurate data for O_3, NO, NO_2, PAN and hydrocarbons. For example, the 39-step lumped parameter model of

Figure 1

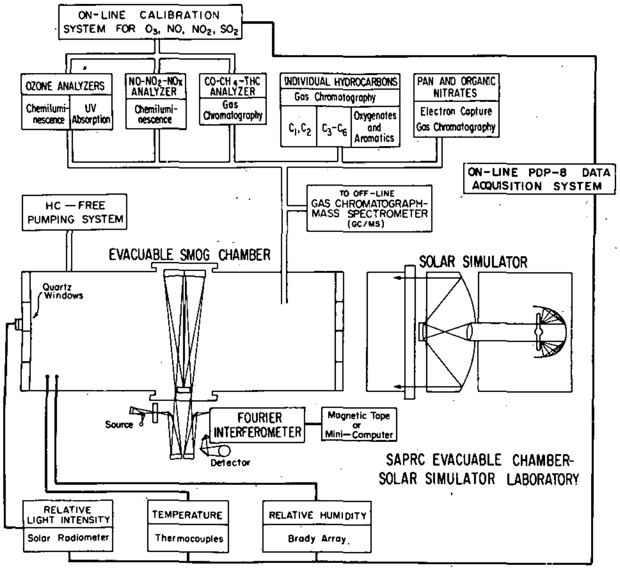


Figure 2

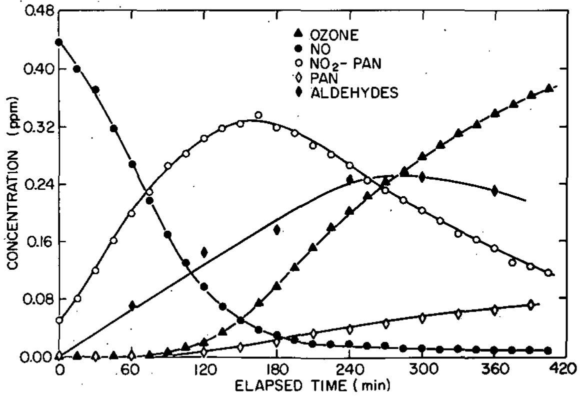
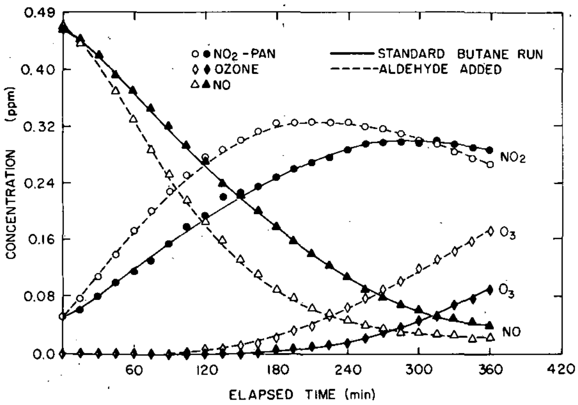


Figure 3



Hecht, Seinfeld, and Dodge[3] predicts, in addition to products traditionally monitored in smog chambers, products such as nitric and nitrous acids, hydrogen peroxide, alkyl nitrites and nitrates, and alkyl peroxides and hydroperoxides. The importance of measuring these species becomes apparent from the fact that for a given set of rate constants three published mechanisms provide substantially different predictions for at least two of these species, hydrogen peroxide and nitric acid, as shown in Figures 4 and 5.

We have begun to obtain data for several of the less easily measured products using our Fourier interferometer long-path infrared system[15] in the evacuable chamber. Preliminary photolysis experiments with a propene/NO_x system have resulted in the identification of products such as acetaldehyde, formaldehyde, PAN, formic acid, nitrous acid, nitric acid, and an alkyl (ethyl) nitrate. The simultaneous rapid scan (8 sec) of the spectral region from 700 to 3200 cm^{-1} and high resolution (0.125 cm^{-1}) afforded by the interferometer permitted good time resolution in measuring the rates of formation of these products. Thus time-concentration profiles could be obtained as shown in Figure 6. In a separate study[16] spectra obtained for the reactions of olefins (ethene, propene, and cis-2-butene) with ozone have resulted in a detailed product analysis. Species observed include acetaldehyde, formaldehyde, formic acid, ketene, methanol, methane, carbon monoxide, and water vapor as well as peroxyformic acid and several α-carbonyl hydroperoxides.

Figure 4 Hydrogen Peroxide Predicted

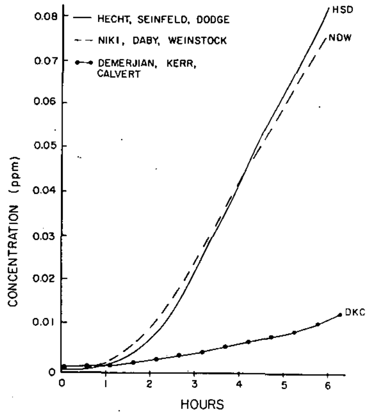
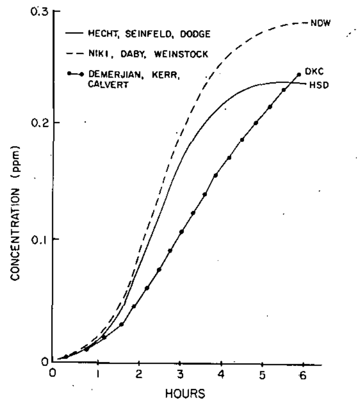


Figure 5 Nitric Acid Predicted



A second powerful analytical tool being employed in the detection of trace organics in these chamber studies (and in ambient air) is a combined gas chromatograph-mass spectrometer (GC-MS). Using a Chromosorb adsorption technique to sample from the chamber, the GC-MS confirmed the presence of species such as propionaldehyde and propene epoxide in the pro-

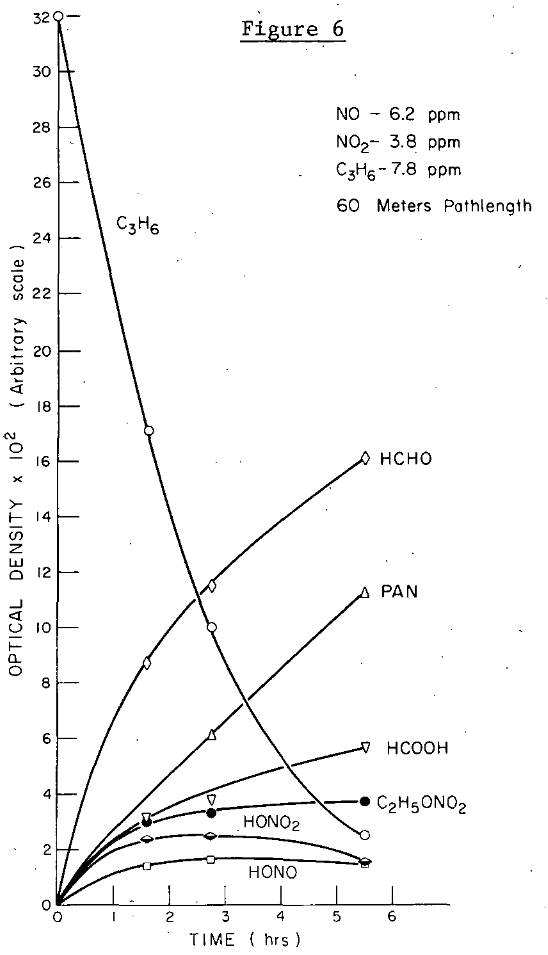


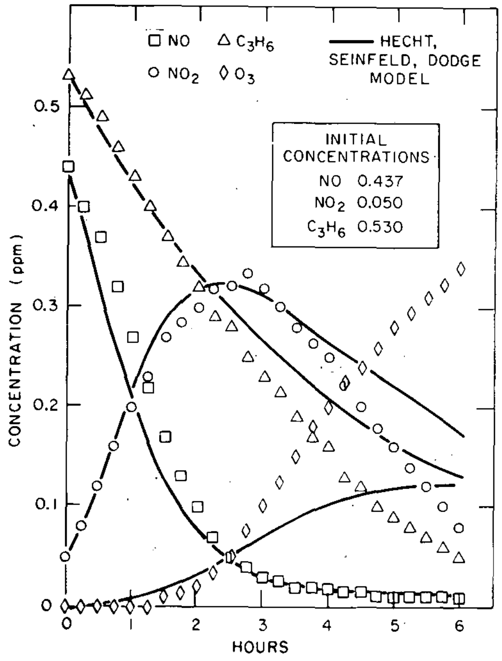
Figure 6

pene-NO_x photooxidations and butyl nitrate in the butane-NO_x system.

We are currently using data of the type presented here for the further development of current kinetic models of photochemical smog. As an example it can be pointed out that some published mechanisms[2,3] do not predict the formation of formic acid, yet we have observed substantial quantities of this species in our propene-NO_x irradiation experiments using the Fourier interferometer, and it has also now been detected in ambient air.[17]

Finally, in the course of our model development program we have generated concentration-time profiles for a large number of species using three published mechanisms[2-4] and a single "best" set of critically evaluated rate constants (an example is shown in Figure 7). We find important differences in these existing mechanisms which must be reconciled in the development of a more accurate and sophisticated mechanism. We believe that the development of such a model will hasten the day when the evaluation of, for example, emission control strategies can be made on a computer rather than in smog chambers or from hindsight after further costly experiments in our society itself.

Figure 7



Acknowledgments

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PHOTOCHEMICAL SMOG KINETICS AND HYDROCARBON REACTIVITY

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Abstract

A detailed mechanism of photochemical smog production has been developed and confidence in its ability to simulate smog chamber observations with economy and speed has been established by comparison of numerical predictions with smog chamber experiments. An approach has also been developed that allows complex hydrocarbon mixtures to be treated as a binary system. The results of these lumped parameter studies will be presented and discussed with emphasis on their application to automotive emissions.

Introduction

We are concerned here chiefly with the purely kinetic aspects of photochemical smog formation. Although understanding the mechanism of photochemical smog production is important in its own right, a detailed mechanism can also provide guidance in the development of an irreducible set of chemical reactions involving the minimum number of species needed to simulate the actual smog process. This simulation model becomes, in turn, an essential element of a multi-box air pollution model presently being developed for the Bay Area Air Pollution Control District. This air quality model, capable of describing the time and spatial distribution of pollutants, is crucial for the formation of effective pollution control strategies and for future land use planning.

Kinetic Modeling

All kinetic mechanisms that have been proposed to describe photochemical smog production have the following characteristics regardless of whether hydrocarbons are treated as specific chemical species or as a lumped hypothetical species. Basically, all kinetic mechanisms employ sets of chemical reaction terms in which each chemical species is described by a time-dependent differential equation. Simultaneous solution of such equations is required because they are coupled with other equations by common non-linear reaction rate terms. Such sets are difficult to solve because of the range of time constants inherent in the reactions. Implicit in these reaction mechanisms is the treatment of a smog chamber experiment as a single phase, well-stirred system of gases subjected to constant radiation flux. The effects of poor mixing, suspended particles and wall surfaces are ignored. The values of the reaction rate constants are either measured or estimated. The increase in computation time that accompanies the addition of each new species to a mechanism requires that the number of species be held to a minimum.

The proposed detailed mechanism incorporates many reactions employed in the tropospheric smog models of Westberg and Cohen (1), Niki (2), and Hecht, Seinfeld and Dodge (3). Also included are relevant reactions used in current stratospheric models (4). Measured values of rate constants are, whenever possible, those recommended by the DOT-CIAP program (4) and by the NBS Chemical Kinetics Survey (5).

The addition of a hydrocarbon to the irradiated NO-NO_2-air system results in the disappearance of the hydrocarbon, the rapid oxidation of NO to NO_2 and the formation of ozone and organic carbonyl compounds. In addition to the generally agreed upon reaction of hydrocarbons with O and O_3, an important process in the oxidation of hydrocarbons is their reaction with OH and HO_2 radicals. Although our mechanism assumes hydrogen abstraction by OH and HO_2 to yield hydrocarbon radicals, the addition of OH and HO_2 to olefins or aromatics would not alter the apparent loss rates of hydrocarbons but the product composition would be changed.

Before discussing the smog chamber simulation, the origins of the OH and HO_2 radicals should be reviewed by inspection of Table I. The associated reaction rate constants for the 62 reactions are listed in Table II. Analysis of the instantaneous reaction rates shows that reaction k_5, the photolysis of HNO_2, is the dominant source of OH early in the photooxidation while the photolysis of H_2O_2, reaction k_{10}, is important at the later stages. The oxidation of RO, reaction k_{42}, the oxidation of HCO, k_{16}, and the termolecular reaction of H+O_2+M, k_{23}, are the dominant sources of HO_2. The results of using the mechanistic scheme outlined in Table I are described in a simulation study and in the testing of a hydrocarbon reactivity scale.

Isobutene Simulation Experiments

The smog chamber data used are shown in Figs. 1 through 3. The experimental values (1) were observed during operation of the SRI chamber at a NO_2 photolysis rate of $k_d = 6.7 \times 10^{-3} sec^{-1}$. The initial conditions for the experiment were: $(i\text{-}C_4H_8)_0$=2.8ppm; $(NO_2)_0$=.0ppm; $(NO)_0$=0.01ppm; $(O_3)_0$=0.001ppm; $(CO)_0$=0.33ppm; (H_2O)=5%RH; and T=298K. The 2-hr simulation required 97 sec of central processing time using a CDC 7600 computer. (The rate constants are listed in Table II).

The agreement between the kinetic model and the experimental results is quite close for species except for the carbonyl products, acetone and formaldehyde. For these compounds, the model predicts lower levels than those measured in the smog chamber after the 100-min irradiation. This discrepancy may be explained by the present model lacking secondary oxidation steps that occur after the initial attack on the isobutene by O, OH, HO_2, and O_3. This refinement can be incorporated in the present scheme if our understanding of the mechanism of the oxidation of hydrocarbon improves. Moreover, quantum yields of primary photolysis products of aldehydes as a function of wavelength are not well determined and should be carefully measured.

Chemistry of Complex Hydrocarbon Mixtures

A complete chemical description of the composition of automotive exhaust, jet engine emissions, and stack gases in general, would present a formidable problem in the large number of species which must be calculated by differential equations in the mechanism. An approach currently under evaluation is to treat a complex hydrocarbon mixture as a binary or ternary system having the chemical reactivity of a reference compound.

The basic assumption in this approach is that the chemical reactivities of the various components 1, 2, 3...n of the hydrocarbon mixture are proportional to their mole fractions, C_1, C_2, $C_3 \ldots C_n$. The criterion for defining chemical reactivity is the time required for a given hydrocarbon to reach maximum NO_2 concentration. This definition gave reactivity indices that gave good agreement with indices calculated using the laboratory rate constants for the attack of a hydrocarbon by OH (10^6 molecules/cc) O_3 (10^{12} molecules/cc) and O atoms (10^6 molecules/cc). Using propylene as the reference hydrocarbon, two complementary definitions of a specific reactivity index are described by these relations:

Specific Reactivity Index,

$$r_i = (dNO_2/dt)_i / (dNO_2/dt)\text{propylene}$$

or, in detailed kinetic form:

$$r_i = \frac{k_{i,O} + k_{i,OH} + k_{i,O_3} + \ldots}{k_{C_3H_6,O} + k_{C_3H_6,OH} + k_{C_3H_6,O_3} + \ldots},$$

where $k_{i,R}$ is the rate constant for the attack on the i th hydrocarbon component by the oxidant, R, times the concentration. Since rate data for interaction of hydrocarbons by hydroxyl or hydroperoxyl is available for a small number of compounds, the formal (and more detailed) definition of r_i was used only to check on the relative scale of r_i values (6) obtained by the rate ratio of time-to-peak for NO_2.

The reactivity of a complex mixture of hydrocarbons may be taken as the summation defined as the propylene-equivalent-concentration, P.E.C.:

$$\text{P.E.C.} = \sum_{i=1}^{n} C_i r_i,$$

where C_i is the mole fraction of the i th component having a specific reactivity index of r_i in an n-component mixture. This approach, assuming the mixture is ideal, allows hydrocarbon mixtures to be treated as a single hydrocarbon species having the overall chemical reactivity of propylene. Although the chain length is longer for olefins than for alkanes and aromatics, the dominant reactive species in car exhaust are the olefins. A compilation of reactivity indices calculated by the above method is available in Reference 6.

As a test of the utility of the P.E.C. approach for lumping hydrocarbons in various fuels gave the following values (P.E.C./ppm):

Regular gasoline	0.612
Premium gasoline	0.532
Kerosene(108-230C)	0.57
Car exhaust, idle	0.549*
Car exhaust, cruise	0.612
Car exhaust, accel.	0.533*
Car exhaust, decel.	0.512*
L.A. atmosphere, avg.	0.46
Car exhaust, mod. comb.	0.42

*Analysis includes only C_2-C_6 hydrocarbons.

It may be significant that car exhaust with modified combustion gives the same P.E.C./ppm value as ambient air samples from Los Angeles (1965). In summary, car exhaust and fuels have a reactivity between ethylene (r_i=0.43) and butene-1 (r_i=0.80).

The results of using the lumped hydrocarbon parameter, P.E.C., to simulate the reactivity of butene-1, propylene, trans-2-butene, butadiene-1,3 and 2-methyl-2-butene in the General Motors smog chamber are listed in Table III. In this numerical simulation, the initial concentration of each hydrocarbon was multiplied by its respective reactivity indices (in this case the Butene-1 reactivity scale was used for programming convenience) to give a Butene Equivalent Concentration. These concentrations were used in the 62-reaction set as starting values and the rate constants for the hydrocarbon oxidation were the butene-1 values. Each simulation was run to the same percent reaction as the chamber.

Considering the approximations made in the P.E.C. approach, agreement between computed and experimental values was found for ozone production by all the olefins. Acceptable agreement was obtained in the formaldehyde predictions. The predicted value for PAN production was an order of magnitude low in the butene and simulations and showed good agreement in trans-2-butene, butadiene-1,2 and 2-methyl-2-butene simulations. On the basis of these encouraging results, the P.E.C. approach was used to simulate the reactivity of hydrocarbons found in auto exhaust and the reactivity index, r_i, set equal to unity.

The next application of the P.E.C. method was a treatment of the mixture of hydrocarbons found in auto exhaust as a two-component system; olefins and alkanes are lumped as butene and aromatic hydrocarbons are lumped as toluene. Since the U.S. Bureau of Mines had run an extensive series of experiments studying the photooxidation of diluted automotive exhaust in the presence of known levels of NO_x, their chamber was chosen for realistic experimental values. Furthermore, these investigators compared experimental values from the smog chamber to an atmospheric sample. The results of the automotive exhaust simulation are shown in Table IV along with the experimental and atmospheric observations. The initial conditions in the smog chamber were: $(NO_x)_0 = 0.27$ ppm, $(HC)_0 = 3.13$ ppmC; $(CO)_0 = 50$ ppm; $k_D = 1.3 \times 10^{-3}$ sec and $(H_2O) = 50\%$RH. The 6-hr simulation required 98 sec of central processor time. Rate constants for butene-1 oxidation were used.

Using a value of 100 for the average molecular weight of hydrocarbons in car exhaust, and an average carbon number of 2.85, a concentration of ~ 1.0 ppm of nonmethane hydrocarbons was estimated by the following relation:

$$(HC,ppm) = \frac{(HC,ppmC)}{\overline{C_n}} = \frac{3.13}{2.85}$$

where $\overline{C_n}$ is the average carbon number of exhaust hydrocarbons. The 1.0 ppm of nonmethane hydrocarbons was divided into an alkane-olefin fraction, (0.85 ppm), and an aromatic fraction, (0.15 ppm). By this scheme, only the alkane-olefin fraction could photooxidize to PAN and the aromatic hydrocarbons would produce benzoylperoxynitrates. The computed results are compiled in Table IV and show satisfactory agreement among the oxidant values (mainly ozone) observed in the atmosphere and in the smog chamber. However, the computed levels of PAN were one order of magnitude below the atmospheric and experimental values. This partial success in simulating the reactivity of automotive exhaust indicates that some smog products may be predicted by the P.E.C. approach. Future work will be directed toward identifying the scope and limitations of the P.E.C. approach.

Acknowledgment

This work was performed under the auspices of the National Science Foundation, Research Applied to National Needs, Grant AG-411.

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TABLE I.

REACTIONS INCLUDED IN DETAILED MECHANISM SIMULATION

Reaction number	*Reaction*								*Reaction number*	*Reaction*							
1	O_3	+	*BUTENE 1	→	*ACTYL	+	*FORMAL	IRR	32	H_2	+	OH	→	H_2	+	H	REV
2	HO_2	+	*TOLYL	→	*BENZYL	+	H_2O_2	IRR	33	OH	+	*BUTENE1	→	*BUTENYL	+	H_2O	IRR
3	NO	+	NO	→	NO_2	+	NO_2	IRR	34	HO_2	+	*BUTENE1	→	*BUTENYL	+	H_2O_2	IRR
4			NO_2	→	NO	+	O	IRR	35	O	+	*BUTENE1	→	*ACTYL	+	*FORMAL	IRR
5			HNO_2	→	NO	+	OH	IRR	36	O_2	+	*BUTENYL	→	*BUTENPR			IRR
6			O_3	→	O_2	+	O	IRR	37	NO	+	*BUTENPR	→	NO_2	+	*BUTOXY	IRR
7			O_3	→	*OD	+	O_2	IRR	38	O_2	+	*ACTYL	→	*ACTPR			IRR
8	*OD	+	H_2O	→	OH	+	OH	IRR	39	NO	+	*ACTPR	→	NO_2	+	*ACPR	IRR
9	*OD	+	N_2	→	O	+	N_2	IRR	40	*ACTPR	+	*ACPTR	→	*DIACTPR	+	O_2	IRR
10			H_2O_2	→	OH	+	OH	IRR	41	NO_2	+	*ACTPR	→	*PAN			IRR
11			HNO_3	→	OH	+	NO_2	IRR	42	O_2	+	*BUTOXY	→	HO_2	+	*MVKET	IRR
12			*FORMAL	→	*HCO	+	H	IRR	43	O_3	+	*MVKET	→	*ACTYL	+	*FORMAL	IRR
13			*FORMAL	→	H_2	+	CO	IRR	44	OH	+	*MVKET	→	H_2O	+	*ACTYL	IRR
14			*FORMAL	→	H_2O	+	CO	IRR	45	HO_2	+	*MVKET	→	H_2O_2	+	*ACTYL	IRR
15			*MVKET	→	*ACETALD	+	*ETYLEN	IRR	46	O	+	*MVKET	→	*ACTYL	+	*FORMAL	IRR
16	*HCO	+	O_2	→	CO	+	HO_2	IRR	47			*ACPR	→	*METANOL	+	CO_2	IRR
17	*FORMAL	+	OH	→	*HCO	+	H_2O	IRR	48	O_3	+	*TOLYL	→	*BENZAL	+	*BENZOYL	IRR
18	O	+	O_2	→	O_3	+	M	REV	49	O	+	*TOLYL	→	*BENZAL	+	*BENZOYL	IRR
19	NO	+	O_3	→	NO_2	+	O_2	REV	50	O_2	+	*BENZOYL	→	*BENOPER			IRR
20	NO	+	NO_2	→	HNO_2	+	HNO_2	IRR	51	NO	+	*BENOPER	→	NO_2	+	*BENOLOX	IRR
21	NO	+	O	→	NO_2	+	M	REV	52	NO_2	+	*BENOPER	→	*BAN			IRR
22	OH	+	CO	→	CO_2	+	H	REV	53	OH	+	*TOLYL	→	*BENZYL	+	H_2O	IRR
23	H	+	O_2	→	HO_2	+	M	REV	54	*BENOPER	+	*BENOPER	→	*DIBENPR	+	O_2	IRR
24	OH	+	OH	→	H_2O	+	O	REV	55	O_2	+	*BENZYL	→	*BENZPER			IRR
25	HO_2	+	HO_2	→	H_2O_2	+	O_2	REV	56			*BENZPER	→	*BENZAL	+	OH	IRR
26	H	+	NO_2	→	OH	+	NO	REV	57	HNO_2	+	HNO_2	→	NO	+	NO_2	IRR
27	H	+	O_3	→	O_2	+	OH	REV	58	O_2	+	*BUTENPR	→	*BUTOXY	+	O_3	IRR
28	HO_2	+	NO	→	OH	+	NO_2	REV	59	NO	+	HNO_3	→	HNO_2	+	NO_2	IRR
29	OH	+	H_2O_2	→	H_2O	+	HO_2	REV	60	O_2	+	*BENZPER	→	*BENZAL	+	O_3	IRR
30	OH	+	NO_2	→	HNO_3	+	M	REV	61			*BUTENPR	→	*ACETALD	+	OH	IRR
31	NO_2	+	O	→	NO	+	O_2	REV	62			H_2O_2	→	H_2O	+	O	IRR

Table II. Reaction rate constants, k_{298K}, used in Ames photochemical model.

Reaction number	*Rate constant (CGS units)*[a]	*Reaction number*	*Rate constant (CGS units)*[a]
1	3.97855E+06	32	3.66010E+09
2	2.00000E+12	33	3.80000E+12
3	1.15120E+05	34	3.80000E+12
4	6.73000E−03	35	1.78653E+12
5	6.73000E−04	36	4.12645E+12
6	2.30000E−04	37	3.09051E+11
7	2.90000E−05	38	3.90702E+11
8	1.68000E+14	39	3.09051E+11
9	1.74000E+13	40	9.00000E+13
10	2.00000E−06	41	4.07000E+10
11	1.90000E−06	42	4.33771E+12
12	4.16000E−05	43	3.97835E+06
13	1.05000E−04	44	8.31254E+11
14	1.05000E−04	45	8.31254E+11
15	8.00000E−05	46	1.78653E+12
16	1.02000E+14	47	2.17573E−01
17	5.00000E+10	48	6.13057E+05
18	2.29700E+14	49	4.44751E+09
19	1.21789E+10	50	4.12645E+12
20	8.80000E+06	51	3.09051E+11
21	2.46960E+16	52	5.30000E+12
22	9.03917E+10	53	2.00000E+12
23	8.11857E+15	54	9.00000E+13
24	1.50019E+12	55	4.12645E+12
25	6.50000E+13	56	1.00000E+12
26	2.78547E+13	57	1.80000E+09
27	1.50444E+13	58	4.10000E+10
28	1.71936E+11	59	4.09000E+09
29	4.78521E+11	60	4.10000E+10
30	5.00000E+17	61	1.00000E+12
31	3.63050E+12	62	2.00000E−06

N.B.: Above rate constants used in simulations; except for changes specified for each smog validation.

[a] Unimolecular Reactions, sec^{-1}
Bimolecular Reactions, cm^3 $mole^{-1}$ sec^{-1}
k_{18}-reaction treated as pseudo-bimolecular, N_2 = M (third body)
k_{20}-reaction treated as pseudo-bimolecular, H_2O = M

TABLE III.

COMPARISON OF SMOG CHAMBER RESULTS AND COMPUTED LEVELS USING THE P.E.C. CONCEPT

[HC] FINAL	[PAN]	[HCHO]	$[O_3]$	$[HC]_0$ INITIAL	r_i C_3H_6	r_i C_4H_8-1	REACTION EXTENT CHAMBER %
BUTENE-1 SIMULATION							
0.30 ppm	0.050	0.90	0.47	2.0	0.8	1.00	85%
0.32	0.004	0.14	0.57	2.0			CALC
PROPYLENE SIMULATION							
0.54	0.350	1.17	0.54	2.0	1.0	1.25	73%
0.69	0.008	0.24	0.58	2.5			CALC
TRANS-2-BUTENE SIMULATION							
0.30	0.600	0.75	0.44	2.0	3.0	3.75	85%
1.26	0.480	3.80	0.65	7.5			CALC
BUTADIENE-1, 3 SIMULATION							
0.30	0.020	0.80	0.48	2.0	1.4	1.75	85%
0.53	0.060	0.91	1.09	3.5			CALC
2-METHYL-2-BUTENE SIMULATION							
0.10	0.850	0.68	0.49	2.0	4.0	10.00	95%
0.48	0.380	3.20	0.37	9.6			CALC

SMOG CHAMBER DATA: J.M. HEUSS AND W.A. GLASSON,
GENERAL MOTORS REPORT GMR-747 (1968)

TABLE IV.

COMPARISON OF POLLUTANT LEVELS FROM AN ATMOSPHERIC SAMPLE, A SMOG CHAMBER EXPERIMENT AND A KINETIC MODEL

SAMPLE	INITIAL REACTANT LEVEL		SMOG LEVEL	
	TOTAL HYDROCARBON ppmC	NO_x ppm	OXID ppm	PAN ppm
ATMOSPHERE (RIVERSIDE, CALIF)*	3.05	0.30		
10/24/68 AT 16:10 PST			0.40	0.034
SMOG CHAMBER (BUR MINES)*	3.13	0.27		
AFTER 2 hr IRRADIATION			0.26	0.034
AFTER 4 hr IRRADIATION			0.49	0.047
AFTER 6 hr IRRADIATION			0.49	0.044
KINETIC MODELLING VALUES				
INITIAL CONCENTRATION	1.0 ppm	0.29		
AFTER 2 hr IRRADIATION			0.21	0.0019
AFTER 4 hr IRRADIATION			0.26	0.0039
AFTER 6 hr IRRADIATION			0.26	0.0056

B DIMITRIADES, U S BUREAU OF MINES REPORT NO. 7433 (1970)

FIG. 1.

COMPARISON OF EXPERIMENTAL LEVELS OF ISOBUTENE, FORMALDEHYDE AND CARBON MONOXIDE WITH MODEL PREDICTIONS

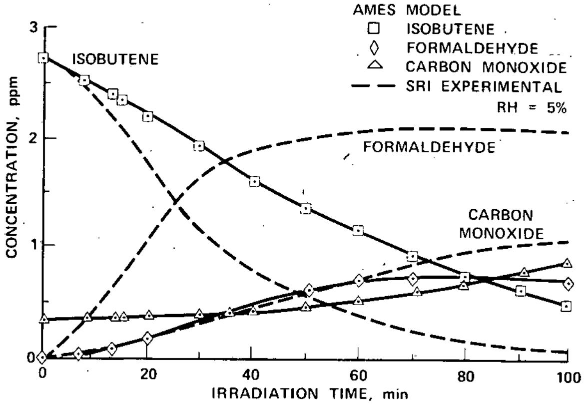


FIG. 2.

COMPARISON OF EXPERIMENTAL LEVELS OF ACETONE AND PAN WITH MODEL PREDICTIONS

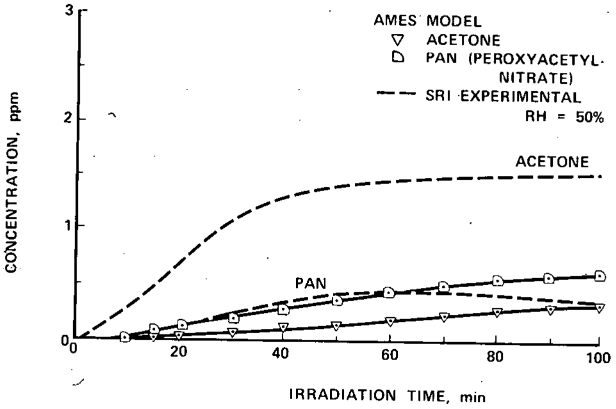
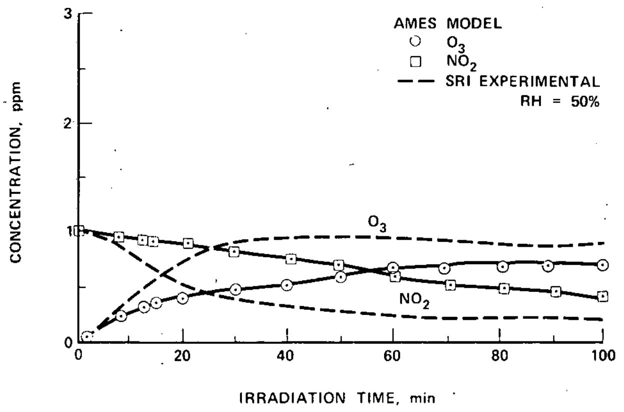


FIG. 3.

COMPARISON OF EXPERIMENTAL LEVELS OF OZONE AND NO_2 WITH MODEL PREDICTIONS



UPTAKE OF TETRAETHYL LEAD VAPOR BY ATMOSPHERIC DUST COMPONENTS*

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Abstract

Exposure of simulated atmospheric dust components to air streams doped with tetraethyl lead (TEL), both in the presence and absence of water vapor, results in uptake of lead by the solids. On a specific surface area basis, the order of increasing amount of lead taken up by the substrates for identical lead exposures is as follows: silicon dioxide < aluminum oxide < carbon black < graphitized carbon black. Sorbed lead is only very slowly removed upon aging. A major effect of aging exposed samples is to convert a substantial portion of the sorbed lead compounds into species which are not removed with n-hexane extraction or moderate heating. The implications are as follows: (1) sorption of organic lead compounds on atmospheric dust components may represent a significant scavenging mechanism, and (2) atmospheric particulates may serve as substrates for conversion of sorbed organic lead to inorganic lead compounds.

Introduction

Considerable attention has recently been focused upon identifying the chemical forms of lead in the atmosphere, in addition to the extent of atmospheric contamination by lead. Recent reports indicate that a significant and highly variable portion of the total atmospheric lead burden may escape collection using high-volume air samplers with conventional filters[1,2,3,4]. Some of the lead passing through these filters consists of gaseous organic lead compounds[5,6]. There is also evidence to support the view that very fine lead-containing particles in certain size ranges may also pass through many filters[7]. Because the escape of a substantial portion of atmospheric lead through conventional filters produces major errors in computing human exposures, there is an urgent need to define the chemical as well as physical forms of lead present in the atmosphere. This information can be used to identify sampling methodologies by means of which the total atmospheric lead content and its components can be routinely and reliably measured. A second major concern is that the biological retention and toxicity of the various chemical and physical forms of lead in the atmosphere may be quite different.

This report deals with the possibility of a third form of lead which may occur in the atmosphere: organic lead compounds sorbed on atmospheric dust particles. The experiments described were carried out to characterize interactions between tetraethyl lead vapor and atmospheric dust components in terms of specificity, extent, and stability.

Materials

The following four solids in finely divided form were selected as simulated atmospheric dust components: Alon (Al_2O_3), Cabosil (SiO_2), Thermax (carbon black), and Graphon (graphitized carbon black). SiO_2, Al_2O_3, and carbonaceous carbon are all known to be major components of atmospheric particulates in polluted areas[8]. Table 1 presents relevant specific surface area and lead content data.

TABLE I.

Properties of Simulated Dust Components

Sample	Pb Content	Area	$\overline{d}$ (est)
Alon	0.27 ppm	87.4 m^2/g	0.017 μ
Cabosil	0.88	195	0.012
Thermax	0.25	8.4	0.36
Graphon	6.0	87.4	0.030

Mean particle diameters were estimated on the basis of the specific surface area measurements, bulk density data, and the assumption of spherical geometry. Submicron sizes are characteristic of suspended particulate matter in urban atmospheres[9]. Moreover, the smaller submicron particles are typically enriched in lead, relative to the concentration of lead found associated with larger submicron particles[10].

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Samples of tetraethyl lead (TEL) were obtained from the Ethyl Corporation and were found to contain 1.06 g Pb per ml. Filters were 47 mm Type A glass fiber filters obtained from the Gelman Co.

Apparatus

The apparatus depicted in Figure 1 was constructed for exposing simulated dust component samples to air streams doped with TEL, both in the presence and absence of water vapor. Solid samples were applied with a spatula to the mounted 47 mm filters. Air flow was maintained during application of the solid. Sufficient solid was added in each case to provide a thin, visually uniform coating.

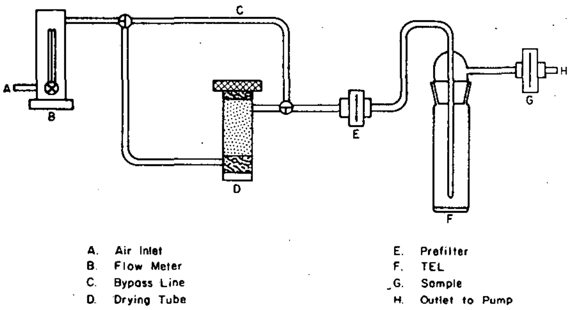

FIG. 1. Apparatus for Exposing Atmospheric Dusts to TEL Vapor

The actual uniformity of solid distribution was checked by determining the mass of solid found in each half of a split filter. In a typical case of five such comparative weighings, the amounts of solid applied to each half of a given filter agreed, on the average, within 2%. Major inhomogenieties in the density of the solid applied to the filters were not detected. The amount applied varied over the approximate range of 0.02 to 0.15 g with lesser amounts used for the higher specific surface area solids. The prefilter was loaded with a 47 mm Gelman Type A glass fiber filter; the purpose of the prefilter is to prevent carryover of drying agent (Drierite) and possible effects by particulate matter already present in the atmosphere.

Procedure

A mechanical vacuum pump was employed to draw laboratory air through the apparatus at the constant flow rate of 5.95 l/min for a period of 30 min for each 0.11 ml dose of TEL. TEL volatilization was normally complete in 20-25 minutes. A calibrated pipet was used to transfer each TEL dose to the impinger. Single TEL doses were employed in all cases with the exception of the samples prepared for the hexane extraction experiments where two TEL doses were used. Blanks were determined by exposing filters to identical TEL dosing conditions. For dry air, the average amount of lead taken up by the filter alone in 16 determinations is 63.0 μg with a standard deviation of 12.6 μg. For undried air, the average amount of lead taken up by the filter alone in 12 determinations is 42.5 μg with a standard deviation of 15.9 μg. The mean blanks are statistically distinguishable at the 99.5% confidence level, as determined by application of the student t test. Blank corrections have been applied to all lead uptake data.

Analysis for lead is by AAS in accordance with procedures reported by Skogerboe[4,7]. Total lead determinations were carried out by analyzing the solution obtained from the extraction with 25 ml 3M HNO_3. Determinations for organic lead were made by analyzing solutions obtained from extraction with 10 ml n-C_6H_{14}.

Results

Results of experiments to determine whether significant lead uptake occurs when simulated atmospheric dust components are exposed to TEL vapor in dry air are presented in Table 2.

TABLE II. Pb Uptake by Dust Components from TEL-Doped Dry Air

Sample	Pb Found	% Monolayer (est)
Cabosil	63.6 μg/m²	6.7
Alon	192	20
Thermax	288	31
Graphon	322	34

Fractional monolayer coverage was estimated in each case on the basis of BET-N_2 specific surface area data and the $Pb(C_2H_5)_4$ molecular cross-sectional area computed from liquid density data and the assumption of spherical molecular geometry. Using the handbook[11] TEL liquid density value of 1.66 g/cm³ yields an estimated TEL molecular cross sectional area of 57×10^{-16} cm². A distinction can therefore be made among the four solids in terms of the degree of lead uptake on a specific surface area basis. The order of increasing lead uptake is as follows: Cabosil < Alon < Thermax < Graphon. In terms of fractional monolayer coverage by sorbed TEL, the range of values is 6.7 - 34% for Cabosil and Graphon, respectively. On a per unit mass basis, the percentages of lead taken up by the four solids are as follows: Cabosil, 0.34%; Alon, 1.2%; Thermax, 0.64%; Graphon, 0.32%. Because lead uptake in these experiments is very likely a surface phenomenon, comparisons between solids are judged more meaningful on a per unit surface area basis than on a per unit mass basis. Nevertheless, the mass percentage data compare closely with those that can be computed for the composition of actual atmospheric particulate matter.

The effect of water vapor on Pb uptake by three simulated dust components was explored by comparing the data above with values obtained using undried laboratory air. For the blank glass fiber filter, Alon, and Thermax, the data presented in Table 3 suggest that the presence of water vapor may suppress lead uptake.

TABLE III. Effect of Water Vapor on Pb Uptake

Sample	Pb Uptake Dry Air	Pb Uptake Lab Air	% Change
Blank	63.0 μg	42.5 μg	- 33
Cabosil	63.6 μg/m^2	88.1 μg/m^2	+ 38
Alon	192 μg/m^2	146 μg/m^2	- 24
Thermax	288 μg/m^2	247 μg/m^2	- 14

On the other hand, the presence of water vapor apparently enhances lead uptake by Cabosil, a known desiccant. Thus it is highly likely that exposure of Cabosil to water vapor results in a surface that is quite different in nature and extent than the original surface. This possibility makes use of the original BET specific surface area of Cabosil questionable with respect to computing lead coverage values in the presence of water vapor. In terms of surface composition, decreases in lead uptake due to the presence of water vapor can be understood in terms of the blocking by water molecules of the higher energy sites upon which TEL sorption can occur. Here, the effect of water vapor would be to decrease the effective surface area with respect to TEL sorption.

The effect of aging samples exposed to TEL-doped dry air was investigated to determine the kinetic stability of lead taken up by the simulated atmospheric dust components. A series of samples of Graphon and Alon, respectively, was identically exposed to TEL. Individual samples were placed in covered, but unsealed Petri dishes for storage in the laboratory. At various time intervals, individual filters were analyzed for lead. The results are shown in Figure 2. The data do not obey simple first-order kinetics. According to Langmuir theory, the rate of desorption should be proportional to the amount sorbed[12]. While the amount of lead remaining does decrease exponentially with time during the first two or three days, the rate of disappearance of lead becomes virtually constant thereafter. The present data represent the results of preliminary experiments and are therefore judged insufficient for development of a detailed mechanistic picture. Nevertheless, it does seem clear that the observed lead loss with time may not be the result of a single depletion mechanism alone. It is possible that the present observations reflect a composite of several processes. Two processes that come to mind immediately are as follows: desorption of TEL, and chemical conversion of sorbed TEL to nonvolatile lead-containing products. The analytical procedure employed for these samples yields only the total amount of lead remaining as a function of time and does not permit a distinction between the various chemical forms of lead.

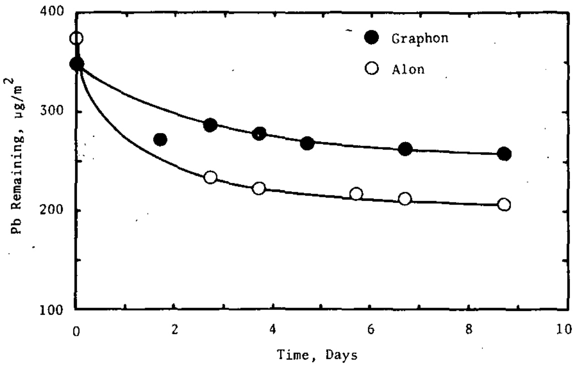

FIG. 2. Effect of Aging on Lead Retained by Dust Components Exposed to TEL Vapor

In an attempt to explore the possibility of conversion of sorbed TEL to nonvolatile lead-containing compounds, samples of dust components were baked at 90°C for 10 hours following exposure to dry air doped with TEL. The results are presented in Table 4 and indicate that sorbed lead is only partially removed under these conditions. Although this temperature is well below the decomposition temperature of TEL (200°C), the possibility that heating accelerates reactions that occur only very slowly under ambient conditions must be considered.

TABLE IV. Effect of Baking for 10 Hours at 90°C

Sample	Pb Uptake Before	Pb Uptake After	% Change
Cabosil	63.6 μg/m^2	54.9 μg/m^2	-14
Alon	192	165	-14
Thermax	288	131	-55
Graphon	322	305	-5.2

A further attempt to distinguish between the forms of lead found on Thermax was made by means of an extraction with n-hexane. Thermax was selected on the basis of the above data indicating a greater fractional lead loss during baking. The exposed sample was halved, and the first half was analyzed for total lead content. The second half was extracted with an aliquot of n-hexane with gentle warming. Both the n-hexane extract and the residue were then analyzed for lead. The results in Table 5 are in qualitative agreement with those of the baking experiments and thus are consistent with the possibility that aging may convert a portion of the sorbed TEL into nonvolatile lead compounds which are not extracted into the organic phase.

TABLE V. Total and Hexane-Extractable Pb

	Half A	Half B		
Sample	Total Pb	Organic Phase	Solid Phase	% Recovery
Thermax, 0.1464 g	130 μg	32 μg	82 μg	88
Blank	40 μg	4.3 μg	26 μg	76
	90 μg	27.7 μg	56 μg	93

Discussion

The results of these preliminary laboratory simulation experiments support the view that atmospheric dust components can sorb TEL from air, both in the presence and absence of moisture. If this process occurs in the atmosphere, the possibility of a third form of lead, in addition to organic lead vapor and inorganic lead particulate, must be considered. These results also indicate that lead taken up by the solids can exist in more than one chemical form, one of which is readily removed by heating or extraction with n-hexane, and the other of which is much more tightly held. The possibility that aging may convert sorbed TEL to other chemical forms of lead is suggested in Figure 3.

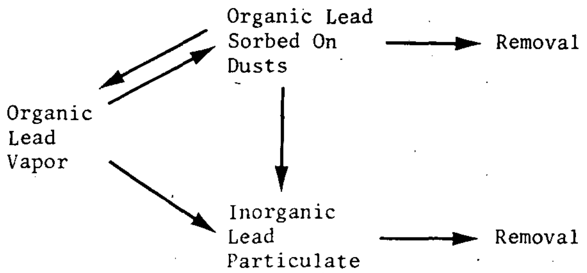

FIG. 3.

In considering these possibilities, it is useful to estimate the quantity of sorbed lead that might occur under atmospheric conditions. If one considers an atmospheric dust concentration of 100 $\mu g/m^3$ of 0.2 μ diameter particles with a bulk density of 3 g/cm^3, the particulate surface area per m^3 of air is approximately 10 cm^2, assuming spherical particle geometry and a roughness factor of unity. Nonspherical particle geometry and roughness factors greater than unity would make this quantity considerably larger. For 30% monolayer coverage by sorbed TEL, the quantity of sorbed TEL per m^3 of air would be approximately 0.3 μg. The potential contribution of lead sorbed on atmospheric dusts to the total lead burden therefore cannot be ignored.

Additional experiments are in-progress to further define the possible role of gas-particle interactions in removing organic lead vapor from the atmosphere. This information is needed to identify and correct possible deficiencies of various sampling techniques for determining the total atmospheric lead burden, in addition to the various forms of lead in the atmosphere. Moreover, some of the rather wide variations in reported atmospheric organic lead values[4,13] may be understandable in part in terms of a partitioning of organic lead vapor between the solid and gas phases, a process which may be profoundly influenced by atmospheric conditions, in addition to the presence or absence of other pollutants.

Acknowledgements

The authors are grateful for the technical assistance of Greg Johnson and Don Dick in analyzing samples for lead. Appreciation is also expressed to the Ethyl Corporation for supplying TEL samples.

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THE COLLECTION EFFICIENCY OF AN ELECTROSTATIC PRECIPITATOR FOR TRACE METALS FROM AN OPEN HEARTH FURNACE

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ABSTRACT

Emission tests in June 1974 both upstream and downstream of an electrostatic precipitator controlling a battery of seven open hearth furnaces resulted in an average particulate collection efficiency of 97.7 percent for three simultaneous sample sets. Specific efficiency tests were also performed simultaneously with Andersen fractionating sampling devices and indicated an apparent minimum collection efficiency at the 4-micron aerodynamically sized particle range. The efficiency decrement at 4 microns is primarily due to transformation of particle sizes within the electrostatic precipitator. Agglomeration of the 1-micron particles to an effective 4-micron size is postulated as the primary reason for the pseudo efficiency decrement at 4 microns. Average particulate concentration upstream and downstream of the precipitator was found to be 0.349 grains/SCF and 0.008 grains/SCF respectively. Total particulate mass emission rates were observed to vary between 35 and 94 lb/hr and resulted in calculated emission factors of 0.16 and 0.46 lb-particulate per ton of steel produced. The mass median diameter of the particles entering the precipitator was found to be 1.56 microns for an average of 3 runs, with the mass median diameter leaving, 1.0 microns.

INTRODUCTION

Emission tests were conducted in June 1974 on the upstream and downstream sides of an open hearth electrostatic precipitator. Based on three sets of simultaneous samples, overall particulate collection efficiency was found to be 97.7%.

Specific efficiency tests were also performed with Andersen inertial particle sizing heads, The mass median aerodynamic diameter of the particulate was 1.56 micron into the precipitator and 1.00 micron at the exhaust stack. Specific efficiency results showed a minimum at the 4 micron size, apparently due to transformation of particle size within the electrostatic precipitator. Agglomeration of small particulate into the 4 micron range is postulated as the primary reason for the apparent efficiency minimum.

Average particulate concentration upstream and downstream of the precipitator was found to be 0.349 grains/SCF and 0.008 grains/SCF, respectively. Total mass emission rates were observed to vary between 35 and 94 lb/hr with correspond to emission factors of 0.16 to 0.46 lb/particulate per ton of steel produced.

FACILITY DESCRIPTION

Open Hearth Process and Facilities

The basic open hearth process depends on a basic, oxidizing slag for oxidation of such impurities as carbon, phosphorus, silicon, and sulphur. The sequence of events in a "heat" (cycle) in the hot metal practice used during the tests is as follows:

1. In the charging and melting period, scrap, limestone, and possibly some ore are charged to and melted in the open hearth furnace.
2. Near the end of the meltdown period, chunks of limestone float up to the slag, while releasing CO_2 according to the reaction $CaCO_3 \rightarrow CaO + CO_2$. This period is called the lime boil.
3. Sometime after the lime boil, the hot metal (up to 75% of the total metallic charge) is added. Hot metal is high in carbon, so a violent reaction accompanies hot metal addition, as carbon is oxidized by the slag and CO is released.
4. During the refining period, impurities are oxidized and dissolved in the slag. Oxygen is occasionally "blown" into the bath during this period, via a jet called a "lance". The purpose of blowing oxygen is rapid oxidation of carbon, and raising the bath temperature to a level suitable for "tapping".
5. When the bath has been sufficiently refined, and the temperature is high enough,

the metal is poured (tapped) from the open hearth furnace.

Throughout the heat, flame comes alternately from two sides of the furnace, from two oil and/or gas burners and constantly from a single burner in the center of the roof. When one end burner shuts off, the other turns on, and the draft changes direction 180°. The purpose of this periodic "draft reversal" is to keep the checker regenerators on either side of the furnace at a temperature suitable for preheating incoming air and for cooling exit gases before they enter the precipitator. The draft reversal cycle is determined by a timer, manually set by an operator. There are seven open hearth furnaces in the shop, all of which are served by the same electrostatic precipitator, manufactured by Joy-Western Precipitation Division.

Exit gases from all seven open hearth furnaces pass through a single mixing chamber before entering the ten precipitator chambers. The gases then proceed through induced draft fans and are discharged via a 22 foot diameter stack at an elevation of 141 feet above grade.

Sampling Locations

In order to determine overall and specific collection efficiency across the open hearth precipitator, existing sampling ports at the exhaust stack were used in addition to ports which were installed according to specific EPA guidelines at the mixing chamber upstream of the precipitator. Refer to Figure 1 18 and 24 sampling points were used in the ESP outlet and mixing chamber respectively. The 18 traverse points were selected on one stack diameter and yielded a relatively flat velocity profile as seen in Figure 1.

Upstream precipitator samples were taken at the mix chamber, refer to Figure 2, which combines the flue gases from all seven open hearth furnaces and feeds them to the precipitator. The purpose of the chamber is to provide adequate mixing of the individual furnace gases and particulates so that a homogeneous stream is presented to the precipitator. This diminishes the variations of particulate resistivity and gas temperature which is important to reliable precipitator operation and optimum collection efficiency. The mix chamber feeds the precipitator via ten ducts and transitions, two of which are take-offs at the top of the mix chamber. Each of these take-off ducts

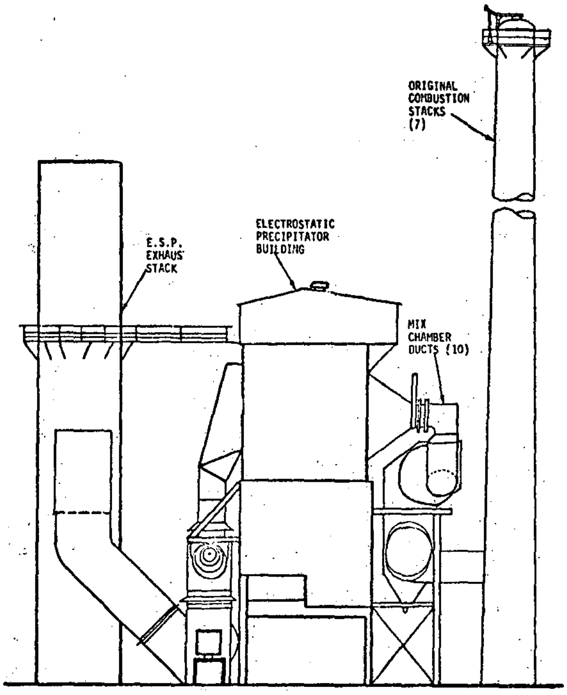

Figure 1. End Elevation of Electrostatic Precipitator Building.

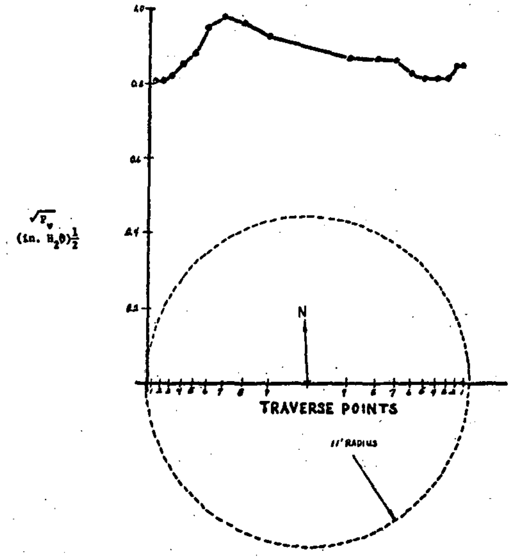

Figure 2. Velocity Profile For Open Hearth Hearth Electrostatic Precipitator Stack.

have an 8' x 7' cross section and were chosen as the upstream sampling location. The sampling strategy assumes a homogeneous mixture of gases and particulates at the mix chamber, thereby yielding representative particulate concentration values at the precipitator inlet. The same particulate concentration is assumed entering all ten precipitator chambers. The particulate not collected then pass into the exhaust stack, where all ten individual precipitator chambers converge into one stream. The total mass flow of gases is then determined at the outlet stack. In this way precipitator efficiency can be computed since total mass flow rate of particulates entering and leaving the precipitator can be computed.

Emission Factors

Results of the grain loading tests and inclusion of gas flow rates and process data resulted in the trace metal emission factors in Table 1. The first samples at each location were preliminary runs, and it should be noted that they are not simultaneous. Runs 2, 3, and 4 are simultaneous at the mix chamber and exhaust stack. Table 1. also presents the emission factors for total particulates. The average of four tests was 0.30 lb-part./ton of steel produced with a range of 0.16 to 0.46. These values compare to 0.35 published in AP-42.[1]

Collection Efficiency

Table 2. contains the overall collection efficiency for test runs 2, 3, and 4. The average value was 97.7%.

Table 1. Trace Metal Emission Factors for an Electrostatic Precipitator Controlled Open Hearth Furnace: June 4, 11, 12, 1974. (Lb. Metal Emission/Ton Steel Produced)

Run#	Cd x10^4	Pb x10^3	Zn x10^2	Cn x10^4	Fe x10^2	Ni x10^4	Total Part.
1	3.6	6.3	3.0	6.3	--	8.0	0.29
2	1.1	7.9	5.4	5.9	1.2	1.1	0.46
3	1.2	3.8	1.9	4.0	5.9	10.9	0.16
4	.81	3.8	2.8	6.4	.89	1.8	0.28
Avg.	1.7	5.5	3.3	5.7	2.7	5.5	0.30

Table 2. Overall Open Hearth Collection Efficiency.

Run Number	Efficiency, %
2	96.5
3	98.9
4	97.5
Average	97.7

Particle size distribution was also determined during each of these tests and the results are shown in Figure The mix chamber exhibited a 1.56 micron mass median diameter and the exhaust stack indicated 1.0 micron. Trace metals were then determined for each stage of the Andersen both up and downstream of the precipitator. The resulting total particulate fractional efficiency curves shown in Figure indicated a marked depression at approximately 4 microns. The tests on 6/11 and 6/12/74 show a minimum collection efficiency of 82 and 96% respectively. This marked decline in efficiency is much greater than that reported in the literature. McCain[2] et al, indicate a fractional efficiency depression at 4 microns, however, the fractional efficiency at the depression was 99.4%, a much greater value than measured in this work. The maximum efficiency reported by McCain was 99.8% at 1.0 micron.

The trace metal fractional efficiency characteristic curve for the test on 6/12/74 is shown in Figure . Note that the depression in collection efficiency reaches a maximum at 4 microns and that the cadmium species exhibits the greatest depression. Figure is typical of tests on 6/11 and 6/13/74.

The collection efficiency minimum near 4 micron particle size is in agreement with a study of the effect of particle size on migration velocity by Henrich[3] Henrich discovered a minimum in migration velocity near 4 micron particle sizes, and suggested that the minimum could have been caused by an interaction between two separate migration mechanisms. A reasonable pair of migration mechanisms would be electrical drift and turbulent diffusion. Electrical drift is most efficient in moving large particles; turbulent diffusion has the greatest effect on small particles. The sum of these two effects could very well produce a minimum in the migration velocity and subsequently in the collection efficiency.

Examination of the total particulate concentration as a function of particle size indicated that an agglomeration mechanism would account for the efficiency decrement at 4 microns. Upstream of the precipitator in the mix chamber a relatively high concentration of submicron material was found. At 4 microns, a definite lack of 4 micron particles was found. The 4 micron particle concentration was the lowest measured as compared to the other size ranges. However, after the precipitator the 4 micron size concentration exhibited a definite relative increase. Transformation of submicron material through the mechanism of agglomeration would produce an apparent collection efficiency decrement at the new transformed size range. The precipitator would in effect be creating particles in the 4 micron size range and the collection efficiency would appear to decline at that point.

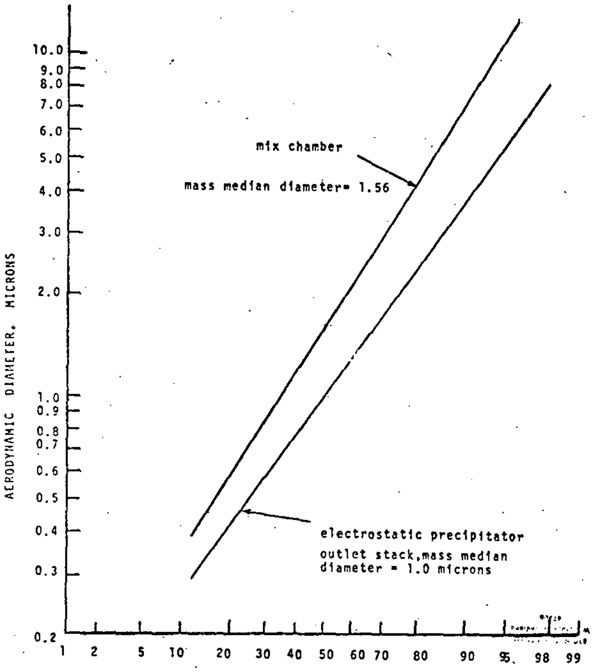

Figure 3. Particle Size Distribution of Open Hearth Fume Before and After Precipitator.

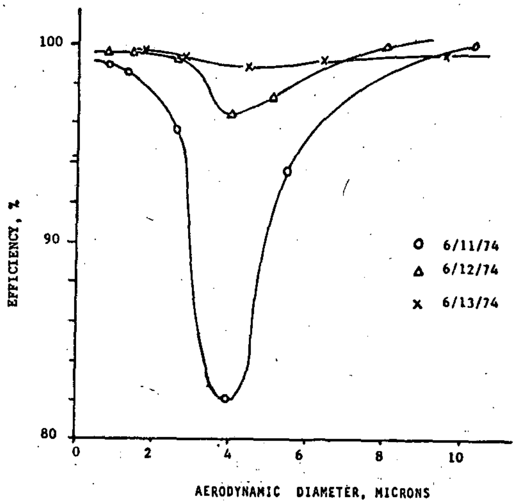

Figure 4. Total Particulate Fractional Efficiency.

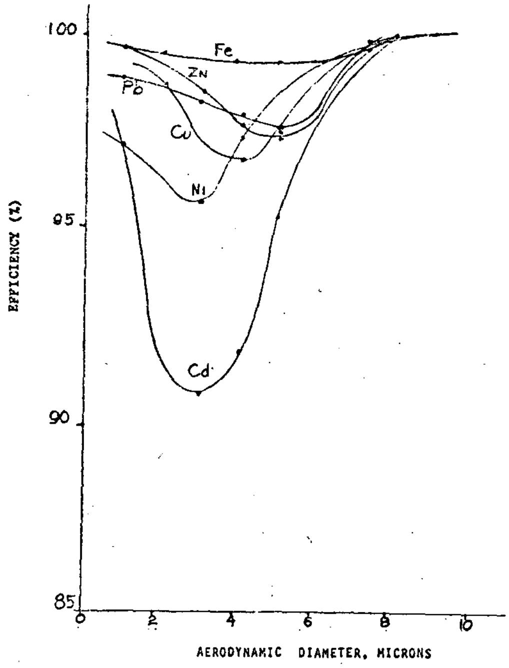

Figure 5. Trace Metal Fractional Efficiency.

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PHYSICAL AND CHEMICAL CHARACTERIZATION OF SELENIUM IN COAL FIRED STEAM PLANT EMISSIONS[1]

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ABSTRACT

Selenium was measured in coal, slag, and fluegas at the Allen Steam Plant in Memphis, Tennessee. Approximately 0.3% of the coal-derived selenium was incorporated into slag. Sixty eight percent of the Se was found on the fly ash particles while the rest was found in the vapor phase. Since the electrostatic precipitators at the plant are very efficient for fly ash removal, 93% of the emitted Se existed in the vapor phase. The major part of Se discharge from the steam plant occurs via fly ash removal to nearby slag ponds. All of the selenium in the slag and flue gas exists as elemental Se and is thus not immediately available for plant uptake. Selenium emission rates from data collected at the steam plant were used to calculate the minimum mobilization of Se from coal consumption in the U.S. and world. Calculations indicate that 1.5 to 2.5 times as much Se is mobilized by man through coal burning as by natural weathering.

INTRODUCTION

Using literature data, Bertine and Goldberg (1971) have postulated that the combustion of fossil fuels may mobilize several trace elements at rates which approach natural weathering processes. In an effort to better understand the mechanisms responsible for this mobilization several investigators have studied the partitioning of trace elements within coal fired steam plants (Billings et al., 1973; Kalb and Baldeck, 1973; Kaakinen and Jorden, 1973; Bolton et al., 1973; Natusch et al., 1974; and Klein et al., 1974). Results from these investigations show that many elements are preferentially incorporated in slag and fly ash or are emitted in the vapor phase. Calculations of trace element emissions thus need to consider these processes so that more realistic predictions of emissions can be made. In addition, the chemical and physical form of these emissions need to be determined so that possible health hazards can be evaluated.

Bolton et al. (1973) have previously demonstrated that a complete mass balance of selenium cannot be achieved by measuring only the solid phases of the material flow in a coal fired-steam plant. This paper describes methods used to sample selenium in coal, slag, fly ash, and the vapor phase in the emissions of the T. A. Allen Steam Plant in Memphis, Tennessee. In addition, the chemical state of selenium was determined for each phase to better understand biological and geochemical implications of these emissions.

EXPERIMENTAL PROCEDURES

Plant description- The plant uses cyclone-fed boilers. Normal coal consumption at 290 MW is about 100 tons per hour. The coal is fed to the boilers in crushed form rather than the more commonly used pulverized form. As a consequence the ash produced by the boilers is about 60% slag and 40% fly ash. Flue gases from each unit are cleaned by an electrostatic precipitator and finally discharged through a 122 meter stack. A block diagram of the Allen Steam Plant is presented in Fig. 1. The number two unit was selected in this study since it recently had been modified by the installation of a new Lodge Cottrell electrostatic precipitator, which is more

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[1] This work was supported by the National Science Foundation - RANN Environmental Aspects of Trace Contaminants Program under NSF Interagency Agreement AG-389 with the U.S. Atomic Energy Commission.

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[4] Industrial Hygiene Department, Oak Ridge National Laboratory.

[5] Operated by Union Carbide Corporation for the U.S. Atomic Energy Commission - Contract Number W-7405-eng-26.

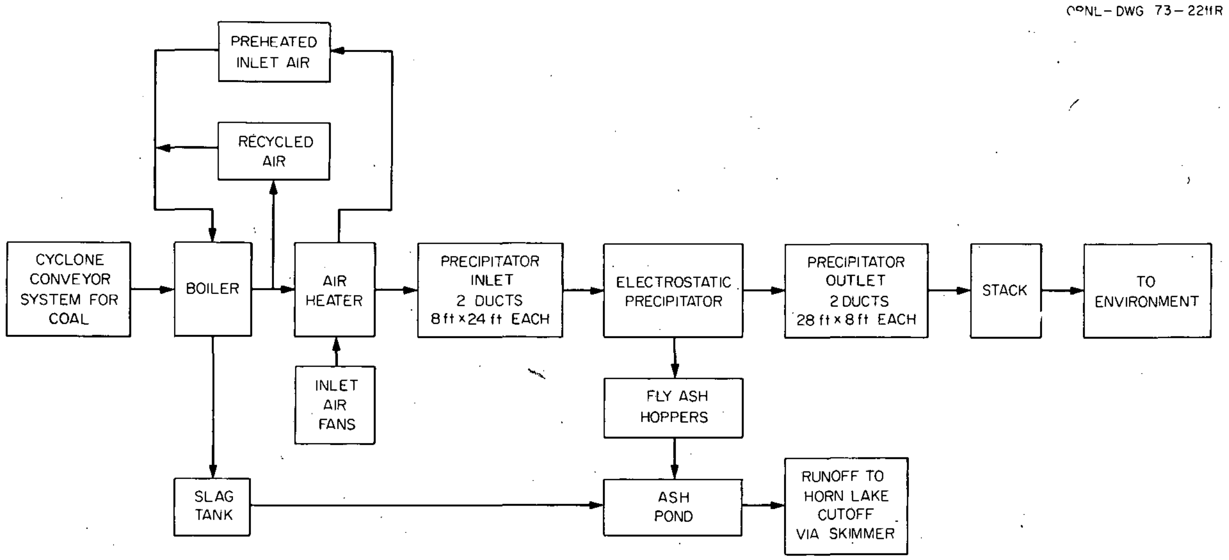

Fig. 1. A block diagram of the T. A. Allen Steam Plant

efficient than the other two units at the plant. This plant thus represents a system with the latest available particulate pollution abatement equipment.

Sampling procedure - Samples for coal, slag, and precipitator inlet and outlet flue gas analysis were obtained in August, 1973 when the plant was operating at 280 MW (e). Coal samples were composited from grab samples taken at 15 min intervals during the flue gas sampling. Grab samples of slag were collected during the periodic flushing of the hopper and are thus not truly representative of the coal samples. The flue gas streams were sampled by a modification of the ASTM method (1971). The flue gas samples were drawn through filters at the precipitator inlet and outlet at a predetermined isokinetic rate. The precipitator fly ash samples were composited for subsequent selenium analysis. The gaseous stream was then drawn through a heated probe to aqueous impinger trains designed to capture vapors of selenium. The impinger train consisted of two 10% Na_2CO_3 solutions immersed in an icebath. Seven runs were made for the precipitator inlet and four for the outlet. Sampling time for each run was 40 min at the inlet and ranged from 2 - 4.5 hrs. at the outlet. Composite samples were then made from the seven inlet and four outlet impinger solutions. The mass flow rate for coal, slag, fly ash, and flue gas, shown in Table 1, was calculated as described by Klein et al. (1974). The data indicates that electrostatic precipitator efficiency for the fly ash was better than 99.5%.

Selenium determinations - Selenium determinations were made using gas chromatography with a microwave emission spectrometric detection system (MES) (Talmi and Andren, 1974). The analysis is based on chelating Se^{IV} with 5-nitro-o-phenylene diamine (PD) to form the thermally stable and volatile piaselenol complex. This is followed by extraction of the piaselenol complex into toluene, separation by a gas chromatic column, and finally, monitoring of the emission intensity of the 204 nm selenium line with the MES.

Coal samples were digested with a mixture of concentrated HNO_3 and $HClO_4$ in volumetric flasks equipped with air condensers. Upon completion of digestion HCl was added to reduce any Se^{VI} to Se^{IV}. The selenium was then complexed with the PD reagent and extracted into toluene for the analysis.

Slag and fly ash samples were leached with H_2O, H_2SO_4, HNO_3, $HClO_4$, HCl, and 1:1 mixture of HNO_3-$HClO_4$. The leaching solutions were then analyzed as described above.

Two sample preparation methods were used to analyze the Na_2CO_3 solutions. One set of solutions were simply extracted after adding HCl and PD reagent. A redox buffer (Br/Br^- solution) and HCl were added to another set for oxidation of any reduced selenium to Se^{IV} (Raihle, 1972). The solution was then heated gently until colorless to expel the excess Bromine. After adding the PD reagent, the solution was extracted and analyzed as above. Subsequent analysis showed that greater than 96% of the Se was trapped in the first Na_2CO_3 impinger solution.

Table 1. Mass flow rate for coal, slag, fly ash, and flue gas calculated for the T. A. Allen Steam plant, Memphis, Tennessee

Coal (g/min)	Slag (g/min)	Inlet fly ash (g/min)	Outlet fly ash (g/min)	Flue gas SCF/min
1.47×10^6	8.14×10^4	7.86×10^4	370	6.21×10^5

The selenium detection limit is approximately 4×10^{-11} g. The validity of the coal, fly ash, and impinger solution determinations were compared with neutron activation analysis. Certified NBS coal and fly ash samples were also analyzed as an independent check. The average relative standard deviation for the determinations was 4.7% and ranged from 2.2% to 9.5%.

RESULTS AND DISCUSSION

Selenium mass balance - Sampling of flue gases is a continuous process extending over several hours; thus any selenium inhomogeneity problems should be averaged out. Since coal and slag were only sampled intermittently, an attempt was made to ascertain the homogeneity of those materials. Results in Table 2 indicate that both coal and slag were homogeneous with respect to Se during the entire sampling period. Analyses of several composite samples of fly ash and impinger solutions are also presented in Table 2.

A mass balance for Se in the Allen Steam Plant is presented in Fig. 2. Extensive fractionation of Se takes place during the combustion of coal. Selenium is very poorly incorporated into slag; only 0.3% of the coal derived Se leaves the system via slag. Approximately 68 percent of the Se is incorporated into fly ash, while the rest is vaporized. Table 1 indicates that precipitator efficiency (defined as the ratio of flow of inlet fly ash to that of outlet fly ash x 100) for removal of fly ash is very good (about 99.6 percent). Consequently, approximately 93 percent of the Se emitted to the atmosphere is found in the vapor phase. The major part of the coal-derived Se is settled in the precipitator hoppers which then is discharged into settling ponds close to the plant.

Table 2. Selenium concentrations in Allen Steam plant samples

Sample	Se (μg/g)
Coal #1[a]	2.2
Coal #2[a]	2.2
Coal #3[a]	2.2
Coal #4[a]	2.2
Slag #1[b]	0.08
Slag #2[b]	0.08
Precipitator Inlet Fly Ash #1[c]	28.0
Precipitator Inlet Fly Ash #2[c]	27.5
Precipitator Inlet Impinger Solution[d]	0.063
Precipitator Outlet Fly Ash	88.3
Precipitator Outlet Impinger Solution[e]	0.088

[a] Coal #1 represents coal particles 1-5 mm in diameter. Coal #2 0.1-1 mm; Coal #3 < 0.1 mm; Coal #4 is a composite of several samples taken at 15 min intervals.

[b] Slag #1 and 2 represents samples taken at two different times.

[c] Samples #1 and 2 represents two different composites made from fly ash collections.

[d] Each gram of composite impinger solution represents 0.066 ft³ of flue gas sampled.

[e] Each gram of composite impinger solution represents 0.134 ft³ of flue gas.

Chemical characterization of Se - The environmental pathways of emitted Se will depend upon its chemical state, both in the particulate matter and in the vapor phase. The expected forms of Se in emissions from combustion processes are Se^0, SeO_2, $SeO_3^=$, and $SeO_4^=$ (Chizhikov and Shchastiliviyi, 1968). Experiments were designed to establish the oxidation

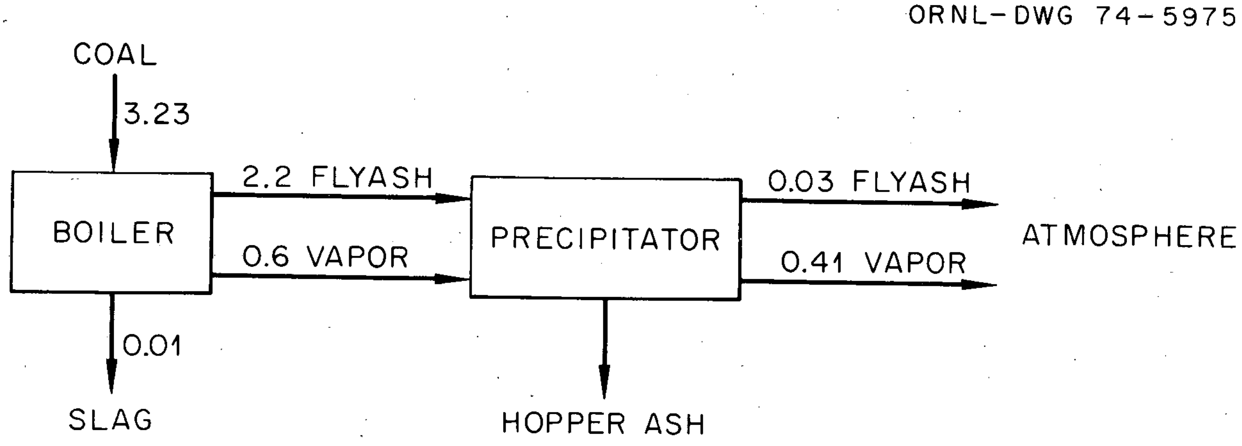

Fig. 2. Mass balance for Se in the T. A. Allen Steam Plant

states of Se in the fly ash, slag, and impinger solutions. These experiments were based on the following chemical properties of the Se compounds:

1. SeO_2, $SeO_3^=$, and $SeO_4^=$ are soluble in H_2O and HCl, but Se^0 is not. The selenite ion is effectively adsorbed by iron oxides (Geering et al., 1968) and will not be leached by water. However, leaching experiments of fly ash with ^{75}Se (added as $^{75}SeO_2$) showed that desorption could be accomplished with 12 M HCl.

2. Se^0 must first be oxidized to $SeO_3^=$ or $SeO_4^=$ before it will dissolve. This can easily be done by HNO_3, H_2SO_4, $HClO_4$, or a Br/Br^- redox buffer (Raihle, 1972).

3. Only Se^{IV} will react with the PD reagent to form the piaselenol complex.

Samples of fly ash and slag were leached with H_2O, 12 m HCl, 18 m H_2SO_4, 16 m HNO_3, and 1:1 HNO_3-$HClO_4$ both at room temperature and at the acid boiling point. Each leached solution was then treated with HCl to ensure the reduction of any Se^{VI} to Se^{IV} (Watkinson, 1966). The Se^{IV} was then reacted with the PD reagent, extracted, and determined as already described. The recovery of Se was found to be very efficient under highly oxidizing conditions, i.e., hot HNO_3, HNO_3: $HClO_4$, and H_2SO_4. No recovery, however, resulted from the H_2O and HCl leachings. It is thus concluded that Se in fly ash and slag exists as Se^0. A control experiment was also performed in which $^{75}SeO_2$ was adsorbed onto a fly ash sample. A 100% recovery was achieved by leaching the sample with 12 m HCl, thus reinforcing the above conclusion that no oxyanions of Se are present in the investigated material.

The PD solution was also added to the impinger solutions before and after the addition of a Br/Br^- redox buffer. The redox buffer will oxidize any reduced Se to $SeO_3^=$ (Raihle, 1972). Selenium could be extracted only after the addition of the redox buffer.

The possibility still exists that SeO_2 in the vapor phase could be reduced after collection in the impinger solutions. This is unlikely, however, since tetravalent Se was found in neither fly ash nor slag. It is thus concluded that all Se in the vapor phase, fly ash, and slag exists as elemental Se.
The formation of Se^0 can be described by Eqs. (1) and (2):

$$SeO_2 + SO_2 = Se^0 + 2SO_3 \quad (1)$$

$$H_2SeO_3 + 2SO_2 = Se^0 + 2H_2SO_4 \quad (2)$$

It seems that excess SO_2 produced in coal combustion processes acts as a reducing agent so that the right hand side of the equation is favored.

Biological and chemical implications - There is a very narrow range between Se toxicity and deficiency in animals. Allaway (1969) states that Se in the range of from 0.04 to 2 μg/g is required in the diet of animals to prevent deficiency. At slightly higher levels (4 or 5 μg/g), however, toxicity results. Selenium is a protective agent against toxic effects of cadmium and mercury (Lisk, 1972).

Selenium has not been shown to be an essential element to plant growth, although several investigators have shown that different plants concentrate Se in nature in varying amounts. Gissel-Nielsen and Bisbjerg (1970) investigated the availability of added Se^0, K_2SeO_4, and $BaSeO_4$ to mustard plants. After a two-year period the total uptake, as a percentage of added Se, was 0.01 percent Se^0, 4 percent K_2SeO_3, and 30 percent K_2SeO_4 and $BaSeO_4$. Lucerne, barley, and sugarbeet uptake was one-third or less for the respective selenium compounds. Results of a review of the variability in Se uptake by plants in seleniferous areas by Rosenfeld and Beath (1964) indicate that the physical and chemical form of Se in soils determines its availability to plants and subsequently to animals. Factors that control the forms of Se are soil pH, redox potentials, microbial activity, and soil mineralogy (Lakin, 1972). In acid soils any $SeO_3^=$ is sorbed onto ferric oxides and made unavailable for further oxidation (Geerig et al., 1968). In alkaline soils Se may be oxidized to $SeO_4^=$, which is readily available for plant uptake. Kubota et al. (1967) reported that 65 percent of the forage crops in the industrial eastern U.S. (acidic soils) contain insufficient Se for the growth of healthy animals and subsequently Berry and Wallace (1974) have suggested that the Se derived from fossil fuel combustion might be desirable for the eastern U.S. Results from this study, however, indicate that Se is emitted as Se^o, which is unavailable for plant uptake. In areas of alkaline soils, such as parts of the arid western U.S., Se may be oxidized to $SeO_4^=$. The potential for toxic effects in such areas must be considered.

Since the latest particulate pollution abatement equipment was installed at the Allen Steam Plant, it is possible to estimate the minimum amount of Se that is discharged into the environment via atmospheric and slag pond emissions. This has been done for the U.S. and the world, and the results are presented in Table 3. A figure of 3 μg/g Se in coal is used for the world-wide concentration (Bertine and Goldberg, 1971). The data are compared to the amount of Se mobilized by the natural weathering cycle. The combined atmospheric and slag pond Se discharges are approximately 2.5 and 1.5 times larger than river mobilization for the U.S. and the world, respectively. In the U.S., the Se emitted to the atmosphere is in itself 25% of that mobilized by U.S. rivers. Since other emission sources are present (i.e., smelting operation of ores, oil burning, refuse burning, etc.), man probably has a profound influence on Se mobilization.

The question of long- versus short-range transport of Se derived from fossil fuel combustion has been considered by several investigators. Weiss et al. (1971) studied Se to S ratios in dated Greenland ice cores and found that S has increased considerably during recent times whereas Se has remained fairly constant. Since elemental Se has a boiling point of about 680°C, the authors postulate that the vapor should condense shortly after atmospheric release to form a solid. One would then expect that Se input into the aquatic and terrestrial environment should be a local effect. Zoller et al. (1974) have recently studied enrichment factors for Se in aerosols at the South Pole. The enrichment factor (EF) is defined as:

$$EF = \frac{(Se/Al)\ aerosol}{(Se/Al)\ crust}$$

Their measured EF was 18,000. Thus, considerable enrichment of Se exists in polar aerosols. The measured EF for Allen Steam Plant emissions is 22,000 which is strikingly similar to the ones found at the South Pole. The aerosol enrichments at the South Pole might also be of biogenic and volcanic origin (Weiss et al., 1971), however, leaving the question of long-range transport unresolved.

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Table 3. The amount of Se mobilized as a result of natural and coal combustion processes

Annual coal consumption (X 10^{14}g)		Annual discharge of Se to the atmosphere (X 10^9g)	Annual discharge of Se to slag ponds (X 10^9g)	Se mobilized by rivers[a] (X 10^9g)
U.S.	6.03	0.25	2.3	1.0
World	28.0	0.82	10.5	7.2

[a] Data taken from Turekian (1971) and Goldbert et al. (1971)

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AMBIENT FORMS OF MERCURY IN AIR

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Abstract

Mercury in air may be separated into particulate, mercuric chloride type compounds, methylmercury (II) type compounds, elemental mercury and dimethylmercury by means of a selective absorption tube sampling system. Combined with emission detection these chemical forms may be detected above 0.3 ng m^{-3}.

Analysis of ambient air in a sampling grid over the Tampa Bay area, at sea, and in homes and buildings indicates that all five forms may be found. Elemental mercury is the chief chemical form found but significant amounts of the other forms are also found. Inorganic mercury on soil is converted to methyl-mercury compounds and elemental mercury.

Introduction

Mercury is perhaps the most widely distributed heavy metal pollutant due largely to the volatility of elemental mercury. Methylmercury halides, dimethylmercury and mercuric chloride are also known to be volatile. Inorganic mercury has been shown to be converted into the more volatile methyl-mercury forms through biological activity by Imura et al (1) and by others. The combination of toxicity and volatility make the study of the environmental chemistry of mercury of prime importance.

Because of the lack of suitable analytical methods, until now little information has been available on the types of mercury compounds and their concentrations in the environment. For example, particulate mercury in air can be determined by activation analysis of filter pads and elemental mercury alone by direct atomic absorption if present above approximately 15 ng m^{-3}. The combination of emission spectroscopy with the use of sequential specific absorption tubes developed by us (2) (3) has provided the needed method for specific detection and high sensitivity for analysis of the volatile mercury forms, and particulate in a great variety of environmental samples. The method has been used in several environmental studies (4).

Sequential Specific Absorption Tube Sampling System

A sampling system was designed for the selective absorption of the several suspected environmental forms of mercury. Amalgamation was first studied. Silvered glass beads and gold coated glass beads were found to rapidly absorb elemental mercury. Dimethylmercury was quantitatively absorbed only on the gold beads thus providing a basis for separation of elemental mercury from dimethylmercury.

After considerable subsequent work sample tube packings were found which would specifically absorb methylmercury(II) chloride and mercuric chloride. A tube containing silicone coated (3% SE-30) on 45/60 mesh Chromosorb-W, HCl, vapor treated, was found to retain mercuric chloride while passing methylmercury(II) chloride, elemental mercury and dimethyl-mercury. Methylmercury(II) bromide or iodide or acetate or other volatile forms are likely converted to methylmercury(II) chloride on the HCl-treated Chromosorb-W tube.

A non-siliconized Chromosorb-W column initially treated with NaOH to 0.15 milliequivalents per gram of column packing was found to quantitatively absorb methylmercury(II) chloride while quantitatively passing elemental mercury and dimethylmercury. Methylmercury(II) chloride is likely converted to the less volatile hydroxide by the alkaline column.

A glass wool filter, 0.30 microns pore size, was used as a particulate filter to complete the stack of absorption tubes. By assembling the absorption tubes in the following order and pumping air through them it was possible to separate mercury from a single air sample into five forms. Sample volumes from 0.025 to 0.200 m^3 were taken. Order of the sampling tubes was as follows: glass wool filter preheated to blank (removes larger particulate only), siliconized Chromosorb-W, HCl vapor treated (removes $HgCl_2$ type compounds and particulate which passes the glass wool filters), Chromosorb-W, NaOH treated (removes CH_3HgCl type compounds) silvered glass beads (removes elemental mercury), gold coated glass beads (removes $(CH_3)_2Hg$).

The efficiency of the individual tubes and the assembled stack was tested using elemental mercury, $HgCl_2$, CH_3HgCl and $(CH_3)_2Hg$ in operation under a variety of temperatures and conditions of humidity. Methylmercury(II) chloride was 83 - 100% retained on the NaOH-Chromosorb-W tube at temperatures as high as 33°C and 85% relative humidity. Mercuric chloride was 90 - 100% retained on the siliconized Chromosorb-W column up to 33°C and 85% relative humidity. Both compounds were tested for one and two-hour pumping periods. Dimethylmercury and elemental mercury were 100% absorbed on the gold and silver coated beads respectively under all conditions tested.

Careful blanking of all sample tubes was necessary to achieve good lower limits of detection for analysis.

Analysis System

After sampling, the stack of tubes were separated and analyzed individually for trapped mercury. Mercury was driven off from each tube by heating and passed through a quartz discharge chamber by means of He carrier gas. A direct current discharge in the chamber was used to excite the 253.65 nm Hg emission line. A conventional type recording spectrometer system described previously was used (5). The gold and silver sections were heated directly into the discharge and de-amalgamated to give sharp mercury peaks when heated to 300 - 400°C. Chromosorb-W tubes were first heated into blanked gold coated bead transfer tubes to eliminate some volatilized interferences from air and to sharpen mercury peak signals. The scanning capability of the system permitted verification of the presence of mercury. Calibration was accomplished by using mercury vapor. Lower limits of detection were found to be near .01 nanograms.

Limitations

Since no other current methods exist for the detection of specific mercury compounds in the 1-20 ng/m^3 range it was not possible to directly compare this method to another one. The identity of methylmercury(II) compounds or mercuric chloride compounds sampled from the environment depends upon comparison to known compounds (i.e. $HgCl_2$, CH_3HgCl, and $(CH_3)_2Hg$). Compounds sampled from the environment did contain mercury as determined by scanning the mercury emission line during analyses.

Methylmercury(II) type compounds and dimethylmercury far above normal concentrations were detected in air above soil treated with mercuric chloride.

H_2S and SO_2 were found to overload the Chromosorb-W (HCl) column if 2-hour pumping times were employed but were not otherwise an interference.

For the most accurate work, very careful handling of the absorption tubes is necessary to avoid contamination.

Mercury in laboratory air is a definite contamination problem.

Applications

The method has been used to study mercury in air in houses, aboard a ship, in school buildings and in a sampling grid in the Tampa, Florida, USA, area.

Tables I and II give data indicating some of our finding. Air over the Sargasso Sea (from shipboard analyses) contained only small amounts of elemental mercury. The larger fraction we believe was from aerosolization of sea water and is likely $HgCl_2$ type compounds. The total mercury in air found at sea compares reasonably well with the amount of mercury in the sea water evaporated into air. Sea water is on the order of 5 - 10 ppb mercury, or 5 - 10 ng/liter. If evaporated, one liter of sea water occupies 1 m^3.

Houses and buildings are obviously the greatest source of air mercury exposure to the general population. Amounts of mercury in buildings ranged from 10 to 100 times higher than mercury in ambient out-of-door air.

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TABLE I Mercury in Air in Buildings and Aboard Ship (R/V Trident)

Sample	ng/m^3 [c]					
	Hg particulate	$HgCl_2$	MMC	Hg°	DMM	Total
Lecture Hall[a] (Before class)	2.9	4.2	12	310	0	367
Same Total only	-	-	-	-	-	351
Lecture Hall (After class)	0	12	25	500	12	549
Same Total only	-	-	-	-	-	557
House[a]						
Bathroom	-	43	4.4	200	0	247
Bedroom	-	0	10	37	0	47
Kitchen	-	12	0	88	0	100
Living room	-	2.7	23	110	0	136
Ship (totals only)[b]						
Laboratory						21
Engine Room						51
Paint Locker						62
Faculty Office (Several) (total only)						110 - 140

[a] Out of doors total ambient Hg, 3 - 6 ng/m^3

[b] Out of doors total ambient Hg, average 7.5 ng/m^3

[c] Uncertainties in data are ± 0.3 ng/m^3 or ± 5%

TABLE II Mercury in Ambient Air

Sample	ng/m^3[b]					
	Hg particulate	$HgCl_2$	MMC	Hg°	DMM	Total
Tampa Area (same day) Suburban Location	2	22	14	4	0	42
Bayside	3	10	54	6	3	76
Urban Downtown	12	0	3	4	1	20
Trapped air over soil treated with $HgCl_2$ (after 1 day)	-	20	20	400	60	500
Trapped air over untreated soil	-	-	-	-	-	3 - 6
Sargasso Sea[a] (underway)	0.1	10	0.2	0.9	0	11
Sargasso Sea[a] (on station)	3.1	0	0.7	1.1	0	4.7
Sargasso Sea[a]	-	-	-	0.89	-	-
Sargasso Sea[a] (underway - near waterline)		7.5, 12.0, 8.1 ng/m^3 Totals only				
(underway - top of deck)		4.0, 11, 2.4 ng/m^3 Totals only				
(on station)		4.0, 0.6 ng/m^3 Totals only				

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[a] South of Bermuda, January 1974

[b] Uncertainties in data are ± 0.3 ng/m^3 or ± 5%

THE EFFECT OF METEOROLOGICAL AND SPATIAL PARAMETERS ON THE CONCENTRATION OF VARIOUS SPECIES OF MERCURY AND ITS COMPOUNDS

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Abstract

A field study to ascertain whether or not alternative mechanisms to the fish cycle provide a practical basis for mercury methylation has been conducted using both air and water samples. Our results strongly suggest that central sewage facilities constitute a widespread source of organic mercury as well as elemental mercury emissions. On the other hand, tests of leached material around a coal-fired power plant indicate that mercury is efficiently trapped by the formation of sulfides.

We have found evidence for organic and elemental mercury emissions covering a concentration range greater than 10^7. The evidence is based on air-sample measurements in cities with populations ranging from twenty to seven-hundred thousand. Particular emphasis was given to meteorological and spatial factors related to central sewage facilities. The concentration of elemental mercury in the atmosphere falls off sharply with increasing distance from the central sewage plant, but the concentration of the more volatile organic forms of mercury increases (for at least several miles) logarithmically with distance. The concentration maxima of the organic mercury emissions appear to be related to population size. Evidence is presented suggesting that the EPA upper limit for mercury in air is being exceeded under certain conditions.

I. Introduction

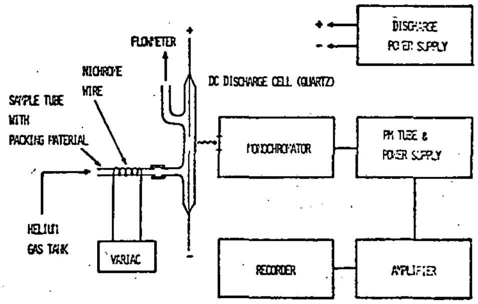
A field study has been initiated designed to determine whether or not organic forms of mercury constitute a potential environmental hazard. It had already been established that relatively significant levels of organic forms of mercury could be found in fish (Jensen, 1969). The purpose of the present field study (Soldano, 1974) is to learn whether alternative sources of organic mercury compounds (both biogenic and non-biogenic) exist, and whether such sources, unrelated to the fish chain, may constitute a health problem (Clarkson, 1972).

II. Experimental Procedures for Water Sample Analysis

A. General Description

To develop a mercury monitoring capability in both air and water, emission spectrographic techniques originated by R. Braman (1971) for detecting mercury were adapted to the present field study.

The apparatus arrangement used is shown in figure 1. It consists of a helium carrier gas source, the mercury sample, an emission type detector cell, and a conventional optical and electronic system. The detector cell is designed to generate a mercury flame path of approximately 2.0 cms. The mercury being carried by helium gas from the sample tube to the detector cell, is excited by a 950-1050 volt electrical discharge. A Jarrell-Ash model 82-020 scanning monochromater is used to monitor the mercury emission at 2537 angstroms. The signal is amplified by a Keithley 417 high speed picoammeter



1. Schematic Diagram of the Equipment Arrangement.

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(full scale 10^{-12} to 10^{-5} ampere). A Texas Instruments strip-chart recorder is used (Picker servo/riter, full scale 10 milliamperes). Photomultiplier voltage, discharge voltage, slit width, amplifier gain and range of the strip-chart recorder all control the total signal gain. The present apparatus is operated with the following ranges of conditions: slit width, 160-330 microns; PM voltage, 900 volts; DC discharge, 950-1050 volts, 31.5 watts/linear inch of discharge, for 10^{-6} to 10^{-8} ampere and 1-10 mV recording range. Full scale on the recorder equaled 20% of the amplifier output.

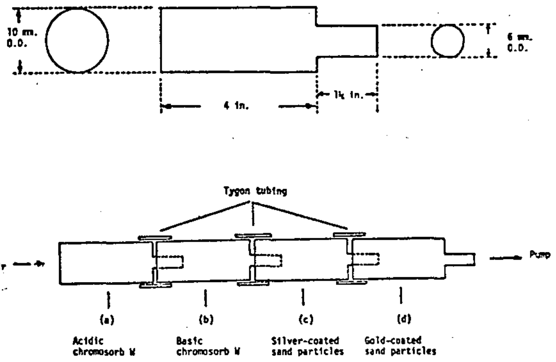
III. Results of the Water Monitoring Program

In the initial development phase of the field study, a program of monitoring mercury in water was initiated. Since coal contains mercury, the environs of the TVA Bull Run Coal Fired Steam Plant was studied. The results from over fifty samples taken in the plant's vicinity attested to the fact that the widespread prevalence of sulfides and the fantastically small solubility product of mercuric sulfide would ensure that any mercury present is effectively trapped. In the absence of a mechanism that would lead to a break down of the mercuric sulfide compound, very little mercury was detectable.

An important clue to a potential source of mercury emissions was discovered in the water phase of our field study when evidence was uncovered indicating that sewage plant gas emissions might contain appreciable amounts of mercury. This finding strongly suggested that an air monitoring field program should be promptly initiated. To implement this study a technique for mercury sampling in the air pioneered by Braman (R. Braman, 1974) was adopted with some modifications.

IV. Experimental Procedures for Air Sample Analysis

The Braman mercury speciation technique involves the stacking of four different materials as shown in figure 2. The first tube encountered by the entering air stream, one containing acidic chromosorb W, is designed to pick up inorganic mercury compounds such as The second material, basic chromosorb W, is selective for alkyl mercury halides. The remaining mercury in the entering air sample is then contacted with a third tube containing silvered Florida sand, (the latter is more resistent to the high temperatures needed to volatilize the adsorbed mercury during analysis). The third tube should adsorb any elemental mercury remaining in the air stream. Finally, the fourth tube containing gold coated sand, is effective in trapping highly volatile dialkyl forms of mercury.

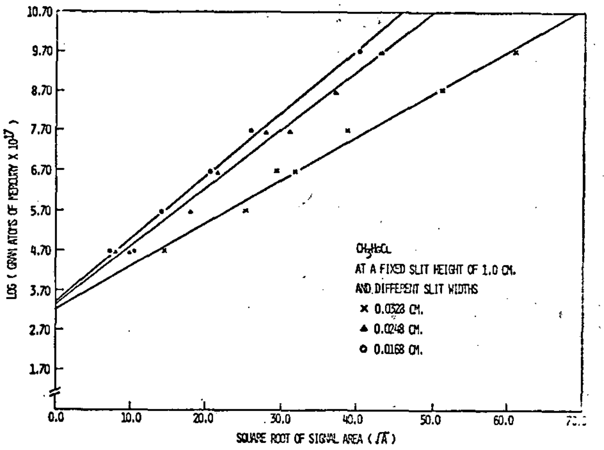


2. Speciation Tubes and Stacking Order.

V. Calibration Curves for Air Monitoring

One microliter of a standard methyl mercury chloride solution is injected into a tube containing chromosorb W, the latter having a specific affinity for alkyl mercury halides. A small volume is used in order to minimize interference arising from the presence of water vapor in the system. Helium carrier gas is passed through the sample tube into the detector cell. At this stage of analysis, the sample tube is kept at room temperature until the signal detected by the monochromater is stabilized. The latter state is indicated by a steady base line shown on the strip-chart recorder. The sample tube containing mercury is heated by a nichrome coil, the latter variac controlled. The increase in temperature causes the mercury compound to evolve from the surface of the packing material and then be carried by helium gas to the DC discharge cell. Due to the presence of mercury in the discharge region at any one time, the temperature is raised slowly. This process is continued until the nichrome wire appears dull red. The signal eventually returns to the previously determined base line indicating that all of the mercury has been carried to the discharge detector cell. The resultant area of the output signal versus time graph is a measure of the concentration of the mercury originally introduced into the sample tube. Known concentrations of CH_3HgCl, were injected into the sample tube and the areas of the resultant graphs of monochromater signal versus time were measured at different slit widths.

A plot of the relationship between known amounts of mercury and the area of the graph of signal versus time generated by the monochromater is shown in figure 3. A linear relationship between the logarithm of the concentration of CH_3HgCl and the square root of the area of the signal from the monochromater time is observed. (Soldano, 1974).



3. The Effect of Changes in Fractional Light Intensity on the Slope of the Linearity between the Logarithm of Concentration of Mercury Versus the Square Root of the Area of the Monochromater Signal Versus Time Graph.

$$\ln (\text{grams atoms of Hg}) \propto \sqrt{\text{area of signal vs. time graph}} \quad \text{eq. 1.}$$

One sees a comparison, as a function of monochromater slit width, of the logarithm of the number of gram atoms of mercury versus the square root of the strip-chart recorder signal area. One notes that the linearity extends over a mercury concentration range greater than 10^5. Moreover, as the fraction of emitted light is decreased by a reduction of slit width, the expected diminution in signal leads to a perceptible change in the slope of the observed linearity. Significantly, the mercury concentration in all three cases extrapolates to approximately the same limiting value.

The above relationship was tested with different mercury compounds. A similiar linear response, one holding over a factor of 10^5 in concentration, was again observed.

In addition to the practical interpolative utility of our empirical relationship, its form is highly suggestive of some elements inherent in the Debye-Huckel complementary field concept; (Debye, 1923) one designed to account for statistical electrical fluctuations of charges in solutions. Analogous to the electrical polarization effects inherent in the Debye approach, Zeegers et al (Zeegers, 1968) have shown that the specific intensity attendant on fluorescence radiance at high optical density can also be described by a square root function involving such factors as Lorentz and Doppler broadening, the Landenburg oscillator coupling constant, the radius of the classical electron and the cell flame path length. In the case of the Debye-Huckel approach, the logarithmic term describes the nature of some ideal standard state with which the system is being compared. At this juncture, however, it is beyond the purpose of this study, which is essentially a field study report, to address ourselves to further description of the factors underlying the relationship we have presented.

VI. Results of a Preliminary Survey for Mercury and Organic Mercury Compounds in Air Near Sewage Treatment Plants

To this point our field studies, with their initial emphasis on monitoring water, gave little indication of any mercury problem. However, when we directed our field efforts to monitoring the air and, more significantly, when we began to focus our field measurements on sewage treatment plant emissions, we obtained results which indicated that the plethora of new, centralized sewage facilities which have been built during the last few years to clean up our waterways, might well constitute a means of collecting much of the industrial mercury emission and then re-emitting it, in combination with the abundant organic products characteristic of sewage systems, into the surrounding air.

Field trips were taken to obtain air samples in the environs of sewage treatment plants ranging from a modern 400 million dollar facility in Washington, D.C. serving approximately one million people, to the smallest one located at Oak Ridge, Tennessee, and serving approximately 20,000 people.

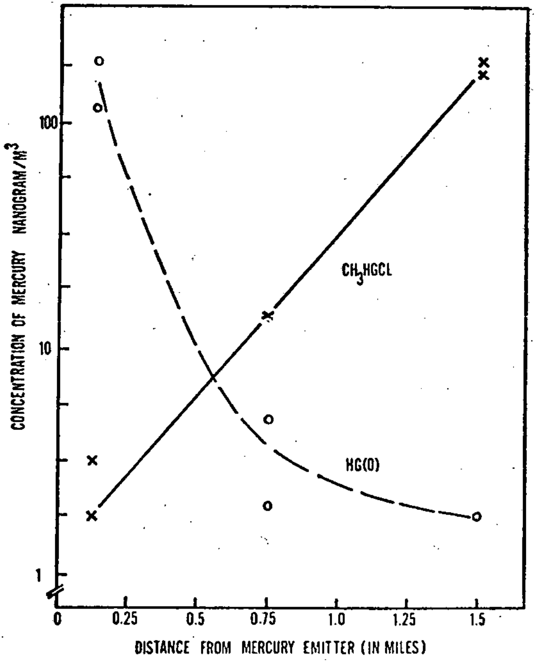
In examining our results the following points should be kept in mind. It quickly became apparent in our field studies that sample location is an important variable. For example, downwind samples were usually higher than those collected upwind from the sewage plant. Equally important, such factors as distance from the plant and elevation of the collection point with respect to the plant were found to affect the overall results. For example, some of the Richmond samples were taken inside the plant proper (samples number 3 and 4, Table I), while others (numbers 2 and 5) were taken close to the plant but at an elevation considerably below the methane gas flame located at the point of emission from the plant. Of greatest significance is the strong indication that the mercury concentration-distance dependency varies with mercury species type. One notes in figure 4 that the concentration of a less volatile species, elemental mercury, [Hg(0)] falls off sharply with sampling distance. On the other hand, the mercury fraction collected in the basic chromosorb W fraction rises sharply with increasing distance. One would expect that if indeed it is the highly volatile methyl mercury fraction that is being collected by the basic chromosorb W, this species should become airborne more rapidly at the point of emission and therefore would not tend to concentrate near ground level at the plant. In fact, the difference in the distance concentration behavior of the two collector fractions shown in figure 4 provides additional support for the thesis that in the field the silver coated sand and the basic chromosorb W are operating with species fractionating efficiency. At this stage of our investigation no attempt has been made to arrive at general distance relationships since it is apparent that the local meteorological patterns may overwhelm purely spatial considerations.

TABLE I

A COMPARISON OF MERCURY CONCENTRATIONS
IN THE AIR AS A FUNCTION OF SPECIES AND LOCATION

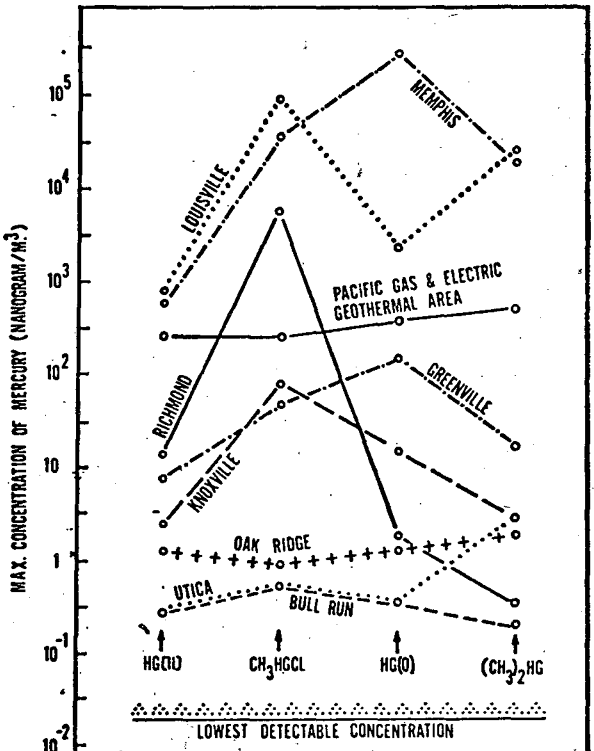
SAMPLE DESIGNATION Set No.	Sample Type	Nanograms of Mercury/Cubic Meter of Air
First Richmond Trip		
(4)	Acidic	2.13
(4)	Basic	62.50
(2)	Acidic	20.00
(2)	Silver	2.50
TVA		
(1)	Acidic	0.43
(1)	Basic	0.83
(1)	Silver	0.53
(1)	Gold	0.33
Oak Ridge, Tennessee		
(1)	Acidic	1.98
(1)	Basic	1.38
(1)	Silver	1.58
(1)	Gold	2.75
Knoxville, Tennessee		
(1)	Acidic	3.75
(1)	Basic	107.50
(1)	Silver	1.75
(1)	Gold	4.00
(2)	Acidic	1.30
(2)	Basic	21.75
(2)	Silver	0.35
(2)	Gold	0.55
Second Richmond Trip		
(1)	Basic	8,750.00
(1)	Acidic	0.25
(4)	Basic	9.50
(5)	Basic	0.85
Memphis Trip		
(25)	Acidic	166.80
(25)	Basic	3,800.00
(25)	Silver	3,330.00
(25)	Gold	132.00
(29)	Acidic	140.00
(29)	Basic	130.00
(29)	Silver	240.00
(29)	Gold	210.00
(38)	Acidic	3,750.00
(38)	Basic	6,250.00
(38)	Silver	600,000.00
(38)	Gold	10,000.00
(27)	Acidic	2,875.00
(27)	Basic	33,250.00
(27)	Silver	5,500.00
(27)	Gold	3,700.00
Second Richmond Trip Cont.		
(2)	Basic	0.53
(3)	Basic	0.50
(2)	Acidic	0.88
(3)	Acidic	0.78
(4)	Acidic	1.25
(5)	Acidic	2.50
(1)	Silver	1.60
(2)	Silver	1.80
(3)	Silver	0.80
(4)	Silver	6.80
(5)	Silver	0.40
(5)	Gold	0.50
Utica Trip		
(4)	Gold	3.50
(4)	Basic	3.25
(6)	Acidic	0.21
(2)	Basic	0.13
(4)	Silver	0.20
(4)	Acidic	0.15
(5)	Silver	0.60
(5)	Acidic	0.38
(6)	Gold	1.68
(6)	Silver	0.33
(5)	Basic	0.80
(6)	Basic	0.95
Greenville Trip		
(3)	Acidic	11.25
(3)	Basic	67.50
(3)	Silver	0.58
(3)	Gold	3.50
(1)	Silver	0.08
(1)	Gold	1.50
(1)	Acidic	0.12
(1)	Basic	0.68
(4)	Acidic	0.30
(4)	Basic	6.50
(4)	Silver	225.00
(4)	Gold	25.00
**(2)	Acidic	7.75
(2)	Acidic	1.23
(2)	Silver	21.25
(2)	Gold	1.55

**Interference



4. A Comparison of the Concentration-Distance Profile of "Methyl Mercury Chloride" and Atomic Mercury Hg(0).

An examination of the field results in figure 5 show that, whereas large concentrations of mercury in the aqueous phase were indeed infrequent, the situation is decidedly reversed as far as mercury in the air is concerned. One is struck by the broad range of mercury concentrations detected (see figure 5



5. The Maximum Concentration of Mercury in the Atmosphere as a Function of Species Type and Location.

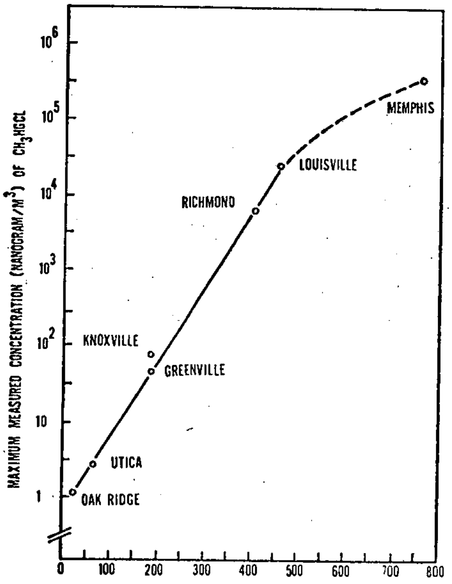
and Table I). For example, in Utica, New York, an airborne concentration of mercury in the vicinity of the sewage plant as low as approximately 0.125 of a nanogram per meter cubed was measured. This particular sample (see Table I) was taken during a snowstorm with the ambient temperature below freezing. The extremely low temperature might account for the fact that a relatively high dimethyl mercury fraction (Table I) was found comparable to that of methyl mercury chloride. It is possible that the lower temperature contributed to an enhanced stability of the dimethyl mercury. The detection of mercury samples in Utica with concentrations of the order$\sim$.1 of a nanogram per meter cubed lend credence to the idea that the numerous measurements found at other sites in the concentration range of$\sim 10^3$ nanograms do indeed represent valid concentration indicators. It should also be noted that our mercury detection system's lower sensitivity limit (.025 nanogram per meter cubed) is comparable to the .01 nanogram per meter cubed cited by Braman (R. Braman, 1974).

A comparison of the collector fractions (fig. 5 and Table I) shows that for most sewage plants surveyed, the largest fraction of airborne mercury was usually found in the basic chromosorb fraction, the latter being designed to filter out the methyl mercury halide component. It should be emphasized that no positive identification of the form of mercury was made on the field samples. The results are simply inferential based on the experimental tests previously outlined. Little interference with the mercury flame emission of the field samples was observed, with one exception. And that exception was very striking! During this measurement (Table I, Greenville sample number 2) the characteristic purplish mercury emission line suddenly shifted to a green color for two-thirds of the sample measurement period. During this time no mercury emission signal was detected by the monochromater. When the source of interference causing the green emission line was depleted, the characteristic purplish mercury color was again noted for the duration of the measurement. This result indicates that trace contaminants other than mercury may exist in some field samples and this particular type is interfering with the mercury emission line. We emphasize again that none of the other measurements listed in (Table I) exhibited such unique behavior.

Another surprising result is the large disparity between the methyl mercury halide fraction and the concentration of mercury in the inorganic compound and dimethyl mercury forms. The concentrations of mercury in the latter catagories appear to be evenly distributed. The actual order is slightly dependent upon the particular facility investigated. It should also be noted (figure 5, Table I) that the airborne concentrations of mercury from sewage plants in the non-methyl mercury catagories are not much different from the low values obtained from a distant (3 miles) air sample of the coal-fired steam plant at Bull Run.

We have also investigated the Pacific Gas and Electric geothermal site in the vicinity of Geyserville, California (figure 5). One notes that the highest concentrations of each form of mercury measured in a predominately high sulfide environment is midway between the relatively low level emissions from the TVA Bull Run Plant and the high results reported for Memphis, Tennessee. The importance of the geothermal measurements lies not in the fact that the mercury concentration levels are reasonably low, but that the concentration of the four different species collected are all comparable. This observation is consistent with the conversion of one form into the other in a strongly non-biogenic environment characteristic of this particular geothermal site.

It is when we turn to (figure 6) that the potentially troublesome implications of our field survey of central sewage plants is revealed. The rationale of this plot is the idea that the degree of industrial activity and resultant mercury emissions are roughly related to the population load on the central sewage facility.



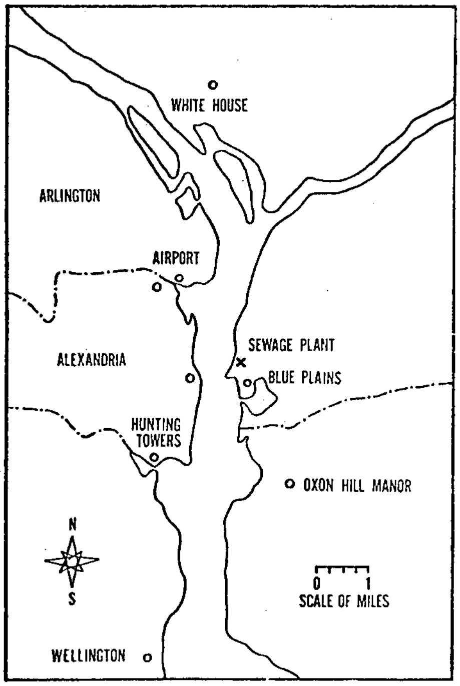
6. A Comparison of Organic Mercury Maxima Detected Versus Population Load on the Sewage Facility.

An examination of (figure 6) shows that there exists (at least over a limited population range) a relationship between the maximum detected concentration of "apparent" organic mercury fraction and the estimated population using the sewage facility. The disturbing point in this correlation is the suggestion that the high values of organic mercury measured in both Louisville and Memphis, values that are considerably above the EPA upper limit of 1,000 nanograms per meter cubed,could have been expected simply from the size of the population load on the central sewage facility. To be sure there is the expected curvature in the case of Memphis but the concentration of mercury obtained at that site remains disturbingly high. These samples were taken over a two day period when the ambient daily temperature was 95° F and the relative humidity was 100%.

We shall now turn to a comparison of the Washington, D.C. field results with those of Memphis, Tennessee in an attempt to describe the meteorological-distance relationships for the different organic mercury species relative to the central sewage plant emissions.

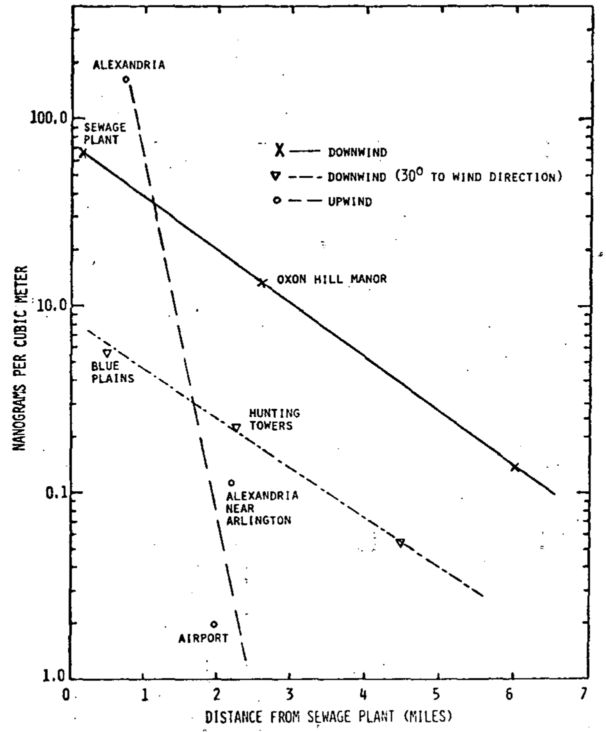
VII. A Comparison of the Sewage Plant Emission Profiles of Washington, D. C. and Memphis, Tennessee

In Washington, (figure 7) we have a large population with relatively low levels of industrial activity. On the other hand, in Memphis we have a high level of industrial activity with the emissions of the central sewage plant complicated by those of the TVA coal fired Allen Steam Plant nearby. In addition, Memphis contains other sources of mercury emissions.



7. A Schematic Map of Washington, D. C.

In (figure 8) one notes a distance-concentration relationship for elemental mercury in Washington, D. C. similiar to that found by Jernelov (Jernelov, 1973) for chlor-alkali plant emissions. The higher solid curve represents the results obtained in a direct downwind direction during a period when the direction of an approximate 30 miles per hour wind was defined by a vector originating at the sewage plant and directed toward Oxon Manor (figure 7). The lower broken line

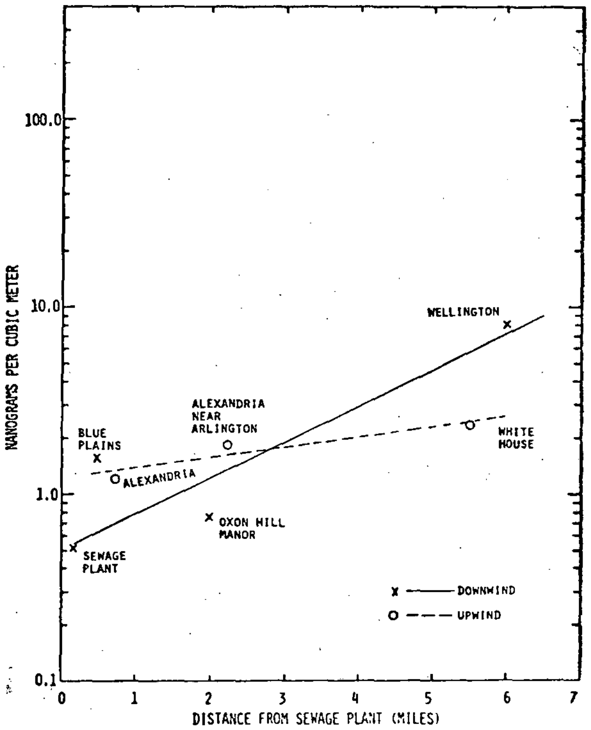


8. The Dependence of Hg(0) Concentration in Air on Wind Direction and Source Distance (Washington, D.C.).

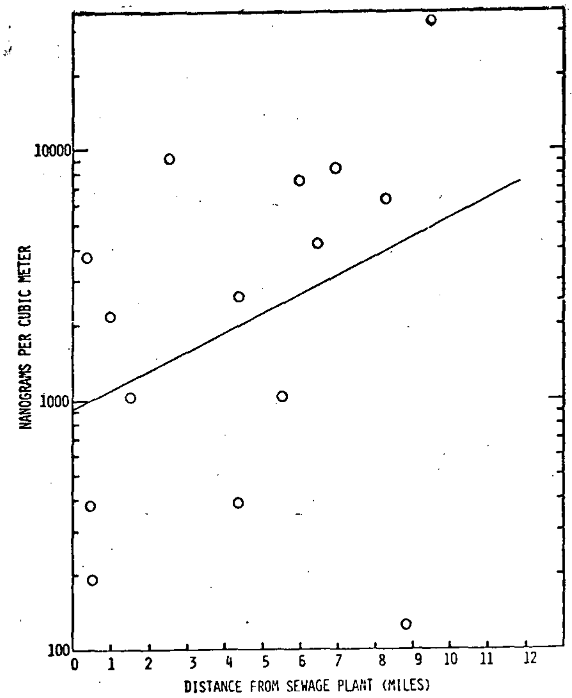
parallel to the direct downwind results represents the concentration-distance profile for downwind locations in Washington, D.C. taken at 30° angle with the wind direction. As expected, these concentrations of elemental mercury are lower. In the case of upwind locations (figure 8) the fall off of mercury concentration levels are much sharper.

Examining the Washington, D. C. sewage plant results for the alkyl mercury halides (figure 9), one again notes that the concentration of alkyl mercury halides increases with increasing separation from the sewage plant. This effect is not as pronounced in the upwind direction.

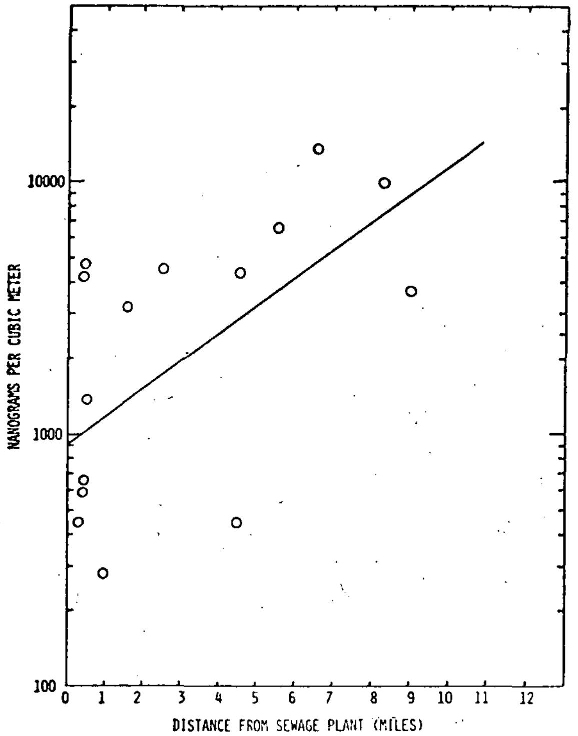
The Memphis results for both alkyl mercury halides, as well as those for the dialkyl mercury form (figures 10, 11) also show a pronounced increase in mercury concentration as a function of increasing distance from the sewage plant. There is, however, a significant difference. The alkyl mercury concentrations measured in Memphis are, for the most part, equal to or higher than the EPA (one thousand nanograms per cubic meter) upper allowable limit. The unusual weather conditions present during the sampling period (i.e. 95° F and 100% relative humidity)



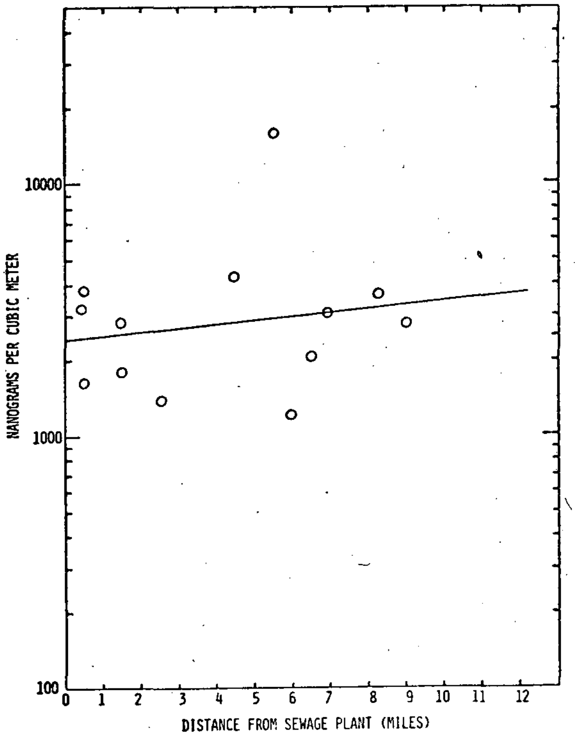
9. The Dependence of CH_3HgCl Concentration in Air on Wind Direction and Source Distance (Washington, D.C.).



10. The Dependence of CH_3HgCl Concentration in Air on Source Distance (Memphis, Tenn.).



11. The Dependence of Dialkyl Mercury Concentration in Air on Source Distance (Memphis, Tenn.).



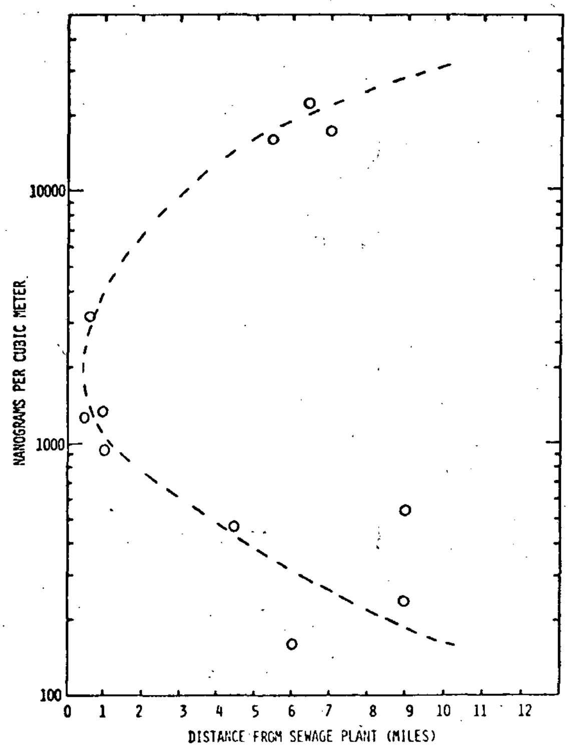
12. The Dependence in Air of the Concentration of the Inorganic Species Trapped by the Acidic Chromosorb on Source Distance (Memphis, Tenn.).

similar to those that accompany weather inversions, might account for these high values. On the other hand, the correlation presented in figure 6 indicates that, for industrial cities of the size of Memphis, these relatively high values for mercury could have been expected, given the right climatic conditions.

When we examine the distance-concentration profile for the inorganic fraction (acidic chromosorb) we are presented with the suggestion that coupled reactions might be taking place in the atmosphere, involving chemical species such as $Hg_2\ Cl_2$, Hg Cl_2, etc., the type of compounds collected in this fraction.

For example, in Memphis (figure 12) we note that the relatively high concentration of these compounds is almost independent of distance. On the other hand, the silvered Florida sand fraction versus distance profile (figure 13) involves two different curves. The lower curve is consistent with the concentration fall off usually found for elemental mercury. Some other species is being collected in the silver fraction giving rise to the upper curve. The interesting point, however, is that the axis of rotation of the overall parabola (figure 13), one that contains no points between the two portions of the parabola, almost coincides with the straight line (figure 12) representing the inorganic mercury fraction. It is possible that the inorganic fraction $Hg_2\ Cl_2$ may be undergoing decomposition into elemental mercury and Hg Cl_2. thereby giving rise to the two portions of the overall parabola.

Another coupling between the inorganic fraction and the dialkyl mercury fraction is suggested in the results involving much lower concentrations of mercury measured in Washington, D.C. There is an indication that the distance-concentration profile for the mercuric form Hg(II) (figure 14) is almost a mirror image of that found for the dimethyl mercury species (figure 15). This relationship may be significant. Parks (1973) has focused considerable attention on the key role Hg(II) plays not only in the volatilization of cinabar under aerobic conditions in sewage sludge. He has also linked the formation under anerobic conditions of alkyl mercury compounds in sewage to the presence of Hg(II). Thus it could well be

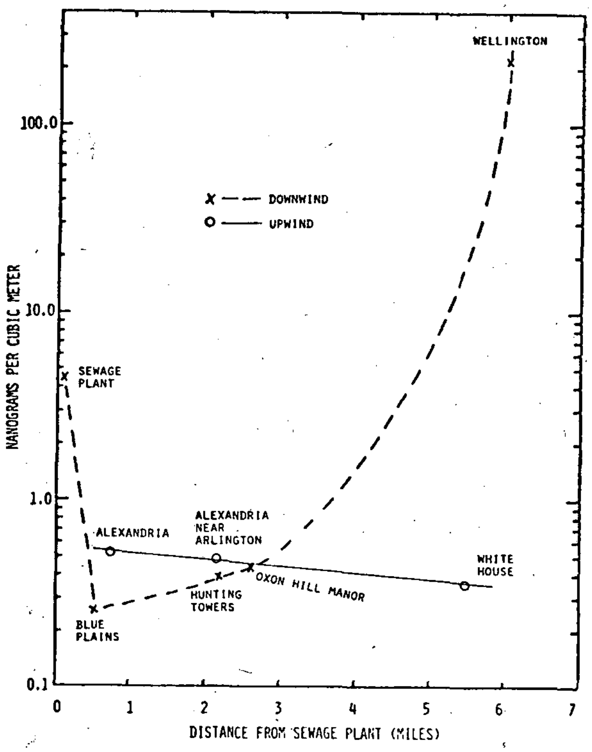


13. The Dependence in Air of the Concentration of the Species Trapped by Silvered Florida Sand on Source Distance (Memphis, Tenn.).

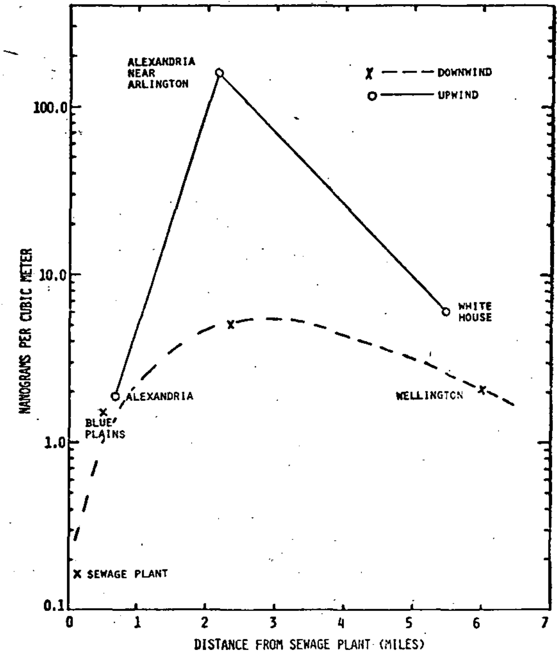
that Hg(II) may play a key role in a definitive interpretation of our field studies in that city. It should also be noted that the mercury measurements in Washington are the only ones so far in our entire field program that also gave indications of significantly high concentrations of the dimethyl mercury form.

IX. Conclusion

Our results show mercury and organic mercury pollution of the air in the vicinity of all of the municipal sewage treatment facilities examined so far. The mercury concentrations in the case of Memphis, Tennessee are so high that they may constitute a health problem. There is also strong reason to believe that some of the more troublesome mercury species, i.e., the alkyl mercury halides, may be reaching a much broader region than the immediate environs of most sewage facilities. This whole problem should be examined in greater detail.



14. The Dependence of Hg(II) Concentration in Air on Wind Direction and Source Distance (Washington, D.C.).



15. The Dependence of $(CH_3)_2$ Hg Concentration in Air on Wind Direction and Source Distance (Washington, D.C.).

Acknowledgment

The authors would like to thank Drs. W. H. Brantley, C. S. Patterson, and C. van Eijk, and Mr. R. Pittman and Mr. W. Caldwell for giving freely of their time and help in furthering this effort. The authors also wish to thank their colleagues in the Chemistry Department for their cooperation.

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INTERMEDIATE RANGE TRANSPORT OF LEAD FROM AUTOMOTIVE SOURCES

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ABSTRACT

A practical urban model to describe the atmospheric dispersion and intermediate range transport of lead from automotive sources has been developed. This model considers only that portion of the emitted lead which has remained airborne sufficiently long to reach air samplers at least 100 meters from major roadways.

The city of Fort Collins, Colorado and the immediate surroundings (125 km^2) was broken down into a series of 32 circular area sources, whose strength was determined from typical daily traffic statistics. The concentration within a particular circular area source is calculated with a uniformly mixed quasi-Lagrangian box model whose mixing height is parameterized so that surface concentrations are the same as if a series of infinite line sources were contributing to the receptor. The circular area sources were selected so that a smooth transition could be made from the box to Gaussian plume model. Concentrations at the downwind edge of the source circle are matched to a continuous point Gaussian plume model which is subsequently used to predict downwind dispersion.

The results indicate that about 45% of the lead consumed by automobiles is still airborne 10 km downwind of the urban area.

INTRODUCTION

The atmospheric dispersion modelling of a group of diffuse area sources is complicated when the source intensities are poorly defined in space and time and the diffusing material exhibits complex behavior. Such is the situation in the modeling of the atmospheric transport of lead bearing particulates from automotive sources. Individual automobile lead emissions vary dramatically with operating conditions, exhaust temperature, load, efficiency and numerous other factors. Thus, defining source strengths in a reasonable and practical manner requires consideration of these factors as well as some actual (but often not reliable) statistics on traffic volume.

In this model, sources are portrayed as circular areas whose emission intensity is determined as if all traffic is uniformally distributed over the area. The use of circular sources allows the transition from a quasi-Lagrangian box model to a Gaussian plume model to be made in a rather smooth step, without the serious surface concentration discontinuities which occur with rectangular area sources especially when source geometries are fixed and the wind directions are variable. The mixing height in the box is a function of stability and is determined so as to give a concentration within the box which closely approximates that calculated from a finite series of line sources aligned perpendicular to the wind.

Downwind of the area source, a standard Gaussian plume model is used to predict surface concentrations. In order to use the Gaussian plume model virtual point sources must be utilized and are located so as to give the vertical and horizontal plume spread corresponding to the radius of the circular area source and the parameterized mixing height.

TEST PROGRAM

Any atmospheric dispersion model which is formulated must be verified to some degree by field measurements if it is to be of any practical value. Two separate test programs were conducted in Fort Collins, Colorado, a residential city of 45,000, so as to better define human exposure to automotive lead in regions with moderately heavy traffic.

A unique air sampling technique was used for the collection of airborne lead containing particles. Spectrographic purity porous-cup graphite electrodes were used as the collectors (Skogerboe, (1972). These cups were doped with a few nanograms of indium, to provide a quantitative comparison in spectroscopic analysis with the emission line of lead or any other heavy metals collected. When ambient concentrations of the metal being investigated are high, a sufficient sample may be collected in as little as five minutes.

A sampling network of 18 stations was established in and around a 125 km^2 area of the city, with one background sampler located remotely in the mountains northwest of the city. Filters were changed three times daily so as to measure morning, afternoon and night average lead levels. A weather station located in the urban area provided data on winds at 18 m and surface temperature. The data collected in this network over a period of 48 hours provided six sets of data for comparison with the model.

A second test program was recently completed in order to determine whether particle settling or surface impaction is playing a role in depleting the airborne particles. For this program many of the original sampling stations were moved to new locations, with fewer stations in the suburbs so that information could be obtained concerning any unusually steep concentration gradient which might be due to settling or impaction.

SOURCE STRENGTH

The initial problem in this study as in any atmospheric dispersion modeling was to establish the pollutant's source strength. Unlike many other automobile exhaust products there is no satisfactory parameterization of automobile lead emissions at the present time. Several investigations (Habibi, 1970; Habibi, et al., 1970) have shown that the lead emitted out the tailpipe varies from 10 to 90% of the lead consumed depending upon operating conditions. Recent studies (Ganley and Springer, 1974) have also shown the size distribution of the emissions vary substantially depending on several of the other factors in operation.

All air samplers were located at least 100 m from all major roadways, so as not to sample the heaviest, fastest setting lead bearing particles. Thus, these particles were not considered available for long range transport and did not enter into the calculations. Consequently, a 45% emission factor was arrived at as that portion of the consumed lead that is available for intermediate range transport. A representative gas mileage was established at 13 mpg. The actual emissions were determined from the average daily vehicle miles per segment of roadway in the city.

Unfortunately, the most recent complete traffic count map available was May, 1969. A more recent count by the State of Colorado at many of the same intersections indicate that the vehicle counts have increased by about 35% in the last four years (this is substantiated by population growth).

Initially, it was assumed that the morning (7:00 a.m. to 12:30 p.m.) traffic accounted for 40% of the total emission, afternoon (12:30 p.m. to 7:00 p.m.) accounted for 40% and nighttime (7:00 p.m. to 7:00 a.m.) was 20%. Using these values in conjunction with mean meteorological factors (wind and stability) for those time periods proved to give poor correlation of the model with data averaged over the similar periods. Traffic statistics were broken down further into hourly percentages of daily total (based on actual hourly counts, and averaged from many locations). Wind data were available from the Fort Collins Weather Station (taken at 18 m) and stability categories were estimated for hourly intervals based on Fort Collins surface temperature and the Denver soundings (60 miles to the south). This procedure worked well for this test but may not be a generally useful approach. Fortunately, during this testing period no major weather systems were forcing the flow in the region, and with this fair clear weather the vertical temperature structure followed a very predictable diurnal cycle. In the second test program an acoustic sounder augmented the data for added determination of mixing height and stability.

DIFFUSION SCHEME

All the tabulated vehicle traffic in a region (usually three to eight sq. km) was considered to be uniformly distributed over the region. The uniform distribution approach, as well as the use of circular area sources, readily yields a rather simple solution. The choice of circular area sources allows the transition from a uniformly mixed quasi-Lagrangian box model to a Gaussian plume model to be much smoother without any serious surface concentration discontinuities or adjustments necessary as for other geometrical types of area sources.

Prediction of concentration at grid points within the source circle are made by assuming a parcel of air enters the circle travelling with the mean wind speed and direction, and transects the circle along a line parallel to the wind direction. If we assume no fallout of lead bearing particles, then as the air parcel travels across the source circle it picks up and maintains all material emitted into it. The concentration in the parcel, assuming no lead is initially contained in it when it starts over the circle, is equal to the emission rate per unit area multiplied by travel time in the source area, and divided by the mixing height. Thus, the pollutant is considered instantaneously and uniformly mixed throughout the volume. The concentration is given by

$$C = \frac{Q_t T}{\pi r^2 H} = \frac{Q_t x}{\pi r^2 HU} \qquad (1)$$

where, $C\left(\frac{\mu g}{m^3}\right)$ is the pollutant concentration, $Q_t\left(\frac{\mu g}{sec}\right)$ is total emission of the source circle, $r(m)$ is the radius of the source circle, $x(m)$ is the distance of travel in the circle, $U(m/sec)$ is the wind speed, $T(sec)$ is the travel time in the circle, $H(m)$ is the mixing height.

Thus, the peak concentration in the circle is given, when $x = 2r$, by

$$C_{max} = \frac{Q2r}{\pi r^2 HU} = \frac{2Q}{\pi rHU} \qquad (2)$$

If we were to apply a Gaussian plume model to a surface point source and wished to determine concentrations along the plume axis for a source strength Q_t, with total plume reflection from the surface, the concentration would be given by

$$C = \frac{Q_t}{\pi\sigma_y\sigma_z U} \qquad (3)$$

where, $\sigma y(m)$ is the standard deviation of the particles displacement in the lateral direction, $\sigma_z(m)$ is the standard deviation of the particles displacement in the vertical direction. Thus, if we consider the downwind edge of the circle to be the point where the box model to Gaussian plume model transition is to take place, the concentration at point A in Figure 1 can be calculated by equation 2 if we set

$$\begin{aligned}\sigma_y &= 3/4\ r \\ \sigma_z &= 2/3\ H\end{aligned} \qquad (4)$$

Several other combinations are possible, the most obvious being

$$\begin{aligned}\sigma_y &= r \\ \sigma_z &= H/2\end{aligned} \quad \text{and} \quad \begin{aligned}\sigma_y &= r/2 \\ \sigma_z &= H\end{aligned} \qquad (5)$$

In Figure 1, a comparison of the isopleths of concentration are given for two of the many combinations of σ_y and σ_z to reproduce $rH/2$. As shown in Figure 1 $\sigma_y = r/2$ and $\sigma_z = H$ appear to underestimate lateral plume growth. Similarly $\sigma_y = r$ and $\sigma_z = H/2$ (not given) tend to overestimate lateral plume growth. The case selected as the best combination, equations 4, gives both a smooth concentration transition across the border of the area source and an acceptable lateral plume growth pattern.

In Figure 1 the concentration field from a uniformly emitting area source was calculated in the following manner. A parcel of air over the area source and travelling with the mean wind picks up and maintains all lead emitted into it. This is considered to be 45% of the total lead consumed due to automobile retention and large particle settling. The mixing height is determined as discussed above. Once the air parcel passes outside of the source region into region 1 the concentration is calculated as being normally distributed with respect with the plume centerline concentration. The plume centerline concentration is determined by the parcel method, with the parcel travelling along the diameter parallel to the wind to the point on the centerline opposite the point of interest in region 1.

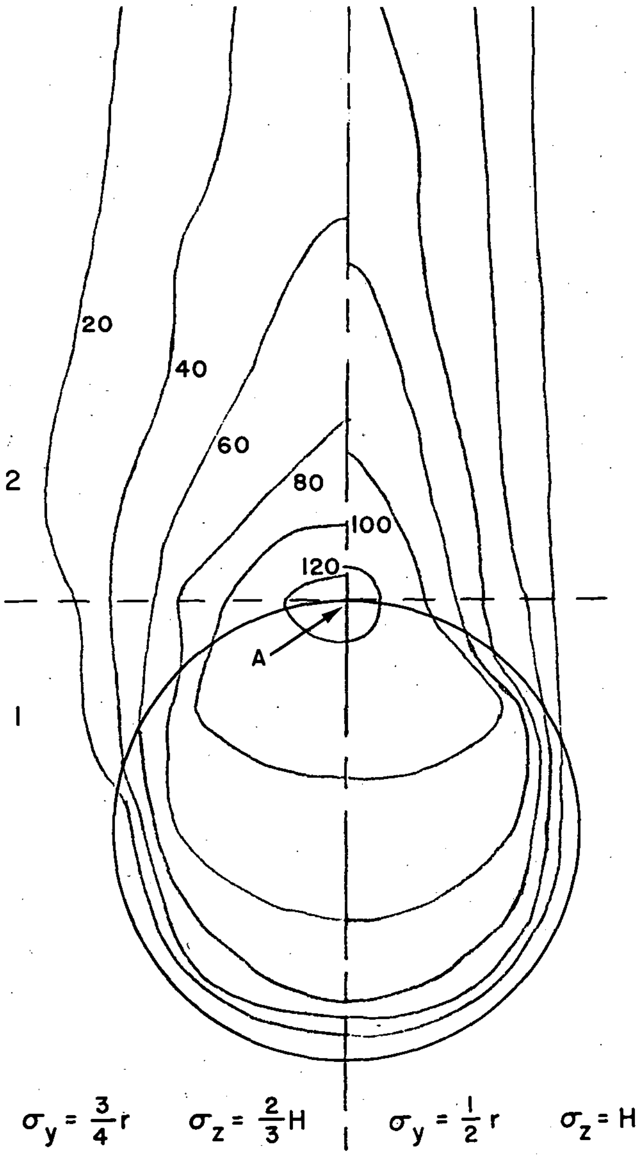

FIG. 1. A comparison of the isopleths of concentration for two combinations of $\sigma_y\ \sigma_z$. Isopleths are labelled in relative units.

When the parcel passes beyond the circle into region 2, the concentration is calculated as if all the pollutant were emitted from a virtual point source, which is located according to the conditions specified in equation 4.

If diffusion is to proceed smoothly downwind from the end of the source area, both σ_y and σ_z must grow continuously beyond this point. However, if the Pasquill-Turner curves are used as the method of predicting dispersion, it should be noted, one will calculate virtual point source locations which will be radically different for the y and z directions in order to give the observed plume spread. These two virtual point sources remain as the apparent origins of the Gaussian plume for all grid points downwind of the box model.

One subtle point, at the transition point we have a instantaneous redistribution of mass. However, because the conditions were matched at the surface and σ_y was judiciously chosen to be equal to 3/4r, the surface redistribution is rather small as seen in Figure 1. The transition becomes less satisfactory at levels above the surface. In general, this technique would provide good concentration estimates to about 50 m above the surface. However, since we are only interested in surface concentrations this does not present a problem in this case. If one were concerned with continuity, for example at 500 m, the concentration step encountered with surface matching may be unacceptable. If this were the situation the basic approach could be applied at any one specific level, but discontinuities at other levels will still remain in this linear mode matching approach. Physically, the transition represents a change in vertical distribution from homogeneous to the height 2/3H, to a normal distribution in the vertical with H now the $3/2\sigma$ point of the distribution.

As a result of this mode matching technique, one is able to maintain continuity in predicted concentrations across the border of the source region at any level desired.

DISPERSION CURVES

It seems to be the rule rather than the exception, that when dispersion modeling is done the "required" data is seldom available so that accurate comparisons with previous investigations can seldom be made. In this program wind measurements were at 18 m and only surface temperature measurements were available. In addition to surface temperature measurement, radiosonde data was available for Denver. Fortunately, during the test period, the weather was quite "well behaved" and the diurnal cycle characteristics of fair clear weather was obvious from the Denver sounding and correlated quite well with the observations in Fort Collins. As a result it was felt accurate estimates of stability could be made from the data available.

At the present time dispersion estimates have been made using the Pasquill-Turner curves only, with some subjective evaluation included; e.g., neither A nor F category has been used and also, the next most unstable case is used rather than that warranted by the stability condition. This shift in curves is partially justified by the conditions of urban and suburban areas under investigation. Fort Collins is a non-industrial, residential city with primarily one and two story buildings.

RESULTS

The basic approach, which has been applied in this study of the intermediate range transport of lead, was to eliminate the large very rapidly settling particulates from consideration by placing the sampling stations at least 100 m from major roadways. Based on size distribution measurements it was felt that the majority of the remaining particulates will behave as a gas. Other studies conducted by the Atmospheric Chemistry Group of CSU's lead project have speculated that gaseous (organic) lead compounds may undergo atmospheric transformations to particulate (inorganic) lead. This study was conducted to determine if a systematic discrepancy between measured and predicted lead levels could be detected. Under certain circumstances these discrepancies could be attributed to secondary processes as additional gravitation settling, surface impaction, or chemical transformation.

Figures 2 and 3 show a comparison of measured and predicted lead levels. The agreement in these cases, as in the other cases tested, is quite good. Thus, it is felt that these secondary processes are not significantly affecting the airborne lead levels in the intermediate transport range. However, it is possible that the processes of settling and gas to particle conversion are counteracting each other. If this were occuring it would not be possible to isolate these processes with the present data.

It should be noted that the ambient lead levels measured and predicted here, represent fair weather transport and diffusion. Thus, in all likelihood rainout and washout play a significant role maintaining the atmospheric budget of lead.

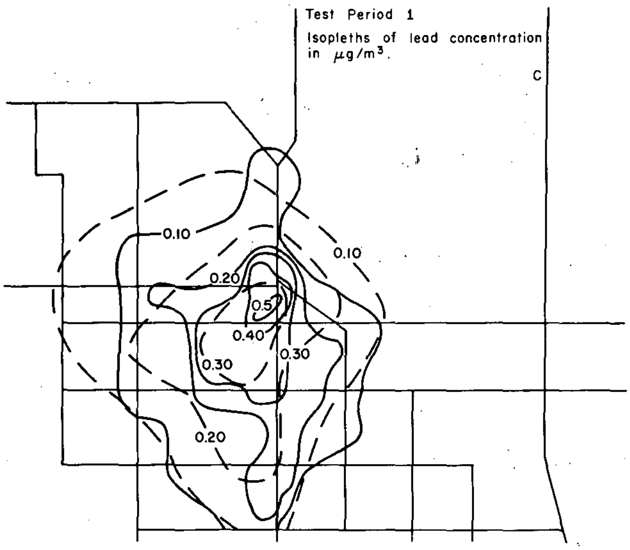

FIG. 2. Abbreviated map of Fort Collins, Colorado, with measured (broken lines) and predicted (solid lines) concentration of airborne lead. Samples were collected from 7:00 a.m. to 12:30 p.m. on May 8, 1973.

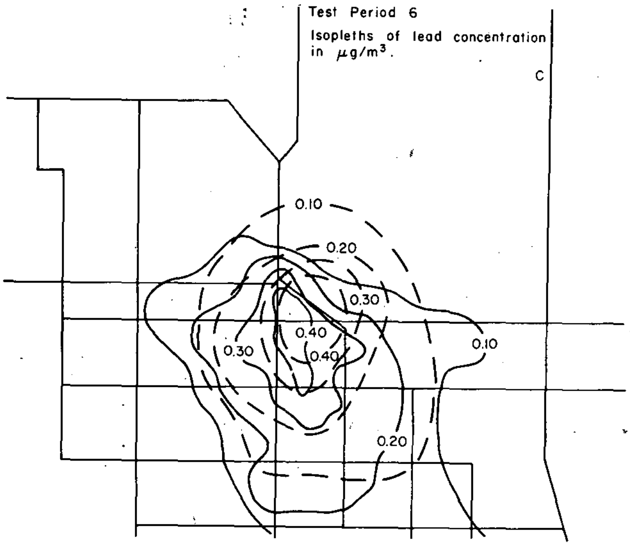

FIG. 3. Abbreviated map of Fort Collins, Colorado, with measured (broken lines) and predicted (solid lines) concentration of airborne lead. Samples were collected from 7:00 p.m. to 7:00 a.m. on May 9 & 10, 1973.

At present, the model is at the point of reasonable prediction of the measured patterns, but it will be tested using other dispersion estimates. In particular, those of McElroy and Pooler, (1968); Bowne, (1973); and Johnson, et al., (1971), will be used and the results using various dispersion curves will be compared. Results showing predicted and measured concentrations will be presented once the sensitivity to various dispersion curves has been established.

DISCUSSION

Assuming that the predictive scheme discussed above is reasonably acceptable, one problem or uncertainty remains. What percentag of the consumed lead (from the gasoline) is sti airborne approximately 10 km downwind of the city (limit of study region)?

Presently, we are assuming that 45% of the consumed lead remains airborne over thes intermediate distances. In other words, 55% of the consumed lead has remained in the vehicle or settled quite rapidly near the roadway and was never seen by any of our air samplers.

However, it is quite unreasonable to expect this depletion of the quasi-airborne lead to cease so rapidly (within 100 m of the source). Thus we should at least intuitively expect some additional settling or impaction on the surface. Some simple schemes were teste with appearingly acceptable results; however, whether this phenomena is actually occuring is unsure for slight adjustments of other paramete such as stability, wind speed, and emission rat can lead to similar results. Now that reasonable pattern agreement is being realized with the model without any unwarranted assumptions, this additional settling or removal mechanism will be incorporated to determine if it can improve results. In particular, it is hoped this "fine adjustment" may help improve the point to point correlation between observations and predictions at sampling stations.

ACKNOWLEDGEMENTS

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POLLUTION TRANSPORT BY CUMULUS CLOUDS

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Abstract

This paper reports on a preliminary numerical study of the effects of the physical characterisitcs of cumulus clouds on the concentration of air pollutants in rain water. If the assumption is valid that cloud water droplets are well mixed vertically as well as horizontally by the motion of cloud air so that the pollutant in the cloud liquid water is uniformly distributed throughout clouds, the observational evidence that the concentration of pollutants in rain water decreases with increasing rainfall rate can be explained. It is emphasized that the dynamics of clouds are an important factor in controlling the concentration of pollutant in rain water.

Introduction

Investigations of the dispersal of pollutants, notably of trace metals from automotive sources along highways, have been focussed mainly on application of the Fickian diffusion equation and on plume models of various kinds (Katen and Reiter, 1973). It has been noted that a measurable fraction of lead-bearing aerosols are dispersed among small enough particle sizes to become virtually unaffected by gravitational settling (Corrin, 1973). Since lead from automotive air pollution has been found on the Greenland ice caps (Fig. 1), we have to assume that these finely dispersed aerosol particles are available for transport processes on a global scale. What governs the movement and deposition of such "volatile" pollutants?

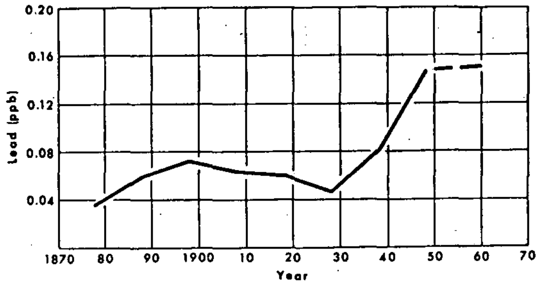

Figure 1. Variation of anthropogenic lead dust fall at Camp Century, Greenland, from about 1880 to 1960, showing the rapid recent increase in man-made particulates in the atmosphere. Lead is measured as parts per billion (ppb). After Murozumi, et al., 1969).

With this question in mind we proceeded to study the fate of certain pollutants through the concept of "residence time" in the atmosphere and through the application of removal processes which came into play on a more or less stochastic basis (Reiter and Bauer, 1974). Results of our work are still preliminary in nature. The conceptual design of our approach looks as follows:

Basically, a pollutant not subject to gravitational settling will be removed either by contact with the ground or by washout and rainout processes. The latter are being modelled in this paper. The former can be handled by the use of eddy diffusion coefficients in the planetary boundary layer, and/or by the concentration of the pollutant in question, times an "affinity factor" which describes empirically the readiness with which the pollutant attaches itself to solid surface. O_3, for instance, is destroyed readily upon contact with organic matter whereas freons have an "affinity factor" of virtually zero.

Our study on wet removal processes will be expanded by applying cloud census data. Presently we have a probabilistic approach in mind which, based upon such census data, will specify the liklihood of an air parcel becoming entrained into (convective) cloud systems of various size and intensity.

Rainout of Pollutants by Convective Clouds

Cumulus clouds are an important mechanism not only for transporting air pollutants from the boundary layer into the free atmosphere, but also for cleansing the atmosphere by precipitation processes. Because of the complexity of cloud physics transport processes of air pollutants by cumulus convection have not been studied extensively. On the other hand, the concentrations of radionuclides and of other pollutants in precipitation have been observed by many authors and the results of observations were summarized by Engelmann (1968, 1971). The tables in Engelmann's papers reveal that concentrations of pollutants in rain water vary over a wide range, depending not only on the chemical nature of the pollutant, but also on the cloud type from which the rain water sample is obtained. However, there is a definite inverse relationship between the concentration in rain and rainfall rate. A rather striking example of this inverse relationship is shown in Figure 2.

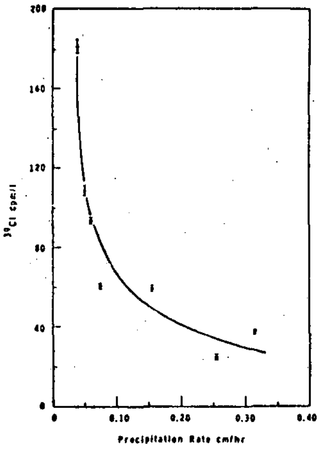

Figure 2. ^{39}Cl concentration as a function of precipitation rate (After Engelmann and Perkins, 1971).

It is important to study the effects of the physical characteristics of clouds on the concentration of air pollutants in rain water. By understanding these effects, the vertical transport processes of pollutants from the planetary boundary layer into the free atmosphere and the cleansing mechanisms of the atmosphere will be understood better. This will lead to more reliable estimates of residence times in the atmosphere of various pollutants from different sources.

This paper reports on a preliminary numerical study of the effects of the physical characteristics of clouds on the concentration of air pollutants in rain water and discusses the transport processes of air pollutants which have their sources below cloud level and are transported into the free atmosphere by cumulus convection. The model used for this study is a one-dimensional and steady-state cumulus model. Precipitation effects are not included into the dynamics of the cloud. The schematic diagram of the model is shown in Figure 3. Although the model is far from real conditions of the atmosphere, several important implications are obtained.

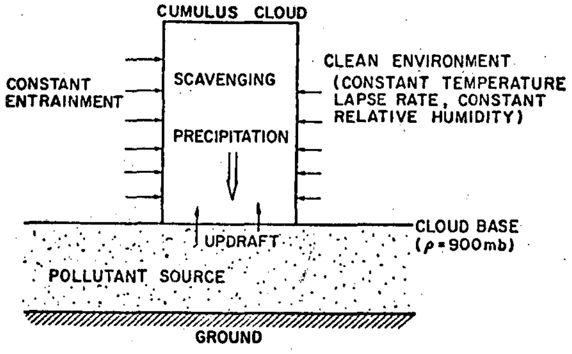

Figure 3. Schematic diagram of the model

Model

(i) Dynamic equations for a cumulus cloud:

The following scheme of a cumulus cloud in a stationary environment is envisaged: The cloud consists of a saturated cylindrical continuous vertical current in a steady state. This continuous current or jet is considered to entrain environmental air through its sides. With these assumptions, the systems of equations for the model cloud are written as follows: (The details of the equations are found elsewhere, for instance, Haltiner, 1959; Srivastava, 1964).

$$\frac{dH}{dz} + EH = E\frac{L}{Cp}q_e - (\gamma_d - \gamma_e) \qquad (1)$$

$$\frac{d(Q + q)}{dz} + E(Q + q) = Eq_e \qquad (2)$$

$$\frac{dw^2}{dz} + 2Ew^2 = 2g[\frac{\Delta T}{Te} - Q] \qquad (3)$$

Here, the symbols are defined as follows:

$H = \frac{L \cdot q}{Cp} + \Delta T$

$E = \frac{1}{M} \frac{dMe}{dz}$ entrainment rate

γ_d: dry-adiabatic lapse rate of temperature

γ_e: lapse rate of environmental temperature

q: water vapor mixing ratio

q_e: value of q in the environment

Q: liquid water mixing ratio

z: height

w: updraft velocity

g: acceleration due to gravity

T_e: environmental temperature

L: latent heat of condensation

C_p: specific heat of air at constant pressure

The first two equations represent, respectively, the conservation of energy and of water substance. Equation (3) is the equation of motion.

It is assumed that the environmental temperature decreases with the constant lapse rate, γ_e, and also that the relative humidity of environmental air, r, is constant throughout the atmosphere. Therefore,

$$T_e = T_{eo} - \gamma_e \cdot Z$$

$$q_e = r\, q_{es}$$

where T_{eo} is the environmental temperature at the cloud base and q_{es} is the saturation mixing ratio of vapor of the environmental air. The vertical distribution of temperature, liquid water content and updraft velocity are obtained by solving these equations with the aid of the Clausins-Clapeyron equation and the hydrostatic equation.

(ii) Equation for pollutant:

The equation of mixing ratio of a pollutant, x, can be obtained from the consideration of the conservation of the quantity x in the portion of the vertical current bounded by the levels z and z + dz as shown in Figure 4.

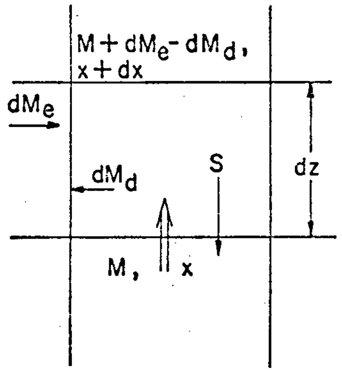

Figure 4. Schematic diagram illustrating entrainment, detrainment and vertical transport of quantity x in a cumulus cloud.

The conservation is expressed by:

$$M \cdot x = (M + dM_e - dM_d)(x + dx) + dM_e \cdot x_e - dM_d \cdot x - M \cdot S \cdot dz \qquad (4)$$

where M is the mass of air which rises vertically through level z within the cumulus cell. x is the mixing ratio of the pollutant in the cumulus cell, x_e is the mixing ratio of the pollutant in the environment, M_e is the mass of air entrained, M_d is the mass of air detrained, and S represents the change of x per unit depth and per unit mass of air due to any source or sink between z and z + dz. By neglecting the term (dM·dz), the equation can be rewritten as

$$\frac{dx}{dz} + Ex = Ex_e + S \qquad (5)$$

$$\text{where } E = \frac{1}{M} \frac{dMe}{dz}$$

If only the scavenging process by cloud water contributes to the term S, we can write

$$S = - \frac{\psi \cdot x}{w} \qquad (6)$$

where ψ is the scavenging coefficient (sec^{-1}) and w is the updraft velocity at z. The scavenging coefficient, ψ, is a function of many physical parameters, such as size distribution of cloud droplets, chemical properties of the pollutant, etc. However, for this preliminary study, ψ is assumed to be expressed by

$$\psi = \psi_o \frac{\rho_a(z) \cdot Q(z)}{(\rho_a \cdot Q)_{=1g/m^3}} \qquad (7)$$

This means that the scavenging coefficient ψ, is equal to ψ_o when the liquid water content is 1 g/m^3 and that ψ varies proportional to the liquid water content. To simplify the problem, the further assumption is made that the air in the environment of the cumulus cloud contains no air pollutant. Therefore, equation (5) yields

$$\frac{dx}{dz} + Ex = -\psi_o \cdot \frac{x}{w} \frac{\rho a \cdot Q}{(\rho a \cdot Q)_{=1g/m^3}} \qquad (8)$$

This mixing ratio of the pollutant at the bottom of the cloud is given by x_o. Dividing the equation (8) by x_o and defining $X=x/x_o$ the equation can be written as

$$\frac{dX}{dz} + EX = -\psi_o \cdot X \frac{\rho a \cdot Q}{(\rho a Q)_{=1g/m^3}} \qquad (9)$$

The solution of equation (9) is given by

$$X=\exp\left(-\int_o^z Edz\right) \cdot \exp\left(\frac{\psi_o}{(\rho a Q)_{=1g/m^3}} \int \frac{\rho_a Q}{w} dz\right) \qquad (10)$$

If there were no scavenging process in the cloud, the solution of the equation (9) is simply expressed by

$$X' = \exp\left(-\int_o^z Edz\right) \qquad (11)$$

Therefore, the amount of the pollutant scavenged in the cloud, T_x, is given by

$$T_x = x_o \int_o^{z_{top}} \rho_a (X'-X)dz \quad (g/cm^2) \qquad (12)$$

where z_{top} is the cloud height and ρ_a is the air density. The total water condensed in the cloud is given by

$$T_{water} = \int_o^{z_{top}} \rho a Q(z)dz \quad (g/cm^2) \qquad (13)$$

Hence, the average concentration of the pollutant in the cloud liquid water, k is

$$k = \frac{T_x}{T_{water}}$$

The ratio of the average concentration of the pollutant in liquid water to the concentration of the pollutant in air below cloud-base is expressed by

$$\left(\frac{k}{xo}\right)_m = \frac{\int_o^{z_{top}} \rho_a (X' - X)dz}{\int_o^{z_{top}} \rho_a \cdot Q(z)dz} \qquad (14)$$

At the present stage, the levels within the cloud which contribute mainly to the precipitation are uncertain. The assumption is made, therefore, that by the motion of air the cloud droplets are well mixed so that the concentration of the pollutant in the liquid water is uniform throughout the depth of the cloud. If this assumption is valid, equation (14) gives the value of the ratio of the concentration of the pollutant in rain water to the concentration of the pollutant in surface air.

(iii) Consideration of different clouds

The equations described in Section (i) which characterize the vertical distribution of updraft velocity, liquid water content, and temperature are solved under different values of physical parameters. By changing the combination of physical parameters, clouds having different physical characteristics are obtained. The following values were used for computation:

(a) Temperature
Cloud base temperature, T = 293°K
ΔT at the cloud base = $T - T_e$ 1°K
(b) Updraft velocity at cloud base
w_o = 50 cm/sec in the case of γ_e = 7.5°K/Km
w_o = 100 cm/sec in case of γ_e = 8.0°K/Km
(c) relative humdity of environment
r = 60, 70, 80, 90 and 100%
(d) Entrainment rate
E = 0.4, 0.6, 0.8 and 1.0 Km^{-1}

With the combination of these parameters, 40 different clouds were obtained. Three of these cases were omitted from the consideration in this paper.

(e) Scavenging coefficient

Davis (1972) reported that from the observational studies the scavenging coefficient ψ, for ^{24}Na is larger than 10^{-4} sec-1 and for ^{38}Cl is between 10^{-3}sec^{-1}. For this reason, the following three different values of ψ_o were chosen:

ψ_o = 0.001, 0.01 and 0.05sec^{-1}

Results and discussion

(i) Vertical distribution of updraft velocity, liquid water content and temperature.

Typical examples of the vertical distributions of T, L. W. C. and w obtained from the calculations are shown in Figures 5a, b and c, respectively. Two different cases are shown. The numerical values of the physical parameters can be obtained from these figures. The solid lines are for a "large" cumulus cloud and the broken lines are for a "small" cumulus cloud. It should be pointed out that these results agree at least qualitatively with the observational results of these quantities: the higher the cloud, the larger the updraft velocity and liquid water content.

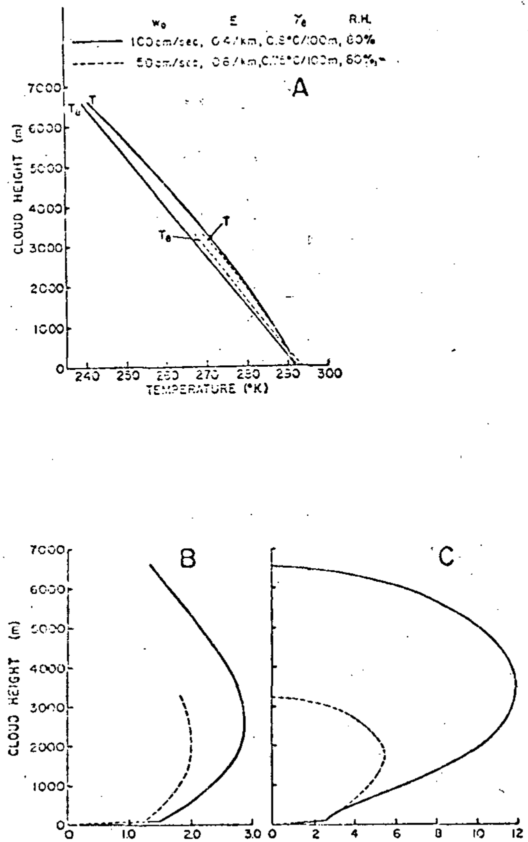

Figure 5. Typical examples of the vertical distributions of temperature (A), liquid water content (B), and vertical velocity (C).

(ii) Total liquid water condensed per unit area of the column of cloud T_{water}, is calculated for each cloud, and the results are summarized in Figure 6. As it is expected T_{water} is larger for higher clouds. In the figures, triangular marks and circular marks are for the clouds grown in an environment having a temperature lapse rate of γ_e = 0.75°C/100m, and, 0.80°C/100m, respectively. It is seen that even if the height of the cloud is the same, the cloud grown in the environment having the smaller lapse rate contains larger amounts of liquid water.

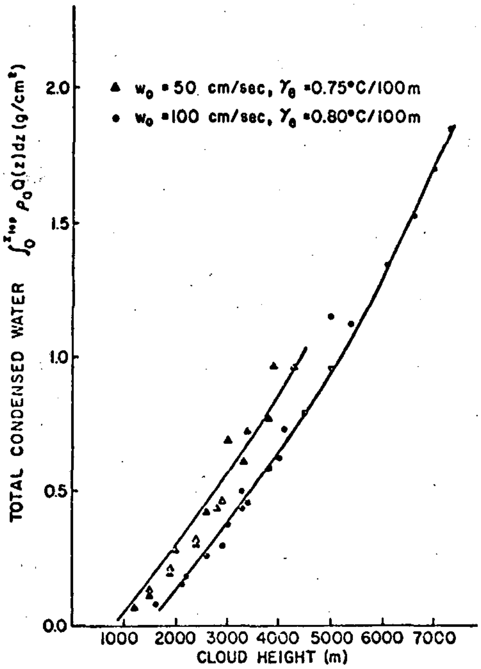

Figure 6. Total liquid water condensed per unit area of the column of cloud versus cloud height

(iii) Vertical distribution of the pollutant in cloud air. The vertical distributions of the pollutant in cloud air are shown in Figures 7a and b for the two different clouds described previously. In these figures, the scavenging coefficient ψ_0 is taken as an independent parameter. In the case of larger values of ψ_0, the relative concentration of pollutant, x/x_0 decreases rapidly with height.

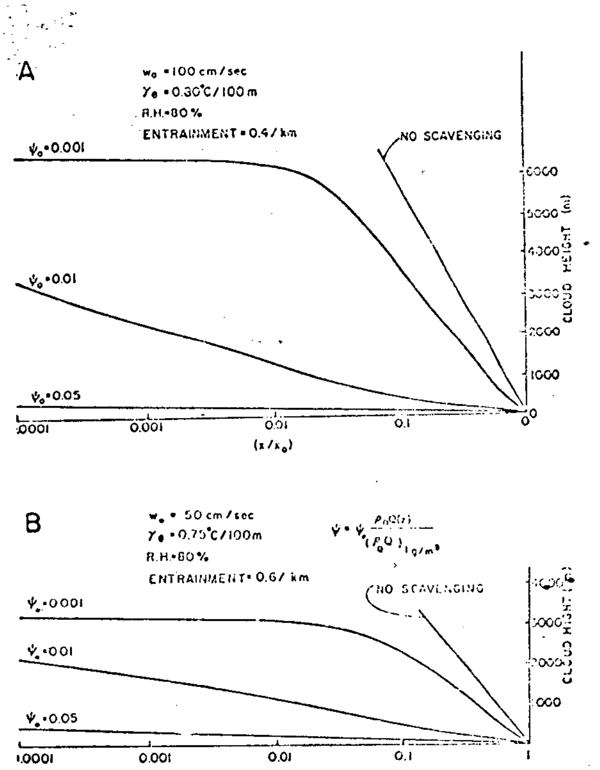

Figure 7. Vertical distributions of the pollutant in cloud air for two different clouds.

The comparison of the two figures reveals that in the smaller cloud the concentration of the pollutant decreases more rapidly with height. This is due to the slower vertical velocity in smaller clouds: The slower the vertical velocity, the longer is the time required for the air to reach the same height above the cloud base. In the case of small values of ψ_o, the concentration of the pollutant in cloud air is significant even in the top portion of a cloud. On the other hand, in the case of larger values of ψ_o, the pollutant is scavenged quickly by cloud water near the lower portion of the cloud. Larger values of ψ_o may be at least qualitatively regarded as corresponding to the scavenging coefficients for hygroscopic material, such as sodium chloride. As described previously, the value of ψ is chosen rather arbitrarily. For future work, improved values of ψ should be chosen.

(iv) Average concentration of pollutant in cloud water as a function of cloud height.

The average concentrations of pollutant in cloud water, which is defined by the equation (14) was calculated for each cloud. Figures 8a, b and c show $(k/X_o)_m$ versus cloud height for ψ_o = 0.05, 0.01 and 0.001 sec^{-1}, respectively.

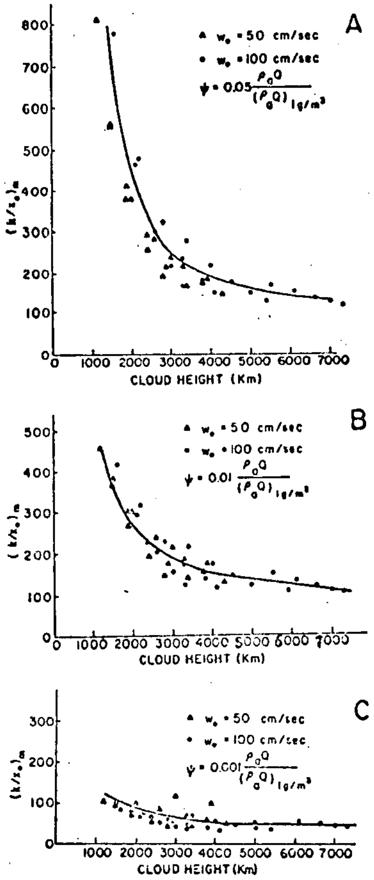

Figure 8. Average concentrations of pollutant in cloud water versus cloud height for different values of the three scavenging coefficients.

In these figures, the triangular marks and circular marks are for clouds grown under the condition of w_0 = 50cm/sec, γ_e = .75°C/100m, and w_o = 100cm/sec, γ_e = 80°C/100m, respectively. The shape of the curve in Figure 8a resembles rather strikingly the curve in Figure 1, in which the observational results of the concentration of ^{39}Cl in rain water versus precipitation rate are shown. It is well known that in general, the precipitation rate from clouds increases with cloud height [Figure 9 from the paper by Austin and Houze (1972)].

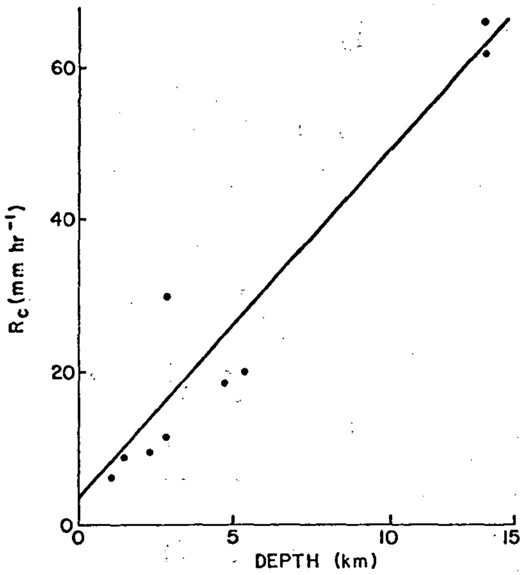

Figure 9. Precipitation rate as a function of cloud depth (after Austin and Houze, 1972).

As is expected, the comparison of Figures 8a, b and c reveals that the larger the value of ψ_o, the larger is the concentration of pollutant in rain water. It should be pointed out that the difference of $(k/xo)_m$ for different ψ_o is large when the height of the cloud is small, and that for the higher clouds the difference of $(k/xo)_m$ becomes smaller for different ψ_o. This can be explained as follows: For the chosen value of ψ_o the scavenging processes in the clouds are so effective that most of the pollutants are scavenged by the liquid water in the lower portion of the cloud. On the other hand, cloud liquid water is fairly uniformly distributed with height as shown in Figure 5b. As a consequence the difference of the average values of $(k/xo)_m$ become smaller for different ψ_o in the cases of higher clouds. It should also be pointed out that for smaller values of ψ_o, the dependency of $(k/xo)_m$ on the depth of the cloud becomes smaller. This reflects the fact that the time required for the pollutant to be scavenged by cloud water is longer under inefficient scavenging processes.

The scattering of the values in the figure can be explained by the fact that each of the model clouds was grown under different environmental conditions.

(v) Average concentration of pollutant in cloud water as a function of total liquid water condensed.

In Figure 10a, b and c, similar to Figure 8a, b and c, the average concentration of pollutant in cloud water versus the total liquid water condensed in the clouds is presented. As has been shown in Figure 6, the total liquid water condensed in the cloud increases with increasing cloud height. Therefore, the shapes of the curves in Figure 10a, b and c are similar to those in Figure 8a. b and c.

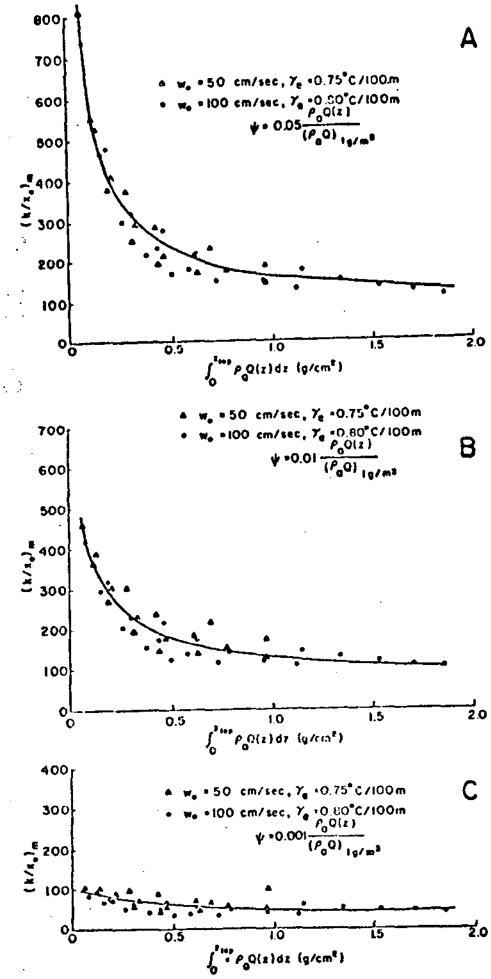

Figure 10. Average concentration of pollutant in cloud water versus total liquid water condensed in the clouds.

CONCLUSION

If the assumption is valid that cloud water droplets are well mixed vertically as well as horizontally by the motion of cloud air so that the pollutant in the cloud liquid water is uniformly distributed throughout the cloud, the results obtained in this preliminary calculation explain, at least qualitatively, the observational evidence that the concentration of pollutants in rain water decreases with increasing rainfall rate. It is emphasized that the dynamics of clouds is as important a factor as the scavenging coefficient in controlling the concentration of pollutant in rain water.

The scavenging process involves many physical parameters of the cloud and many microphysical mechanisms. Incorporation of these parameters and mechanisms into a numerical model is a difficult task. An effort should be made to undertake such a task in order to understand the processes of vertical transport of pollutants by clouds, and the eventual removal of certain pollutants from the atmosphere. It should then be possible to estimate the impact of certain pollutants on the global environment by referring back to climatological data on atmospheric transport and precipitation processes.

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SOME ATMOSPHERIC TRANSPORT CHARACTERISTICS OF SUSPENDED PARTICULATES AND ASSOCIATED TRACE CONTAMINANTS AROUND THE SOUTH END OF LAKE MICHIGAN

by
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Abstract

Selected daily isopleths for total suspended particulate and associated trace contaminants are analyzed for atmospheric transport characteristics. It is possible to clearly isolate certain meso-scale atmospheric transport characteristics from single day isopleth analysis reveals only area source pollution levels, not point sources. It is postulated that point source identification from atmospheric transport patterns can be achieved only from accurate hourly meteorological data, in conjunction with known point source inventory strengths, and under environmental conditions that essentially eliminate refloatation from terrestrial surfaces.

Introduction

The area around the south end of Lake Michigan is extremely complex from an atmospheric transport viewpoint. There are several major terrestrial surface features that account for this complexity. This rectangular geographical area consists of about half land and half water. (See Figure 1.) The Lake Michigan shoreline changes a full 180° in orientation from almost north-south to east-west then to south-north again. A unique topographic feature is that of 200 to 300 feet elevations rise over the first 5 to 10 miles from the Lake Michigan shoreline. This is due to the presence of a glacial moraine that surrounds much of the south end of Lake Michigan. Further, the land use is highly varied too; from urban, suburban, intenstive industrial areas, as well as open country.

Intensive "heat islands" and "heat sinks" or cold areas exist because of these highly varied terrestrial surfaces. The water surfaces are colder than the land surfaces in the spring and summer but warmer in the autumn and winter. The City of Chicago and some heavily industrial areas produce "heat islands" while the rural areas produce "heat sinks". All of these natural or man-made features produce many observable meso-scale atmospheric circulations.

In the area around the south end of Lake Michigan a land-lake breeze, similar to that of land-sea breeze circulation, commonly exists. An observable "lake front" is often produced on the land areas during midday under many synoptic conditions. This unique feature of the greater Chicago area as illustrated in Figure 2 was documented by Lyons in 1973 (3). A "lake front" sky is illustrated in Figure 3. This photograph was taken October 20, 1973 near noon. The Chicago Lake Michigan shoreline is shown in the foreground.

The net result of all these contrasting terrestrial surfaces is the existence of many meso-scale atmospheric wind systems and transport patterns. Further, these patterns can change almost hourly and nearly always change from one day to another. Therefore, averaging over time periods of more than a few hours produces effects that are likely to be mean results that represent several atmospheric transport conditions.

In an attempt to isolate and understand the effects of the many atmospheric transport patterns on air quality, individual days on the U.S. Environmental Protection Agency (EPA) observational schedule for total suspended particulate (TSP) were analyzed over a 12-month period. Results for some selected days from this effort are reported herein illustrating some of the basic patterns of atmospheric transport in the study area.

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Data Sources And Methods

Figure 4 shows the locations of all high-volume air sampling sites used in the analysis. The isopleth analysis for TSP as well as for trace metals were produced using data from sampling sites or points illustrated in Figure 4. The isopleths represented in the various figures were drawn using linear interpolation between sites. All available site data were used in each case. These data were secured from 82 air sampling sites through the cooperation of the following nine agencies:

1. Division of Air Pollution, State Board of Health, State of Indiana.
2. Division of Air Pollution Control, City of Gary.
3. Department of Air Quality Control, City of East Chicago.
4. Air Pollution Control Department, City of Hammond.
5. County Health Department, Lake County, Indiana.
6. County Health Department, Porter County, Indiana.
7. Division of Air Pollution Control, Michigan City, Indiana.
8. Department of Environmental Control, City of Chicago.
9. Cook County, Department of Environmental Control.

Meteorological data were obtained from the National Weather Service. Figures representing daily isopleth analysis contain estimates of the mean 24-hour wind speed as well as the resultant wind speed, in mph. These numbers appear below the 24-hour mean wind direction in these figures. Also, these figures representing daily analysis contain mean 24-hour temperature in degrees Fahrenheit. Mean values for wind and temperature were derived from hourly values. The resultant wind is the vector sum of wind directions and speeds divided by the number of observations. Resultant wind speed will equal mean wind speed when the winds are from only one direction for the 24-hour sampling period. Thus, the resultant wind speed is a measure of the wind direction consistancy.

A "wet day" is a day in which at least 0.10 inches of precipitation was recorded at Midway Airport in Chicago. Table 1 reports the precipitation amount recorded by the National Weather Service, Chicago, Midway Airport for Figures 5 through 14.

Table 1. Precipitation recorded at Chicago's Midway Airport on the day of total suspended particulate measurements as well as three days previous for each sample day reported in this study.

Figures	Date	Precipitation
5 & 6	Jan. 28, '73	0.02"
Dry	27	T
Day	26	0.00
	25	0.00
7 & 8	Apr. 4, '73	0.15
Wet	3	T
Day	2	0.04
	1	0.25
9 & 10	Jan. 16, '73	0.00
Dry	15	0.00
Day	14	0.01
	13	0.00
11 & 12	Jan. 10, '73	0.00
Dry	9	0.00
Day	8	T
	7	T
13 & 14	Mar. 5, '73	0.35
Wet	4	0.02
Day	3	0.01
	2	0.26

* Trace, less than 0.01 inches.

Discussion

Each sixth day during a given month is designated as an air quality observation or measurement day by the U.S.-EPA. This standardized schedule produced a common observational day among the nine cooperating state and local agencies on four to five days each month. Each of these EPA scheduled days were analyzed for 1973. Several sample days have been chosen during January, March and April of 1973 to illustrate some of the atmospheric transport characteristics in the study area.

To illustrate the effect of refloatation on TSP and the trace metal cadmium compare January 28 with April 4, 1973, represented by Figures 5, 6, 7 and 8. The meteorological transport conditions are almost identical except for terrestrial surface conditions. On January 28 the land surfaces in the study area are dry and on April 4 they are wet (see Table 1). On both days the winds are steay out of the North at 360°. The average wind speed is near 15.5 mph. Both days have 100% cloud cover with near neutral stability conditions existing over most of the 24-hour observational period. Surface temperatures represent only a conservative seasonal change off Lake Michigan water surface.

The on-shore transport of air pollutants as represented by TSP values result in similar patterns on both days (See Figures 5 and 7). However, the meausred amounts are 25 to 50% higher on the dry day, January 28, when compared to the wet day, April 4. Similar relative differences exist for the cadmium determinations (see Figures 6 and 8). Since both days have wind speed well above the critical level for refloatation, it is assumed that differences of this magnitude must be largely due to refloatation (1). The weekly sampling day adds additional validity to this deduction. January 28, 1973, was a Sunday which usually produces lower area source emissions of TSP values than other weekdays (4). The sampling day of April 4, 1973, occurred on a Wednesday. Further, it should be noted that rather low TSP values were measured in most areas within the City of Chicago for the wet day, April 4, while the reverse is true for the dry day, January 28. Also, these north on-shore winds with good flushing speeds produce smaller area-source patterns on the wet day for both TSP and cadmium amounts. Flushing winds decrease TSP concentration by increasing mixing and lateral transport of airborne pollution (5).

Winds from the south and southeast varying from 100 to 200° in compass readings represent the reverse type of atmospheric transport around the south end of Lake Michigan. These winds produce off-shore transport along the shoreline oriented East-West where much heavy industrial sources exist in northwestern Indiana and in the extreme southeastern areas of Chicago. This type of transport day is represented in Figures 9 and 10, for Tuesday, January 16, 1973. On this sample day the winds were consistently out of the SSE at 190° at 16.5 mph. It was a dry day with near neutral stability conditions.

Such meteorological transport conditions improve air quality conditions in the heavily industrialized areas of NW Indiana and SE areas of Chicago. These conditions effectively flush these heavy source areas, transporting pollution over Lake Michigan where there are no high-volume samplers. At the same time an increased deterioration in air quality, as measured by recorded TSP values, is observed from the Loop area north in Chicago (see Figure 9). This situation will be pronounced if the wind speeds are above 10 mph with surfaces dry. Such conditions produce refloatation which could account for high values of TSP on January 16, 1973, in northern part of Chicago and Cook County, Illinois. This deduction is strengthened by the fact that on wet days with strong south to southeast winds TSP values are lower and much more uniform over the entire study area.

The cadmium levels associated with TSP measurements were high in the SE industrial areas of Chicago and in the northern areas of the City (see Figure 10). Cadmium, as well as the other trace metals zinc, lead and copper, increases in high-volume pad TSP measurement on dry days with strong off-shore winds from the south and west. Days with on-shore winds from the north and northeast, even on dry days, show much lower cadmium levels. These results (compare Figures 6, 8 and 10) suggest that a considerable amount of trace metals as measured by TSP catches on high-volume pads if refloated from soil, street, and building surfaces within the urban and suburban environments. Further evidence is revealed in Figures 6 and 8 showing higher cadmium values only in known source areas with on-shore north winds, but generally much lower values over the entire area.

Figures 11, 12, 13 and 14 illustrate examples of days with direct on-shore and off-shore winds for most of the highly urbanized areas around the south end of Lake Michigan. In Figures 11 and 12 on Wednesday, January 10, 1973, winds were below critical refloatation speeds and were rather steady from the southwest at 230°. Land surfaces were dry. Unstable conditions prevailed over most of the 24-hour period. A weak mesoscale lake front developed during the afternoon hours.

These meteorological conditions produced only minor evidence of refloatation. It is likely that the lake front circulation did contribute to the transport of TSP inland from known heavily industrialized source areas along the lake shore. The isopleth analysis for TSP and associated cadmium values are representative of known source areas. In this case, one could conclude that little atmsopheric transport took place with respect to source regions.

Figure 13 and 14 for Monday, March 5, 1973, reveal the opposite directional atmospheric transport conditions. The winds are from the northeast and variable. Unstable conditions prevail. The land surfaces are wet. These environmental conditions would produce little or no refloatation. Such atmospheric transport conditions produce good inland transport of TSP and associated trace metals from the heavily industrialized areas located near the lake shore. The TSP producing areas are revealed rather definitely under these inland transport conditions. Known source areas for cadmium are more sharply revealed in the isopleth analysis of Figure 14.

There are many other combinations of atmospheric transport source areas and surface conditions that could be illustrated. But the preceding sample day analyses and discussion of them represent some of the main atmospheric transport conditions. In general, there are a greater number of days with wet surfaces when the wind is from the north and northwest. Winds from these directions normally represent post cold front conditions, and higher wind speeds. This is most fortunate from an air quality viewpoint since refloatation is held to a minimum.

The City of Chicago experiences its poorest air quality on days when the atmospheric transport is from southeast. Surface winds or boundary layer winds that blow from the quadrant of NE to SE (45 to 135°) are normally associated with an approaching low pressure storm center. The surfaces are usually dry. The speeds are normally less than 10 mph, but persist for 12 to 18 hours. These atmospheric transport conditions are very effective in transporting the heavy TSP condition of the heavily industrialized areas of SE Chicago and the lake shore areas of NW Indiana.

Summary

Isopleth analysis of the total suspended particulate, cadmium and other trace contaminants clearly suggest that intensely polluted areas around the south end of Lake Michigan are a result of certain atmospheric transport configurations. These transport configurations are related to both macro- and meso-scale atmospheric circulation patterns. The mesoscale transport patterns are reinforced by the terrestrial surface features which include both land and water, urban and rural areas plus topographical features that help mesoscale circulation patterns to persist. These patterns usually persist only a few hours and almost never more than a day or two. The atmospheric transport of aerosol pollutnats is further complicated by the refloatation of particles from polluted terrestrial surfaces. This phenomenon makes the identification of small area sources difficult and the identification of point sources almost impossible. However, individual days conducive to minimal refloatation produce rather clear small area source configurations under known atmospheric transport conditions.

Acknowledgements

This tudy was sponsored by the National Science Foundation, Research Applied to National Needs, grant number GI 35106 through the Institute for Environmental Health at Purdue University. The high-volume data on air quality was provided by the City of Chicago, Department of Environmental Control; Department of Environmental Control, Cook County, Illinois; Division of Air Pollution Control, City of Gary; Department of Air Quality Control, City of East Chicago; Air Pollution Control Department, City of Hammond; Division of Air Pollution Control, Michigan City; County Health Department, Lake County; County Health Department, Porter County in Indiana, and the Division of Air Pollution, State Board of Health, State of Indiana. The meteorological data was obtained from the U.S. Department of Commerce, National Oceanic and Atmospheric Administration, National Weather Service Office at Midway Airport, Chicago, Illinois. The assistance freely given by personnel within these organizations, institutes and offices was absolutely necessary for the success of this research effort.

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List of Figures

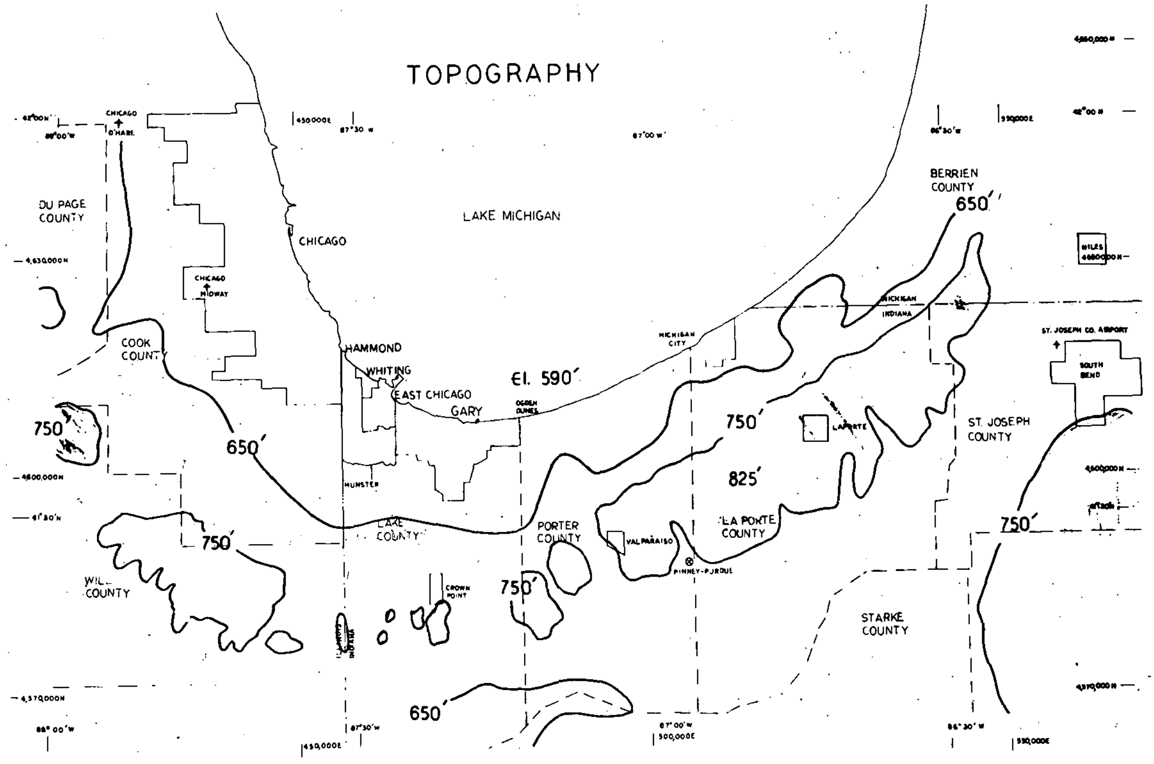

Figure 1. Topographic features around the south end of Lake Michigan.

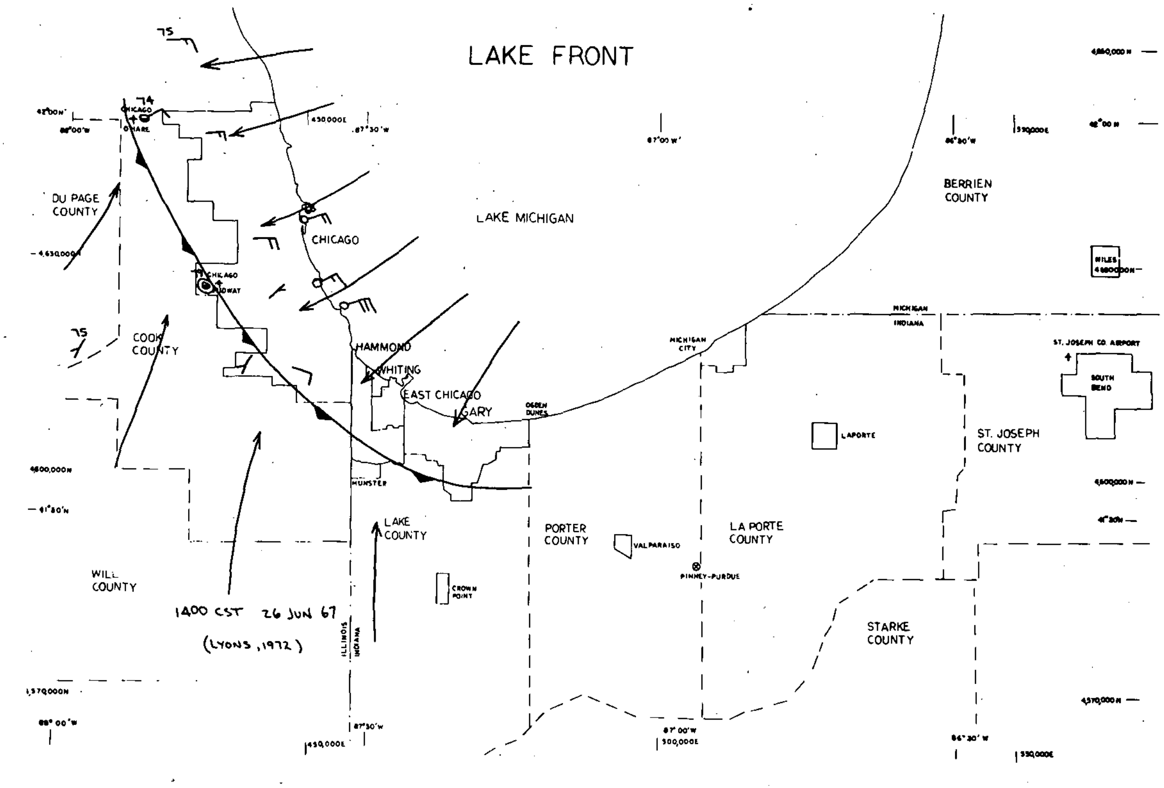

Figure 2. A synoptic illustration of the "Lake Front" at 1400 CST 26 June, 1967. (after Lyons '72)

Figure 3. A photo taken from a light aircraft at near noon 20 October, 1973, of a well developed "Lake Front" over Chicago.

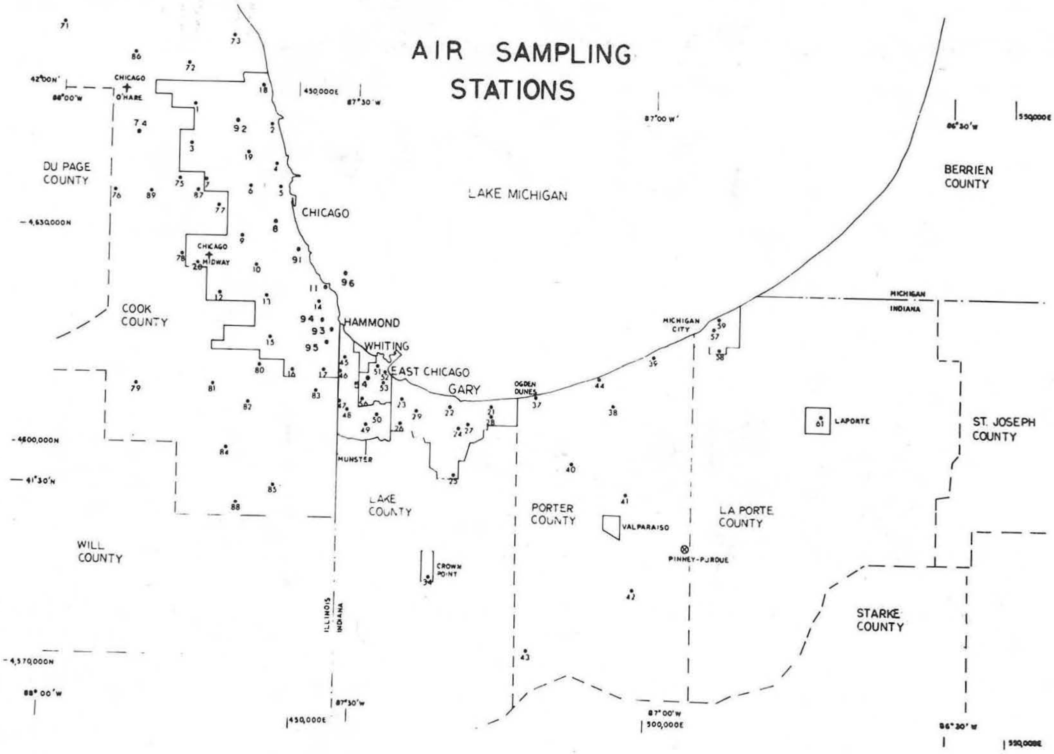

Figure 4. The geographic location and number code for the high-volume air sampling stations used in the study around the south end of Lake Michigan.

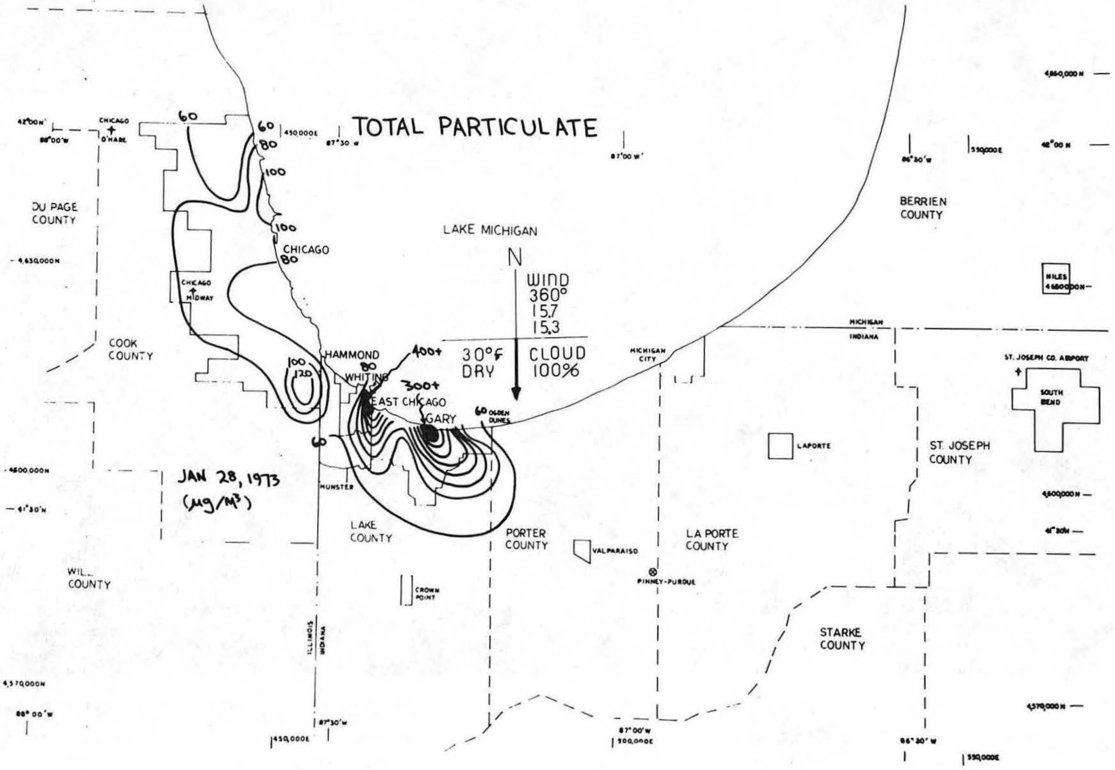

Figure 5. Isopleth analysis for total suspended particulate on 28 January, 1973.

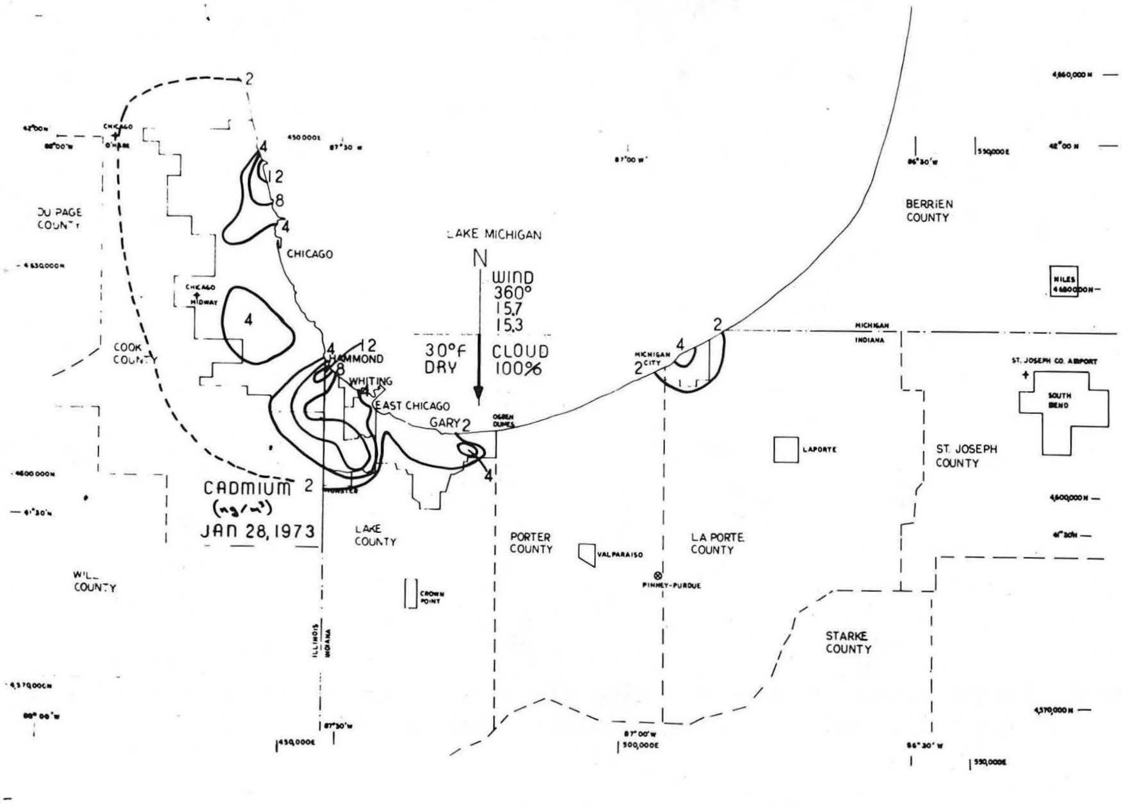

Figure 6. Isopleth analysis for cadmium on 28, January, 1973.

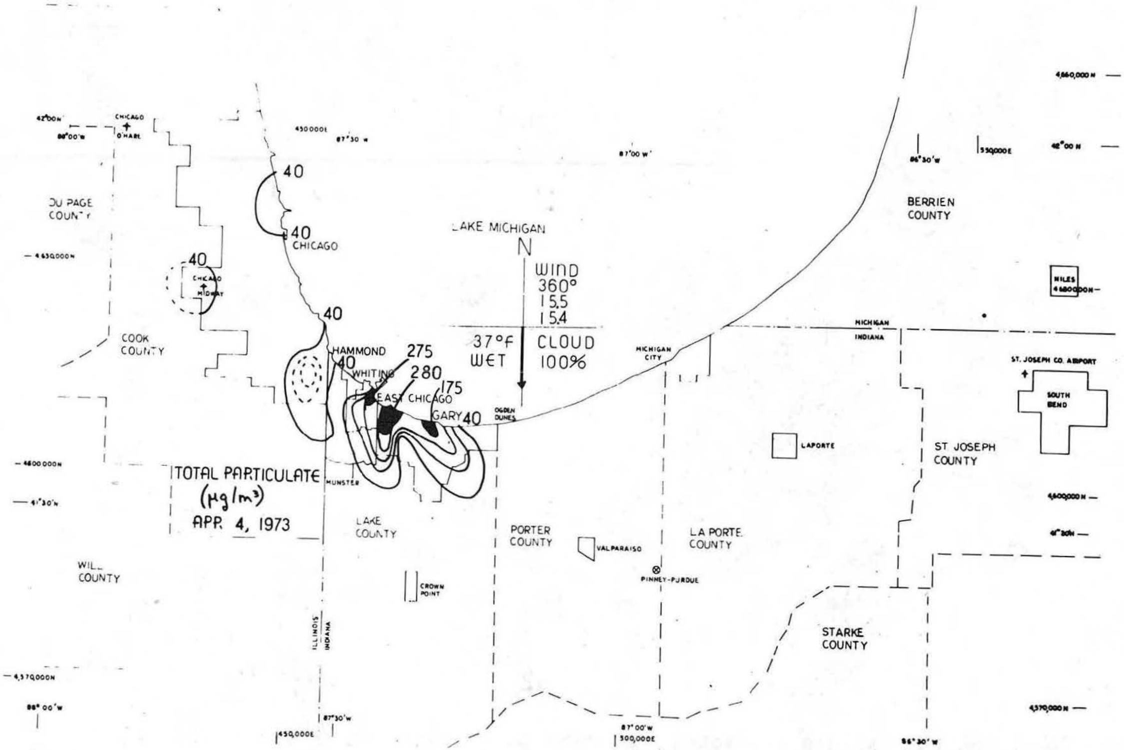

Figure 7. Isopleth analysis for total suspended particulate on 4 April,1973.

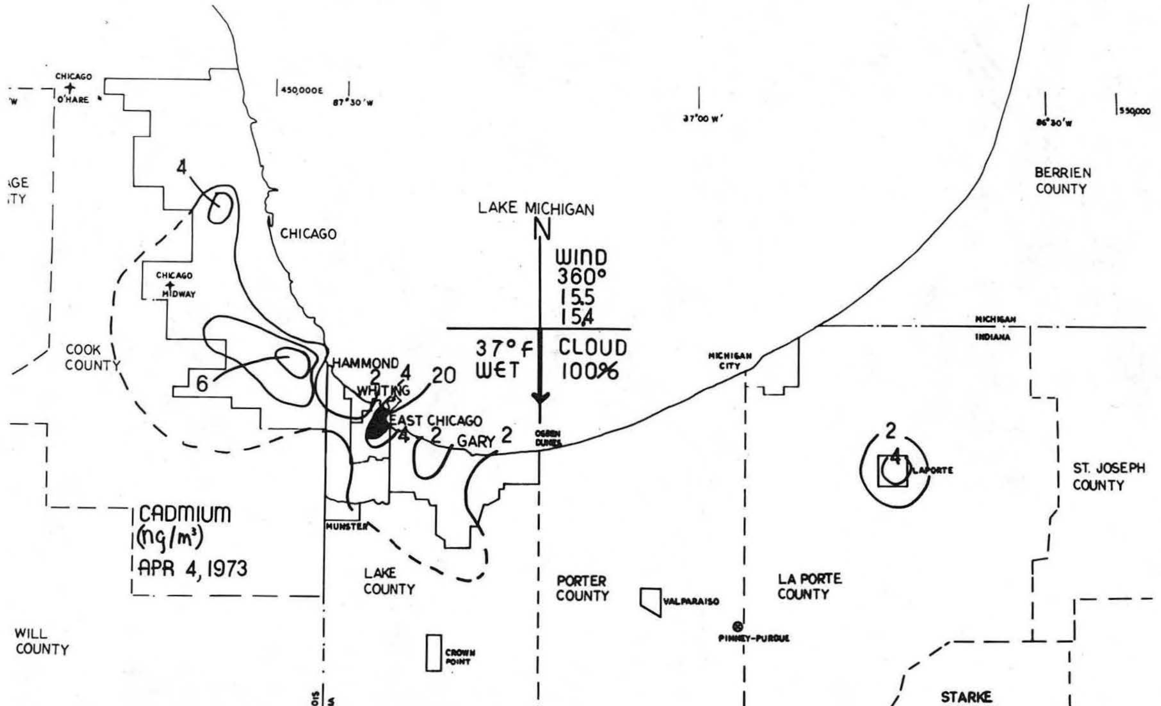

Figure 8. Isopleth analysis for cadmium on 4 April, 1973.

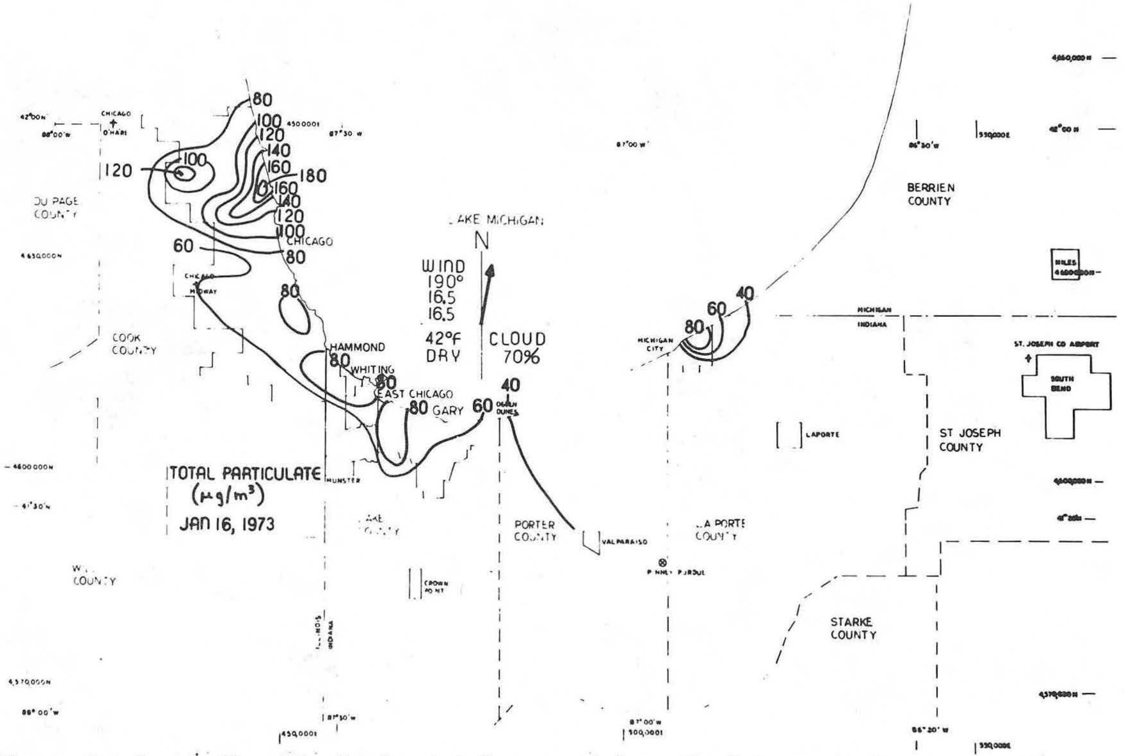

Figure 9. Isopleth analysis for total suspended particulate on 16 January, 1973.

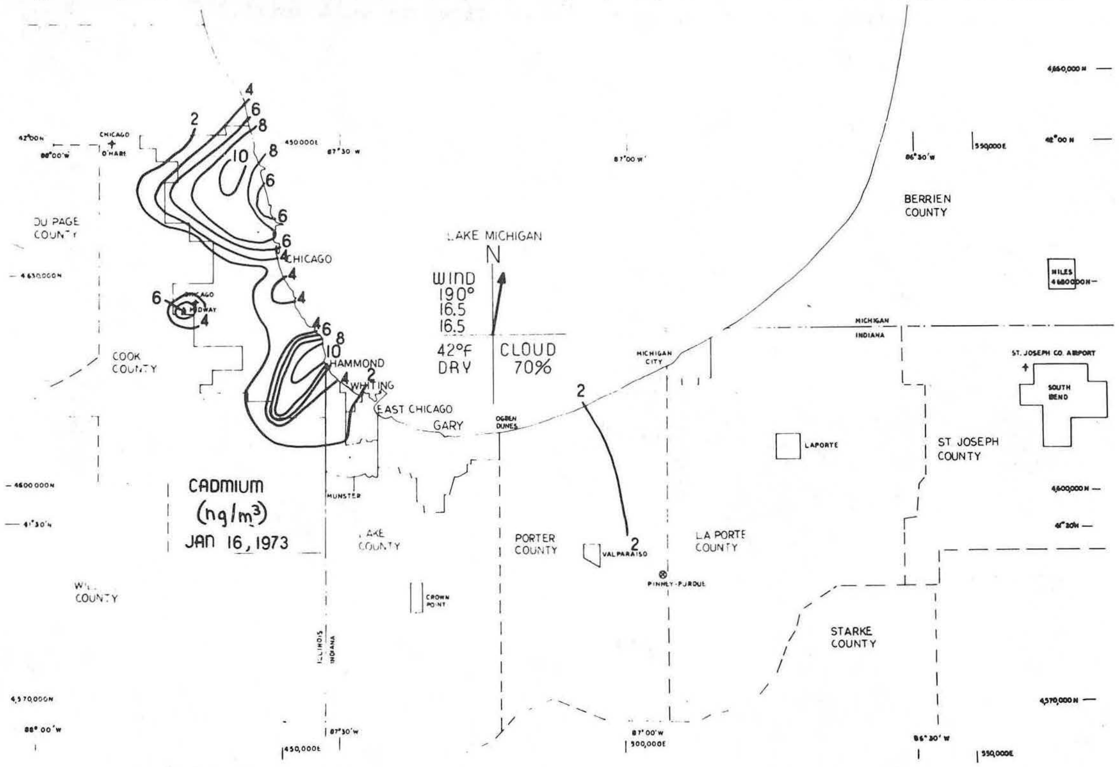

Figure 10. Isopleth analysis for cadmium on 16 January, 1973.

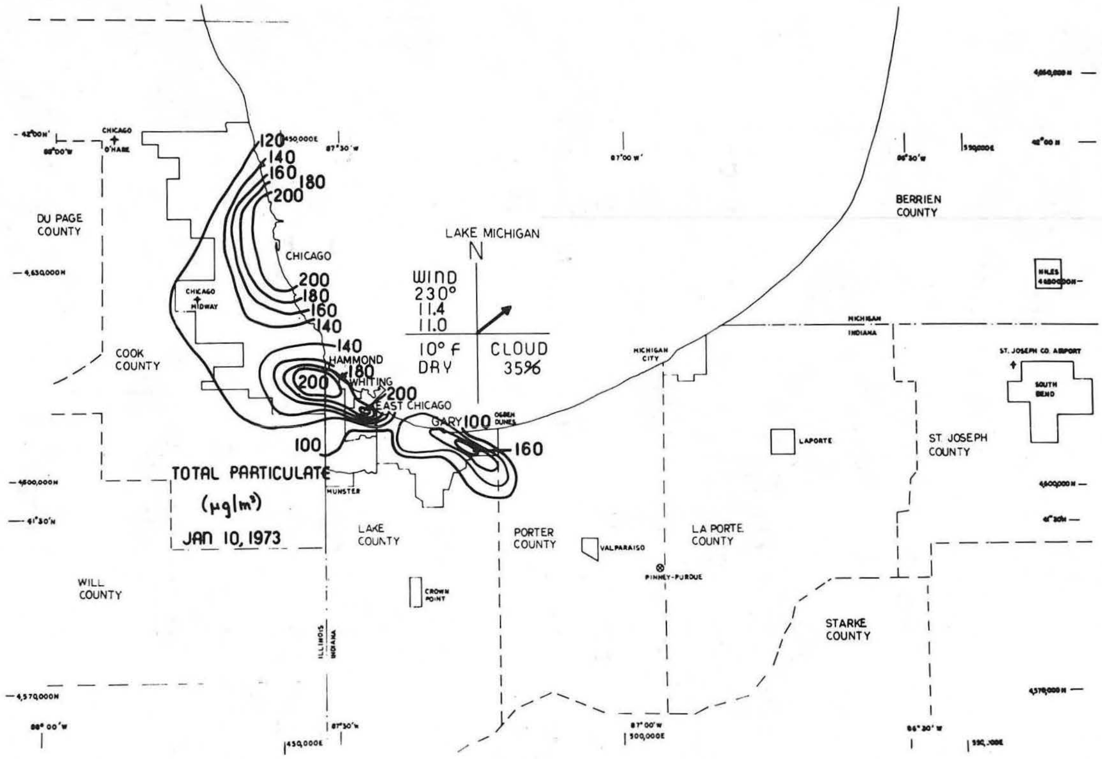

Figure 11. Isopleth analysis for total suspended particulate on 10 January, 1973.

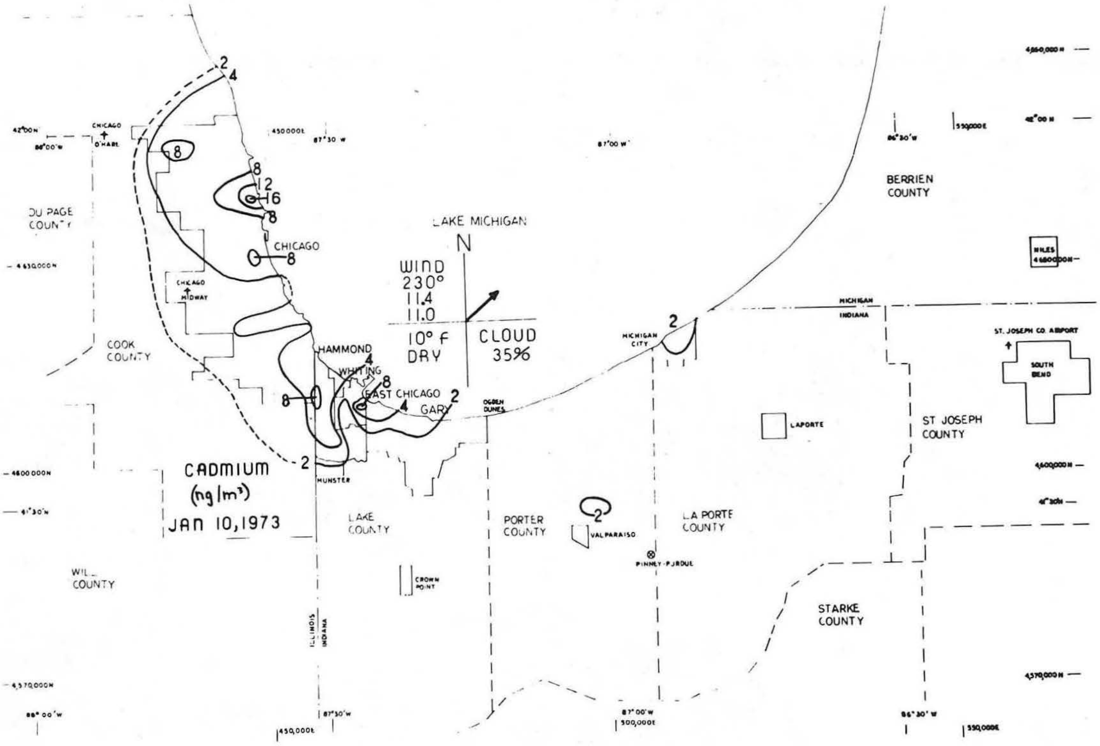

Figure 12. Isopleth analysis for cadmium on 10 January, 1973.

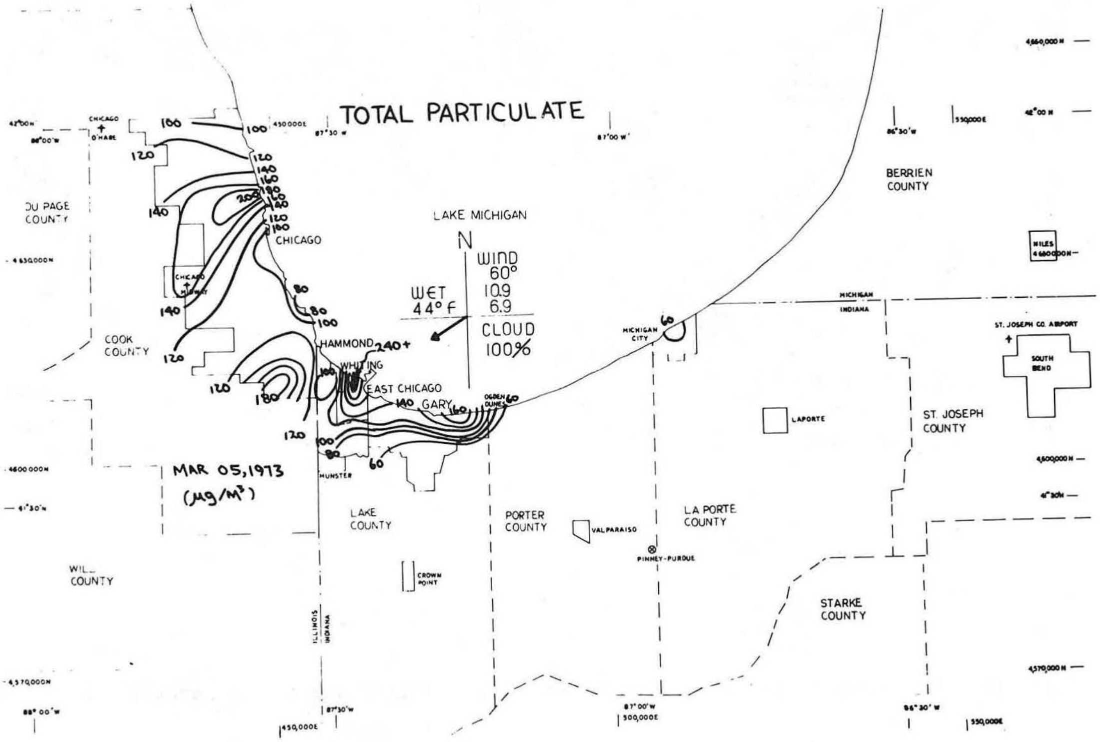

Figure 13. Isopleth analysis for total suspended particulate on 5 March, 1973.

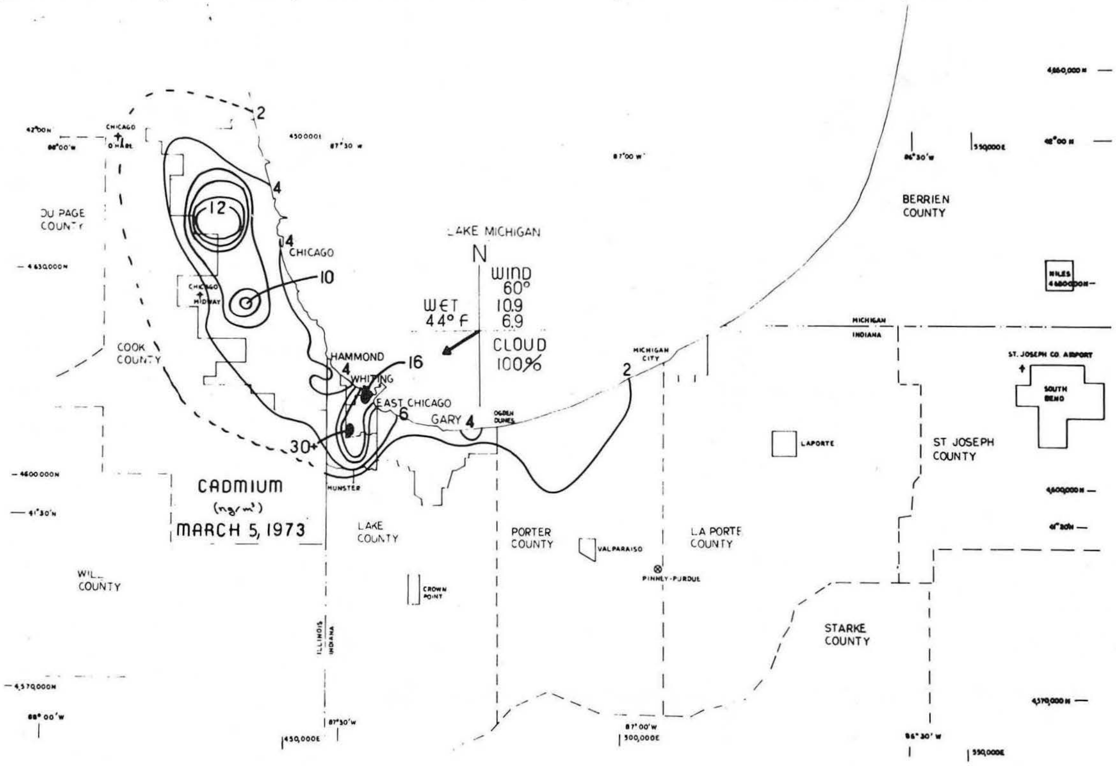

Figure 14. Isopleth analysis for cadmium on 5 March, 1973.

PHYSICAL MODELING OF THE TRANSPORT OF AUTOMOTIVE EMISSIONS IN A CITY STREET CANYON

D.J. Lombardi*
R.S. Thompson*
J.E. Cermak**

Abstract

Measurements of tracer-gas concentrations were made over a physical model of downtown Fort Collins, Colorado placed in an environmental wind tunnel. The tracer-gas was released from two line sources to simulate two lanes of traffic along the main street. A thick turbulent boundary layer with neutral thermal stratification was used to simulate the atmosphere. Steady-state mean concentrations were measured in a street canyon and on the building faces forming the canyon. The non-dimensional concentration coefficients determined from the laboratory data were compared to those obtained from prototype data. The site of concentration data revealed similar trends; however, since only one set of field data was available for comparison the degree of similarity cannot be evaluated at this time.

List of Symbols

C	measured concentration	ML^{-3}
U	local mean wind speed	LT^{-1}
u	longitudinal wind velocity fluctuation	LT^{-1}
U_o	mean free-stream wind speed	LT^{-1}
W	street width	L
Q	source strength	MT^{-1}
L	source length	L
χ	dimensionless concentration coefficient	
Z	Height	
δ	boundary layer thickness	

Subscripts

l	denotes laboratory parameter
f	denotes field parameter

M - mass; T - time; L - length

Introduction

The levels of pollutant concentrations produced in city street canyons resulting from contaminants released in automotive exhaust has become of much concern in recent years. Physical modeling of atmospheric dispersion over urban areas the size of a few blocks to square miles will provide reliable information on the buildup and transport of atmospheric contaminants.

The physical modeling approach is preferred over field investigations because it is much less costly and geometrical as well as meteorological parameters can be varied systematically. Meteorological parameters can be controlled and adjusted in a wind tunnel while in a field study experimentalists must wait for nature to provide the critical combinations of wind speed and direction which are of most interest. The complexities of topography and irregular building shapes and orientation make computer simulation of flow patterns very difficult in most cases.

A paper presented by the same authors at the First Annual Trace Contaminants Conference discussed the techniques and limitations involved in performing an atmospheric diffusion study in a boundary-layer wind tunnel. The similarity conditions which must be met were discussed in some detail. For more information on these aspects of physical modeling see Cermak, J. E. et al.[1]

Recently others have examined the nature of urban diffusion using the physical modeling approach. Jacko et al.[2] examined the effect of city geometry on the ground-level dispersion of air pollutants. Hoydysh and Chin[3] performed a theoretical and experimental investigation of pollution dispersion in street canyons.

This paper describes a study of automotive emission dispersion in a model of a single street canyon--one city block of downtown Fort Collins, Colorado. The Atmospheric Science Department of Colorado State University performed a full-scale field study in this block which provided a data base for comparison of full- and small-scale results.[4] The primary objective of this effort was to determine the degree of agreement between the physically modeled concentration distributions and the full-scale distributions.

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Model Details

A 1:200 scale model of a 16-block area of downtown Fort Collins, Colorado, was studied in the Colorado State University (CSU) Environmental wind tunnel[1] (see Fig. 1). This included the street-section of Fort Collins analyzed in the Atmospheric Science Department, CSU, field study (see Fig. 2).

The model was constructed primarily of styrofoam. Faces of the buildings along the one-block portion of the street of primary concern were made of plexiglas so that sampling ports could be drilled into them. Small blocks one-inch square shown in the background of Fig. 3 were used along the upwind fetch to develop a suitable boundary layer. These blocks were scaled to the roughness of the residential area surrounding the business district which was studied.

Automotive emissions were simulated with the release of a dilute mixture of Krypton-85 in air. Two line sources the length of the city block were used to model the traffic lanes of the street. The line-source construction shown in Fig. 4 was such that the tracer gas was emitted from the source with negligible velocity.

Tracer-gas sampling ports were drilled into the building faces and the building tops as shown in Fig. 5. Street-center concentrations were sampled through small brass tubes mounted through the street surface as shown in Fig. 6. Sampling ports on the building face, building top, and street center were arranged to permit measurement of concentrations in three cross-sectional planes: one in the center of the block with taps corresponding to locations sampled in the field study, and two others at locations where the building shapes differed from those at the center of the block. In addition to these street-canyon sampling locations a portable vertical rake was placed downwind of the street to determine the vertical concentration distribution within the contaminant plume.

Velocity Measurements and Flow Visualization

The mean velocity distribution within the boundary layer over the model was measured with a pitot tube. The profiles for several locations upwind and over the street canyon verified that the boundary layer was fully developed. Vertical profiles of mean velocity and turbulent intensity directly above the center of the street canyon were measured with a hot-film anemometer. As indicated in Fig. 7, the mean velocity increases as the 0.3 power of distance above the zero-displacement plane. Figure 8 shows the manner in which the turbulence intensity is 15 percent at the building height (~ 6 cm) and decreases to 1 percent at the 80 cm level.

Since no temperature stratification was introduced in the tunnel flow only a neutrally-stable atmosphere was modeled.

Flow visualizations were made by placing continuously emitting point sources of a

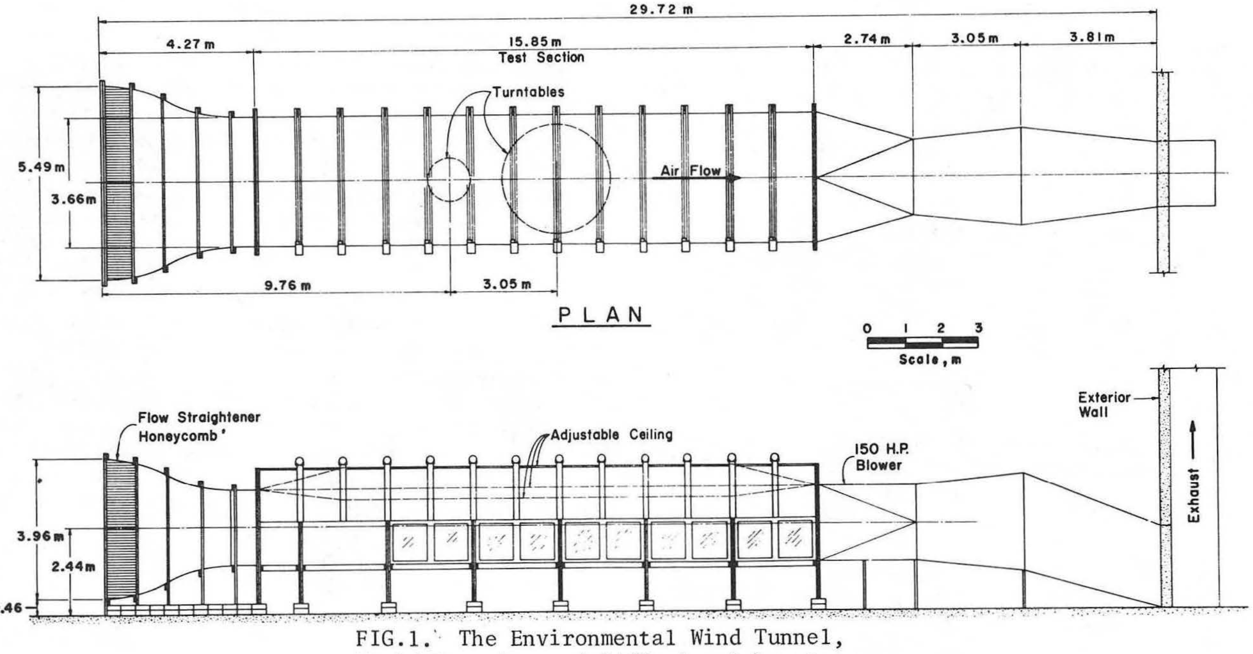

FIG.1. The Environmental Wind Tunnel, Fluid Dynamics and Diffusion Laboratory, Colorado State University.

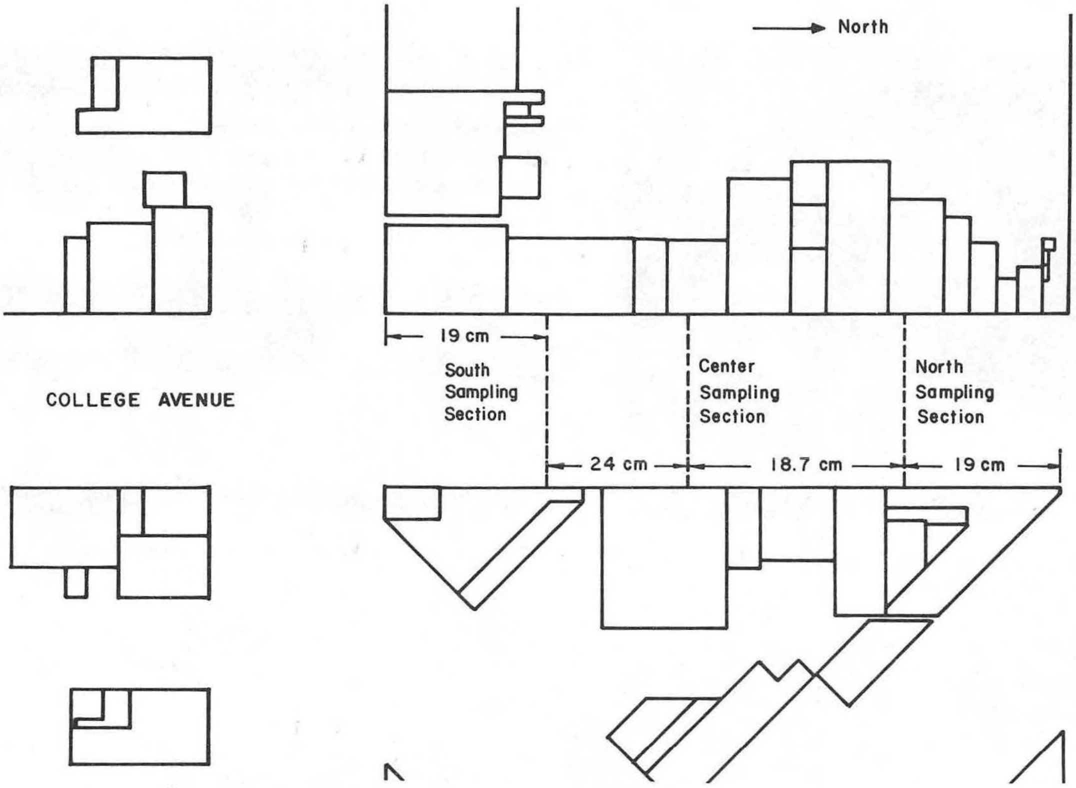

FIG.2. Plan view of Fort Collins model showing sampling cross sections.

FIG. 3. Scale model of Fort Collins, Colorado. Scale is 1:200.

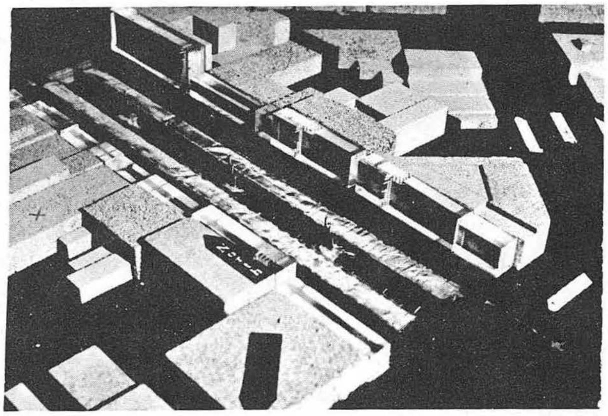

FIG. 4. Section of the city where concentration measurements were made. Line sources were embedded in the street surface and sampling ports were installed for such measurements

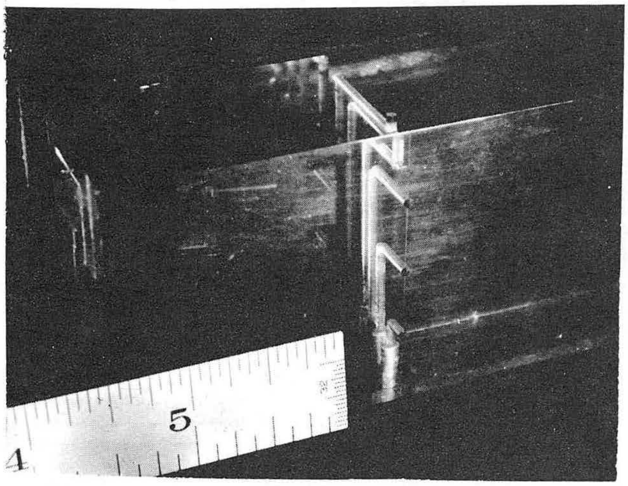

FIG. 5. Gas sampling ports in the building faces and building top.

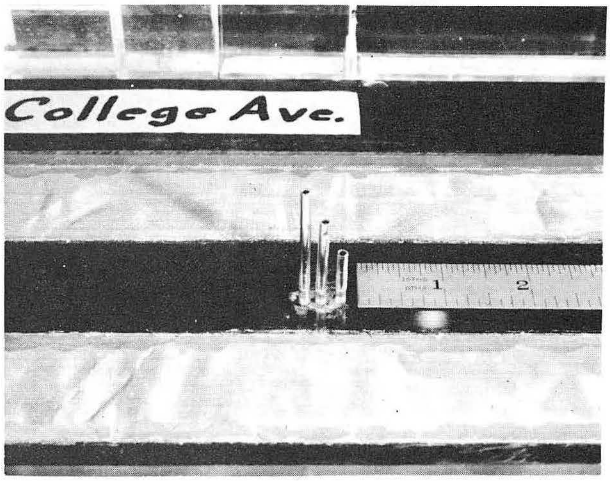

FIG. 6. Street center sampling ports.

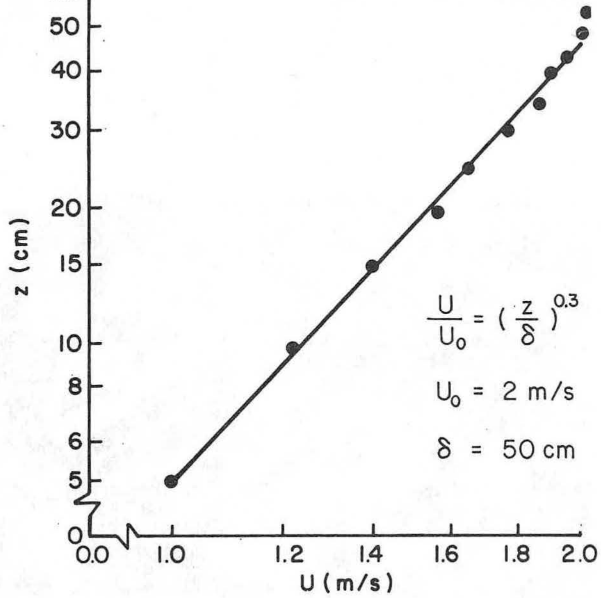

FIG. 7. Mean velocity profile over the model.

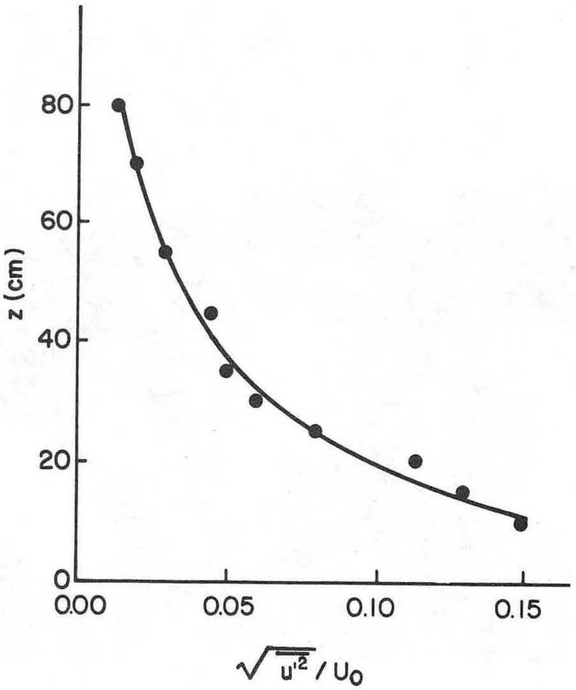

FIG. 8. Turbulence intensity profile over the model.

smoke producing chemical at various points on the street surface. Several interesting aspects of the velocity field in the street canyon were observed.

One of the more pronounced observations was the existence of a vortex motion in the street canyon when the street was oriented perpendicular to the wind. This was also observed in the previous study of a uniform city with much deeper street canyons.[1] The ratio of building height to street width for the sampling area was approximately 1:4 whereas the ratio for the uniform city was 1:1.5.

Interesting flow was observed when the mean wind was set at an angle of 45° to the street--the southeast wind direction. For this wind direction the vortex motion took the form of a swirling helix traveling down the street. Motion near the street surface was toward the northeast.

The building located at the northeast street corner is the tallest building on the street. It is approximately twice as tall as neighboring buildings. A strong updraft exists along the face of this building as shown in Fig. 9 for a wind direction. This updraft entrains smoke from the opposite side of the street and from neighboring buildings nearly one quarter of a block away.

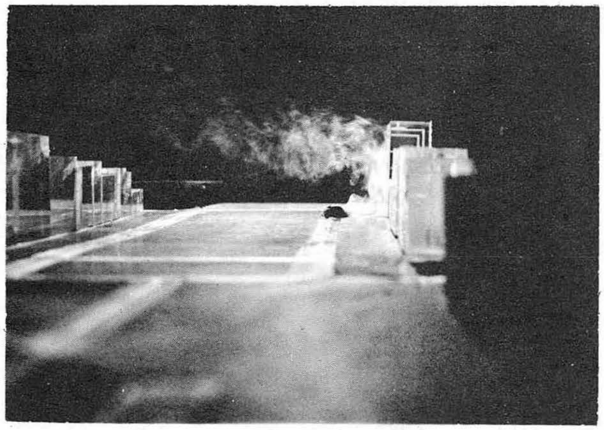

FIG. 9. Smoke tracer showing updraft on face of tallest building. Wind is from the southeast.

Concentration Measurements

Gas samples were drawn through each port in the street canyon and collected in separate retaining bottles. These samples were then analyzed individually to determine the contaminant concentrations at the specified locations. The procedure is discussed in more detail by Chaudhry and Cermak.[5]

Non-dimensional laboratory concentration coefficients were expressed in the form:

$$X_1 = \frac{C_1 U_{o1} W_1}{Q_\ell / L_\ell}$$

where C_1 is the measured concentration, ML^{-3}
U_{o1} is the free-stream wind speed, LT^{-1};
W_1 is the street width, L; and
Q_1/L_1 is source strength per unit length, $MT^{-1}L^{-1}$.

Concentration data were taken for seven wind directions. The most complete set of field data was obtained for a northeast wind--the following discussion will be restricted to this case.

In Figs. 10-12, concentration coefficients are shown for the street canyon sampling points at the three cross-sections where data were taken.

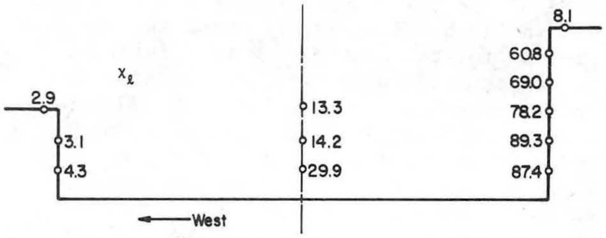

FIG. 10. Non-dimensional laboratory concentration coefficients for the north cross section of the block. Wind is from the northeast.

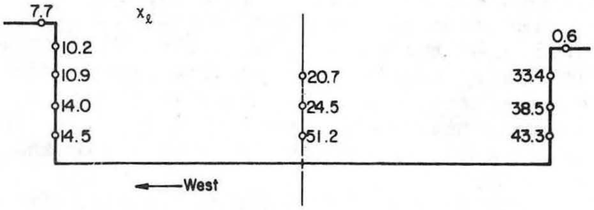

FIG. 11. Non-dimensional laboratory concentration coefficients for the south cross section of the block. Wind is from the northeast.

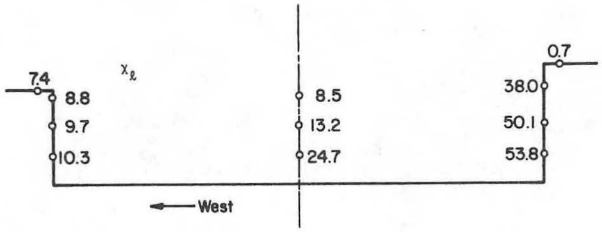

FIG. 12. Non-dimensional laboratory concentration coefficient for the center cross section of the block. Wind is from the northeast.

In the north cross section, Fig. 10, the advective effect of the mean flow is revealed by the distribution of surface concentration coefficients. A current of air not mixed with tracer gas enters the street canyon from the north and ventilates the western building faces since there are no buildings directly upwind to resist flow. Updraft on the east face of the large building for a southeast wind noted by flow visualization is also present for the northeast wind. This air motion causes the highest concentration to occur on the face of the building and have values more than 20 times the value found directly across the street. It is noteworthy that the vertical gradient of concentration on this face is small. Also, the rooftop concentration is 9 percent of the maximum observed at street level.

At the opposite end of the street the amount of ventilation by tracer-free air is small. Most of the air entering this south cross section has entrained a large amount of tracer-gas ingredients while traveling the length of the line source. Mixing is very efficient during this transport process as evidenced by the uniform concentration distribution shown in Fig. 11. The ratio of east-side to west-side concentration coefficients is about 1:3 as compared to 1:20 at the northern cross section. The street-center concentrations are also higher due to the accumulation of tracer gas as the flow proceeds down the street. It is also interesting to examine concentration coefficients at the rooftop level. On the western rooftop this value is nearly the same as that found on top of the tall building at the north end of the street.

The center cross section, Fig. 12, corresponds to the section of street examined in the field study. The roof-level concentration the eastern side of the street is very small. On the western side of the street the concentration is again close to that on top of the tallest building. The ratio of west-side to east-side concentration is about 1:5.

In summary, for a 45° orientation of a street to the wind direction, the following characteristics of the flow pattern were observed. Where contaminant free air enters a street canyon, low contaminant concentration levels occur. The helical vortex, swirling down the street transports street-level contaminants toward the upwind building faces. Tall upwind buildings enhance the updrafting motion of the vortex. These mechanisms produce higher contaminant levels on upwind building faces. Mixing of the contaminants as they are transported down the street results in more uniformity in concentration levels at downstreet cross section. Rooftop contaminant levels can be on the order of 10 percent of the maximum concentration levels on the street surface.

Comparison of Model Data and Field Data

The raw field data for the center section are presented in Fig. 13. Meteorological parameters, vehicle rate, and carbon-monoxide concentrations in parts per million are included. To relate concentration measurements to source strength in a form which can be compared to the non-dimensional concentrations obtained in the laboratory, an automotive emission factor is required.

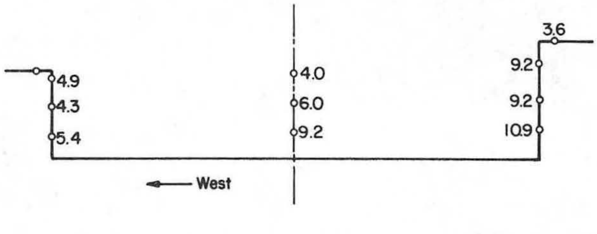

FIG. 13. Raw field data for the center cross section of the block. Values are carbon monoxide concentrations measured in parts per million. Wind is from the northeast.

An automotive emission factor of 112.5 grams of carbon-monoxide per mile was assumed. Emission factors for specific locales are difficult to estimate correctly. This number was based on emission factors for light-duty vehicles at high altitudes, corrected for average vehicle speed.[6] Multiplying by the vehicle rate gives a line source strength with dimensions of $ML^{-1}T^{-1}$.

No background concentration was present in the wind-tunnel flow. The field data, however, included contributions of CO from upwind sources. To compare the field and laboratory data the field background concentration was removed. Note that the laboratory concentration on the eastern rooftop was negligible. Thus, the field concentration at the corresponding point (3.6 ppm) was taken to be the background value and was subtracted from concentrations at all other data points.

A free-stream wind speed for the field experiment is not available. To compare field concentrations with laboratory concentrations a free-stream wind speed must be estimated. At one location at rooftop level in the street center, velocity measurements are made for both the field and laboratory studies. The ratio of the free-stream laboratory measurement to the measurement at this location can be applied to estimate the free-stream field velocity. This ratio is 1.95 which upon multiplication by the field wind speed at this location gives a free-stream wind speed of 3.6 m/sec.

Non-dimensional field concentration coefficients were formulated as follows for comparison with the laboratory coefficients:

$$\chi_f = \frac{C_f U_{of} W_f}{Q_f / L_f}$$

where C_f is the measured concentration (expressed in grams per cubic meter) minus the background level; U_{of} is the mean free-stream wind speed in the field; W_f is the actual street width; and Q_f/L_f defines the source strength per unit length of the street in the units grams of CO $s^{-1}m^{-1}$.

The non-dimensional field concentrations are shown in Fig. 14. Ratios of laboratory concentration coefficients to field coefficients are presented in Fig. 15.

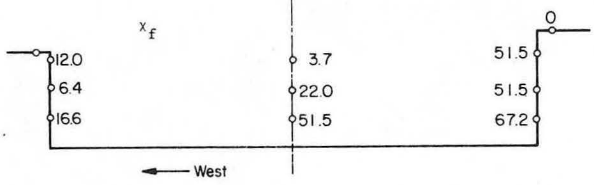

FIG. 14. Non-dimensional field concentration coefficients for the center cross section of the block. Wind is from the northeast.

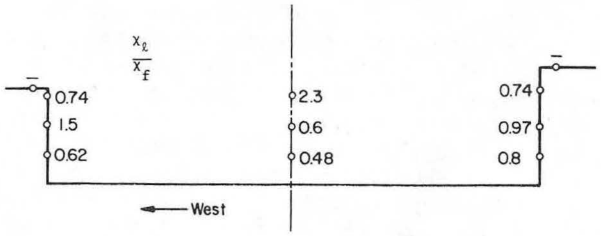

FIG. 15. Ratio of non-dimensional laboratory concentration coefficients to non-dimensional field concentration coefficients.

Discussion

The ratios of the laboratory concentration coefficients to the field concentration shown in Fig. 15 deviate from unity, and there are several reasons why these deviations exist. The field samples that were taken were 15-minute samples. During this period the wind direction probably varied and the wind velocity was not constant. However, in the wind tunnel these parameters did remain constant. Furthermore, the motion of automobiles in the streets was not modeled in the laboratory. This motion could alter the flow patterns in the streets.

There are also some uncertainties concerning the emission factor used to normalize the data from the field measurements. The number used was an average value, as mentioned above, but it did not include the effects of parked cars idling in the street. Also this number was not a weighted average incorporating corrections for vehicle age, vehicle type (light duty, heavy duty, etc.) or vehicle make.

Finally, in correcting the field data the background level used for CO was not a constant as it was assumed to be. There are contributions from several nearby streets and intersections that produce a non-uniform background in air entering at different points of the street canyon.

Concluding Remarks

The results of this study show that by using the physical modeling technique, the concentration levels at various locations in an urban street canyon can be estimated with sufficient accuracy to reveal the effects of wind direction and street canyon geometry. This method is applicable to any passive gaseous contaminant or trace contaminant which does not settle appreciably and disperses as a gaseous contaminant.

An investigation of this type reveals where the highest concentrations of pollutants will exist and what the effects of buildings of different geometries will be on the pollutant concentration levels. Furthermore, the relationship between rooftop concentration levels and those that exist in the streets can be obtained to determine street-level air quality from air-quality monitors placed on building tops.

Acknowledgment

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We also wish to thank Mr. Paul Katen of Colorado State University for making field data available.

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LONG-PATH AMBIENT-AIR MONITORING WITH TUNABLE LASERS -- PARTICIPATION IN THE ST. LOUIS REGIONAL AIR POLLUTION STUDY (RAPS) OF THE ENVIRONMENTAL PROTECTION AGENCY*

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Abstract

The resonance absorption technique employing tunable semiconductor diode lasers has been utilized to perform integrated-path monitoring of atmospheric pollutant gases over long distances. Recent measurements carried out in Massachusetts showed continuous laser monitoring of atmospheric CO to have a sensitivity of a few parts per billion over a 0.6 kilometer path. The laser system has now been incorporated into a mobile van and transported to St. Louis, Missouri to participate in the first Regional Air Pollution Study (RAPS) of the U. S. Environmental Protection Agency. The main purpose of RAPS is to evaluate various mathematical models for predicting pollutant concentrations around urban areas. Since the grid size for such models is usually of the order of 1 kilometer, a long-path laser technique is ideal for providing the input data and checking model accuracy. In addition, pollutant variability studies will be performed at selected sites in an attempt to understand reasons for possible differences between the long-path data and those obtained from more conventional point-sampling instruments.

Introduction

One of the most promising applications of tunable lasers is in the area of detection and measurement of ambient air pollutants [1-3] . Many atmospheric pollutant gases, such as NO, C_2H_4, SO_2, CO, O_3, and CO_2, have already been detected by various tunable laser techniques [2,4-9]. In this paper we will describe a tunable <u>diode</u> laser system which has been used to measure <u>ambient</u> concentrations of carbon monoxide over long outdoor paths. The laser source was one of the Pb-salt types [10,11] that have several inherent advantages, such as small size and ease in wavelength tunability, compared to other types of tunable lasers. A $PbS_{1-x}Se_x$ laser was tailored chemically ($x=0.18$) to operate in the 4.7-μm wavelength region in close coincidence with the fundamental vibrational band of CO centered at 2145 cm^{-1} [12]. Exact frequency matching and tuning through the CO absorption lines was easily achieved by varying the injection current, which changes the junction temperature and thus the laser wavelength.

The detection used was that of resonance absorption [1,13,14] wherein the laser is tuned to an appropriate CO absorption line, and derivative detection [1,2] used to determine the gas concentration over the path. Primary innovation in this present system is the use of a commercially-available closed-cycle cryogenic cooler [15], instead of liquid helium, to provide the low operating temperature (~15 K) for the diode lasers; and this was an important factor in extending the well-established laboratory-based diode laser spectroscopic techniques to the practical, fieldable system reported here.

Carbon monoxide is an important pollutant in the atmosphere today, especially in metropolitan areas where the density of automobiles is high. (The CO content of automobile exhaust can be as large as 10% by volume.) In addition to their harmful and poisonous effects, CO molecules play an integral part in the formation and conversion of other pollutants such as NO, O_3, and NO_2 [16] . Traditionally, the amount of CO in ambient air has been measured by point-sampling instrumentation based on conventional infrared techniques. However, the limitations of these standard methods become ob-

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vious in cases where the *average* pollutant concentration over a *large* area is needed. The long-path tunable laser system to be described here represents a development in the direction of a versatile and reliable monitoring system for such *in situ* ambient-air measurements; and *with* the eventual utilization of the new widely-tunable diode lasers [17], several different pollutant gases can be monitored sequentially. A multi-pollutant capability would be extremely useful since many pollutants interact strongly with each other, and the time evolution of their concentrations can be incorporated into the mathematical models, along with meteorological and topological data, for advance prediction of air pollution levels [18].

In August 1974 our laser monitoring van was driven to St. Louis, Missouri for a two-month period of measurements of ambient CO levels at various sites. Preliminary measurements, taken with support from the U. S. Environmental Protection Agency, will be discussed later in this paper.

Field Measurement Setup

Field measurements were performed at our Antenna Range near Hanscom Field, Bedford, which is located approximately 20 miles west of Boston. The most essential components of the laser optical system are indicated in Fig. 1. The $PbS_{0.82}Se_{0.18}$ laser was mounted inside a closed-cycle cryogenic cooler, CTi Model 21 [15], and its emission was collimated by an Al-coated off-axis parabolic mirror M-1, 12 cm in diameter. After the beam was transmitted over the 305-meter path to a corner-cube retroreflector M-2, it was reflected back over the same path to a Ge beam-splitter, finally impinging on the InSb infrared detector.

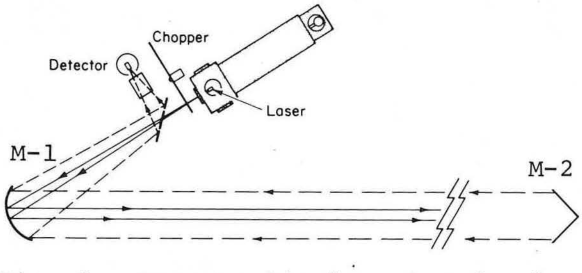


Fig. 1. Laser optical system for long-path monitoring.

Measurement and Calibration Techniques

Tunable laser experiments have been performed in various laboratories to determine absorption coefficients, linewidths, and line shapes of atomic and molecular transitions [19]. Field measurements of gases in the ambient air are similar to the laboratory measurements. For example, transmission intensity dips caused by CO absorption along the 0.6 km path (round-trip distance between laser and retroreflector) at our field site were easily detected, as shown in Fig. 2. In Fig. 2(a) an absorption dip due to the CO P(7) line is shown, indicating the presence of this gas along the outdoor path. In Fig. 2(b) a very short path was used to provide an effective "zero-ppm" scan.

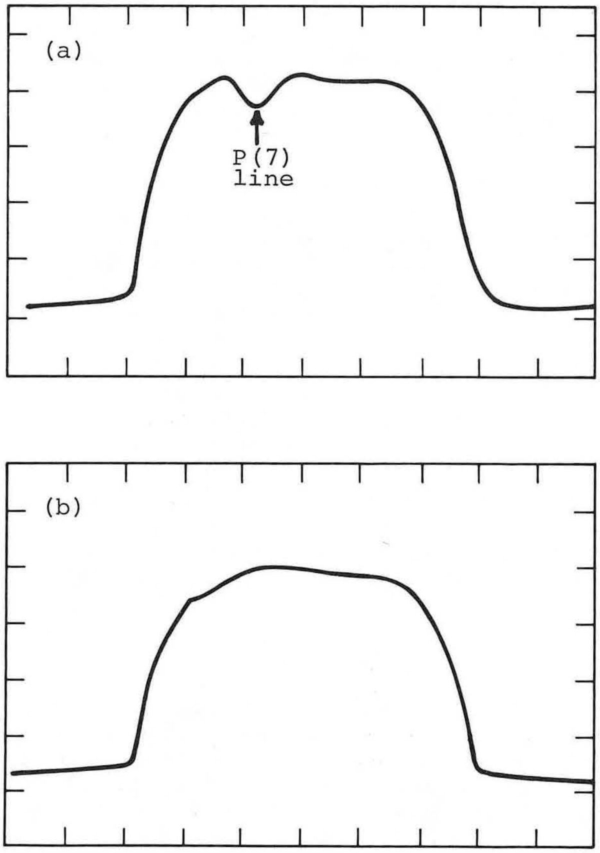


Fig. 2. Oscillogram of (a) long path (0.6 km) transmission of tunable diode laser radiation, showing dip at CO P(7) line (2115.63 cm^{-1}) due to ambient CO. In (b) the path was shortened by placing retroreflector near collimating mirror. Horizontal scale: 0.5 msec/div. Vertical scales: arbitrary.

For any type of tunable laser with adequate stability and power, the major factors limiting sensitivity for air monitoring will be related to the atmosphere itself. We found that thermal effects along the outdoor path were the main cause of optical degradation, and overcame these by a unique technique of derivative spectroscopy. This method involves tuning the laser to the side of an appropriate absorption line of the gas to be monitored, modulating the diode current (hence, the laser frequency) at 10 kHz, and synchronously detecting the first derivative of the signal. (Under ideal conditions the first derivative will be zero in the absence of that particular gas in the atmosphere.) At this high frequency the effect of turbulence is minimized since the atmosphere is "frozen" in the time scale of a few oscillations. The chopper shown in Fig. 1 provided the "direct" transmission signal; and by dividing the first-derivative signal by the "direct" signal, long-term atmospheric effects [20] (e.g. beam-steering at sunrise and sunset) are reduced.

Calibration was achieved using the 10-cm cell shown in Fig. 1. Since the pathlength ratio during our field measurements was 1/6100, a calibration gas of 1000 ppm of CO (in air) in the cell produces the same signal as 164 ppb over the long path. Linearity was checked by using several different mixtures of CO in air.

CO Monitoring Results and Discussion

The most sensitive CO monitoring performed over the 0.6 km path is shown in Fig. 3, which represents a 12-minute run of the ratioed signal using the P(4) line. The peak-to-peak noise in a time corresponding to the integration time is no more than the width of the recording pen - or 5 ppb in this case.

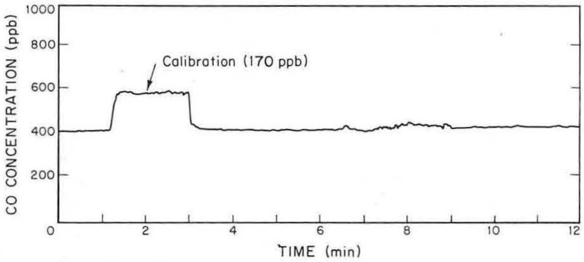
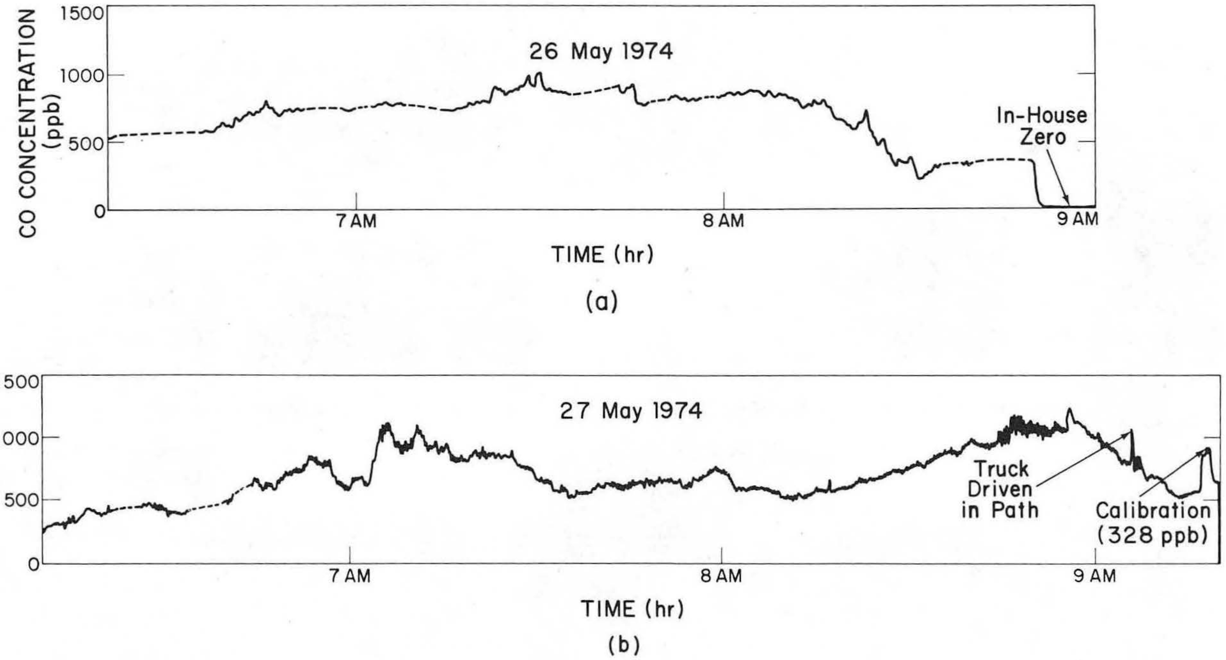


Fig. 3. Laser monitoring of ambient CO over 0.6 km path using the P(4) line. Integration time was 1 sec.



(a)

(b)

Fig. 4. Laser monitoring of CO over 0.6-km outdoor path on two successive mornings, using P(4) line centered at 2127.69 cm^{-1}. Wind shifted from W to SE at 8 AM.

The slight increase in ambient CO level between 6 and 9 minutes was caused by an automobile which was driven along the path to generate more CO.

Several measurements were performed essentially unattended for several days. The only problem was that vertical beam steering occurred during the early morning and evening hours due to varying temperature gradients along the outdoor path. Figures 4(a) and (b) were taken in early morning on successive days to demonstrate the system's capability for unattended monitoring over several hours. The dashed lines indicate times when checks were being made of the system or when anomalous perturbations (such as sunlight impinging on the infrared detector) caused an erroneous measurement. A general rise in CO level occurred as commuter traffic increased toward 8:00 a.m. Since the field site is only a few miles northwest of Route 128 (a major highway), it is not surprising to see a secondary increase in CO level in Fig. 4(b) when the wind shifted from its normal westerly direction.

Since the ambient CO level at our field site was usually below 1 ppm, we did not have any of the problems which are associated with nearly complete absorption of the laser beam at line center. In laboratory simulations of this condition we found that the calibration becomes nonlinear at high pollutant levels. This problem can be avoided in the field by: (1) tuning the laser further away from line center; (2) reducing the path length; or (3) using a weaker absorption line.

St. Louis Regional Air Pollution Study

In August 1974 our diode laser monitoring van, shown in Fig. 5, was driven to St. Louis, Missouri for preliminary measurements in conjunction with the U. S. Environmental Protection Agency's first Regional Air Pollution Study. At the time of this Trace Contaminants Conference a few measurements had already been made at the St. Louis University site; and during the subsequent two-month period measurements were made at two other sites as well, in Missouri and Illinois.

Comparisons were made between our laser measurements of ambient CO and

Fig. 5. Diode Laser Air-Monitoring Van

those obtained using bag samples which were filled while walking along the laser beam path. Gas chromatography was used to determine the CO concentrations in the bag samples, and several comparisons between these and the laser measurements over a 0.3 km path are listed in Table I.

TABLE I. Comparative CO Measurements

Run No.	Laser (ppm)	Bag (ppm)
1	0.55	0.61
2	0.60	0.62
3	0.39	0.56
4	1.65	1.07
5	0.87	1.02
6	3.1	2.3
7	2.13	1.93
8	0.95	0.85

There is generally good correlation between the laser and bag-sample measurements. In fact, total agreement would be expected only if the pollutant concentration was invariant over the entire path.

Figure 6 shows the CO concentration in St. Louis, as deduced from the first diode laser measurements there. Although the actual monitoring used a 1-sec time constant, this curve was redrawn with an approximately 5-min time constant to indicate more clearly the trends over the 5-hour period. The CO level rose from 0.5 ppm in mid-afternoon to nearly 2 ppm at the time of peak commuter traffic. A complete report of these St. Louis measurements is in preparation. A comprehensive technical article describing our initial long-path monitoring of CO will soon be published [21].

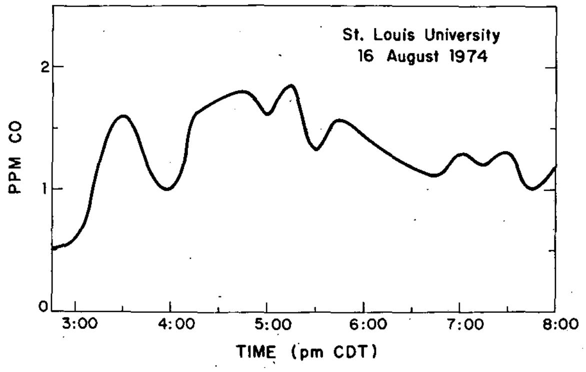


Fig. 6. Laser monitoring of CO at St. Louis University. Pathlength = 0.2 km.

Acknowledgments

We are indebted to J. O. Sample for competent technical assistance throughout this program, and to A. R. Calawa, T. C. Harman, M. J. Manfra, and L. J. Belanger for providing the diode lasers. We also acknowledge the fine cooperation of John Peterson of Cryogenic Technology, Inc., and technical suggestions and support from Drs. W. A. McClenny and Lucian Chaney of the U. S. Environmental Protection Agency.

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FEASIBILITY OF THE REMOTE DETECTION OF POLLUTANTS USING RESONANT RAMAN SCATTERING

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Abstract

We present calculations of the resonance Raman cross-section for several diatomic molecules. We use these results along with recent measurements of large resonance enhancements in NO_2 and SO_2 to estimate the sensitivity of a Lidar system based on the resonance Raman effect.

In this paper, we wish to assess the implications of recent measurements of large resonance Raman cross-sections in NO_2(1) and SO_2(2) for remote detection of these pollutants in the atmosphere by means of a Lidar system. We shall also present calculations for the resonance Raman cross-sections of various diatomic molecules and use these calculations to expand our estimates of the sensitivity of a resonance Raman Lidar system.

Raman Lidar systems have been used for some time to study major atmospheric constituents.(3) However, the fact that Raman cross-sections are quite small ($\sim 10^{-30}$ cm^2/sr) has made this technique difficult to use to detect minor atmospheric constituents such as pollutants. In spite of this difficulty, S. Nakahara et al.(4) and Melfi et al.(5) have reported detection of SO_2 in power plant stack plumes at a range of 200 m at night, and Hirschfeld et al.(6) using a powerful doubled ruby laser have been able to measure SO_2 concentrations of 30 ppm at 200 m in full day-light with a good signal to noise ratio.

It is well known that Raman cross-sections are enhanced if the laser source is tuned close to an absorption line in a gas. Such enhancements could dramatically increase the sensitivity of a Raman Lidar system. Most measurements of the resonance Raman effect(7) have been made in I_2 vapor, where large enhancements have been observed.(10) Recently, we have measured a resonance Raman cross-section of 1.7×10^{-24} cm^2/sr(9) in I_2 with an excitation wavelength of 5466.36 Å and Penney et al.(2) have reported a cross-section of 10^{-25} cm^2/sr for SO_2 with a laser excitation near 3002 Å. These cross-sections are, respectively, 4×10^6 and 2.6×10^4 times the Raman cross-section for N_2 at equivalent excitation wave-lengths. Resonant inelastic scattering cross-sections(11) of the order of 10^{-20} - 10^{-21} cm^2/sr have also been observed for OH(12,13), and Wang and Davis(13) were able to measure atmospheric concentrations of OH at a level of 2 parts in 10^{13}.

We have just completed an extensive search for large enhancements of scattering into the ν_2 Raman mode of NO_2 using a nitrogen-laser-pumped dye laser. The investigation was carried out by tuning the laser through most of the visible absorption spectrum of NO_2 between 4200 Å and 6100 Å with a laser band-width of .1 Å. We will present the details of these experiments elsewhere,(1) but wish to report that we have seen large resonance enhancements and have measured a cross-section of 5.6×10^{-27} cm^2/sr for narrow band ($\sim$1Å) re-emission into the ν_2 Raman mode at the peak of one of the resonances for 1mm of NO_2 plus 1 atm of N_2 buffer gas. All of these measurements, along with the results of the following calculation, allow one to make reasonable estimates of the sensitivity of a resonance Raman Lidar system operating under various conditions.

One can easily estimate the resonance Raman cross-section for diatomic molecules which have known oscillator strengths and Franck-Condon factors. For an infinitely narrow exciting laser near an isolated absorption line, the cross-section can be written, approximately, as:(14)

$$\frac{d\sigma}{d\Omega} \approx \frac{e^4\, \omega_\ell\, \omega_s{}^3\, |\langle I|r|M\rangle|^2\, |\langle M|r|F\rangle|^2\, \rho_I}{\hbar^2\, c^4\, [(\omega_\ell - \omega_o)^2 + \gamma_T{}^2]} \qquad (1)$$

where $\langle I|r|M\rangle$ is the matrix element from the initial to intermediate vibrational-rotational state, while $\langle M|r|F\rangle$ is the matrix element between the intermediate and final state. ω_ℓ is the laser frequency, ω_s the scattered frequency, ω_o the central frequency of the resonance and ρ_I is the relative thermal population of the initial vibrational-rotational state. γ_T is the pressure broadened linewidth. This expression is valid if γ_T is dominated by inelastic collisions and is larger than the linewidth due to the combination of natural, doppler, and hyperfine broadening. For most molecules at atmospheric pressure, the linewidth is, in fact, primarily due to pressure broadening. Even though the assumption that γ_T is dominated by the contribution of inelastic collisions may be invalid, a calculation based on that assumption will provide a lower limit for the cross-section.

We can rewrite Eq. 1 in terms of the oscillator strength, f, and the Franck-Condon factors S_{ij} by making the substitution:

$$|\langle I|r|M\rangle|^2 = \frac{\hbar}{2m\omega_o}\,\frac{f\,S_{IM}}{3}$$

$$|\langle M|r|F\rangle|^2 = \frac{\hbar}{2m\omega_o}\,f\,S_{MF}$$

The factor of 3 in the first matrix element occurs because we assume that the oscillator strength is equally divided between the P, Q, and R branches of the absorption line. For $\omega_\ell = \omega_o \simeq \omega_s$ we get:

$$\frac{d\sigma}{d\Omega} \quad \frac{r_o^{\,2}\,\omega_s^{\,2}\,S_{IM}\,S_{MF}\,f^2\,\rho_I}{12\gamma_T^{\,2}} \qquad (2)$$

where r_o is the classical radius of the electron. For molecules where the oscillator strengths and Franck-Condon factors are known,(15-25) we can use Eq. 2 to make an estimate of the resonance Raman cross-sections. We assume that the molecules are initially in their ground vibrational state and choose the intermediate and final vibrational states to maximize $S_{IM}S_{MF}$. We also choose the initial rotational state with the maximal thermal population and use standard methods to calculate ρ_I.(26) We choose γ_T on the basis of our previous work (9) with I_2 where we found $\gamma_T = 2 \times 10^{10}$ radians/sec for 1 mm of I_2 in one atm of N_2. The results of these calculations as well as experimentally determined cross-sections are presented in Table 1.

Molecule	Electronic Transition	Vibrational Transition	λ_L(Å)	$\frac{d\sigma}{d\Omega}(\mathrm{cm}^2/\mathrm{ster})_{\mathrm{CALC.}}$	$\frac{d\sigma}{d\Omega}(\mathrm{cm}^2/\mathrm{ster})_{\mathrm{EXP.}}$	Ref.
CO^+	$A\ ^2\Pi_i - X\ ^2\Sigma^+$	0-1, 1-1	4913	2.5×10^{-20}		15
SO	$A\ ^3\pi_0 - X\ ^3\Sigma^-$	0-2, 2-0	2579	1.3×10^{-20}		16
OH	$A\ ^2\Sigma^+ - X\ ^3\pi_1$	0-0, 0-1	3064	2.4×10^{-22}	$\sim 10^{-20} - 10^{-21}$ (11)	17,18
NO	$A\ ^2\Sigma^+ - X\ ^2\pi$	0-0, 0-3	2262	1.3×10^{-23}		19,20
I_2	$B\ ^3\pi^+_{0u} - X\ ^1\Sigma^+_g$	0-25, 25-1	5466.36	1.2×10^{-24}	1.7×10^{-24}	21,22
SO_2	$\tilde{A}\ (^1B_1) - \tilde{X}\ ^1A_1$		3002		1×10^{-25}	
$^{79}Br^{81}Br$	$B\ ^3\pi^+_{0u} - X\ ^1\Sigma^+_g$	0-28, 28-1	5264.0	7.8×10^{-27}		23,24
NO_2	$\tilde{A}\ (^2B_1) - \tilde{X}\ ^2A_1$ (?)				5.6×10^{-27}	
CO	$a\ ^3\pi - X\ ^1\Sigma^+$	0-0, 0-1	2063	4.5×10^{-30}		15
Cl_2	$A\ ^3\pi^+_{0u} - X\ ^1\Sigma^+_g$	0-15, 15-3	4933	7×10^{-31}		23,25

TABLE 1: Resonant Raman cross-sections for various small molecules determined either experimentally or from Eq. (2).

We would now like to consider the practical implications of resonantly enhanced Raman cross-sections for pollutant detection by means of a Lidar system. For such a system, the number of signal photons detected is:

$$S = 2.69 \times 10^5\ \eta N \frac{E}{\hbar\omega_o}\,\frac{AL}{R^2}\,\rho\frac{d\sigma}{d\Omega}\ e^{-[\alpha_s+\alpha_o]R}$$

with

η - total detection efficiency (optical and quantum efficiency)
N - number of laser pulses
E - laser pulse energy (joules)
ω_o - laser frequency (radians/sec)
A - collector area (cm^2)
L - range increment (m)
R - range (km)
ρ - concentration of pollutant (ppm)
$\frac{d\sigma}{d\Omega}$ - Raman scattering cross-section (cm^2/sr)
α_o - atmospheric absorption coefficient at laser frequency
α_s - atmospheric absorption coefficient at scattered frequency

The number of counts collected during the same number of pulses from skylight is:

$$B = \eta\ N\ \frac{W(\omega_s)\Delta\lambda}{\hbar\omega_s}\ A\ \phi\ \frac{2L}{c}$$

with

$W(\omega_s)$ - background irradiance at the scattered wavelength ($watts/cm^2$ srÅ)
$\Delta\lambda$ - detector bandwidth (Å)
ϕ - detector field of view (sr)
ω_s - Raman shifted frequency
$\frac{2L}{c}$ - gate time for range increment (sec)

A useful measure of the sensitivity of a Lidar system can be obtained by considering the signal to noise ratio (SNR). When detecting scattered light with wavelength >3000 Å, we will assume that the noise is dominated by the fluctuations in the backgroud irradiance, so that $SNR = S/\sqrt{B}$. For detection at wavelengths <3000 Å, where the stratospheric ozone layer effectively absorbs sunlight, and for nighttime detection, we will assume that the noise is caused by fluctuations in the signal, so that $SNR = \sqrt{S}$. We will ignore, in this paper, the possible problems associated with additional background due to the fluorescence of aerosols.(27) This background may cause trouble for a Lidar system which depends on ordinary Raman scattering. However, since the useful resonance cross-sections are at least 3 orders of magnitude larger than ordinary Raman cross-sections, we feel justified in ignoring this problem for the purposes of our illustrative calculations.

Suppose we now choose reasonable receiver parameters (i.e. $\eta = .1$, $A = 10^4 cm^2$, $\phi = 10^{-5}$ sr, $\Delta\lambda = 1$ Å) and a laser transmitter which emits a beam of $10^3 cm^2$ cross-sectional area. In order to comply with the laser safety standard for direct viewing, (28) we will limit the laser energy to .05 mJ/pulse for a repetition rate of 100 Hz. This limitation applies for lasers with wavelengths >4000 Å. For shorter wavelengths, the limits appear to be less stringent, but since there are no standards for very short pulses, we will assume the same standard as for wavelengths >4000 Å. We use the data of Baum and Dunkelman (29) to evaluate α_0, α_s and that of Knestrick and Curcio (30) for $W(\omega_s)$. We further assume a range resolution of 10 m and calculate the concentration of pollutant which yields SNR = 10 with an integration time of 100 sec. In Figure 1, we present the results of that calculation for NO_2, SO_2, and NO using the cross-sections in Table 1.

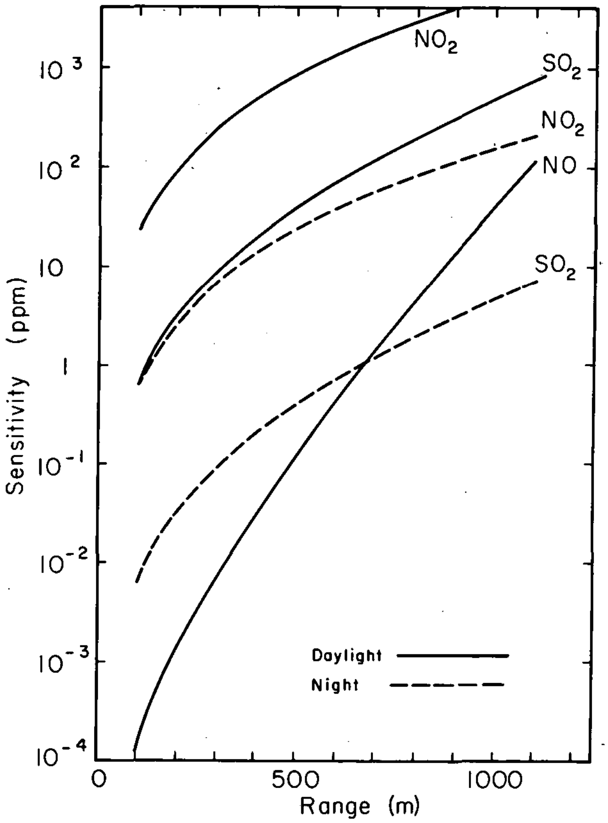

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FIG. 1: Lidar sensitivity vs. range for E = .05 mJ and N = 10^4 pulses assuming a signal to noise ratio of 10 and a visibility of 10 km.

Figure 1 shows that, with the marginal exception of daylight detection of NO_2, a Lidar system making use of resonance Raman scattering can easily detect the pollutant concentrations typical of smoke plumes (>10 ppm) at a range of a few hundred meters using lasers with only very modest energies. A useful comparison can be made with the recent report(6) of detection of SO_2 using ordinary Raman scattering. In that case, the laser used had an average power of .4 watts and an energy per pulse of .2 joules, and was able to detect 30 ppm at 200 m with SNR ∿ 10. Our calculation shows that using a laser of 5 mW average power and .05 mJ/pulse, one could achieve a sensitivity of a factor of 10 better by making use of the resonance Raman effect. In addition, if there is an enhanced cross-section in SO_2 for λ_0 <2800 Å comparable to that for λ_0 = 3002 Å, then the resonance Raman Lidar sensitivity for daylight detection of SO_2 will be the same as for night-time detection, since sky background interference with the detected radiation will no longer be a problem. The fact that the SO_2 absorption spectrum shows features at λ <2800 Å similar to those at λ ∿3000 Å leads one to expect that comparable enhancements will be found for such wavelengths.

Using presently available technology, one could construct a nitrogen laser-pumped dye laser which has the required pulse energy and repetition rate(31) and by using non-linear doubling crystals could extend its tuning capability to ∿2300 Å.(32) In order to detect NO, however, one needs a laser at 2260 Å. At present, the non-linear crystals available for frequency doubling to this wavelength are not very efficient.(33) However, at least one efficient technique for up-conversion of light with λ > 2500 Å to span the wavelength region 2000-2350 Å has been reported.(34) It should be noted that even if the efficiency of conversion of visible light to light at 2250 Å were only ∿.01%, there would still be enough sensitivity to monitor smokestacks at ∿200 m.

Figure 1 also shows that monitoring of ambient concentrations (∿.1 ppm) at distances of order 1 Km is certainly out of the question, given the safety constraint we have imposed on the calculation. If one could be sure that there will be no eye exposure to the light from the Lidar transmitter, then one might be able to use high-energy tunable lasers to gain the required sensitivity.

In conclusion, it seems to us that the advantages in sensitivity and safety associated with the use of resonance enhancements in a Raman Lidar system outweigh the additional problems associated with the use of a tunable laser as a Lidar transmitter. The fact that an instrument for use in populated areas will probably have to comply with stringent eye safety standards implies that the use of resonance enhancements will be the only avenue to a workable Raman Lidar system for remote smokestack monitoring.

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"Use of Ion Beams for Monitoring California's Aerosols"

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Abstract

The State of California's Air Resources Board has operated an aerosol monitoring network of up to 14 stations since January, 1973, using impactors for particle sizing and using accelerator beams for most of the subsequent analyses for elemental content. Two stage Lundgren impactors with after filters provide for particle sizing, operating at flow rates of 0.5 to 1.0 cfm. Normally, 24 hour samples are taken in the size ranges of 0.1 to 0.5 µm, 0.5 to 5 µm, and 5 to 20 µm effective aerodynamic diameter at unit density. Each week 21 samples from each impactor are sent by U.S. mail to the Air Quality Group of the Crocker Nuclear Laboratory for analysis. Most analyses are performed using 18 MeV alpha particle beams from the 76" isochronous cyclotron. Ion-excited x-ray emission (IEXE) is used for elements sodium and heavier. Alpha scattering, for simultaneously measuring the elements hydrogen through sodium, is being added to the system for the 1974 program. The aim is to routinely report results for particles in these size ranges that add up to the total mass present, results that should equal Hi-Vol mass measurements when the maximum Hi-Vol particle size is limited to 20 µm. Problems involving blank purity, contamination in handling, and analytical limitations will be discussed. Once results are present in an array for each size range, with all particle collection and analytical corrections included, elements are correlated one to another through each month within each size range and mean elemental ratios taken. This aids greatly in identifying primary aerosol sources. Correlations are later taken between each element and eight major gaseous pollutants measured routinely by the A.R.B. network, and visibility/aerosol correlations are also extracted. Results are reduced for publication every three months in the California Air Quarterly.

Introduction

The abstract of this paper relates what has been the main thrust of the NSF/RANN supported ion-beam analysis program at Davis-monitoring California's aerosols. What is not included there is the rationale behind such a program. Why does the State of California support an aerosol monitoring study on a long term basis? And what information is expected from such an effort? Once these questions are answered, reasons for the use of ion beams also becomes evident.

Requirements for a Monitoring Program

The problem derives from the very nature of atmospheric aerosols. Since the aerosols are liquid and/or solid in the midst of a gaseous medium, each has an interface with the medium which defines a size and shape. This enormous complication is absent in the case of gaseous pollutants, and from it arises three very important aerosol properties:

1) Due to the change of the complex index of refraction at the interface, aerosols with effective diameters close to a wavelength of light, scatter light very effectively, reducing visibility.

2) Aerosol particulates can be generated or can grow to be relatively enormous agregations of atoms. A 2 µm particle, about the mass median diameter, is composed of perhaps 10^{11} atoms, which can consist of any combination of elements from hydrogen to uranium.

3) Since the aerosol particulate has mass, it can be separated from the gaseous medium through settling, impaction, diffusion, etc., leading, for example, to retention of fine aerosol particles deep in the lung.

These complications make aerosol measurements more difficult than gaseous measurements. The concept of an instrument that would continuously read out all relevant aerosol parameters is untenable. Designing a meter capable of identifying the thirty elements normally present in amounts above 1 ng/m^3 in urban aerosols strains the imagination, and adding to this the individual distributions, element by element and chemical by chemical, of mass with size, makes the problem impossible.

The question then comes down to how much needs to be known to allow an air quality agency to identify aerosol sources, transformations, transport, and sinks, evaluate health hazards and welfare problems? The answers will never be agreed upon by all, but the Davis program-

1. Chose three size ranges, 0.1 μm to 0.65 μm, 0.65 μm to 3.6 μm, and 3.6 μm to 20 μm, and rejected particulates above 20 μm.
2. Used 24 hour averaging periods for most measurements, with continuous sampling and long term placement at a site, often over one year.
3. Used up to 14 sites to cover various aerosol problems throughout the state.
4. Perform elemental analysis on every sample.

It was felt that such a program represented a minimum level of activity necessary to obtain vital information in a relatively short period. However, the number of samples thus generated was enormous - a 10 station network would generate ∿ 11,000 samples/year, exclusive of calibration and repeat runs.

Thus, the first requirement for the analytical system was low cost per analysis, even at some loss in sensitivity. It was felt that the information gained from 10 samples at nominal 3 ng/m^3 sensitivity for many elements was for more than from one sample at 1 ng/m^3 sensitivity, the costs being about equal.

The second was broad range, multi-element capability for lightly loaded samples, since light elements such as Na to Cl contributed most of the mass normally present of elements heavier than sodium, while elements such as selenium, cadmium, mercury, and lead were important from health considerations. The very light elements, H → F, compose about 80% of the mass of the average California urban aerosol, and these elements are now also being measured on significant numbers of samples. The combination of low cost/analysis and multi-element capability resulted in the extraordinary fact that the cost per positive elemental determination during the first year was about 20 cents.

Other requirements involved large throughput capabilities, which further encouraged automation. Non-destructive analysis was likewise very desireable, since many of the samples are also being analyzed by XRF, SEM, ESCA, and optical spectroscopy.

These requirements were well met by use of ion-excited x-ray analysis by elastic scattering of alpha particles for elements H → Cl.

Preliminary Results of the Program

The results of the efforts of the first year have been gratifying, despite numerous problems that had to be solved in the collection of suitable aerosol samples. Analytical systems problems were almost non-existent, with the ∿ 1,000 analyses required each month being completed during a single day.

Although the results are still in the process of interpretation, several interesting facts are evident:

1) Much of the mass seen during each month occurred in correlated element sets specific to known sources. Correlation coefficients as high as 0.99 were common among such sources as soil (Al, Si, K, Ca, Ti, Mn, and Fe), automotive effluents (Br, Pb), sea salts (Na, Cl), and fuel oil combustion sources (S, V, Ni). This aided reduction of the data in areas where these sources were likely to exist.

2) Monthly mean values often varied in a regular fashion from month to month, revealing dramatic changes in air chemistry, source strengths, and meteorology. The summer/winter pattern in sulfur particulates appears to isolate photochemical sulfate production from direct combustion sources of sulfate, while the Br/Pb ratio appears highly correlated with the chemical reactivity of the atmosphere.

3) With extensive knowledge of aerosol composition by size, and with the availability of weather and gas pollutant data from standard instrumentation, multi-variate analyses have been able to isolate effects such as visibility degradation by specific source.

4) Correlation of aerosol source tracers with gas pollutants often provides unambiguous information on gas pollutant sources.

Summary

In summary, the analytical techniques developed in part by the NSF/RANN program have allowed California to initiate a continuous research effort through its monitoring programs. By this means, statistically meaningful relationships are being developed that will allow the state to effectively evaluate air quality problems and devise cost-effective methods for amelioration.

A NON-METHANE HYDROCARBON MONITOR USING CRYOGENIC SEPARATION*

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Abstract

Methane has a higher vapor pressure than any other hydrocarbon. Because of this, methane can be separated from the other hydrocarbons in ambient air by condensing the heavier ones on a suitably cold surface. A methane separator based on this idea has been constructed and tested with bottled gas mixtures. The device trapped more than 95% of all the non-methane hydrocarbons used and had no measureable effect on methane. We are now constructing a complete monitoring instrument using this concept. Its design is discussed here.

Introduction

Because of their involvement in the photochemical reactions that generate oxidants in polluted atmospheres, the U.S. Environmental Protection Agency (EPA) has set national primary and secondary ambient air standards for hydrocarbons corrected for methane[1] (i.e., total content of hydrocarbons other than methane). However, no areas are presently required to monitor non-methane hydrocarbons (NMHC) for at least two reasons. It is argued that if oxidant levels remain within air quality standards, hydrocarbons should also be at acceptable levels (this is still somewhat controversial). Also, the currently designed reference method for measurement of NMHC[2] is complex, costly, and marginal in its ability to operate unattended and provide sufficiently accurate data.

In the near future, the EPA will publish performance standards and test procedures for instruments to monitor three air pollutants: ozone, sulfur oxides, and carbon monoxide. Because of the difficulties mentioned above for NMHC, and similar problems with oxides of nitrogen, they will publish only guideline performance and test information for instruments to measure these pollutants. This leaves some uncertainty concerning both required performance and the size of the market for NMHC monitoring instruments. However, monitoring of NMHC (and decisions based on the indicated levels) could be a valuable part of the air pollution control strategy for areas with oxidant problems, and the availability of good instrumentation would encourage this.

The reference method for measurement of NMHC uses a gas chromatograph with flame ionization detector to measure methane.[2] A similar detector (in some cases the same one) measures total hydrocarbons in another part of the air sample, and the NMHC level is obtained by subtraction. This technique is inherently a batch process, and current versions of the instrument provide 5 to 12 samples per hour. The gas chromatographic column separates methane from the other hydrocarbons in the air sample and the flame ionization detector measures the amount of methane in the sample. The essential function of the column is separation of methane from other hydrocarbons. The required measurement is also possible with many other separation techniques.

Methane (CH_4) is the lightest, most volatile hydrocarbon, so it is possible to separate CH_4 by condensation of the heavier hydrocarbons in an air stream. We have assembled and tested a simple device using this idea[3] which achieved better than 95% separation of CH_4 from other hydrocarbons. Basically a tube at 77° K traps the heavy hydrocarbons, so that of the hydrocarbons in a stream of ambient air, only the CH_4 remains in the trap effluent. The processed air containing only methane is sent to a flame ionization detector alternately with an unprocessed ambient air sample and the NMHC level is obtained by subtraction. Figure 1 is a flow schematic for this device. Figure 2 shows typical data obtained with the instrument.

The device described above was an experimental one, designed to test the concept. We have been encouraged to build and test a more sophisticated unit that would be more nearly like a commercial air pollution monitor.

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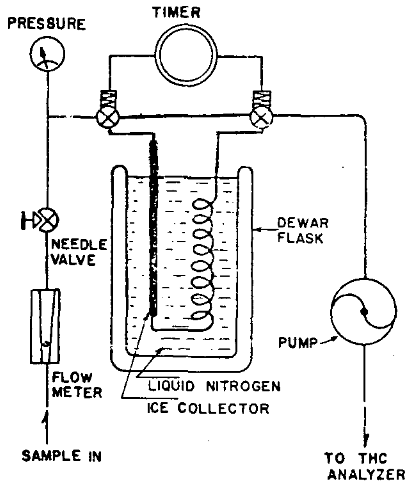

FIG.1. Schematic diagram of the experimental methane separator.

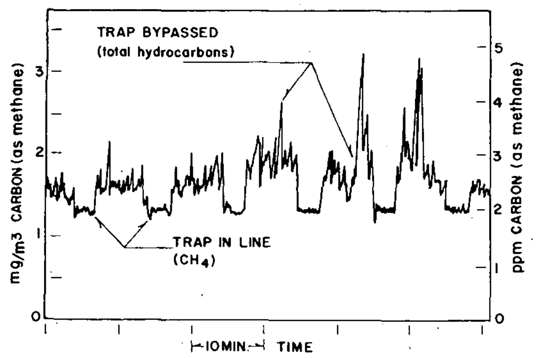

FIG. 2. Typical data from a total hydrocarbon monitor when used with the methane separator. This recording was obtained at about 2:00 p.m. in downtown Eugene, Oregon.

Design of a Monitoring Instrument

There are several alternatives for NMHC monitoring systems that could use the cryogenic separation technique. One can make an add-on unit for use with any of a number of commercial total hydrocarbon (THC) monitors (and there are already many units in the field). Or one can design a complete system including sample conditioning, detection, and signal processing. For an add-on device, the cryogenic trap system must process a large enough sample to satisfy requirements of the commercial THC monitors in use. For a complete instrument, the trap system is designed to match one particular detection system, and the signal processing can also be made more convenient. Refrigeration can either be supplied by use of liquid nitrogen or by a closed cycle cooler such as those available from Cryogenics Technology, Inc. and Air Products and Chemicals.

While an add-on device would be very useful to the many agencies that already own total hydrocarbon monitors, it is much easier to perform definitive tests on a complete system. Therefore, we decided to build and test a complete system using liquid nitrogen cooling, and follow this with a modification that employs a closed-cycle cooler. As time permits, we will also give advice, and help agencies construct their own add-on device for a particular application. We are currently working with the Oregon Department of Environmental quality on an add-on device they plan to use for research purposes.

Device Description

The monitoring instrument under construction will include all the systems needed to meet EPA's indicated requirements, and will provide convenient data processing. The unit is designed to operate unattended for at least three days, automatically sampling ambient air and generating signals (analog and digital) proportional to the ambient air hydrocarbon content corrected for methane. The design can be conveniently broken down into three systems: (1) the air sample flow system; (2) the signal processing system; and (3) the liquid nitrogen control system. These systems will be described below.

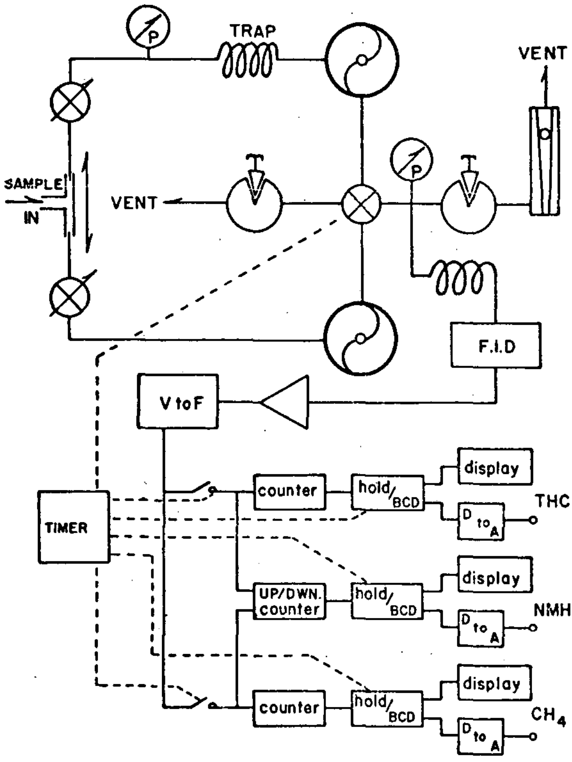

FIG. 3. Schematic diagram of the non-methane hydrocarbon monitor.

Flow System

The sample flow system is shown schematically in Figure 3. The system is designed to operate at a sample flow rate of about 100 cc/min in each line. This is sufficient to supply the 50 cc/min required by the detector and an excess large enough to allow the pressure regulators to function properly. The total 200 cc/min sample is split near the inlet, one-half going through the line containing the trap, the other half through the bypass line. The restriction (needle valve) in the upper line and the pump combine to maintain the trap pressure low enough to avoid air condensation. The bypass line also contains a needle valve in order to adjust the bypass flow to match the flow through the trap. Ambient air that has passed through the trap will contain only methane. The bypassed stream contains all the ambient hydrocarbons, and the four-way valve alternately routes CH_4-only or -THC samples to the detector. Another gas stream is released through the vent. The volumes of the two sample paths and the flow rates are adjusted so that a THC sample and the following CH_4-only sample were both collected at the same time. Thus the difference of the two adjacent signals will represent non-methane hydrocarbon content of the same aliquot of ambient air.

Pressure in the sample line leaving the four-way valve is controlled by an up-stream pressure regulator. The capillary restrictor leading to the flame ionization detector meters the flow to the detector, and the excess is vented to the atmosphere. The flow-meter on the vent tube is used to indicate flow rates of the two sample streams during set-up.

Electronics

The signal processing system is also shown schematically in Figure 3. It is designed to provide both digital and analog signals that indicate the measured levels of methane, and total hydrocarbons and the derived non-methane fraction.

After initial amplification, the analog detector signal is converted to a frequency proportional to the analog voltage in a voltage to frequency converter (V to F). This frequency is routed to a counter and the cycles counted for a period controlled by the timer, providing a count proportional to the average analog signal over the period. The maximum count is transferred to a module that holds the value and converts it to binary coded decimal (BCD) format for output or digital display. A digital to analog converter (D to A) converts this value to an analog signal for a strip chart recorder. Signals corresponding to CH_4 and to THC are routed to separate counters, and an up/down counter is used to compute the difference corresponding to NMHC.

Refrigeration and Control

The liquid nitrogen system and the cryogenic trap are shown in Figure 4. The trap is located inside a dewar flask. During normal operation, the liquid nitrogen level is maintained above the level of the main (hydrocarbon) trap by a gravity-feed reservoir. This supply reservoir will hold enough liquid nitrogen for three days' operation and it can be automatically filled from a larger storage container if desired.

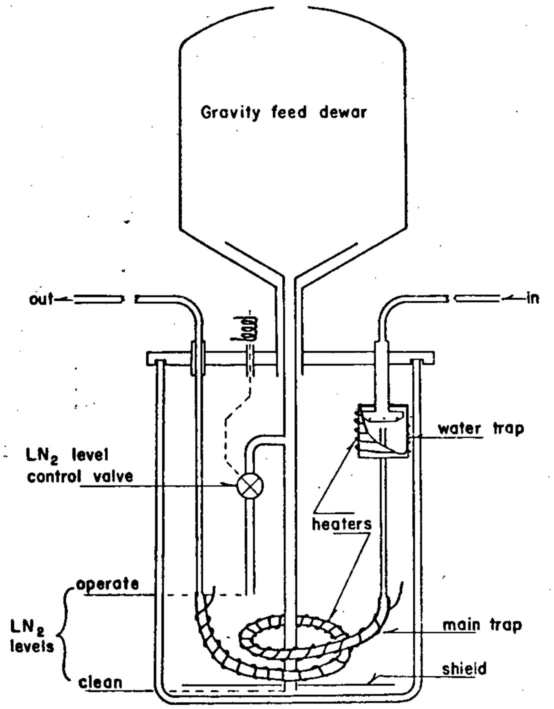

FIG. 4. NMHC monitor liquid nitrogen and trap system.

Approximately once a day, the hydrocarbon and water traps must be warmed and the condensate (mainly water) flushed out. To do this, the liquid nitrogen is lowered below the trap level. The lower dewar is a sealed container, so evaporated nitrogen gas can only escape through the feed tube or through the tube extending below the LN_2 level control valve. If this control valve is open, LN_2 will remain at the "operate" level. Closing this valve causes pressure to increase on the liquid surface, forcing liquid nitrogen up into the upper reservoir until the liquid level in the lower dewar is below the lower fill tube opening. With this technique of transferring liquid nitrogen between reservoirs, the heating and cooling cycle can be accomplished with relatively little cryogen consumption.

To accomplish the trap cleaning cycle,

the LN_2 level control valve is closed and power is applied to the heaters on both traps. The LN_2 level drops below the shield just above the bottom of the dewar. The heaters raise the trap temperature to about 110° C., the condensate is evaporated and flushed out the vent. After sufficient time the heaters are turned off, the LN_2 control valve is opened, and the LN_2 returns to the "operate" level.

Trap Design

The trap system itself consists of a main trap (for hydrocarbon collection) operated at 77° K and a relatively warm water trap. For high collection efficiencies, it is apparently important to maintain turbulent flow conditions and this requires some attention to flow rates as low as 100 cc/min. Air enters the water trap through several small (0.015 in.) diameter holes, and the high velocity jets strike the outer walls which are at a temperature of about -20° C. Ice builds up from these points and slowly fills the trap. The ice trap is large enough to accommodate the several cc's of ice and snow that result from about thirty hours' operation at a 25° C. dew-point. (This corresponds to about 30,000 ppm water vapor in the inlet gas.) The hydrocarbon trap is a 75 cm.-long section of ¼-inch copper refrigeration tubing filled with anodized aluminum shot about 1 millimeter in diameter. A short plug of pyrex wool is inserted about each 15 cm. This seems to encourage turbulence and considerably improves trapping efficiency.

Conclusion

This system is now nearly assembled. After completion, some tests will first be performed using prepared gas mixtures and laboratory instrumentation. The design of some of the components will possibly change during this testing phase. Afterwards, our plans include some field tests in Oregon and additional tests in St. Louis in conjunction with the EPA's Regional Air Pollution Study (RAPS).

The preliminary tests we have performed with our current trap design indicate greater than 95% collection of C_2H_4, C_3H_8, $i\text{-}C_4H_{10}$, and $n\text{-}C_4H_{10}$, and the ability to tolerate as much as 30,000 ppm vapor for over 30 hours. More comprehensive performance data will be published as soon as it is available.

Acknowledgements

We wish to thank Dr. R.K. Stevens of the EPA National Environmental Research Center for his helpful guidance during this development, and Mr. Michael Cromar, who helped construct and test the first device.

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TRACE CONTAMINANTS IN THE ATMOSPHERE

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My function this morning is to report to you on the past two days' sessions dealing with atmospheric aspects of trace contaminants research. While I am flattered that our conference chairman has asked me to serve in this role, I must confess having one reservation. It is not possible to convey in the time available all of the findings and research applications that were presented at our sessions. Considerably more new data were presented and discussed during the past two days than can be thoughtfully considered this morning. I would like to congratulate Dr. Tisha Novakov on selection of Asilomar for this year's Annual NSF-RANN Trace Contaminants Conference. At least for this Coloradoan, the combination of scientific purpose and setting has been most rewarding. I trust that I speak for all in expressing thanks for the tireless and successful efforts of this year's Conference Chairman.

My interpretation of our Chairman's charge to "rapporteurs" is to summarize highlights of our sessions with respect to the following areas:

1. Air Chemistry
2. Sources
3. Transport
4. Methods and Instrumentation.

What I will try to do is summarize some of the developments that seem particularly striking. The hope is that those attending other sessions may be encouraged to utilize in their own programs some of the findings and techniques described at our sessions. One example that comes to mind immediately would be the separation-identification procedures described by Rod Skogerboe for identifying the chemical forms of lead in soil, plants and on air filters. While the application in this case was for lead from automotive sources, other uses may be seen for identifying the chemical forms of other trace metals, perhaps in quite different matrices. Another example is the approach described by Bill Zoller for tracking down a municipal incinerator as a source of atmospheric particles substantially (10^5 times) enriched in certain toxic metals. A third example is the ion-beam technique developed by Tom Cahill and coworkers for simultaneously determining a multiplicity of elements in atmospheric dusts, including low-atomic number elements. These are but three examples; there are many others.

In the context of Dr. Pitts' remarks at the plenary session on the opening day, I believe that attendees were made keenly aware of this nation's need to mobilize its talent pool of environmental-energy specialists. As Dr. Pitts pointed out, cost-effective strategies for managing environmental contamination problems require technologies solidly founded on scientific facts. An example of the scientific pay-off that can be realized by cooperation and collaboration among concerned specialists can be seen in the development of the airshed model discussed by Dr. Pitts. This discussion was most helpful to all in emphasizing the important role that the scientific community can play in developing the needed body of scientific information. In Dr. Pitts' words, "You have to know what you've got."

Dr. Pitts and coworkers coauthored the leadoff paper at our first session, "Air Chemistry." Particularly striking to me was the progress made in modeling the photochemical processes in the atmosphere by simulation experiments carried out in laboratory smog chambers. The combined gas-chromatography, mass-spectrometry analytical methodologies led to detection of new products in propylene-NO_x photooxidations. The kinetic data are being utilized in validating models for chemical transformations in smog. Progress in developing the kind of mechanistic information needed for models of real predictive value is most encouraging. Also encouraging is the development and application of newer techniques, such as Fourier infrared interferometry, for determining constituents such as formic acid, nitric and nitrous acid, and alkyl nitrates. These new developments were discussed by Dr. Winer of the Cal-Riverside group.

Along the same line, developing a predictive model for photochemical smog processes from laboratory simulation studies, R. F. Reinisch (NASA-Ames) discussed development of a numerical model with emphasis on modeling hydrocarbon mixtures characteristic of engine exhaust. Here, the emphasis was on simplified inputs and outputs, rather than on elucidation of specific reaction mechanisms. A feature of this particular model is the definition of a reactivity parameter by means of which complex hydrocarbon mixtures were treated.

A "state of the science" report on certain unstable atmospheric species of importance in air pollution reactions was provided by Snelson of the IIT Research Institute. The discussion helped focus attention on the need for more kinetic and thermodynamic data for certain key species, especially NO_3.

Lead alkyls in the atmosphere was the subject of two presentations by representatives of Colorado State University. Corrin reported development of a sampling-analysis approach for measuring picogram quantities of specific lead alkyl compounds in the atmosphere. Sampling was accomplished with hexane bubblers at -78°C; analysis was by gas chromatography using an electron capture detector operated in a pulsed mode. Edwards reported on laboratory simulation experiments in which atmospheric dust components were exposed to tetraethyl lead vapor. The data suggest that sorption of organic lead vapor on atmospheric dusts may be important in scavenging and breakdown mechanisms. These studies both relate directly to the problem of detecting and defining the fate of organic lead in the atmosphere.

Trace gas analysis of power plant fumes via small aircraft was discussed by Davis from the University of Maryland. Airborne samples from a power plant plume were obtained with an aircraft equipped with on-board instrumentation for determination of SO_2, O_3, and NO/NO_2. The data were used to develop models which interrelate the concentrations of certain plume components under various conditions. These studies helped focus attention on the need for more information in the atmospheric chemistry of SO_x. Researchers from Purdue University reported measurement of electrostatic precipitator efficiency at an open-hearth furnace. This study was especially valuable in illustrating some of the practical aspects of field sampling under, to say the least, rather difficult conditions.

The second session dealing with atmospheric aspects focused on sources. Zoller from the University of Maryland discussed release of trace metals from coal-fired power plants and municipal incinerators. The data presented should prove highly useful for inventorying and identifying sources of trace metals in urban areas. Incinerators were found producing particles greatly enriched in some of the more volatile metallic elements. This problem may assume major importance as power production from incineration becomes more widespread.

Construction of a materials balance for selenium inputs and outputs at a coal-fired power plant was reported by Andren and coworkers from the Oak Ridge National Laboratory. Most of the Se emitted is associated with fly ash particles with the remainder in the vapor phase. The implication is that man mobilizes appreciably more selenium through coal burning than occurs naturally through weathering.

Jacko and coworkers from Purdue also reported on trace metal emissions from a municipal refuse incinerator. Again, this type of study points out the importance of including incineration operations in inventories of trace metal emission sources.

Braman from the University of South Florida reported a speciation study of mercury compounds in air. Collection is accomplished by a selective absorption tube, and analysis is carried out by an emission technique. Detection limits are in the fractional nanogram range per cubic meter of air. Although elemental mercury is the chief form found, five chemical forms of mercury were found in significant amounts. In soil, inorganic mercury is converted to methyl mercury compounds and elemental mercury. In a study reported by Soldano of Furman University, sewage facilities were implicated as possible major sources of airborne mercury emissions in urban areas.

The third session dealt with transport of contaminants in the atmosphere.

Katen from the Colorado State University environmental lead project team described development of a practical urban model for intermediate-range transport of automotive lead from traffic sources. Predictions of downwind lead concentrations were validated by extensive field sampling and deal with that portion of lead emissions which does not settle out within 100 m of a highway. A major result is that about 45% of the lead consumed by automobiles is still airborne 10 km downwind of Fort Collins.

Atmospheric transport of automotive lead was also the subject of an investigation report by Hudson from the University of Illinois. A mathematical model was developed for atmospheric transport of particulates over level terrain. A network of streets is represented as a set of finite-length line sources of varying intensities. A major difference between predicted and observed air-lead values was ascribed to background, i.e., lead advected into the system from distant urban sources.

A contribution from investigators at Purdue dealt with analysis of a large body of atmospheric particulate and trace metal data in terms of atmospheric transport characteristics. Newman suggested that source identification requires hourly meteorological data, rather than daily information.

Transport of air pollutants by cumulus clouds was discussed by Hemni from Colorado State University. Cumulus clouds play an important role in transporting pollutants and in atmospheric cleansing. The paper focuses on calculating vertical transport of air pollutants from the boundary layer by cumulus clouds. The influence of various physical parameters, including humidity and precipitation, was discussed in terms of effects on the rate of vertical transport of pollutants.

A wind-tunnel simulation technique was described by Thompson of Colorado State University to model dispersion of automotive emissions in a city street canyon. Pronounced effects of local building geometry were detected, and localized concentration inhomogeneities were striking, even under moderate crosswind conditions. Validation of some major effects was provided by comparison with field data in downtown Fort Collins. Physical modeling of pollutant dispersion clearly provides a powerful predictive tool, particularly at elevations below rooftop where no fully satisfactory mathematical model presently exists.

At this point we met for an extremely useful informal session on aerosol chemistry. New data were discussed, and mechanisms for SO_x-NO_x interactions were explored. Data were exchanged and discussed on an off-the-record basis. My compliments go to Dr. Novakov for arranging this fine opportunity to explore new concepts.

The fourth and final session dealt with analytical methodologies and instrumentation.

Grant and Proctor from Stanford Research Institute reported on use of the differential absorption backscatter technique for remote measurement of pollutants. A dye laser served as the light source which, for a single pair of pulses, allowed NO_2 concentrations to be determined with an uncertainty equivalent to 0.05 km ppm. This type of approach also shows considerable promise for application to measurement of SO_2 and O_3.

Hinkley from MIT described use of tunable semiconductor diode lasers for remote sensing. Continuous laser monitoring of atmospheric CO with a ppb sensitivity was reported. The system has been incorporated in the St. Louis RAPS study for EPA. The advantages of this approach to remote sensing should be substantial.

Use of resonance Raman scattering to the remote sensing of pollutants was discussed by Robrish of the Lawrence Berkeley Laboratory. The scattering cross-section of NO_2 was measured, and the implications were discussed in terms of development of monitoring instrumentation.

Procedures for nondestructive separation of environmental lead compounds from soil and plant matrices were discussed by Skogerboe from Colorado State University. Application to the problem of identifying the various lead compounds present was discussed and examples were presented with emphasis on use of x-ray difractometry. Possible mechanistic explanations for formation of the various lead compounds found in air, soil and plants were explored.

Cahill from the University of California-Davis described use of ion beams for monitoring aerosol composition. Both alpha and ion-excited x-ray emission were used in the procedures described; the latter source is used primarily for sodium and elements above in mass number. Some of the advantages of the ion-beam technique in the context of an ongoing, major monitoring program were discussed. Data from analysis of actual atmospheric samples were presented to demonstrate the breadth of the technique in terms of simultaneous multielemental analysis.

In a paper authored by LSU investigators working with Professor West, an atomization-combustion technique was described for producing H_2SO_4 and metal-oxide aerosols. The atomizer-burner is similar to the type used in flame photometry. The materials this produced have been used as reference materials in x-ray fluorescence and ring-over studies. The aerosol-generation technique should be of particular interest to anyone needing a convenient source of particulates for laboratory simulation studies.

Our session closed with papers on cryogenic sampling of air pollutants and high-energy, tunable lasers for remote sensing.

I would like to close with several observations of a general nature. First, I am most encouraged by the willingness of the various investigators to discuss preliminary data and work still underway. It is precisely at this stage that the information is so very helpful to colleagues working on parallel problems. The research scientists and engineers clearly recognize that their counterparts at other institutions and agencies are an important component of the community of information users. Yet at this stage of development, projects are only infrequently the subjects of technical papers presented at traditional professional society meetings. Thus the NSF-RANN meetings of this type can play a vital role in accelerating the rate of information transfer and utilization within the scientific community, in addition to the benefits to society in general. The second observation is that the work presented was directly tied to problems of major national importance in assessing and managing environmental quality. What I find so very encouraging here is the vast amount of good, usable science emerging from these programs. The papers presented at our sessions provide ample and convincing proof that not only is the scientific pay-off useful and utilized, it is also very good science. I am most pleased to have had the opportunity to participate in the program.

UNSTABLE ATMOSPHERIC SPECIES THAT HAVE NOT BEEN FULLY CHARACTERIZED

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Abstract

The mode of formation of many pollutants in the atmosphere is not well understood. Reaction mechanisms invoking the intermediacy of unstable chemical species leading to specific pollutants are often proposed. In many cases the unstable intermediates themselves are poorly characterized. In this paper the current state of knowledge with respect to the characterization of some of these intermediates believed to be of importance in atmospheric pollution will be presented. Particular emphasis will be devoted to NO_3 and the organic radicals RC(O)O, RC(O)OO, RCC, ROO and RO. Some thermodynamic and kinetic deficiencies due to poor characterization of these species will be noted.

LEAD ALKYLS IN THE ATMOSPHERIC ENVIRONMENT

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Abstract

A rationale is presented which stresses the need for the determination of specific lead alkyls in the urban environment. The present distinction between "particulate" and "organic" lead is shown to lead to ambiguity and confusion in interpretation. In view of the anticipated low level of lead alkyl concentrations and the necessity for reasonable sampling times an analytical method for specific alkyls was developed sensitive at the picogram level; this method involved techniques of sampling and gas chromatograph determination. Sampling was accomplished with hexane bubblers at -78C. The hexane solutions were concentrated under vacuo at -78C to a volume approximately 2 percent of what originally employed in collection. The column of 20 foot length was packed with 5 percent Carbowax 6000 on DMCS Chromosorb W previously treated with 8 percent NaOH. The electron capture detector (tritium) was operated in the pulsed mode. Certain complications were encountered and solutions worked out. Preliminary results obtained in a cooperative study of lead alkyl concentrations as a function of distance from a heavily travelled highway will be presented.

THE COLLECTION EFFICIENCY OF AN ELECTROSTATIC PRECIPITATOR FOR TRACE METALS FROM A OPEN HEARTH FURNACE

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University, Lafayette, Indiana

Abstract

Emission tests in June 1974 both upstream and downstream of an electrostatic precipitator controlling a battery of seven open hearth furnaces resulted in an average particulate collection efficiency of 97.7 percent for three simultaneous sample sets. Specific efficiency tests were also performed simultaneously with Anderson fractionating sampling devices and indicated an apparent minimum collection efficiency at the 4-micron aerodynamically sized particle range. The efficiency decrement at 4 microns is primarily due to transformation of particle sizes within the electrostatic precipitator. Agglomeration of the 1-micron particles to an effective 4-micron size is postulated as the primary reason for the pseudo efficiency decrement at 4 microns. Average particulate concentration upstream and downstream of the precipitator was found to be 0.349 grains/SCF and 0.008 grains/SCF respectively. Total particulate mass emission rates were observed to vary between 35 and 94 lb/hr and resulted in calculated emission factors of 0.16 and 0.46 lb-particulate per ton of steel produced. The mass median diameter of the particles entering the precipitator was found to be 1.56 microns for an average of 3 runs, with the mass median diameter leaving, 1.0 microns.

THE RELEASE OF TRACE METALS FROM HIGH TEMPERATURE COMBUSTION SOURCES: COAL-FIRED POWER PLANTS AND MUNICIPAL INCINERATORS

W. H. Zoller, G. E. Gordon, E. S. Gladney,
R. R. Greenburg, and J. J. Bors
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Abstract

A pulverized coal-fired power plant and a municipal incinerator have been studied to evaluate their importance as sources of the anomalously enriched trace metals in urban atmospheres. The power plant has been found to have minor enrichment of volatile elements relative to Al. The incinerator, on the other hand, emits material containing large quantities of volatile elements with very high enrichments relative to crustal materials. The importance of incinerators in urban regions will be discussed.

TRACE METAL EMISSIONS FROM A MUNICIPAL REFUSE INCINERATOR

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Abstract

One of the potentially significant sources of heavy metals to the urban environment is the municipal refuse incinerator. The work described took place during a two-week period of sampling at the Nicosia Municipal Incinerator in East Chicago, Indiana. Eleven stack samples as well as grab samples of other process streams including scrubber input water, scrubber effluent water, and scrubber residue were analyzed for cadmium, lead, zinc, and copper. The resultant data were used to generate mass emission rates of metals from the incinerator to the atmosphere and the East Chicago sewer system. Also determined are trace metal emission factors averaged over the sampling period.

ATMOSPHERIC TRANSPORT OF LEAD PARTICULATES FROM AUTOMOBILE EXHAUST IN AN 86-SQUARE-MILE ECOSYSTEM

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Abstract

Atmospheric lead concentrations were measured as a function of both time and position in a rural area adjacent to Urbana-Champaign, Illinois during the period August, 1973 to February, 1974. The results were interpreted by means of a mathematical model which has been developed for predicting the atmospheric transport of particulates of any size distribution. The lead is emitted from finite length line segments representing a network of city streets and rural highways. The model can be used to predict the dispersion of pollutants in any region of flat terrain. The inputs required for the model are the coordinates of the highway segments, traffic counts, and meteorological conditions. The measured mean rural concentration is 0.227 microgram per cubic meter with a standard deviation of 0.116 microgram per cubic meter. Most of the lead in the rural area is transported into the area from distant sources with the contribution of automobiles in Urbana-Champaign and local highways being minor. Measurements were also made of particle size distributions and deposition rates to the ground.

LASER REMOTE MEASUREMENTS OF NO_2, SO_2, AND O_3

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Abstract

Experiments using the differential absorption backscatter technique for the remote measurement of air pollutants are being conducted at SRI. A dye laser operating between 440 and 450 nm has been used to measure BO_2 in a sample chamber 365 m from the transmitter. Particulate matter and molecules in the atmosphere provide a distributed reflector to send light back to the receiver near the laser. The laser measurements agreed well with in situ measurements. A single pair of laser pulses allowed NO_2 concentrations to be determined with an uncertainty equivalent to 0.05 km ppm. An ADP or ADA crystal generating the second harmonic of dye laser light currently is being used to produce signals in the 280 to 310 nm region. These signals will be used to measure SO_2 and O_3 in a manner similar to that used for NO_2.

IDENTIFICATION OF ENVIRONMENTAL LEAD COMPOUNDS

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Abstract

Procedures will be described which permit the nondestructibe separation of environmental lead compounds from soil and plant matrices. The identification of lead compounds contained in the separated fractions will be discussed. Possible mechanistic explanations for the lead compounds identified will be examined.

GENERATION OF STANDARD AIRBORNE PARTICULATES: X-RAY FLUORESCENCE STUDIES

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Abstract

A convenient and precise method has been developed for the generation of standard metal salt particulates and sulfuric acid aerosol. The method of generation essentially simulates the process that occurs in industrial plants and incinerators responsible for the discharge of metal oxide particulates and sulfuric acid aerosol in ambient atmospheres, viz, the combustion of metal and sulfur bearing fuels and other substances. The generator consists of an atomizer-burner of the type used in commercial flame photometers, mounted at the base of a miniature glass stack. The burner is operated using oxygen/or hydrogen. A dilute solution of the desired metal or mixture of metals is aspirated into the flame, where it decomposes to yield the neutral metal atoms, which then recombine with oxygen to form metal oxide particulates in the size range of 0.1-5 micrometer. For the generation of sulfuric acid aerosol, a dilute solution of sulfuric acid is aspirated into the flame. The aerosols, moving up the stack at a steady and controlled rate can be collected by means of the sampling probe using a suitable filter medium. Standard metal particulates or sulfuric acid aerosol sample can be made using this method for evaluating new analytical procedures and also for interlaboratory comparisons. Also, standard composite samples containing acid aerosols, soot, silica, and metal particulates can be generated using this method. The application of generated standard particulates as reference material for x-ray fluorescence and ring oven studies, will be discussed.

A HIGH ENERGY TUNABLE COHERENT SOURCE FOR REMOTE POLLUTANT MEASUREMENT

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Abstract

We have developed a high energy post coherent source suitable for remote pollutant detection by the differential absorption method. The coherent source is pumped by a Q-switched Nd:YAG oscillator-amplifier chain operating at 10 pps with up to 500 nj per pulse. $LiNbO_3$ angle tombed p parimetric oscillator efficiently converts a 1.06 M pump radiation to 1.4 micrometer to 4.4 micrometer tunable output with band widths less than 0.1 cm (minus). Mixing further extends the tuning range to 18 micrometer. The source is controlled by a PDP 11E 10 mini-computer which also has a real time data system for remote pollutant measurement. The tunable coherent source and its application to remote pollutant measurement will be described.

III. WATER AND SOIL

A SCHEME FOR THE DETERMINATION OF OPTIMUM SAMPLING SITES FOR SOIL AND VEGETATION*

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Abstract

A technique is presented which allows estimation of the required number and distribution of sampling sites necessary to accurately specify soil and vegetation data. The heart of the technique is an interpolation algorithm which estimates sample values at points, without actually collecting samples at these points, by using a weighted sum of the eight nearest field samples. The technique can be applied to any system in which the spatial locations of the sampling sites are fixed and accurately known. Additional requirements are that the field samples do not change rapidly with time and that the source of the parameter being measured is not distributed over a large area.

Introduction

The selection of sampling sites for a field sampling program is a matter of considerable importance, especially when one considers the expense of collecting and analyzing samples. Thus, a technique which allows one to estimate sample values, without actually collecting field samples, is easily justified.

The assumption is made that the final product desired from a field sampling program is a spatial distribution function which gives the value of the parameter being measured at every separately resolvable point within the study area. In order to form this spatial distribution function, the study area is divided into a large number of subareas. Field samples are obtained for a limited number of these subareas. The sample values for the other subareas are then estimated by the use of an interpolation algorithm. The interpolation algorithm forms the estimate by using a weighted sum of the eight nearest sample values. The weighting is performed so that samples near the point for which the estimate is being made are weighted heavier than more distant samples. The problem is to choose the minimum number of sampling sites which allow the estimate to be made with a required accuracy.

The interpolation algorithm is an extension of a technique developed by Crain and Bhattacharyya [1] for use with geophysical data. While they dismissed their method for geophysical data, it appears to be suitable for estimation of a surface with relatively few maxima and minima.

The error criterion is the mean-square error between the true spatial distribution and the estimated spatial distribution. Since the true spatial distribution is unknown, a computer simulation is used. This is accomplished by assuming a spatial distribution, sampling and estimating the spatial distribution, and then computing the error as a function of the number of samples used in forming the estimate.

Two different spatial distributions are assumed; Gaussian and exponential. These are analyzed for two different distributions of the sampling sites. For both cases, the sampling sites are random. For the first case, both the north-south and the west-east coordinate of a given sampling site is a uniform random variable. This results in an even distribution of sampling sites over the study area. For the second case, the radial distance from the center of the study area to the sampling site obeys a Rayleigh probability density function. This scheme insures that the density of the sampling sites is

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greatest where the spatial distribution is changing most rapidly. This is certainly a desired condition.

Curves are presented which illustrate estimation accuracy as a function of the number of samples. The results show that for a 10,000 meter by 10,000 meter study area, an accuracy of 20 percent can be obtained with approximately 100 samples while accuracies of 5 percent require in excess of 400 samples. As expected, a Rayleigh distribution of the sampling sites is preferred. In addition, the assumed shape of the spatial distribution does not significantly impact the required sample size. Thus, guidelines on required sample sizes are established.

Sample Interpolation

In order to illustrate the estimation algorithm, it is applied to soil data in the vicinity of the AMAX smelter in the New Lead Belt of Southeast Missouri.

The sampling site locations are illustrated in Figure 1. It is clear that the sampling sites do not form a regular grid over the 10,000 meter by 10,000 meter study area. In addition, sample estimates may be required for positions which are not sampling sites. Thus, data interpolation is often required. The result of the interpolation is a spatial display which yields sample values, either real or estimated, for every separately identified position in the area.

The first step in the generation of these spatial displays is to divide the study area into a spatial matrix of data cells. The size of this matrix is arbitrary and depends upon the application. For this study, the spatial matrix is a 64 x 64 matrix denoted A_{ij}. Thus, the spatial matrix for this study, illustrated in Figure 2, contains 4096 data cells. This size was chosen as a compromise between accuracy and computing requirements.

The first matrix subscript, i, indexes the columns of the matrix, which represent the N-S position of the sampling site, and the second subscript, j, indexes the rows of the matrix, which represent the W-E position of the sampling site. The individual values of the matrix elements represent the concentration of the element under investigation in the specific spatial location corresponding to that entry in the matrix. Obtaining a chemical analysis for each of the 4096 specifically identified positions in the study area is usually precluded by the large cost of such an extensive sampling and analysis program. Thus, use of an algorithm to estimate the chemical parameters for a large number of the matrix elements is easily justified.

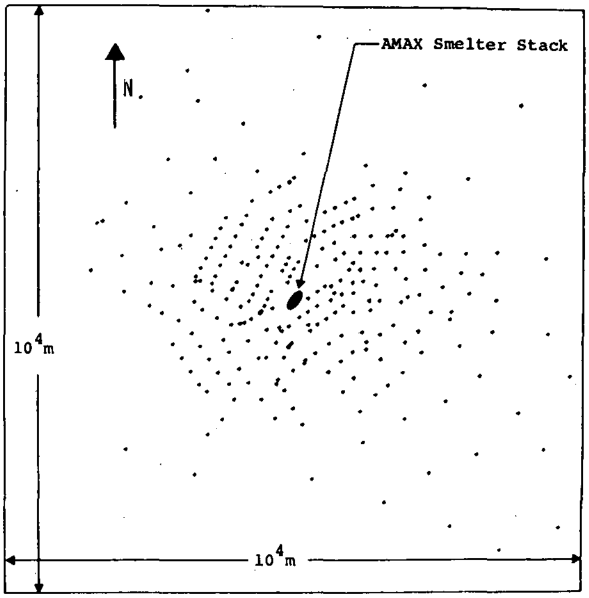

FIG. 1. Sampling Site Locations.

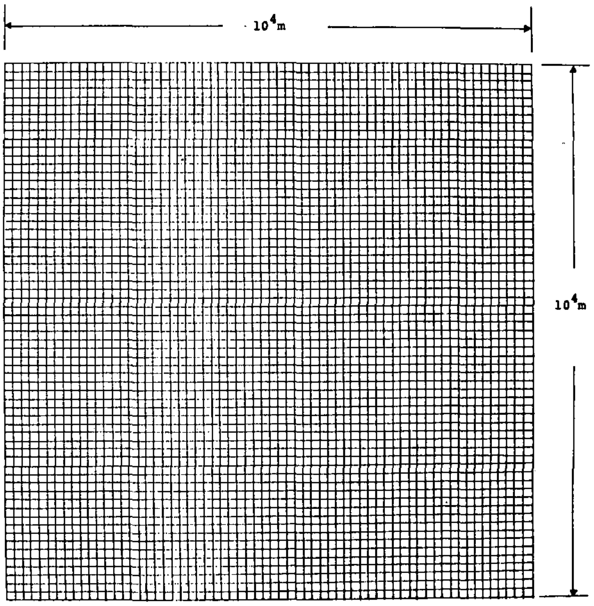

FIG. 2. Spatial Matrix.

In order to efficiently handle the bookkeeping, a second matrix is computer generated. This matrix contains three rows and a column for each field sample available. The first row, $B_{1\ell}$, corresponds to the sample values resulting from chemical analysis. The second row, $B_{2\ell}$, corresponds to the N-S position of the sample and the third row, $B_{3\ell}$, corresponds to the W-E position. These general matrix elements are denoted by $B_{k\ell}$.

Initially, the algorithm scans the available field data and places each field sample in the corresponding cell of the spatial matrix. If more than one field sample falls into the same cell, the cell value is taken as the average of those field samples falling in that cell. The algorithm then searches the spatial matrix for those data cells which do not contain field sample values. When one such cell is identified, A_{IJ}, the $B_{k\ell}$ matrix is then searched for the eight <u>nearest</u> cells for which data exists. This is accomplished by determining the eight data cells for which the distance function

$$(B_{2\ell} - I)^2 + (B_{3\ell} - J)^2 \qquad (1)$$

is a minimum. The estimated value for A_{IJ} is computed using the relationship

$$A_{IJ} = \sum_{h=1}^{8} \frac{K B'_{1h}}{\sqrt{(B'_{2h}-I)^2+(B'_{3h}-J)^2}} \qquad (2)$$

where K is a normalizing constant given by

$$\frac{1}{K} = \sum_{h=1}^{8} \frac{1}{\sqrt{(B'_{2h}-I)^2+(B'_{3h}-J)^2}} \qquad (3)$$

The values B'_{2h} and B'_{3h} in (2) and (3) are those values of $B_{2\ell}$ and $B_{3\ell}$ for which (1) is a minimum.

The interpolation equation, (2), is structured such that each of the eight values is weighted inversely proportional to the distance from the cell of interest and is normalized so that if the eight sample values are equal, A_{IJ} is equal to each of the eight B_{1h}.

A typical result of plotting the completely filled spatial matrix is illustrated in Figure 3. The height of the surface represents the concentration of lead in the soil. The peak near the center roughly makes the location of the smelter stack. This spatial display was generated using the field sampling sites in Figure 1. Approximately 250 cells of the spatial matrix contain field samples. Thus, approximately 3850 sample values were interpolated.

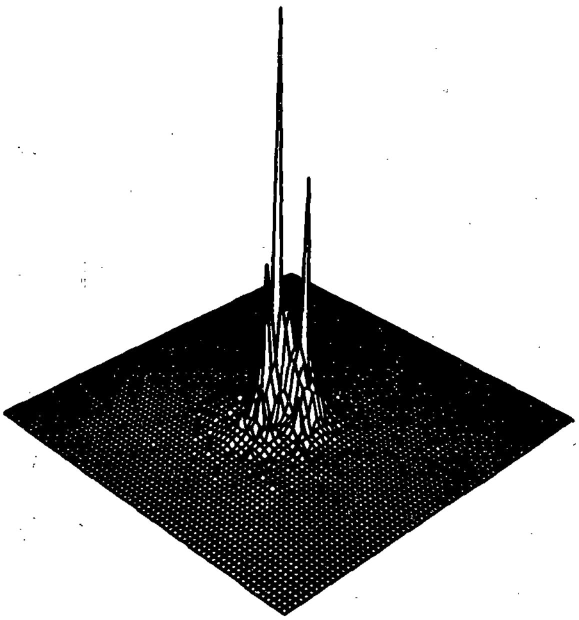

FIG. 3. Interpolated Spatial Display.

In order to separate large scale trends from highly localized effects, the spatial display of Figure 3 can be filtered. In addition, filtering smooths errors induced by the interpolation algorithm and also tends to smooth field sampling errors. This filtering is accomplished by taking the fast Fourier transform of the spatial display, filtering and inverse transforming. The fast Fourier transform used is the binary radix routine HARM of the IBM Scientific Subroutine Package [2]. This is a three dimensional transform routine, but is used in this application with only two dimensions. The filtering is accomplished by an element by element multiplication of the transformed array by a filter array. The filter used is a simple two-pole smoothing filter. The result of filtering the spatial display of Figure 3 is illustrated in Figure 4. Filtered spatial displays are also useful for generating contour maps [3]. Documentation for all computer programs utilized for generating spatial displays and filtering those spatial displays are contained in a separate report [4].

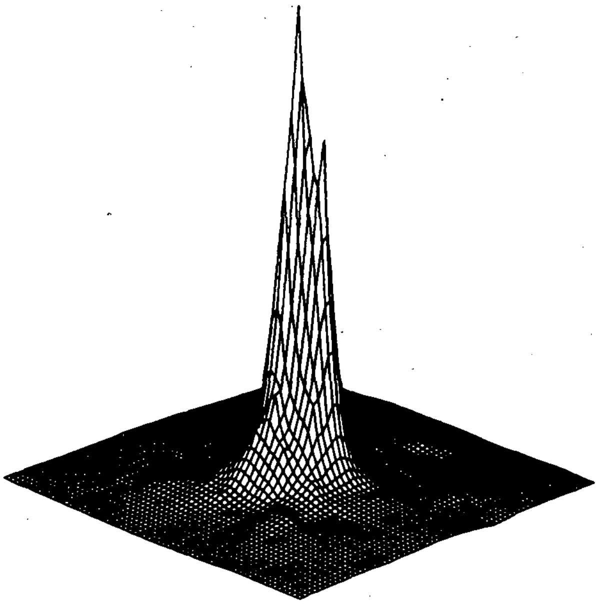

FIG. 4. Filtered Spatial Display.

Estimation Accuracy

The estimation error in generating a spatial distribution is defined as the normalized mean-square error between the interpolated spatial distribution and the true spatial distribution from which the field samples are extracted. Thus, the estimation error is calculated by first forming

$$E = \iint_A [S(x,y) - \bar{S}(x,y)]^2 dx\, dy, \quad (4)$$

where $\bar{S}(x,y)$ is the interpolated spatial distribution, $S(x,y)$ is the true spatial distribution from which the field samples are extracted and A is the study area. To be meaningful, the error must be normalized by

$$V = \iint_A S(x,y) dx\, dy, \quad (5)$$

which is the volume under the true spatial distribution over the study area, A.

The problem is to determine the total number of field samples, and the distribution of the sampling points required to form an interpolated spatial distribution, $\bar{S}(x,y)$, satisfying a given accuracy requirement.

Since the true spatial distribution, $S(x,y)$, is unknown, computer simulation is used. Two spatial distributions were simulated, one having a Gaussian shape

$$S(x,y) = ke^{-x^2/2\sigma_x^2} e^{-y^2/2\sigma_y^2} \quad (6)$$

and one having an exponential shape

$$S(x,y) = ke^{-\alpha|x|} e^{-\beta|y|} \quad (7)$$

These are illustrated in Figures 5 and 6, respectively.

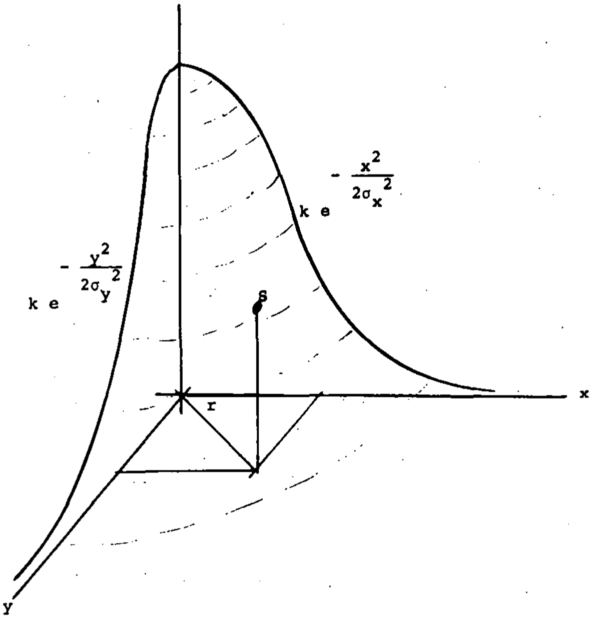

FIG. 5. Gaussian Spatial Distribution.

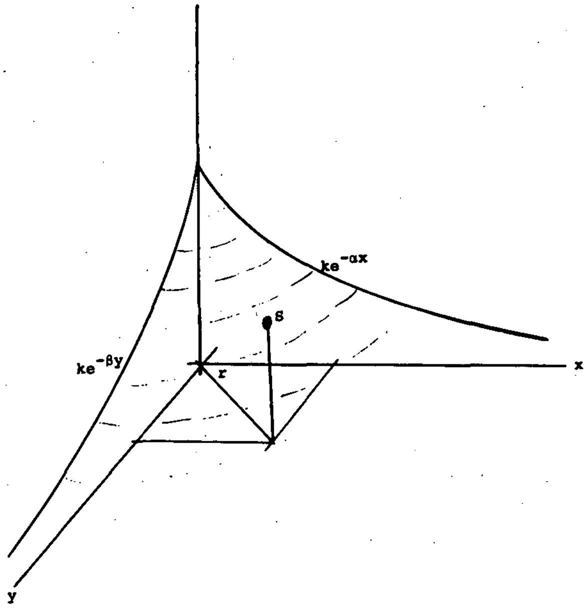

FIG. 6. Exponential Spatial Distribution.

Two different sampling profiles were assumed. For both cases, the location of the sampling site is random and defined in terms of a probability density function. For the first sampling profile, referred to as a uniform sampling profile, both the x and y coordinates of the sampling sites obey a uniform probability density function [5]. For this case, every possible sampling site is equally likely. The second sampling profile is such that the x and y coordinates of the sampling sites obey a Gaussian probability density function having zero mean and a variance of 2 units. For this case, the radial distance from the center of the study area to the sampling site r, obeys a Rayleigh probability density function [6]. For this reason, this particular sampling profile is referred to as a Rayleigh sampling profile. Since the Rayleigh profile extracts more samples where $S(x,y)$ is changing rapidly, it should give better results.

The sampling sites are defined in terms of a random variable; thus, a random number generator is used to select the sampling sites. Different selections of sampling sites can be obtained by using different "seed" numbers in the random number generator. For each simulation, three different sampling profiles, all having the same statistical properties, were generated by using three different seed numbers. The variation of estimation accuracy as the seed is changed gives an indication of the sensitivity of estimation accuracy to small changes in the sampling profile. Typical sampling profiles for uniform and Rayleigh sampling are illustrated in Figures 7 and 8, respectively.

The mean-square estimation error, as a function of the number of field samples, is illustrated in Figure 9 for a spatial distribution having a Gaussian shape. The sampling is assumed uniform. The parameters, σ_x and σ_y, which specify the spread of the spatial distribution, are both equal to unity. For the sampling profiles selected by seed numbers 30777 and 52479, the decrease in estimation error is approximately exponential up to approximately 250 field samples. Beyond this sample size, the improvement gained by collecting additional field samples is slight. The sampling profile selected by seed 13589 is obviously inferior.

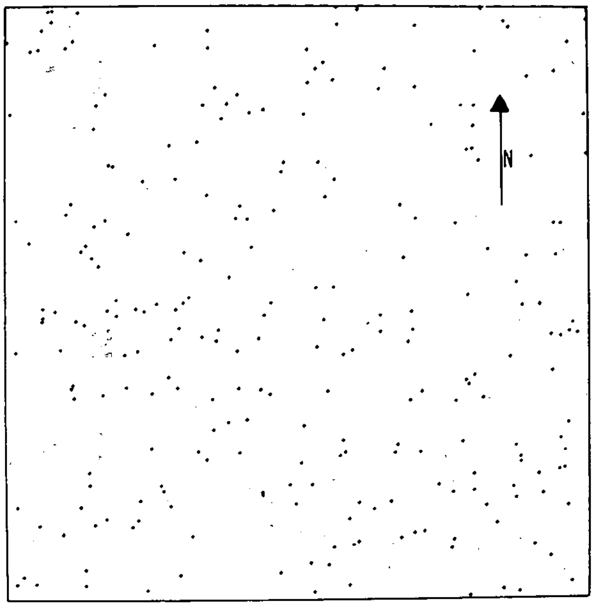

FIG. 7. Uniform Sampling Profile.

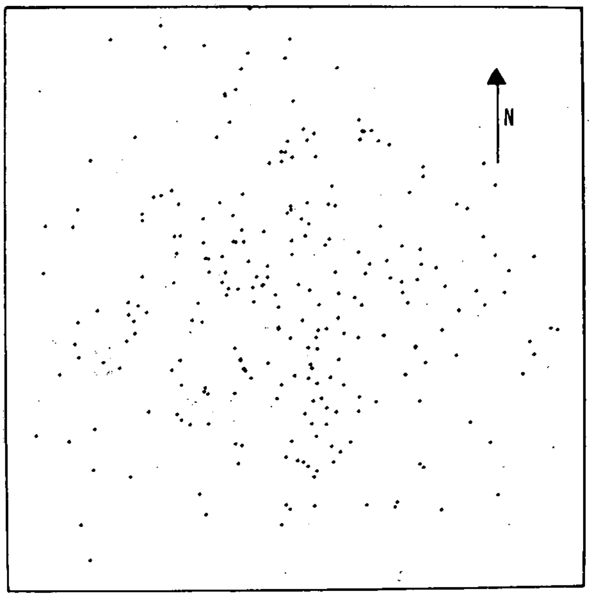

FIG. 8. Rayleigh Sampling Profile.

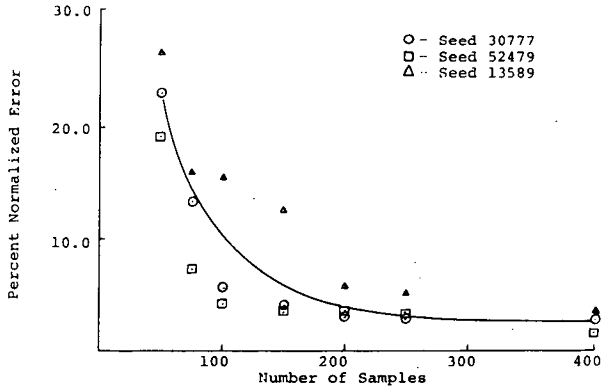

FIG. 9. Estimation of a Gaussian Distribution with Uniform Sampling.

If the same Gaussian spatial distribution is estimated using Rayleigh sampling, the estimation error behavior illustrated in Figure 10 results. It is readily apparent by comparing Figures 9 and 10 that Rayleigh sampling produces a lower error for the same number of samples after approximately 100 field samples have been collected. The improvement achieved with Rayleigh sampling is, on the average, approximately a factor of 2, if between 250 and 400 field samples are collected. In addition, the variation in mean-square estimation error is less sensitive to the sampling profile selection with Rayleigh sampling.

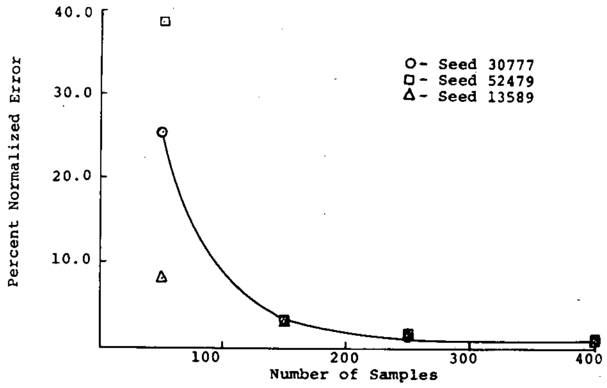

FIG. 10. Estimation of a Gaussian Distribution with Rayleigh Sampling.

The same analysis was conducted assuming an exponential spatial distribution. The results are illustrated in Figures 11 and 12 for uniform and Rayleigh sampling, respectively. For both cases, the parameters α and β, which adjust the spread of the spatial distribution, are both equal to unity. Once again, the improvement achieved with Rayleigh sampling is significant, being a factor of 2 or 3 if between 250 and 400 field samples are collected. Also, the variation in error is less sensitive to the sampling profile with Rayleigh sampling.

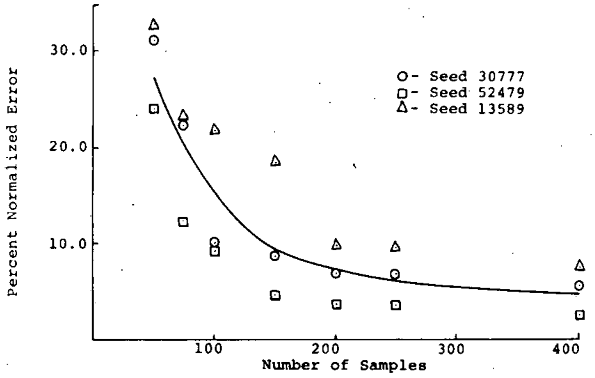

FIG. 11. Estimation of an Exponential Distribution with Uniform Sampling.

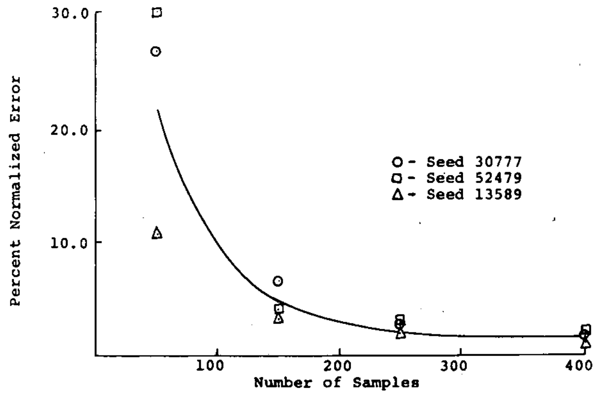

FIG. 12. Estimation of an Exponential Distribution with Rayleigh Sampling.

Conclusions

The word optimal in the context of the title is defined as the sampling profile which satisfies a given accuracy requirement at lowest cost. This typically translates into the sampling profile which satisfies a given accuracy requirement with the smallest total number of samples.

An algorithm has been presented which estimates sample values at points where field samples are lacking.

This is accomplished by a linear weighting of the eight nearest field samples. By the use of such an algorithm, the total number of samples required to form a spatial distribution can be reduced if sample values can be estimated accurately.

The technique has been applied to two simple cases; a Gaussian and an exponential spatial distribution from a point source forcing function. The result yields the number of field samples required to estimate a spatial distribution with a given mean-square accuracy. A second result is the increase in estimation accuracy obtained by increasing the size of the field sampling program. Thus, a possible way to use the technique is to collect a limited number of field samples to determine the general shape of the spatial distribution. Using this spatial distribution as the true surface, sampling profiles can be generated and the estimation accuracy computed for each profile. The field sampling program can then be completed using the best profile.

Since only two simple cases have been considered, much remains to be accomplished before general conclusions can be drawn. These include a study of the effect of a distribution of forcing functions, a study of appropriate error criteria and a study of different spatial distributions.

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Identification of Diatoms by an Optical Pattern Recognition System for Use in Water Quality Monitoring**

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Abstract

An optical pattern recognition system is described that is capable of rapidly identifying diatom species from prepared slides. The system is based on the construction and subsequent correlation of laser generated Fourier transform holograms that act as spatial frequency filters. The results of experiments relating to rotation and discrimination of various species are discussed and the importance of this rapid data gathering system to water quality control efforts.

Introduction

The development of environmental quality control techniques is a necessary prerequisite for both the management and optimal use of aquatic ecosystems. These techniques should provide rapid information of the physical, chemical and biological quality of the aquatic ecosystem. Unfortunately, the generation time of biological information has been so long that corrective actions are often initiated too late. As a result, inappropriate arbitrary controls are often imposed on industry that are likely to overprotect or underprotect the biological integrity of the receiving system.[1] The variability of the system's biological "state" is an important parameter and the more rapidly its nature is determined, the more accurately can control measures be applied, especially when coupled to information regarding the physical and chemical characteristics of the system. However, conventional methods of biological analysis often require length processing times before the necessary information is obtained. Thus, it has been difficult to fit the controls to the precise needs of the system.

This paper describes a prototype system, based on the concept of coherent optical spatial filtering, that rapidly counts and identifies diatoms from prepared slides.[1-3] The justification for using these algae for purposes of monitoring water quality has been well established by Patrick et al.[4] In addition, Kaesler and Cairns[5] have shown that the diatom portion of the aquatic microbial community is satisfactory for determining the overall structural response of the whole ecosystem. The close chemical and physical association of the diatoms with their environment allows for a relatively fast response (i.e. community structure response) to environmental perturbations.[6] The capability of rapidly monitoring this response by noting shifts in numbers of species and their abundance relationships would considerably reduce the lag time of data feedback.

Methods

The spatial filtering technique involves the optical pattern recognition and counting of diatoms. This process utilizes laser generated Fourier transform holograms as spatial frequency filters[7] that select diatoms of one particular structure from a mixed population (i.e. the system identifies a particular species from a many-species

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population). An optical filter can be constructed for any diatom of interest. Each filter contains the structural characteristics of the diatom stored as spatial frequencies. In order to identify a given diatom from an unknown sample, the diatom's filter must be optically correlated against the entire unknown sample of diatoms. Whenever there is a good correlation (i.e. a signal to noise) ratio from the matched filter a dot of light appears on an output screen. The screen is scanned in the x-y plane and all the dots, their intensities and locations are automatically recorded and stored in a computer (PDP-11-40). Orientation and size variations of diatoms can be accounted for by rotation and translation of the filter.

At the present time, the prototype system is designed to accept only 35 mm. positive transparencies of the diatom inputs. The microphotographs are taken from standard prepared diatom mounts using phase contrast microscopy. Eventually, this intermediate input preparation phase will be by-passed by interfacing the microscope directly with the optical system, thus facilating more real-time analysis.

Shown in Figure 1 is a diagram of the optical system for filter construction and correlation studies of the optical filter. The construction of the filter is accomplished by placing the diatom transparency in the Input Plane and allowing the Fourier Transform Lens (FTL) image to combine with the reference beam passing through the lens C2. The resulting image at the Filter Plan is the optical filter.

In order to carry out the correlation study of this optical filter, a transparency of unknown diatoms is inserted in the Input Plane and the reference beam is blocked. The correlation between the Input Plane and the diatom filter in the Filter Plane is outputted on the scanner mirrors G1 and G2. The image of dots corresponding to the correlation signal is then picked up by a photodiode (P.D.) and recorded (L.P.) as well as stored into a PDP-11-40 (not shown) computer. The computer analyzes the various signal to noise ratios for each diatom, determines the confidence level for the correlation signal and displays on a storage scope all the signals received. Figure 2 shows some typical signal to noise ratios for various diatoms. The rotation angle corresponds to a study of small rotations about the original axis for which the filter was made. Shown in Figure 3 is a drawing of the overall optical processor.

Discussion

Thus far, the system has been able to discriminate a variety of diatom species from a mixed population. Preliminary studies concerning diatom orientation and sizing differences have been conducted and indicate the levels of discrimination possible.[1] Further research is currently underway to determine how these levels may be improved upon, in addition to the effects of background materials present on the input slide and the difficulties of computer control of the system.

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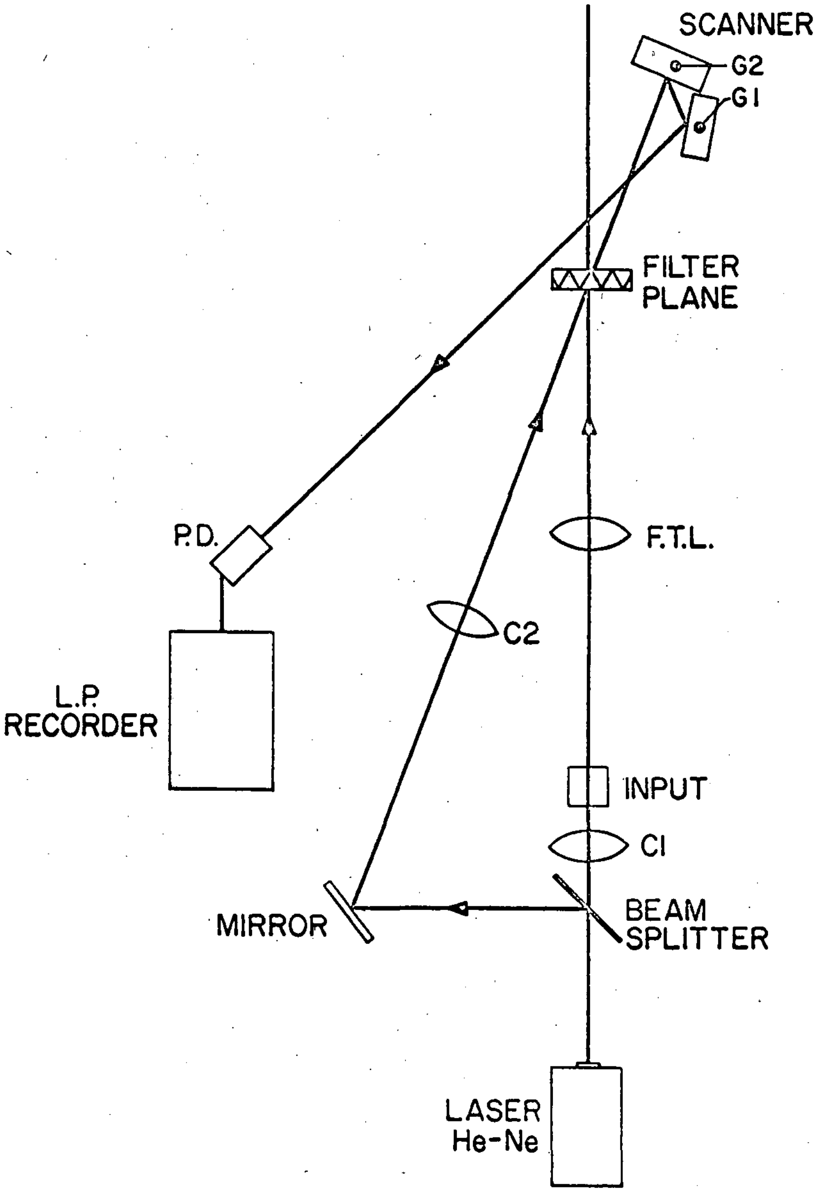

FIG. 1. Schematic drawing of the optical processor. (C1,C2) are the signal and reference beam collimators; (F.T.L.) Fourier Transform Lens; (G1, G2) the galvanometer mirror scanner; (P.D.) the photodiode detector; (L.P.) light pen recorder.

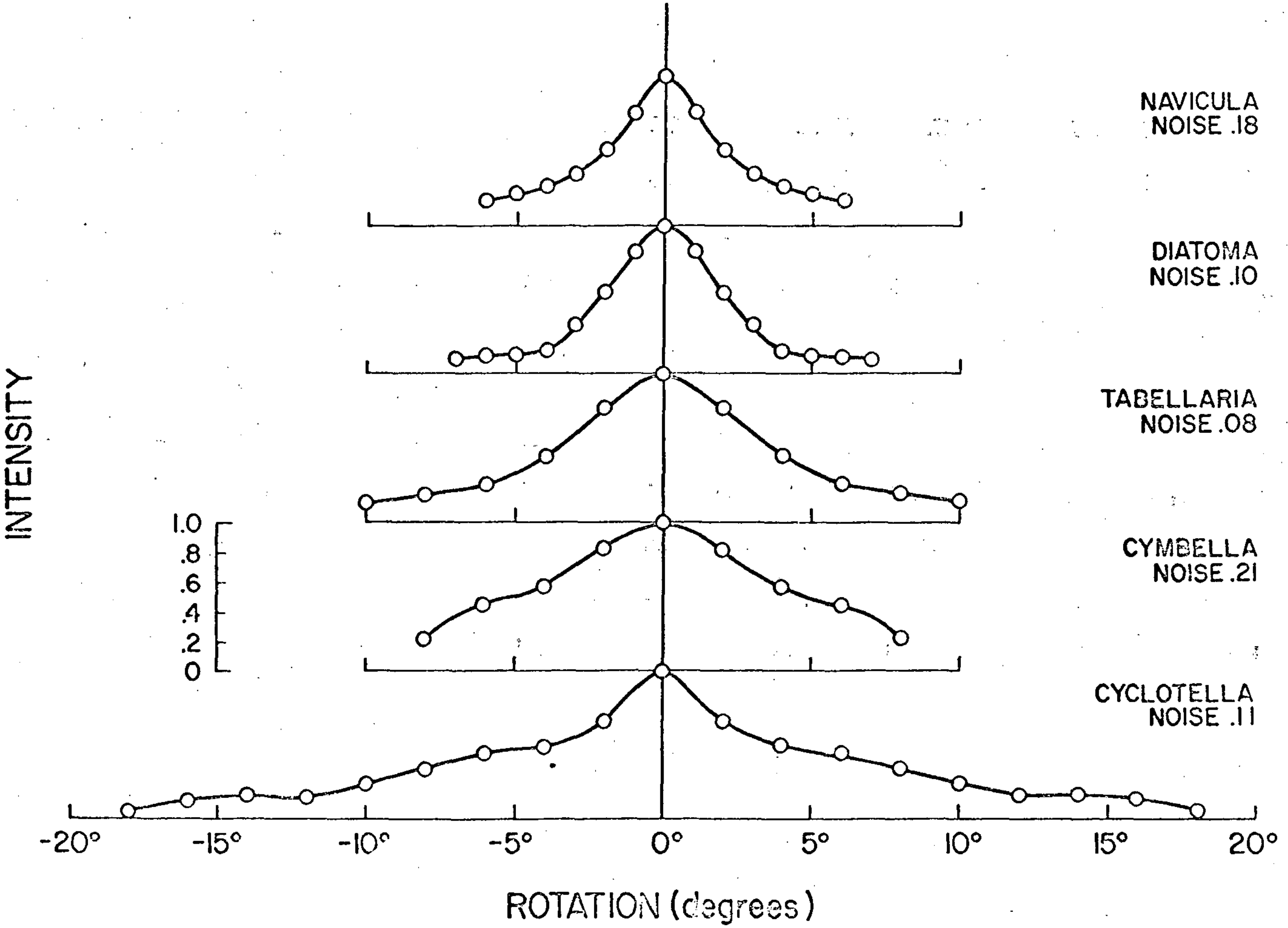

FIG. 2. Correlation function for various filters matched against the general input scene. The filter plane was rotated about its center. All intensity curves have been normalized to one.

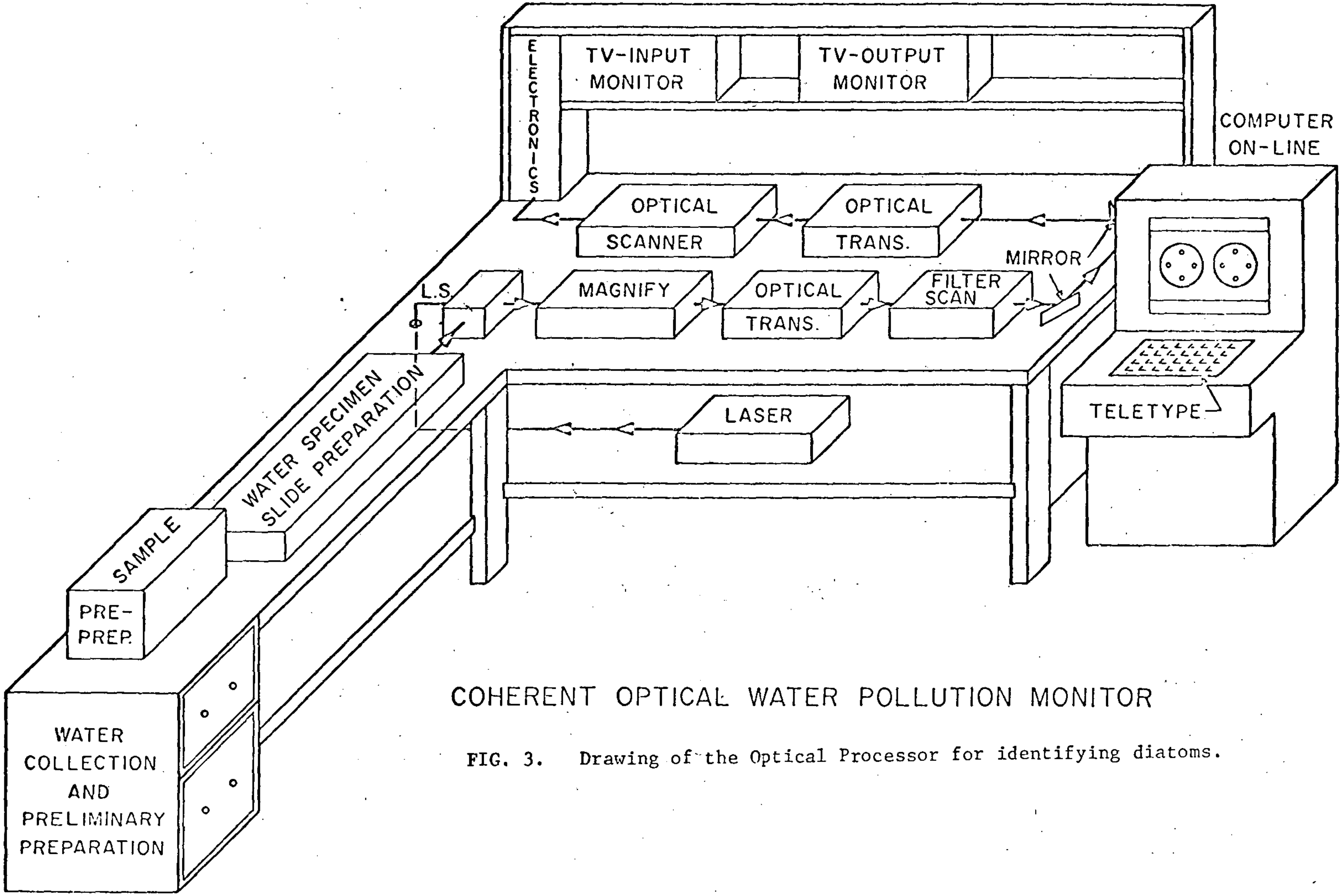

FIG. 3. Drawing of the Optical Processor for identifying diatoms.

THE APPLICATION OF FLUORESCENCE POLARIZATION IMMUNOASSAY TECHNIQUES TO THE DETECTION OF ORGANIC ENVIRONMENTAL CONTAMINANTS

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Abstract

Existing immunochemical methods for the detection of organic contaminants are reviewed, and the specific phenomenon of fluorescence polarization is discussed in detail. The essential feature of applying this phenomenon to an immunoassay consists in first labeling the contaminant of interest (antigen) with a fluorescent label, and then observing the degree of polarization of the fluorescent light when standard quantities of the labeled antigen and its antibody, together with the unknown, are allowed to interact. The dependence of polarization upon the extent of reaction between the antigen and antibody forms the basis for the quantification and immunoassay. Reaction between the antigen and antibody results in an increase in size of the kinetic unit and a retardation of the rotary brownian motion, which in turn is manifested by an increase in the polarization of fluorescence. In the presence of unlabeled antigen in the sample, a smaller percentage of the labeled antigen is bound to the antibody, and in this circumstance the polarization observed will be lower. Hence, the standard immunoassay curve which can be constructed from this type of data would show the polarization of fluorescence for certain standard chosen experimental conditions plotted as a function of the amount of unlabeled antigen, which determines the quantity of the unknown present. This detection technique is characterized by extremely high sensitivity and specificity. Recent results for a number of organic compounds of interest are presented, and include a typical pesticide, fungicide, antibiotic, and hormone.

Introduction

Immunology as a subject is logically concerned with the immunity of living organisms to harmful agents regardless of their origin, and includes resistance to disease, hypersensitive reactions as exhibited by allergic persons, and tolerance and rejection of foreign tissue, such as those encountered in organ transplants. In this case, however, we will take a more restricted view of the definition and apply it to the mechanisms and techniques involved in the detection and measurement of organic contaminants of environmental interest.

A substance which when injected into an animal stimulates the animal to produce antisera capable of reacting with the substance in a highly specific manner is referred to as an antigen, and the specific protein produced is referred to as an antibody. These antibodies belong to a group of serum proteins known as immunoglobulins. The production of these antibodies as a result of the injection of the antigen takes place over a period of many weeks, and matures after about two months. In general, "good" antigens are usually of large molecular size (>40,000), partially digestible by enzymes, and are recognized as being foreign by the antibody-producing animal. It will be recognized immediately, of course, that almost all the compounds of environmental interest, such as fungicides, herbicides, pesticides, and many other synthetic organics, do not have a large molecular weight and would appear therefore to be incapable of stimulating antibody formation. Fortunately this is not the case, and so-called partial antigens or haptens are capable of being produced and reacting with a specific antibody.

Haptens are defined as partial antigens which alone cannot induce antibody information, yet in conjugation with a suitable carrier can produce antibody against themselves as well as against the carrier-hapten complex. Examples of such carriers include ovalbumin, bovine serum albumin, fibrinogen, and many others. In summary, the hapten once conjugated with a suitable carrier can stimulate antibody production.

The remarkable feature about this antibody stimulation is that some antibody will be produced which is highly specific in its reaction with the hapten alone. It is this phenomenon which allows us to use immunological techniques in the detection and quantification of organic contaminants of relatively low molecular weight, and under a variety of practical conditions.

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Review of Immunological Techniques

Any means of applying an immunochemical reaction to a detection problem ultimately relies upon a reaction occurring between an antigen or hapten and its specific antibody. Perhaps the most general means by which this interaction can be employed in measurement and detection has come to be known as "competitive binding assay". In practice, this method requires two essential reagents. These are a labeled form of the substance to be detected or measured and an antibody specifically directed against this substance. The principle of the assay involves a preliminary measurement of the binding of the labeled antigen (substance being detected) with its antibody and then, a determination of the extent of the *inhibition* of this binding by known quantities of the unlabeled antigen, which corresponds to the unknown. From these data, a standard curve can be constructed which shows the degree of binding by the labeled antigen under certain specified standard conditions as a function of different amounts of the unlabeled antigen or unknown added.

The usual method of labeling the antigen to be identified requires the introduction of a radioactive label. When such a radiolabel is used, an essential and crucial step in the radio-immunoassay (RIA) is to separate physically that portion of the labeled antigen which is bound to the antibody from that which is unbound or free. Only in this way is it possible, by radioactive counting, to determine what fraction of the radiolabel remains bound, or is being bound, in the presence of the unknown.

Alternatively, a simple direct way of implementing competitive binding principles in an immunoassay is to employ a fluorescent label instead of a radiolabel. The fluorescent label then allows the assay to be carried out in principle either by fluorescence polarization measurements, or in some cases by fluorescence intensity measurements. Unlike RIA, no separation of the bound and free forms of the labeled antigen is necessary, since a simple, rapid optical measurement gives the essential information without any physical separation whatsoever.

The application of the immunological techniques to the analysis of residue amounts of organic contaminants appears to be of relatively recent origin, and Ercegovitch[1] in 1971 gave an excellent review of work in this area. This appears to be limited to work carried out by him at Pennsylvania State University on the herbicide aminotriazole and on parathion with sensitivities in the microgram range, and by Centeno[2] and Haas and Guardia,[3] using a tanned cell hemiglutination inhibition test with detection limits of 0.1 μg and 1.0 μ for DDA and malathion, respectively. At approximately this time Dandliker had also been successful in developing antibody to DDA, and used it in a more refined immunological technique with potential detection sensitivity in the subnanogram-to-picogram range. This technique is referred to as a fluorescence polarization immunoassay.

The Physical Basis of Fluorescence Polarization Immunoassay

To adequately understand the basic principles of fluorescence polarization in an immunoassay, some basic discussion of the polarization phenomenon itself must be presented. In classical terms, the emission from a single molecule may be regarded as radiation from a single oscillating dipole; this radiation has an oscillating electric field parallel to the direction of oscillation of the dipole and is said to be polarized in the same direction.

For simplicity, assume that the direction of the absorption and emission oscillators in a single molecule are the same and that they are rigidly fixed with respect to the geometric axis of the molecule. Furthermore, assume the molecule is to be rigidly fixed in position during the interval between absorption and emission (typically 10^{-8} sec). The probability of absorption of light is proportional to the square of the magnitude of the component of the electric vector of the exciting light in the direction of the oscillator. This probability is proportional to $\cos^2\theta$, where θ is the angle between the incident field E which is parallel to the Z axis, and the direction of the absorption oscillator. Because the probability of absorption falls off as θ increases, molecules oriented so that θ is small are preferentially excited, while those with large θ have little chance of absorbing. Since the absorption and emission oscillators are parallel, the emitted light will be partially polarized with a degree of polarization P. This quantity is defined[4] in terms of the intensities, I, polarized either parallel or perpendicular to the incident electric field.

It can be shown by suitable integrations that the maximum value of P that can be observed with linearly polarized light is one half. Now if the molecules are subject to rotary brownian motion instead of being rigidly fixed, then the molecular rotation taking place between the time of absorption and emission may be expected to result in values of P lying between one-half and zero.

The dependence of polarization upon the extent of reaction between the antigen and antibody forms the basis for the quantification and immunoassay. Reaction between the antigen and antibody results in an increase in size of the kinetic unit and in retardation of the rotary brownian motion, which in turn is manifested by an increase in the polarization of fluorescence. In the presence of unlabeled antigen in the sample a smaller percentage of the labeled antigen is bound to the antibody, and in this circumstance the polarization observed will be lower. Hence, a standard immunoassay curve, which can be constructed from this type of data, would show the polarization of fluorescence for certain standard chosen experimental conditions plotted as a function of the amount of unlabeled antigen, which essentially determines the unknown.

Preparation of Reagents Required for the Assay of Environmental Contaminants

Basically, two techniques are available for the synthesis of the fluorescent derivatives: first, classical organic syntheses, and second, free radical labeling. The organic synthesis adopted clearly depends on the structure of the contaminant itself and will vary widely. Alternately, a mixture of the substance to be labeled, together with a fluorescent dye, is irradiated. The multiplicity of free radicals formed during the irradiation then affords a mixture of compounds, some of which will generally be fluorescent-labeled derivatives.

The choice of dye involves the consideration of several factors, the most important being that the wavelength of excitation and emission should be chosen so as to minimize interference from any other fluorescent molecules which happen to be present in the samples to be tested. A wide range of dyes is available for labeling purposes, and includes fluorescein, dansyl, and indocyanine green.

The preparation of an antibody against a contaminant begins by coupling the pesticide to a highly immunogenic molecule such as ovalbumin, and introducing the complex into rabbits by means of intradermal injections. The initial immunization yields "primary response" antibodies, which are usually of fairly low specificity. Booster immunizations can be given and secondary response antibody collected, which is generally more specific and of higher titer.

Experimental Results

A number of assays have been conducted using this technique, and the resulting sensitivity and specificity have been extremely encouraging.

A specific example of the curves obtained for an assay of 2-Aminobenzimidazole is shown in Figures 1 and 2, where the rate of change of polarization as a function of time for varying concentrations of inhibitor is given. The resulting standard inhibition curve is shown in Figure 3, from which one can conclude that a detection limit of 300 pg/ml can be obtained.

To obtain a measure of the specificity, an inhibition experiment was carried out using benzimidazole as opposed to 2-Aminobenzimidazole, the structures of which are shown in Figure 4. The rate of change of polarization with benzimidazole are found to be two orders of magnitude slower than with 2-Aminobenzimidazole, which indicates a remarkably good specificity considering that no special effort had been made to obtain high specificity antibody. In Figure 5 the results of the assay of a number of other organic compounds are shown, together with their detection sensitivity.

Conclusions

In conclusion we see that a new assay technique for organic compounds has been developed which has a high degree of specificity and a detection sensitivity in the nanogram-to-picogram range. The assay is rapid and can be carried out by personnel with very little training, which makes it particularly valuable for field use.

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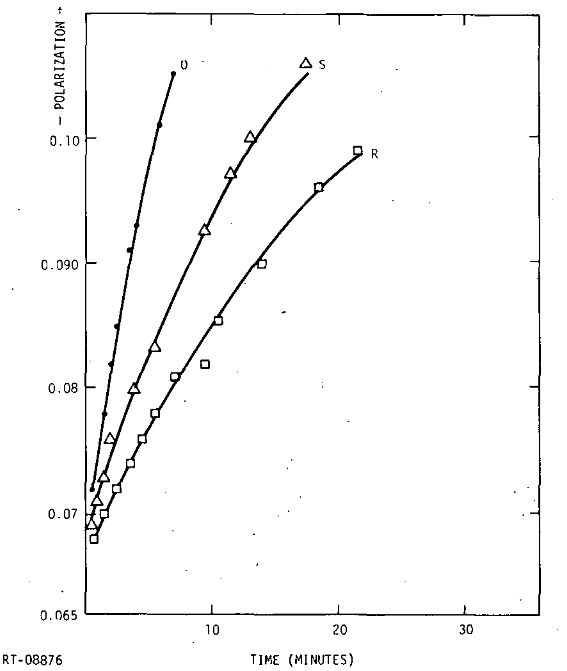
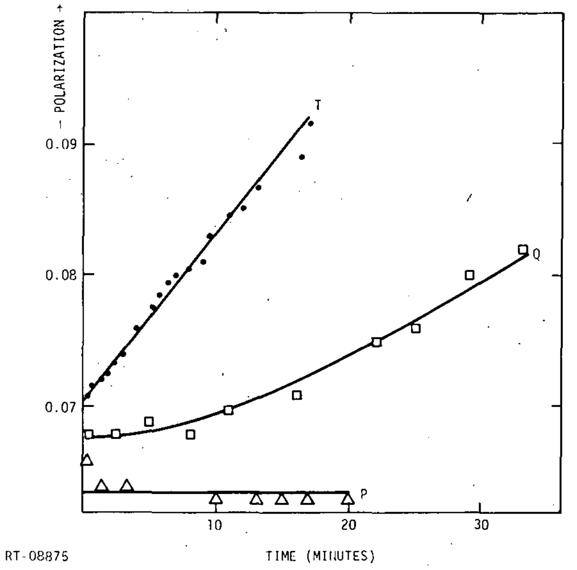


RUN	INHIBITION LEVEL (M)	$(dP/dt)_i$	LOG $(R_1 \times 10^4)$	INHIB. (ng/ml)	LOG CONCEN. (ng/ml)	LOG CONCEN. (pg/ml)
O	0	6.7×10^{-3}	1.83	0	---	--
S	3.33×10^{-8}	3.2×10^{-3}	1.51	4.43	0.644	3.64
R	10^{-7}	1.9×10^{-3}	1.28	13.3	1.124	4.12

Fig. 1. Rate of change of polarization as a function of inhibitor concentration



RUN	INHIB. LEVEL (M)	$(dP/dt)_i$	LOG $(R_1 \times 10^4)$	INHIB. (ng/ml)	LOG CONCEN. (ng/ml)	LOG CONCEN. (pg/ml)
T	3.3×10^{-7}	1.26×10^{-3}	1.10	44.3	1.644	4.64
Q	10^{-6}	3.9×10^{-4}	0.59	133	2.124	5.12
P	10^{-5}	0	--	1330	3.124	6.12

Fig. 2. Rate of change of polarization as a function of inhibitor concentration

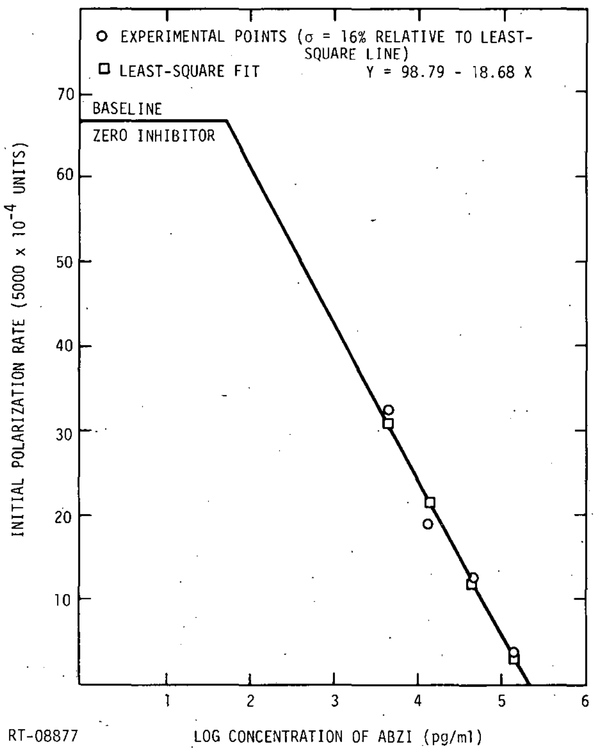
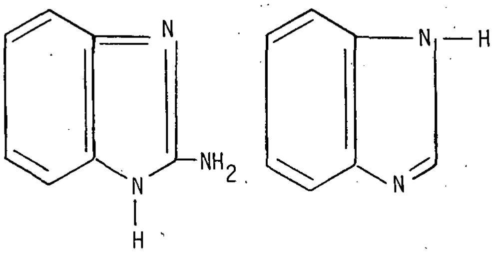


Fig. 3. Standard inhibition curve



2-Aminobenzimidazole (MW = 133)

Benzimidazole (MW = 118)

Fig. 4. Structure of benzimidazole and 2-Aminobenzimidazole

Compound	Detection Limit (g/ml)
DDA	0.5×10^{-9}
2-Aminobenzimidazole	300×10^{-12}
Penicilloyl Hapten	1×10^{-9}
HCG	100×10^{-12}
Diethystilbestrol	100×10^{-9}

Fig. 5. Detection limits of some compounds of interest

TRACE ELEMENT DISTRIBUTIONS ON WALKER BRANCH WATERSHED[1]

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ABSTRACT

Distributions (g/ha) of cadmium, lead, and zinc on Walker Branch Watershed, a forested ecosystem in east Tennessee, were developed from data on concentrations of these elements in leaves, branches, bole, roots, and litter for four major forest types of this system. Tree species used in these budget calculations accounted for greater than 85% of the total standing crop of aboveground vegetation. Forest types consisted of shortleaf pine, oak hickory, chestnut oak, and yellow poplar and included both overstory and major understory (redbud, black gum, dogwood, etc.) species. Element concentrations were determined on pooled samples by isotope dilution spark source mass spectrometry (IDSSMS).

The elemental budgets indicate that, on Walker Branch Watershed, the organic litter compartment contains the greatest percentage of accumulated cadmium, lead and zinc. Of the living components, the lateral roots have the greatest accumulation of these three elements. These ecosystem compartments exhibiting accumulation are suggested as possible loci for primary toxic effects.

INTRODUCTION

The understanding of natural processes governing circulation of trace toxic elements in the biosphere is a prerequisite for assessment of the environmental behavior of these materials. Long-term ecological behavior of trace elements including pathways and rates of dispersion, residence times in various components of ecosystems, and chemical transformations are largely unknown. In an effort to develop the information necessary for evaluation of ecosystem cycling of trace elements, distributions of the trace metals cadmium, lead, and zinc have been determined for the major vegetation components of a forested watershed in east Tennessee (Walker Branch Watershed). Initially, concentrations of these three elements were determined in both overstory and understory species comprising 88% of the vegetative biomass on Walker Branch Watershed. These data represented our first year's effort as was reported at the first Annual NSF Trace Contaminants Conference.[1] During the current year, these concentration data have been combined with vegetative biomass data obtained in the IBP-Eastern Deciduous Forest Biome program[2] to arrive at distributions of cadmium, lead, and zinc accumulation in vegetation on Walker Branch Watershed. The purpose of determining distributions of trace metals in natural forested ecosystems is to assist in identifying sites of accumulation (species or ecosystem compartments) and critical ecosystem pathways. This type of inventory is essential to implementation of forest ecosystem models of trace element circulation. Jointly these models and established data bases may then be used in developing monitoring strategies for other forested ecosystems by defining the critical pathways and ecosystem components which must be included in a routine surveillance program. Development of monitoring strategies for trace toxic elements is a major contribution of this research. Proper implementation of these strategies can maximize the amount of information obtained while minimizing the number and kinds of samples to be obtained.

SITE DESCRIPTION

Walker Branch Watershed is located on the U. S. Atomic Energy Commission's Oak Ridge Reservation in eastern Tennessee. The 97.5-ha watershed ranges in elevation from 265 to 360 m above sea level and is underlain by dolomitic limestone. Streamflow from the watershed is

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[1] This work was supported by the National Science Foundation — RANN Environmental Aspects of Trace Contaminants Program under NSF Interagency Agreement AG-389 with the U.S. Atomic Energy Commission.

[2] Operated by Union Carbide Corporation for the U.S. Atomic Energy Commission — Contract Number W-7405-eng-26.

measured with calibrated V-notch weirs; precipitation is monitored at five sites with recording rain gauges. Samples for analysis of the chemical composition of rain, dry particulate fallout, and streamflow are collected at these gauging stations. Detailed descriptions of the watershed and its facilities are available.[3-5]

The climate of the Oak Ridge area is typical of the humid Appalachian region. Mean annual precipitation is about 136 cm and temperature averages 14.7°C. Streamflow from the watershed averages 52% of the precipitation with the remaining 48% being lost through evapo-transpiration. The detailed hydrologic cycle of Walker Branch has been characterized,[4] and simulation models are being developed for prediction of the dynamic responses of mineral cycles to environmental variables.

Soils of the Fullerton and Bodine series occupy greater than 95% of the watershed area.[5] These soils are classified as typic paleudults (formerly termed red-yellow podzolics) and are well drained, acid, infertile, and commonly contain abundant chert. These are residual soils formed over the weathering dolomitic bedrock. Most of the watershed is composed of slopes ranging from 10 to 60%.

Forest vegetation of the watershed has a mean basal area of 20.8 m^2/ha and is typical of the oak forests of the Ridge and Valley Physiographic Province. Four major associations of overstory vegetation are present:[6] pine, yellow poplar, oak-hickory, and chestnut oak. The pine association is composed primarily of shortleaf pine (Pinus echinata) with lesser amounts of Virginia pine (P. virginiana) and generally occurs on ridge tops. The yellow-poplar (Liriodendron tulipifera) type occurs along stream channels and on lower slope positions. Chestnut oak (predominantly Quercus prinus) occupies more xeric ridge positions. The oak-hickory (Quercus spp. - Carya spp.) association occurs on slope positions intermediate between the ridge tops and stream bottoms.

MATERIALS AND METHODS

Forest Inventory Data. The vegetation inventory system consists of 298 permanent, nested circular plots which were established using a stratified random design.[6] Initially, in 1967, each tree >1.2-cm DBH was identified by species, assigned a permanent number, tagged at 1.5 m aboveground and measurements of diameter and height were recorded.[3,6] Frequency of trees <1.2-cm DBH within 60-cm-height classes was recorded by species. Resurvey measurements (1970 and 1972) included DBH, mortality since plot establishment (recorded separately for standing dead and fallen stems), and ingrowth (growth of trees into the next largest diameter class). The total survey represents information on ∿11,000 stems >1.2-cm DBH. These data form the basis for describing biomass pool sizes, and dynamics associated with ingrowth, outgrowth, mortality, and transfers to woody litter. The present summary of trace element distribution is based on the 1970 stand inventory for trees >1.2-dm DBH.

Biomass Estimation Procedures: Aboveground Components. Estimates of aboveground forest biomass were based on allometric relations between various weight components (i.e., branch, bole, and foliage) of individual trees and their DBH. Allometric relations were derived from extant dry-weight data collated by Sollins and Anderson[7] for about 40 species in the southeastern U.S. including about 250 trees with DBH >10 cm. Even with this large amount of harvest data, only a few species were sufficiently well represented along a range of DBH to warrant derivation of single species allometric relations.[8] Therefore, regressions were developed from the pooled data.[2]

Biomass Estimation Procedures: Belowground Components. Estimation of belowground biomass pools utilized two procedures. Stump weight, defined as the central root plus large laterals to a 60-cm radius, was obtained from regression analysis on DBH.[2] Lateral root biomass beyond the 60-cm radius was determined from excavation of soil pits (75 by 75 cm) to the depth of the major rooting zone (∿60 cm). Excavated soil was dry sieved in the field; root organic matter was returned to the laboratory, washed in tap water over sieves, and dried at 100 C. Periodic microscopic examination indicated this washing treatment was sufficient to remove soil material without damaging root structure. Ash values of roots >0.5 cm diam were comparable to ash values of aboveground woody material (5-8% dry wt). Ash values of roots <0.5 cm diam were higher on the average, but did not exceed 15% dry wt.

Litter Organic Matter Estimates. For each forest type, six plots representative of a range of slope (5 to 55%) were sampled intensively to determine litter pool sizes and annual variation.[9] At intervals of two to three months, three 1-m^2 subplots were randomly selected on each of the 24 permanent inventory plots. Woody material >2.5-cm diam was removed from this entire subplot. A 0.25-m^2 subarea was used to obtain samples of O_1 and O_2 litter for weight and element content analyses. The separation of O_1 and O_2 litter horizons was accomplished in the field on the basis of O_1 organic material being recognizable to species and O_2 being branches and twigs (<2.5-cm diam) from other O_1 material was completed in the laboratory. Woody litter (material >2.5-cm diam) inputs were estimated from windfall estimates of permanently tagged trees averaged over the entire forest type.

Trace Element Analyses. Samples of vegetation and soil were obtained from transects on Walker Branch Watershed.[1] Vegetation sampling (leaves, first year twigs, branches and bole) was confined to the 11 major tree species (listed in Table 1); trace element content of root material was determined from samples of root mass collected during excavations of soil pits in representative stands of major forest types. Litter samples consisted of O_1 and O_2 horizons from representative plots of each major forest type. Trace element content (Cd, Pb and Zn) was determined by isotope dilution spark source mass spectrometry (IDSSMS) and are accurate to ±5%. Detailed procedures of treatment during chemical analysis are summarized elsewhere.[1]

RESULTS

Concentrations of Cd, Pb and Zn in biomass and organic matter components of forests on Walker Branch Watershed are summarized in Table 1. Species sampled comprise 88% of the total forest biomass, and are representative of both overstory and understory species. Lead concentrations generally were higher in components of hickories, black gum, dogwood, sourwood and black oak. Shortleaf pine, hickories, dogwood, sourwood and black gum exhibited above-average levels of Cd, while only hickories and black oak contained above-average levels of Zn. Generally trace element concentrations in O_2 litter were higher than those in O_1 litter. Lead and Zn concentrations of O_1 and O_2 litter horizons in the pine forest type were similar, while Cd levels in oak-hickory O_2 litter were 3X lower than levels in the O_1. Trace element concentrations in root tissues were consistently higher in roots <0.5-cm diam. Concentrations of Cd, Pb and Zn in roots <0.5-cm diam were equal to or greater than the arithmetic average of trace element levels in foliage.

Trace element concentrations (Cd, Pb and Zn) in woody species and litter, and above- and belowground biomass of major forest types (Table 2) were used to estimate the accumulations of these metals in

Table 1

Summary of Trace Element (Cd, Pb and Zn) Concentrations of Biomass and Organic Matter Components on Walker Branch Watershed

Species	Element (ppm)								
	Pb			Cd			Zn		
	Foliage	Branch	Bole	Foliage	Branch	Bole	Foliage	Branch	Bole
Shortleaf Pine	4.2	1.0	0.35	0.48	0.3	0.21	10	6.3	3.5
Chestnut Oak	3.2	1.3	0.65	0.16	0.11	0.02	14	1.4	0.2
Red Maple	3.2	5.9	1.6	0.17	0.34	0.24	19	13.0	8.2
Hickories	7.8	4.9	2.8	0.38	0.39	0.33	36	11.0	14.0
Tulip Poplar	2.7	3.1	0.63	0.29	0.03	0.03	15	4.8	2.6
White Oak	3.0	1.6	0.44	0.12	0.03	0.05	18	3.6	3.1
Red Oak	2.1	0.8	0.74	0.35	0.08	0.11	17	3.4	3.1
Blackgum	6.0	4.6	0.64	0.38	0.06	0.12	15	9.6	5.8
Dogwood	10.4	5.2	2.8	1.10	0.04	0.31	16	12.0	5.3
Sourwood	4.1	3.6	4.0	0.84	0.24	0.15	21	6.0	3.7
Black Oak	5.2	3.5	2.2	0.69	0.30	0.14	28	9.7	5.3

Forest Type

	Yellow Poplar			Chestnut Oak			Oak Hickory			Pine		
	Pb	Cd	Zn	Pb	Cd	Zn	Pb	Cd	Zn	Pb	Cd	Zn
	ppm											
Litter												
O_1 leaf	31	0.79	58	27	0.42	42	25	0.62	48	31	0.26	56
O_2	42	1.00	130	51	0.81	110	35	0.20	125	37	0.60	59
Roots												
< 0.5 cm diam	12	0.74	59	9.2	0.57	24	25	0.33	35	7.4	0.43	40
.5–2.0	3.1	0.15	14	3.7	0.34	16	8.3	0.33	20	2.0	0.3	16
> 2.0	2.4	0.33	14	1.8	0.23	12	3.6	0.36	14	1.7	0.2	10

Table 2

Summary of biomass for forest types on Walker Branch Watershed[a]

Component	Forest type			
	Yellow Poplar	Chestnut Oak	Oak Hickory	Pine
	kg/ha X 10³			
Foliage	3.9	4.7	4.2	4.6
Branch	21.2	30.3	26.9	27.2
Bole	83.5	102.9	90.5	89.6
Stump	15.3	19.0	16.1	17.0
Roots >2.0	3.2	2.9	8.1	1.8
Roots 0.5–2.0 cm	5.5	4.6	6.4	5.8
Roots <0.5	7.9	7.5	9.3	6.8
O_1	6.6	7.0	8.7	10.9
O_2	7.5	18.4	18.1	15.7

[a] After Harris et al. 1973.

organic matter of the watershed area. As an example of the pattern observed, Table 3 summarized the distribution of Pb in aboveground biomass among major tree species in the oak-hickory forest type. Trace element accumulation generally follows the biomass contribution of each species; exceptions are those species known to accumulate trace elements (e.g., hickories, red maple).

Table 3

Lead Distribution Among Major Species in Oak-Hickory Forest Type

Species	% of Total Biomass	g/ha				% of Total Lead
		Foliage	Branch	Bole	Total	
Shortleaf Pine	0.67	0.07	0.22	0.25	0.54	0.23
Chestnut Oak	20.0	1.91	5.96	10.38	18.25	7.7
Red Maple	5.1	1.58	16.75	14.67	33.0	14.0
Hickories	23.6	7.30	33.60	66.80	107.7	45.7
Yellow Poplar	2.8	0.53	4.20	2.97	7.7	3.3
White Oak	28.8	1.36	5.05	4.75	11.16	4.7
N. Red Oak	0.3	0.10	0.25	0.93	1.28	0.54
Blackgum	2.7	1.51	6.70	2.95	11.16	4.7
Dogwood	0.04	0.55	1.10	1.60	3.25	1.4
Sourwood	4.7	1.36	5.16	16.58	23.1	9.8
Black Oak	6.2	0.70	3.50	7.80	12.0	5.1
All others	5.1	0.61	2.44	3.70	6.75	2.9
Total	100.0	17.58	84.75	133.31	235.89	100.0

Table 4

Standing pools in three size classes of lateral roots on Walker Branch Watershed

Size Class	Forest Type			
	Yellow Poplar	Oak-Hickory	Chestnut Oak	Pine
	Cadmium (g/ha)			
<0.5 cm	6	3	5	3
0.5–2.0 cm	1	2	2	2
>2.0 cm	1	1	1	1
Total	8	6	8	6
	Lead (g/ha)			
<0.5 cm	95	198	73	58
0.5–2.0 cm	17	46	20	11
>2.0 cm	7	11	6	5
Total	119	255	99	74
	Zinc (g/ha)			
<0.5 cm	466	277	189	316
0.5–2.0 cm	77	110	88	88
>2.0 cm	43	43	37	31
Total	586	430	314	435

Trace element pools of Cd, Pb and Zn contained in root biomass are summarized in Table 4. Biomass data from the limited number of root pits (N=10) were averaged over all forest types. These mean lateral root biomass estimates are: 7.9x10^3 kg ha^{-1} roots <0.5 cm diam); 5.5x10^3 kg ha^{-1} (roots 0.5-2.0 cm diam) and 3.1x10^3 kg ha^{-1} roots >2.0 cm diam). Thus, differences among trace element contents are attributable to concentration differences in this treatment. Root biomass (average of all forest types) in the size classes, <0.5-cm diam, 0.5-2.0 cm diam and >2.0-cm diam, was distributed in the ratio of 2.55:1.77:1. With respect to Cd, only distribution in the oak-hickory and pine forest types approaches this ratio. Distribution of Cd in yellow poplar and chestnut oak forest types reflects higher concentrations in roots <0.5-cm. Distribution of Pb and Zn reflect consistently higher concentrations in roots <0.5-cm diam. Present analyses do not distinguish whether trace elements are incorporated in root tissue, absorbed on soil particles on root surfaces or associated with mycorrhiza.

Among forest types, litter organic matter as O_1-leaf averaged 8.3 x 10^3/kg ha^{-1} (36% of total litter) and O_2 averaged 14.9 x 10^3 kg ha^{-1} (Table 5). Trace element distribution in litter was similar with an average of 28% of the litter-cadmium, 32% of litter-lead and 27% of litter-zinc found in the O_1 litter compartment. There were two notable exceptions. In the oak-hickory type, 60% of the litter-cadmium was in the O_1-leaf compartment; this probably reflects the high leaf concentrations observed in hickories and the relatively slow decay rates of hickory leaf litter (W. A. Thomas, unpublished data). In the chestnut oak forest type, O_1 leaf litter contained only 13 - 17% of Zn, Cd, Pb pools. Low foliar concentrations in the dominant <u>Quercus prinus</u> may account for this distribution pattern.

The contributions of each forest type to the total accumulation of Cd, Pb and Zn on Walker Branch Watershed were estimated from the mean trace element pools in each forest type, as well as the transitional

Table 5

Standing pools of cadmium, lead, and zinc in O_1 and O_2 litter components for four forest types on Walker Branch Watershed

Forest type	O_1 organic matter (10^3 kg/ha)	Pollutant conc in O_1 leaf (g/ha)			O_2 organic matter (10^3 kg/ha)	Pollutant conc in O_2 leaf (g/ha)		
		Pb	Cd	Zn		Pb	Cd	Zn
Pine	10.9	338	2.8	610	15.7	580	9.4	926
Chestnut oak	7.0	189	2.9	294	18.4	938	14.9	2024
Oak-hickory	8.7	217	5.4	418	18.1	633	3.6	2262
Yellow poplar	6.6	204	5.3	382	7.5	315	7.5	975
Mean	8.3	237	4.1	426	14.9	616	8.9	1546

stands, and the percent of the watershed area occupied by each forest type (Tables 6, 7, and 8). Deviations of trace element distribution from that which would be expected on a simple area basis are attributable to the characteristics of the dominant species. Shortleaf pine bolewood, for example, exhibits low concentrations of Pb, average concentrations of Zn and high concentrations of Cd. Chestnut oak bolewood, on the other hand, exhibits low concentrations of Cd, Pb, and Zn.

Table 6

Above-ground standing pool of cadmium (g/ha) by forest types and vegetational components on Walker Branch Watershed

	Forest type				
	Yellow Poplar	Oak Hickory	Chestnut Oak	Pine	Transition
% Area	8.1	10.7	12.1	14.8	54.0
Area (ha)	7.9	10.4	11.8	14.4	52.7
			g/ha		
Foliage	1.2	1.3	1.3	1.8	1.3
Branch	3.2	5.3	4.1	5.2	3.6
Bole	8.5	13.6	7.5	13.3	10.4
Total	12.9	20.1	12.9	20.2	15.3
% of Total	6.5	13.4	9.8	18.6	51.7

Table 7

Above-ground standing pool of lead (g/ha) by forest types and vegetational components on Walker Branch Watershed

	Forest type				
	Yellow Poplar	Oak Hickory	Chestnut Oak	Pine	Transition
% Area	8.1	10.7	12.1	14.8	54.0
Area (ha)	7.9	10.4	11.8	14.4	52.7
			g/ha		
Foliage	13.6	17.6	14.9	16.6	15.6
Branch	70.3	84.8	58.3	46.6	65.0
Bole	88.4	133.3	87.4	99.9	100.6
Total	172.4	235.6	160.7	163.1	181.2
% of Total	7.7	13.9	10.8	13.3	54.2

Table 8

Above-ground standing pool of zinc (g/ha) by forest types and vegetational components on Walker Branch Watershed

	Forest type				
	Yellow Poplar	Oak Hickory	Chestnut Oak	Pine	Transition
% Area	8.1	10.7	12.1	14.8	54.0
Area (ha)	7.9	10.4	11.8	14.4	52.7
			g/ha		
Foliage	64.8	81.1	71.0	54.8	71.8
Branch	140.8	116.9	115.7	148.0	141.8
Bole	364.6	541.9	240.5	378.5	378.1
Total	570.2	720.1	427.2	581.3	591.6
% of Total	8.0	13.2	8.9	14.8	55.1

DISCUSSION

These budget calculations utilize analytical results from pooled samples of biomass and organic matter components. While analytical errors are within ±5% of the reported values of Cd, Pb and Zn levels, estimates of biological and spatial variability of trace element content cannot be obtained from pooled sample analyses. Conclusions drawn from such a general survey should only serve to guide such additional analyses as are necessary to establish patterns of biological and spatial variation, and to suggest directions for research on loci of trace element accumulation in the ecosystem and the potential effects of accumulation on biological processes.

A principle functional attribute of ecosystems is the recycling of essential elements through processes of uptake, accumulation, and death of autotrophic components, and microbial immobilization and mineralization of element content in detritus. This same complex of biological processes would influence the transport and accumulation in ecosystems of nonessential, potentially toxic, trace elements. In the context of biogeochemical cycles, carbon (as organic matter) and water can conveniently be viewed as "carrier" systems, alternately acting to transport or accumulate elements.

Given that elemental input to the ecosystem is a continuing process, it can be expected that during the course of time, phenomena of bioaccumulation, differential uptake and chemical fixation can lead to accumulation or conservation of mineral elements essential to the continued growth or maintenance of the ecosystem. For Walker Branch Watershed, accumulation and conservation of nitrogen at the expense of considerable energy (carbon) has been shown.[9,10] It has also been established from input-output relationships that the Watershed is accumulating trace elements (Anders Andren, unpublished data). While knowledge of the input-output balance indicates that net accumulation of trace elements is occurring, components within the ecosystem (e.g., soil, organic matter, living biomass) must be examined to determine what biotic or abiotic processes are contributing to the net accumulation. In the case of trace toxic elements, these loci of accumulation represent stages in critical pathways which either influence transport in foodchains leading to man or potentially impair functioning of ecosystem processes due to toxification as has been shown for decomposition processes in Swedish forests heavily polluted with Cu.[11] Observations in the immediate environs of a lead smelter in the Crooked Creek Watershed (southeastern Missouri) of apparent accumulation of litter organic matter (A. Watson and R. J. Luxmoore, personal communication) and depauparate amounts of fine roots (A. Watson and W. F. Harris, unpublished data) merit closer examination to determine the extent to which ecosystem function is impaired and whether trace element accumulation is a causal agent.

The concept of organic matter as a sample "carrier" of trace elements appears to hold satisfactorially for most components of the forest biomass budget on Walker Branch Watershed. Mean percentages of living tissue closely agree with relative distribution of Cd, Pb and Zn (Table 9). Clearly, certain taxa such as hickories contain higher levels because of their differential uptake patterns. This is evidenced in the oak-hickory type by the fact that hickories contribute 24% of the total aboveground biomass which contains 46% of the Pb accumulation in aboveground biomass (Table 3).

Table 9

Standing pools (g/ha) of cadmium, lead, and zinc in the vegetative components of Walker Branch Watershed

	Biomass (10^3 kg/ha)	% of Living Biomass	g/ha (% of total pool)		
			Cd	Pb	Zn
Foliage	4.4	2.8	1 (4.0)	16 (4.7)	69 (6.2)
Branch	26.4	17.0	4 (16.0)	65 (19.0)	141 (12.8)
Bole	91.6	58.8	11 (44.0)	102 (29.9)	381 (34.6)
Stump	16.8	10.8	2 (8.0)	21 (6.2)	70 (6.4)
Lateral Roots	16.5	10.6	7 (28.0)	137 (40.2)	441 (40.0)
Total Living Vegetation	155.7	100.0	25 (100.0)	341 (100.0)	1102 (100.0)
Litter (O_1 & O_2)	23.2		13	853	1972
Total Vegetation	178.9		38	1194	3074

An exception to the concept that organic matter acts as a sample "carrier" of trace elements is the lateral root component. Lateral roots comprise only 11% of the living forest system; yet 28% of the Cd accumulation and 40% of the less mobile Pb and Zn accumulation is associated with root organic matter (Table 9). Of this accumulation associated with lateral roots, 60% (Cd) to 77% (Pb) is associated with the highly active pool of roots <0.5-cm diam (Table 4). Other studies in a yellow poplar forest and a loblolly pine plantation have demonstrated that this large pool of biomass ($\sim$8.0 x 10^3 kg ha^{-1}) is annually renewed and the sloughed organic matter is catabolized in heterotrophic metabolism.[12,13] As stated earlier, the present general survey does not permit detection of specific locations of trace elements associated with roots, whether accumulated in root tissue, associated with mycorrhizal activity or associated with adhering soil mineral or organic particles. The latter explanation seems implausible based on measured mineral ash content (5% to 15%) and concentrations of Cd, Pb and Zn in soil. This pattern of trace element distribution suggests that one possible ecological effect of accelerated trace element input may be related to rhizosphere physiology. Impaired water or nutrient uptake, whether the result of toxification of mycorrhiza or direct impairment of root physiology, could seriously affect forest production and subsequently other aspects of ecosystem function. The question requires much additional research to ascertain critical trace element levels, the extent to which forest productivity would be depressed and other contributing factor interactions.

The forests examined on Walker Branch Watershed are all second growth; the accumulating biomass and litter organic matter pools are not in equilibrium with annual detritus inputs. The historical pattern of trace element inputs is unknown. Therefore, the patterns of accumulation of trace elements in litter are affected by several processes operating over long temporal scales, including the litter decay characteristics which result in litter organic matter residence times ranging upward from 1+ years (yellow poplar). Thus, the correlations between litter organic matter accumulations and corresponding trace element burdens are not clear. However, in this relatively unpolluted forest ecosystem, Cd, Pb and Zn are accumulating in litter horizons of the soil. Litter (O_1 + O_2) accounts for 13% of the total forest organic matter (excluding soil organic matter); this fraction of organic matter contains an average of 34% of total Cd in all organic matter, 71% of Pb and 64% of Zn (Table 9).

Some of this accumulation in litter might be attributable to the root distribution since certain forest types typically have significant root extension in the O_2 litter horizon (oak-hickory, chestnut oak and pine). Yellow poplar, however, exhibits little or no root extension in the O_2 horizon and has a similar portion of the total trace element burden in organic matter in litter (37% of Cd, 63% of Pb, and 53% of Zn vs mean distributions above). In light of this behavior at low to moderate levels of trace element input, the documentation of impaired ecosystem processes in heavily polluted systems can be expected.[11]

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THE IMPACT OF LEAD MINING AND MILLING OPERATIONS ON STREAM WATER QUALITY IN SOUTHEAST MISSOURI

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Abstract

This paper summarizes the results of intensive studies to determine if changes in water quality have occurred in the Clark National Forest area since it became the site of the world's largest lead mining and milling operations. These studies have included 3½ years of bi-weekly analysis of filtered and non-filtered heavy metal levels, as well as some 17 physical and chemical parameters of pollution at 23 control and non-control stream sites in the area; sampling and analysis of runoff water from a smelter watershed and a control watershed; analysis of stream sediments of Clearwater Lake, the only long term holding basin in the area; analysis of the leachates from soils near the smelter both in the natural state and after saturation with lead and/or zinc; and analysis of a meander system for polishing the tailings ponds commonly used by this industry as a treatment device.

These studies have shown that the region has experienced only minor increases in dissolved heavy metals from the soil to the streams and out of the ecosystem as very fine suspended solids, particularly during runoff, is a major transport mechanism. There is evidence that this material may be building up in Clearwater Lake, though it is possible that this is not a permanent sink. Leachates from grossly contaminated soils do not present a problem to the ground water of the region. The meander treatment system has been very successful in eliminating both the massive algal blooms which had developed below the effluents of many of those mine-mill operations, and the heavy metals which they trap. This algae which has concentrated lead to levels as high as 17,000 μg/g dry weight and choked the streams has virtually dissappeared; the normal levels of algae which do exist now have lead contents in the range of 250 μg/g. Furthermore, studies by the Missouri Department of Conservation, based on benthic diversity indices, indicate that the stream has returned to pre-mining water quality levels.

Introduction

The investigations summarized in this paper were performed in order to: 1) evaluate the effects which the development of the world's largest lead mining district, known as the New Lead Belt or Viburnum Trend of Southeast Missouri, would produce on the quality of the streams draining the Clark National Forest area surrounding these operations; 2) to evaluate the role which these water systems play in the transport of heavy metals through and out of the forest ecosystem; and 3) where possible, to explore techniques for improving the water quality of the region.

The study area has been described in detail in a recent National Science Foundation Report (1). Surface rock outcroppings and the mine aquifer consist of dolomite and limestone. Because of the topography of the region no stream receives the discharge of more than one mine-mill complex (1). Numerous smaller streams, in close proximity to these operations, are unaffected by the mining activity and serve as control streams.

The mine-mill activities produce two potential sources of water pollution: 1) mine water from the subsurface operation, and 2) mill waters used for the ore concentration process. The mine water contains colloidal ore particles, grease, oil, and nutrients from the unspent explosive materials. The mill water contains not only elevated heavy metal concentrations, but also organic reagents used in the milling process. Background studies on these organic reagents have been reported by Jennett and Wixson (2) and the geochemical nature of these effluents have been described by Bolter and Tibbs (3). The waste waters from these mine and mill operations do not normally find their way to the surface stream systems until they have received treatment in, at least, a single tailings pond. A summary of the factors contributing to environmental changes in water quality is shown in Table 1.

TABLE 1. Summary of factors contributing to environmental change.

I. Mine Water
  - Natural Nutrient Load of Subterranean Water
  - Fuel Spills
  - Oil Spills
  - Hydraulic Fluid Spills
  - Small Mineral Particles in Mine Effluent
  - Blasting Agents - Spills and Partially Oxidized Compounds are Nutrients
  - Highly Variable Mineral Content of Ore

II. Mill Operation
  - Chemical Spills
  - Variable Mineral Content of Ore May Cause
    - A. Excessive Use of Reagents and Loss of Toxic Chemicals to Effluent
    - B. Low Recovery of Heavy Metals During Pulse of Very Rich Ore
  - Chemical Reagents Not Adsorbed to Concentrate Are Released in Effluent
  - Improperly Placed Concentrate Piles Allow Dispersal of Heavy Metals

III. Tailings Ponds
  - Improper Design of Placement of Ponds, Insufficient Size or Number
  - Insufficient Retention Time
  - Release of Toxic Milling Reagents to Streams
  - Release of Organic and Inorganic Nutrients to Streams
  - Release of Finely Ground Rock and Mineral Particles to Stream

Procedures

Samples for the general water quality studies have been taken on a bi-weekly basis for the last 3½ years at 23 sites. Background data at most of these sites exist prior to mining activities (3). In addition, two automated runoff sampling stations were established - one on a control watershed and one on the smelter watershed - to determine if heavy metals washed from the soil to the streams.

Quantitative determinations of the metallic content of the water in both dissolved and suspended states, and of the stream sediments, were made by the Environmental Trace Elements Laboratory of the University of Missouri using atomic absorption techniques (1). The separation between dissolved and suspended matter was made by assuming that water passing a 0.45 micron Millipore filter contained only dissolved material.

Chemical and physical parameters other than metals were measured in accordance with "Standard Methods" (4).

Samples of stream and lake sediments were taken at irregular intervals during the course of this study. These samples were always passed through an 80 mesh sieve prior to digestion and analysis to remove large gravel. A more complete description of the techniques will be found in reference (1).

Results

A. General Studies

Table 2 summarizes the maximum, minimum, and average values for lead and other metals which have been found in the streams of this region. The mass flows of heavy metals are based on the average concentrations of the element times the annual average flow (where available) not including runoff. Dissolved cadmium mass flows were not calculated since the levels were generally too low for accurate analysis.

A summary of the physical and chemical parameters of water quality for 15 of the 23 principal sampling stations is shown in Table 3. There were few obvious differences to be found between the physical and chemical quality of control streams and those receiving mine-mill effluent.

A statistical review of the data from these tables is still being made, however, some facts are known. The dissolved heavy metal content of these waters is minimal; however, a comparison of the filtered versus unfiltered stream water samples has shown that considerable quantities of heavy metals are present in a finely divided, suspended particulate state. Two points are of interest: first, almost all of the high dissolved readings have occurred during the last year and secondly, virtually all of these readings both total and dissolved have been associated with periods of rainfall runoff.

During normal dry weather flow, both the dissolved and suspended lead content of the water are well below the 0.05 parts per million limit set for drinking water by the U. S. Public Health Service and the 0.1 part per million effluent standard set by the Missouri Clean Water Commission for this type of waste discharge. Bolter (3) has pointed out that the streams characteristic of this region are high in carbonate and consistently average between pH 7.0 and 8.0 and, therefore, any dissolved heavy metals which may find their way into the streams are probably rapidly precipitated as insoluble carbonates. Since most of the particles are in the colloidal or near colloidal size range, they should be transported to a reservoir, ocean, or be deposited in some other aquatic body providing long-term sedimentation conditions. This phenomenon has not been noted in most conventional monitoring programs since both state and federal agencies routinely used filtered samples as the basis of their analyses for heavy metals.

A review of the physical and chemical data has consistently shown the turbidity and suspended solids levels at, or near, the industrial outfalls, are as a general rule far higher than those of the receiving streams and the heavy metals were generally associated with these solids.

A major environmental problem in the mine-mill receiving streams has involved the transport of heavy metals under conditions where mine and mill effluents have stimulated excessive biological growths in receiving streams. These dense gelatinous mats of algae and their associated aquatic populations have coated some stream beds causing aesthetic problems, blocking photosynthetic energy input and limiting normal stream populations (2). The biological mats act as living filters which trap dilute nutrients, sediments which are high in trace metals, and filter out finely ground particles of rock flour, tailings, and minerals which escape the flotation processes and tailings reservoirs. However, these growths are only temporary accumulations of materials since they become detached as they decompose or break loose during periods of high runoff and are carried into other ecosystems. A procedure for eliminating this growth is discussed later in this paper in section F.

B. Metal Transport in Runoff

The route of lead from tails, concentrate piles, transport vehicles, and the smelter aerially to the soil having been established by Bolter (1), the question whether or not the soil was the ultimate sink arose. A limited study of the "Old Lead Belt" of Missouri by Hemphill (1), a lead mining and milling region since the mid-1800's, indicated that soil lead levels were nearly the same as the New Lead Belt. Since geochemical studies of the soil by Bolter had indicated that the lead was tenaciously held in the top soil layer, it was assumed that the isolated high values of lead in unfiltered water samples found during periods of high runoff might be a significant transport phenomenon.

In order to check this hypothesis automated runoff water quality stations were constructed on two watersheds. The control watershed was located 6 miles from the smelter and was assumed to have no input of any kind from any industrial source. The other watershed drained a smelter area, whose primary heavy metal input was material deposited on the soil. The samples were analyzed for lead, zinc, copper and cadmium as well as 11 other physical and chemical parameters of water quality to determine any changes in the water's natural properties. The data presented here will devote itself to lead; more detailed information is available, however (1).

Figure 1 shows the rainfall intensity, runoff, and lead values for filtered and unfiltered samples for a selected storm on the control watershed, and Figure 2 shows similar data from the smelter watershed during the same storm. The total lead content in the smelter watershed runoff is 3 to 5 times as large as from the control. Similar patterns are also available for zinc. During the peak runoff period, the peak concentration occurs implying that large masses of material would be moved during heavy storms (the storm shown is the approximate equivalent of a 1 inch storm). It is extremely difficult at present to estimate the mass flow of heavy metals from the lead belt under runoff conditions; a study, however, has recently been initiated by the University of Missouri-Rolla working jointly with Oak Ridge National Laboratory to model a part of the smelter watershed in order to produce an estimate of this mass flow.

Note the differences in the storm rainfall intensity on the two watersheds which are 6 miles apart; this variance is typical of the Ozark region. Rain was trapped in wide-mouth polyethylene jars and the pH measured and found to average 5.5. During periods of peak runoff, the stream pH falls approximately 0.5 units. Since the rainfall affects pH only slightly (generally less than 1 unit), it should not be surprising to find only very small increases in dissolved metallic matter. The interesting point is the abrupt major increase in the metal content of the suspended solids.

Anomalous cadmium values were also found in the runoff from the smelter watershed. This was surprising since it is rare to find this element naturally in the waters of this region. The element is present in very small amounts in the lead ore, however, and it is apparently present in abnormal amounts in the smelter solid wastes, lagoon effluents, and in the leaf litter surrounding the smelter. Similar relationships for zinc and copper in unfiltered runoff can be shown, indicating that runoff transport may be a major transport phenomenon for all heavy metals.

Following the runoff studies, the question arose as to where would this material ultimately end up if it is being transported from this system and whether a sink could be found following the severe rainfall and flooding which occurred in the spring of 1973. The only sites for such an aquatic sink of heavy metals were the Clearwater Lake sediments or in temporary sinks in the stream sediments of the region.

C. Sedimentation Characterization

Studies of the stream sediments of the region were performed for several reasons including: 1) to provide basic data for the aquatic biologists, 2) to determine, if possible, whether the suspended heavy metals came largely from the washed-in soil or if it came from the resuspension of sedimented solids on the stream bottom, and 3) to develop data on maximum possible concentrations of lead which fish and other life forms might be exposed to in the streams. A summary of the results of these studies is presented in Table 4.

TABLE 4. Heavy metals concentration in the sediments of typical streams in the New Lead Belt

Station No.	Sample Site	Metal Conc. μg/g* Pb	Zn	Cu	Cd	Mn
5	Strother Creek	518	332	36	0	1503
7	Black River	798	163	38	0	1015
#10	Upper Bee Fork	38	79	17	0	1126
13	Lower Bee Fork	213	204	28	0	1269
##11	Tailings #1	785	2058	80	0	16490
###12	Tailings #2	543	1020	42	0	10033

*All average values; # indicates streams with no mine-mill activity; ## samples taken directly from tailings pipe from 1st settling pond; ### samples taken directly from tailings pipe from 2nd settling pond.

Several interesting factors emerged confirming the sediment transport phenomenon. First, only very low levels of lead and other metals are found in the sediments. Second, what little lead was found was generally in the 325 mesh or finer range; this is to be expected because although the ore is ground to 90 percent finer than 200 mesh, the heavy metals minerals are as a whole more friable and grind even finer. Third, while the soils of the region contain appreciable quantities of clay (9-12 percent), there is virtually no clay in the stream sediments (based either on size or geochemical character). The heavy metals in the suspended solids during runoff must be washing directly from the soil into the stream and out of the ecosystem. There is, therefore, a major sediment transport phenomenon occurring. This phenomenon is starting to be recorded in literature from other countries (5).

D. Reservoir Sediment Studies

In the New Lead Belt, most mill wastewaters and mine waters ultimately flow into two major receiving streams, Logan Creek and the Black River. Logan Creek receives wastes and mine water from only one mine, while the Black River receives a majority of the wastes and mine water from five mining operations. The velocity patterns of these receiving streams are of such character that fine particles do not obtain the quiescent conditions required for sedimentation and therefore these particles are carried along in the flow until these conditions are satisfied.

In the case of both the Black River and Logan Creek, these quiescent conditions are found in Clearwater Lake located at Piedmont, Missouri. The lake is approximately 30 miles from the last of the 5 mine-mill discharges on the Black River and approximately 25 miles from the single mine discharge on Logan Creek. In addition to the two arms of Clearwater Lake which receive waste water flow, there is a third arm, receiving flow from Webb Creek, which is not exposed to any type of mining waste products. A benthic sediment sampling program was therefore initiated and a summary of the results for lead is shown in Figure 3. These preliminary results would seem to indicate that increased heavy metals concentrations can be expected in the sediments where they are exposed to mining waste discharges.

It could logically be argued that one would expect higher levels of lead, zinc, and copper from the mining region due to surface mineralization; however, no such natural surface anomalies have ever been found by any researcher. The data from the Webb Creek arm of the reservoir is very consistent and ranges from 15-22 ppm for lead and zinc. This is the normal background level expected for the New Lead Belt control streams and confirms the belief that no unusual surface mineralization is occurring. Logan Creek is only slightly higher ranging from 20-30 ppm lead and zinc with only 1 mine in its basin. The data from the Black River Arm (with 5 mines) is far more erratic than the other two arms with the data for lead and zinc varying from 18 to 50 ppm. However, most of the sediments of this arm contain 35 to 50 ppm lead and zinc, and this arm is most subject to washout since it drains by far the largest area. Most of the sediments from this arm would be expected to travel to the dam face and mix with the other sediments and the data indicates that this does occur. All the arms of the lake should have uniform amounts of metal in the sediments. This obviously is not the case. As of yet, not enough data exists to state that the metals are definitely from the mines but the indication is that they are. Several areas remain to be evaluated: first, if the metal-laden sediments are building up, how fast is it occurring and would it ever build up to dangerous levels and secondly, how much is carried out of the reservoir during turbulent periods and into the Mississippi River system. Another question which should be studied relative to these sediments is under what conditions can these heavy metals be released to the environment? Upstream spills of acid will obviously dissolve this material allowing it to be transported from the system. Under less alkaline water conditions, runoff can affect stream pH more than in the New Lead Belt. It is also possible that the heavy metals can be released by anaerobic organisms in the bottom sediments. Release of precipitated heavy metals has not been observed in waste water treatment plant anaerobic digestor studies, but these treatment devices encourage methane formers, not acid production, and have a highly alkaline environment as compared to normal stream and lake sediments. Since humic and fulvic acids are known to mobilize heavy metals, it is logical to assume that volative acids will too; this then implies that excessive organic loads to heavy metals bearing sediments could pose an environmental hazard. The literature on the effects of heavy metals on various types of anaerobic organisms is extremely limited so this hazard cannot be evaluated currently.

E. Soil Leaching Studies

Even though the literature is clear that most heavy metals move very slowly vertically, experiments were initiated in the fall of 1973 to determine the potential existing for ground water pollution in the New Lead Belt. Since there were very few wells in highly contaminated areas and since most of these made extensive use of galvanized piping, laboratory column studies of soils were initiated . The soils selected were from the two watersheds previously described.

The samples were dried, weighed, cation exchange capacities (CEC) measured and then they were packed in glass columns. Triple distilled water with enough carbon dioxide in it to produce a pH of 5.5 (similar to rain water) was then used to leach the soils of any readily available heavy metals. Following this, each column was loaded with either lead or zinc acetate until the effluent equalled the influent (this was defined as break-through). At break-through, the columns were allowed to rest 6-8 weeks and the process repeated to determine if time was a factor in heavy metal retention. The control soils originally contained an average of 17.7 μg/g of Pb and 21.0 μg/g of Zn, with a CEC of approximately 15 meq/100g; the smelter watershed soils contained an average of 1300 μg/g Pb, 127 μg/g Zn, and had a CEC of approximately 14.5 meq/100g.

The results showed when the natural soil samples were leached, no detectable amounts of lead and zinc were released. Further, it was found that the smelter soil could hold between 60% and 70% before movement occurred. The resting period did increase the amount of lead which the soil could hold indicating that over a long period, the soil holding capacity would approach (but not equal) the CEC. Experiments showed lead was held twice as firmly as zinc; this was true, regardless of whether zinc was used to replace lead or vice versa.

Using Clark National Forest Hydrologist estimates of the amount of leachates and assuming the soil was saturated with lead (based on 100 percent of CEC), it would take 100 years for the lead to move 1 foot. Obviously, no danger currently exists or is likely to ever exist to the ground water of the region from soil pollution.

F. Meander System for Mine-Mill Effluent Treatment

The meander system in Strother Creek is entirely artificial and was conceived by University of Missouri-Rolla Environmental Engineers in cooperation with the AMAX Lead Company Engineering staff who designed and built it. During the 1971-73 study period, consideration was given to whether or not an inexpensive, effective treatment process could be developed which would contain and control the excessive algal growth and the associated heavy metals which they trapped. The problem with designing such a process was that the cause of this excessive growth had never been proven and it was, therefore, decided that a series of broad, shallow, rapidly flowing meanders should be built which would stimulate or encourage the growth of the algae on company property and simultaneously trap any suspended heavy metals. In order to prevent the algae and heavy metals from escaping the system, a sedimentation pond was placed at the end of the meanders with a well baffled outlet. (See Figure 4 for a plan view of the system.)

The project has been successful at eliminating problem algal growth downstream, to the extent that the stream is no longer one of the major algal study sites. Furthermore, what algae currently exist have a significantly lower lead content (Figure 5). Extensive analyses of the water and sediments of these meanders have shown that the total metal content and, therefore, the heavy metals ratio as defined by the State of Missouri (6) has declined.

Figure 6 is a plot of the heavy metals ratio at various points in the lagoon-meander treatment system (raw data on this system is still being evaluated). In this case, the ratio has been calculated on unfiltered, as well as filtered samples to demonstrate the system's effectiveness at removing suspended particulate heavy metals. Below the meander and lagoon system, Strother Creek rarely exceeds the allowable concentrations for any heavy metal except during severe storms when the algae in the meanders break loose and the final sedimentation chamber is less efficient due to temporary turbulence generated. Studies are still underway: 1) to determine under what conditions the system fails and 2) to try and develop design criteria which will allow design optimization and transfer of this system to mines in other areas.

A recent report by Ryck and Whitely (7) of the studies of changes in benthic populations in the New Lead Belt has shown that as a result of this meander system, the stream's character has returned to its pre-mining quality.

Summary and Conclusions

Based on these studies, the following conclusions can be made:

1. Dissolved heavy metals as a result of favorable pH, alkalinity and hardness conditions do not appear to present a significant hazard to the ecosystems of the New Lead Belt streams.
2. Suspended solids transport of heavy metals is a major transport phenomena for heavy metals. The long term implications and the effect these solids produce on downstream reservoirs and other ecosystems is currently unknown.
3. It does not appear likely that soil, even where heavily contaminated with lead or zinc, would produce leachates dangerous to ground water in this area.
4. The efficiency of the meander system in treating mine-mill tailings pond effluents has been clearly shown. The incidence of algal blooms and the heavy metal content of downstream vegetation has decreased significantly and the benthic productivity has returned to levels found prior to mine production.

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0 0 0 0 4 2 0 2 3 0 5

Table 2 Metal Concentrations of Streams at 23 Sampling Sites in the New Lead Belt Study Area

DISSOLVED METAL CONTENT

Element	Station Number																						
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23
Pb max.	.280	.022	.010	.130	.061	.075	.066	.012	.045	.160	.031	.022	.120	.059	.110	2.62	14.8	2.35	2.60	.760	.180	.020	.153
min.	<.005	<.005	<.005	<.005	<.005	<.005	<.005	<.005	<.005	<.005	<.005	<.005	<.005	<.005	<.005	.009	.010	.010	.050	.023	<.005	<.005	.005
mean	.026	.009	.006	.012	.014	.011	.009	.006	.009	.008	.008	.008	.015	.011	.014	.465	1.256	.495	.577	.264	.026	.008	.041
mass flow lb/yr	581	196		135	232	86	6900	396	606	147			276	146	188								
Zn max.	.460	.084	.027	.250	.097	.034	.036	.023	.128	.088	.170	.190	4.80	.117	.091	21.0	16.5	32.0	8.40	4.10	.103	.010	.560
min.	<.010	<.010	<.010	<.010	<.010	.005	<.010	<.010	<.010	<.010	<.010	<.010	<.010	<.010	<.010	<.010	.012	<.010	.210	.840	<.010	<.010	<.010
mean	.063	.018	.011	.068	.028	.013	.013	.011	.019	.014	.088	.087	.307	.017	.024	5.465	5.397	7.34	3.455	1.892	.025	.010	.132
mass flow lb/yr	1391	394		771	478	103	9832	729	1251	261			5567	222	317								
Cu max.	.039	.015	.010	.010	.011	.018	.018	.010	.024	.010	.010	.012	.063	.010	.095	.060	.330	.016	.120	.131	.010	.010	.032
min.	<.010	<.010	<.010	<.010	<.010	<.010	<.010	<.010	<.010	<.010	<.010	<.010	<.010	<.010	<.010	<.010	<.010	<.010	<.010	<.010	<.010	<.010	<.010
mean	.012	.010	.010	.010	.010	.010	.010	.010	.011	.010	.010	.010	.013	.010	.015	.017	.034	.013	.027	.023	.010	.010	.014
mass flow lb/yr	263	226		114	172	84	7835	666	712	181			235	133	202								
Cd max.	.010	.010	.010	.012	.010	.013	.010	.010	.010	.015	.031	.018	4.00	.028	.048	4.75	5.50	.180	4.70	1.50	.025	.008	.177
min.	.000	.000	.000	.000	<.001	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.002	.004	.001	<.010	.180	<.001	<.001	.004
mean	.007	.006	.006	.006	.006	.007	.006	.006	.006	.007	.008	.007	.206	.008	.009	2.178	2.097	.070	1.52	.748	.010	.003	.043
mass flow lb/yr																							
Mn max.	.550	.054	.011	1.82	.680	.012	.010	.018	.840	.020	2.48	2.34	1.02	.054	1.06	.590	.650	.510	.700	4.10	.072	.041	.480
min.	<.010	<.010	<.010	<.010	<.010	<.010	<.010	<.010	<.010	<.010	<.010	<.010	<.010	<.010	<.010	<.010	<.010	<.010	.073	.083	<.010	<.010	<.010
mean	.062	.014	.010	.128	.111	.010	.010	.010	.052	.011	1.247	1.285	.462	.015	.124	.315	.346	.104	.408	1.808	.017	.017	.089
mass flow lb/yr	1363	312		1459	1895	82	7534	692	3455	202			8394	194	1653								

Element	Station Number																						
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23
Pb max.	.200	.100	.100	.100	.830	.100	.100	.680	.120	.920	.350	.110	.340	.020	.100	26.5	14.8	8.10	12.9	1.40	.220	.045	.250
min.	<.005	<.005	<.005	<.005	<.005	<.005	<.005	<.005	<.005	<.005	<.005	<.005	<.005	<.005	<.005	1.65	.450	.230	.200	.180	<.005	<.005	<.005
mean	.029	.011	.010	.013	.081	.011	.014	.035	.019	.009	.060	.035	.034	.007	.018	7.161	5.078	2.155	2.006	.506	.037	.018	.054
mass flow lb/yr	643	249		151	1389	111	10315	2316	1246	158			622	97	243								
Zn max.	.180	.153	.026	.280	.175	.032	.018	.026	.208	.057	.430	.280	.155	.019	.109	12.4	15.5	33.0	7.60	4.20	.042	.020	.600
min.	<.010	.008	<.010	<.010	<.010	.008	.008	<.008	<.010	<.008	<.010	<.010	<.010	<.008	<.010	.960	.037	<.010	.700	.780	<.010	<.010	.019
mean	.043	.017	.011	.060	.043	.011	.011	.011	.018	.012	.151	.133	.043	.011	.022	5.027	5.694	7.742	3.287	1.963	.014	.014	.145
mass flow lb/yr	966	369		686	743	88	8107	751	1196	221			783	143	287								
Cu max.	.025	.027	.029	.036	.036	.035	.028	.032	.026	.030	.140	.030	.033	.026	.157	.340	.330	.210	.950	.053	.032	.018	.037
min.	<.010	<.010	<.010	<.010	<.010	<.010	<.010	<.010	<.010	<.010	<.010	<.010	<.010	<.010	<.010	.017	.014	.013	.011	<.010	<.010	<.010	<.010
mean	.011	.011	.011	.011	.012	.011	.011	.011	.011	.011	.021	.012	.011	.011	.017	.093	.071	.038	.097	.021	.012	.011	.015
mass flow lb/yr	246	237		128	206	88	8000	716	702	201			206	140	224								
Cd max.	.010	.016	.010	.010	.016	.010	.010	.012	.010	.012	.010	.015	.010	.010	.010	5.55	6.70	.190	4.30	1.60	.018	.005	.200
min.	.000	.000	.000	.000	<.001	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.280	.016	.011	.280	.190	<.001	<.001	.004
mean	.008	.008	.007	.007	.008	.007	.007	.008	.007	.008	.007	.008	.007	.007	.007	2.451	2.596	.062	1.758	.779	.006	.002	.046
mass flow lb/yr	168	169		83	134	59	5484	500	489	139			132	99	98								
Mn max.	.640	.620	.042	.070	.690	.028	.200	.064	.960	.034	3.40	2.42	1.06	.088	1.12	.660	.730	.500	.830	4.50	.010	.041	.480
min.	<.010	<.010	<.010	<.010	.019	<.010	<.010	<.010	<.010	<.010	.660	.540	<.010	<.010	<.010	.038	<.010	.010	.120	.080	<.010	<.010	<.010
mean	.062	.037	.012	.032	.133	.011	.017	.012	.049	.012	1.656	1.512	.406	.021	.117	.364	.389	.106	.456	1.941	.010	.017	.089
mass flow lb/yr	1391	821		367	2279	88	13125	807	3238	225			7363	279	1553								

Table 3 Summary of physical and chemical parameters of water quality.

	Stations														
	#1	#2	#3	#4	#5	#6	#7	#8	#9	#10	#11	#12	#13	#14	#15
pH	8.10	7.45	7.74	7.73	7.73	7.66	7.58	8.2	8.1	8.0	7.6	7.6	8.0	7.4	7.6
Temperature	0-25°C	0-25°C	0-25°C	0-25°C	0-25°C	0-25°C	0-25°C	0-25°C	0-25°C	0-25°C	0-25°C	0-25°C	0-25°C	0-25°C	0-25°C
Turbidity (JTU)	3.7	2.9	1.2	1.0	7.7	1.3	.76	1.0	1.0	1.0	8.0	6.5	1.2	3.4	2.0
Dissolved Oxygen (DO) (ppm)	5.4	4.6	4.7	5.5	5.5	5.6	5.3	5.6	5.2	5.5	5.9	5.9	5.4	5.3	5.9
Alkalinity (mg/l)	180	200	198	152	150	150	150	144	156	135	152	144	145	30	80
Hardness (mg/l) Calcium	150	140	210	100	95	100	100	75	80	75	110	110	110	15	50
Total	300	280	360	250	235	200	210	155	160	135	260	260	260	30	110
Chloride (mg/l)	0	0	30	20	0	0	0	0	0	0	0	0	30	0	0
Chem. Ox. Dem. (COD) (mg O_2/l)	30	20	50	40	75	95	35	15.0	20.0	30	31	20.0	50	40	20
Phosphorus (mg/l) Ortho	.1	.1	.1	.1	.1	.1	.1	.1	.1	0	.1	.1	0	.1	.1
Total	.3	.3	.4	.3	.2	.1	.1	.2	.1	.1	.3	.2	.1	.1	.1
Nitrite mg/l	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Nitrite mg/l	.1	.1	.2	.1	.2	.1	.1	.2	.1	.1	.2	.1	.1	.1	.1
Nitrogen mg/l Ammonia	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Total Organic	26.4	8.4	30.2	25.7	16.4	18.0	12.0	15.6	10.0	22.4	16.4	17.6	35.3	25.7	30.2
*Specific Conductance (μmho/cm)	360	200	260	450	100	160	340	300	380	280	750	750	740	120	340

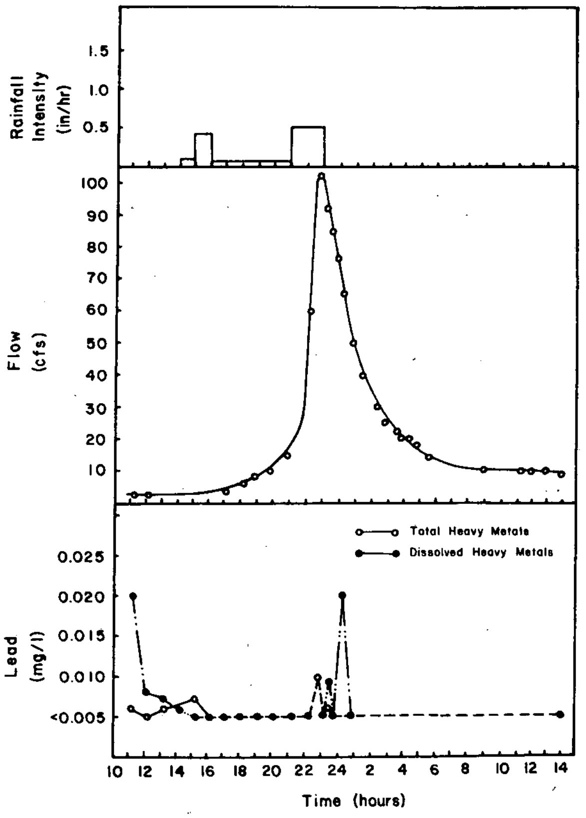

FIG. 1. Selected runoff data from a control watershed in the New Lead Belt.

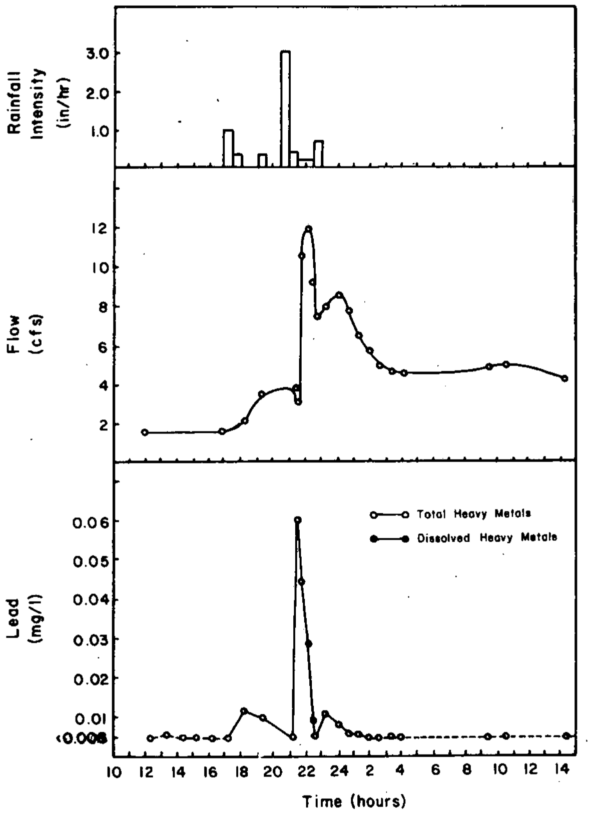

FIG. 2. Selected runoff data from the smelter's Crooked Creek watershed.

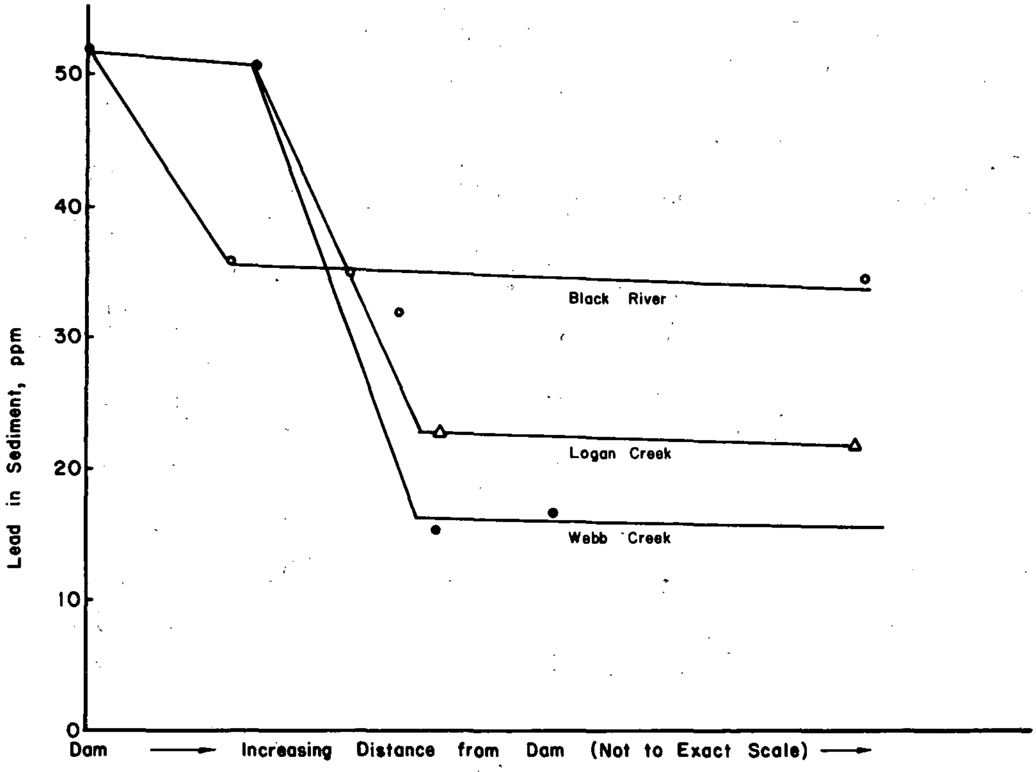

FIG. 3. Lead in sediments of Clearwater Lake.

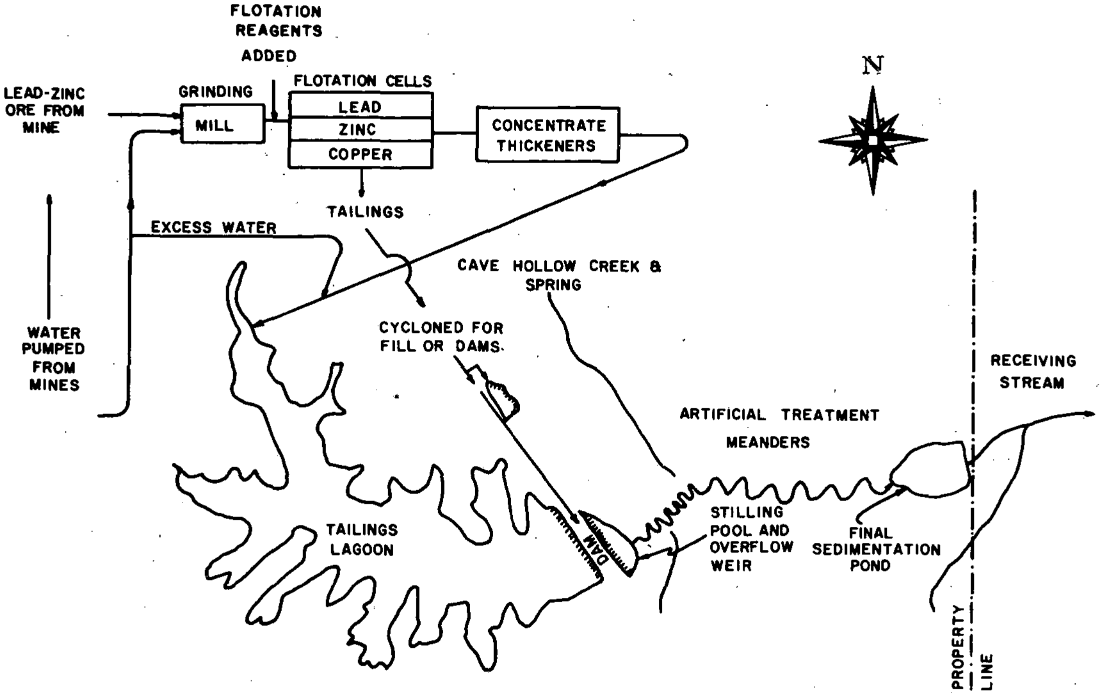

FIG. 4. Schematic of a mine and mill operation using a lagoon followed by a meander section and final sedimentation.

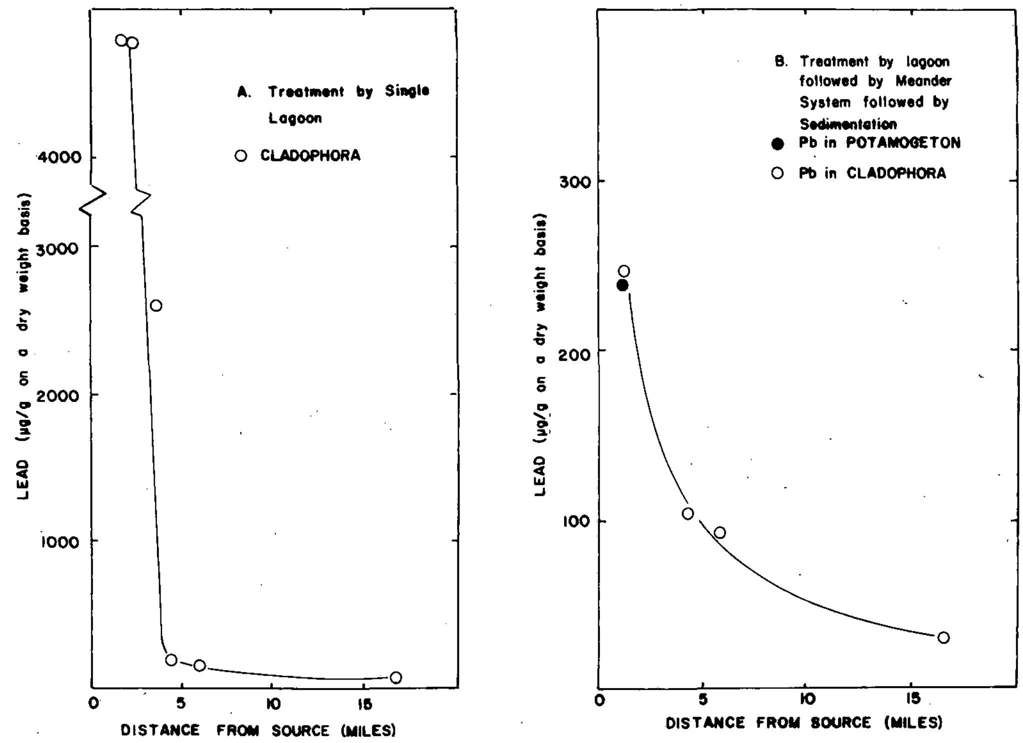

FIG. 5. Lead in algae as a function of distance from a typical mine tailings lagoon before and after meanders construction.

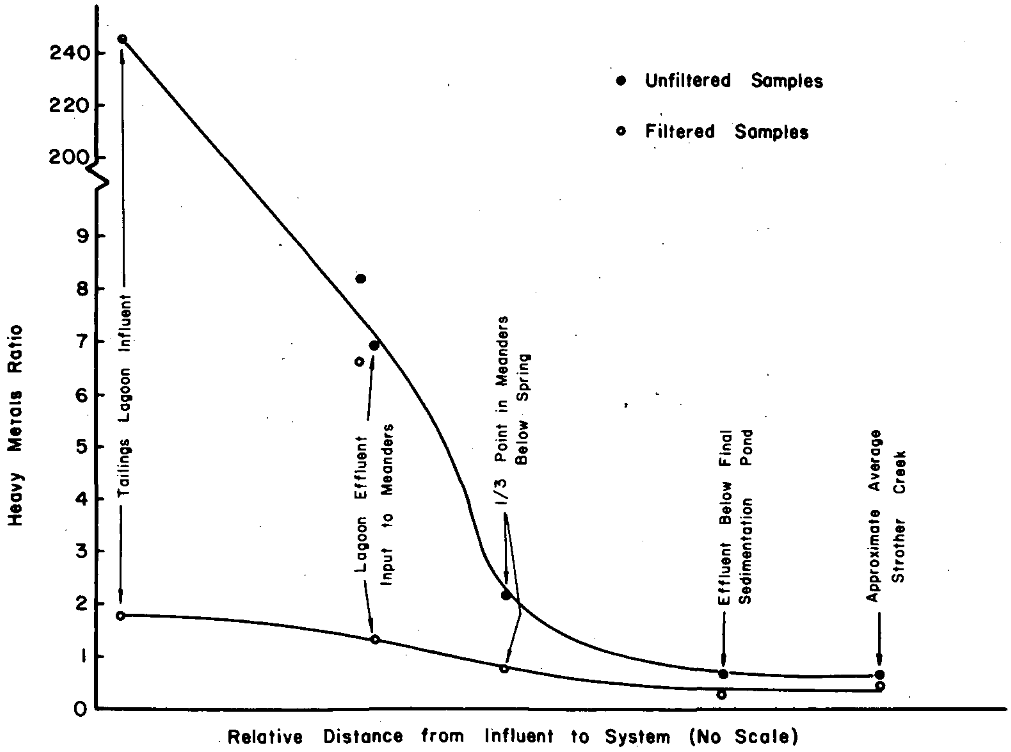

FIG. 6. Heavy metals ratio in a lagoon-meander treatment process.

FIRST-ORDER SIMULATION RUN FOR LEAD TRANSPORT THROUGH CROOKED CREEK WATERSHED - NEW LEAD BELT MISSOURI*

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Abstract

The Unified Transport Model (UTM) was used to simulate the transport of Pb in one of the land segments (.45 sq. mi. area) of a 1.3 sq. mi. area at the head of the Crooked Creek Watershed. The head of this watershed is adjacent to the AMAX mine-smelter complex and hence provides a good location for validating a transport model. Hourly precipitation and other meteorological input data were obtained from stations as close as possible to the mine-smelter. Geographic type input data were obtained from U. S. Geological Survey topographic maps. The Atmospheric Transport Model (ATM) part of the UTM was used to compute wetfall and dryfall deposition values for Pb due to three known sources in the area: the smelter stack and two area sources. The ATM predicts values of total monthly deposition that are within a factor of two of measured monthly deposition rates. Soil input data were taken from soil survey maps of neighboring Dent County. The Wisconsin Hydrologic Transport (WHTM) part of the UTM uses a simple ion-exchange model to simulate the movement of lead (effective distribution coefficient = 1000) through the homogeneous land segments comprising the watershed. For the 1972 water year simulated, the WHTM shows a factor of 10 build-up of lead at the soil surface and predicts a flushing of lead from the watershed after a couple of medium-to-heavy storm events. The simulation also predicts that the stream flowing through the segment runs dry approximately three weeks following the last storm preceding a long dry period.

Introduction

The work to be described below is intended to be of the nature of a progress report on the first serious attempt to apply the Unified Transport Model [1] (UTM) to a forested watershed adjacent to a lead mine and smelter. The UTM is being applied to the study of Pb transport in order to calibrate and validate the model and to aid the Pb industry and various government regulatory agencies to assess what impact Pb mining activities have on a national forest. This work is a result of a collaboration between the Ecology and Analysis of Trace Contaminants (EATC) project at ORNL and the New Lead Belt Study Project at the University of Missouri - Rolla (UMR).

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**Prime contractor for the U. S. Atomic Energy Commission.

The Model

The version of the UTM being used for the Crooked Creek Watershed study is shown in Figure 1. It is composed of two basic programs: a hydrologic transport model (WHTM) [2] and an atmospheric transport model (ATM) [3]. The ATM uses the historical precipitation data and rain gage location data required by the WHTM. The ATM employs a Gaussian plume model and a wind resuspension model, together with a procedure for treating the geometries of the emission sources in relation to receptor points, to simulate atmospheric transport of pollutants. Three types of emission sources may be used: point, line, and area. In the WHTM the PRECIP group of subprograms processes the raingage inventory and historical precipitation data. The LAND group of subprograms simulates the response of a vertical column through the land segment on a quarter-hour basis. The cross-sectional area of the column is 1 sq. ft. The CHANL group of subprograms uses the output from the simulated response of the various unit land areas as input to a prescribed network of reaches, determines the channel routing times, and generates a hydrograph.

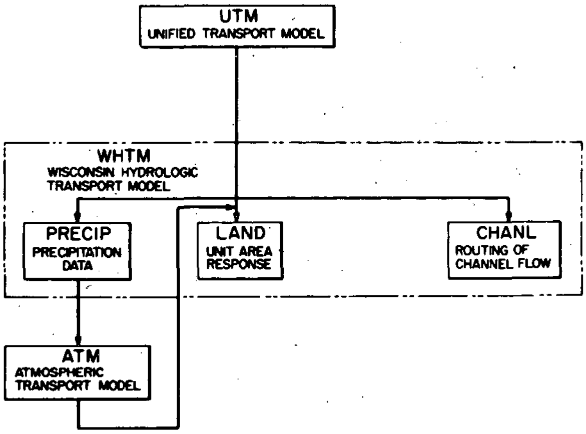

Figure 1. Schematic Diagram of the Unified Transport Model Showing How the Atmospheric Transport Model Couples to the Wisconsin Hydrologic Transport Model.

Most of the effort in simulating the hydrologic response of a watershed must be spent on the LAND group of subprograms. A conceptualization of the hydrologic response of a land segment is shown in Figure 2. Several items deserve emphasis at this point. Incoming precipitation falls on the vegetation, which usually is considered to include grass, leaves, litter--any plant material that is located above the actual soil. In a forested watershed, the impervious area runoff comes predominantly from the stream beds, banks and flood plains. Evapotranspiration occurs at the potential rate for the interception and upper zone storages, depleting the former before taking anything from the latter. Hence, when the evapotranspiration is low, i.e., during the winter and early spring, the streams will flow for longer periods following a storm than they do in the summer.

A simple first-order ion exchange model simulates the movement of a trace toxicant through a land segment. Figure 3 shows how this model is used. It is employed in

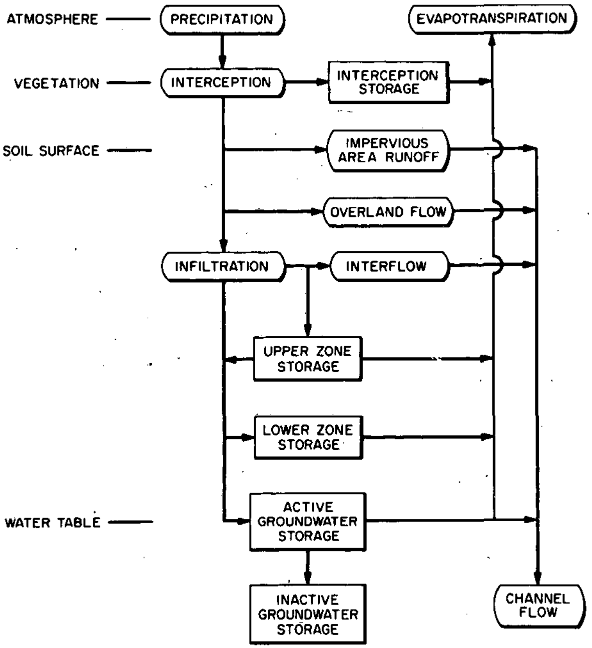

Figure 2. Hydrologic Flow in a Land Area Segment.

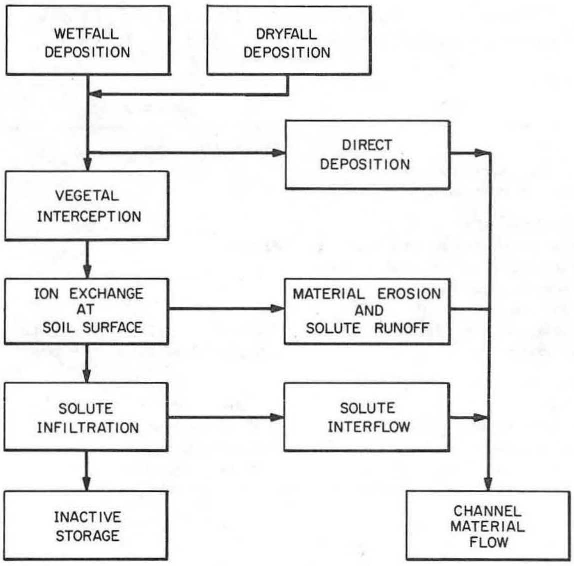

Figure 3. Material Flow in a Land Area Segment.

tandem with the hydrologic response. Lead in the rain (wetfall deposition) and in the dust which settles (dryfall deposition) is computed by the ATM and supplied as input to the land segment simulation. Three components of Pb flow to the stream channel are shown. There is a fourth, not shown, coming from the groundwater. However, the component which always seems to dominate all the others is that associated with overland flow and erosion. Once these four lead flow components reach the stream, there is no further ion exchange. If the toxicant treated by this simulation model resides at the land surface, as seems to be the case for Pb on the Crooked Creek Watershed, then the treatment of overland flow and erosion becomes very important and poses a serious challenge to the model.

The Watershed

Crooked Creek Watershed for the purposes of this study is a 1.3 square mile area of land lying at the head of Crooked Creek. Figure 4 shows a topographic map of the Crooked Creek headwaters area. The study area lies inside the boundaries defined by the roads shown, which form roughly an inverted triangle. This study area lies near the center of the "Viburnum Trend" or "New Lead Belt" area of southeast Missouri. The roads run roughly along the ridge tops. The mine and smelter shown in the center lie on a major divide separating the Meramec and Black River drainage basins. The grey areas indicate the extent of forest cover. The forest in the watershed area is composed primarily of oak.

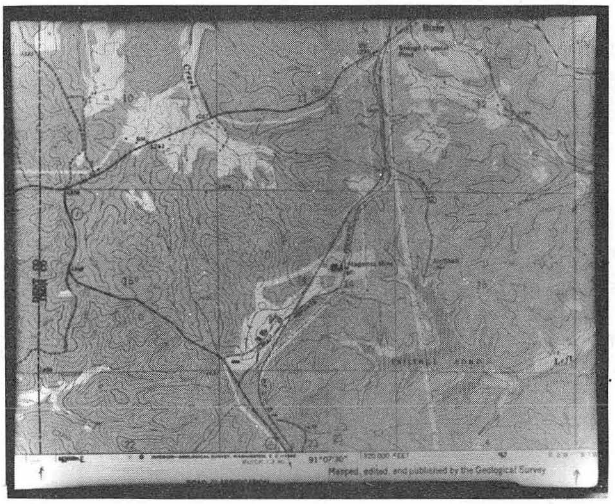

Figure 4. Topographic Map Showing Approximate Extent of Forest Cover in the Crooked Creek Watershed Study Area.

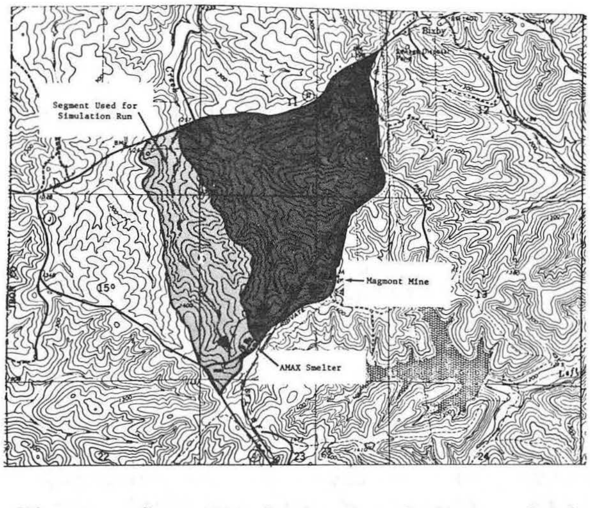

Figure 5. Crooked Creek Watershed Study Area Boundaries.

The precise boundaries of the Crooked Creek Watershed study area are shown in Figure 5 encompassing the total area which is shaded. The long light grey segment was chosen for simulation since it initially appeared the easiest one to simulate. A wet-dry stream flows the length of this segment. The white "X" on the ridge knob adjacent to the grid line marks the centroid of the segment and is used as the receptor point for the Pb depositions computed by the ATM. All the sources of Pb affecting this segment are assumed to be located at the smelter.

The First-Order Simulation

A first-order simulation run, for the purposes of this talk, consists of using the best input data for the model which is available for the area under study. This input data includes what data can be gotten from preliminary measurements of water balance and toxicant distribution in the study area. A rough picture of the dominant processes involved in the toxicant transport is important and helps in estimating parameters and interpreting results. The following agencies have been very helpful in supplying data and other information of value to the Crooked Creek study: U. S. Weather Bureau, U. S. Forest Service, the Soil Conservation Service, and the Missouri State Geological Survey.

Table I shows the input required by the ATM and where it was obtained. The most difficult data to get are the stability wind rose data and the source characteristics. St. Louis is about 90 miles NEN of the watershed and was the closest source of five-year averaged stability wind rose data. This data can now be used for simulation runs spanning a period of several years.

The Pb source strengths are shown in Table II. The only source where a lot of assumptions had to be made was the vehicular traffic source. These assumptions [4] included the number of vehicles at the smelter, their frequency of movement and average distance traveled, the amount of concentrate dust suspended by the tires, etc. Order of magnitude accuracy was all that was hoped for in these assumptions. The simulated deposition rates at the centroid of the segment are shown at the bottom. Notice that the simulated dryfall deposition is 2-3 orders of magnitude greater than the wetfall deposition. A Wong wetfall-dryfall sampler has been operating on the watershed for several months. Data for comparison should soon be available. The simulated deposition rates are calculated on the basis of continuous emission rates for the

TABLE I. Input Required for the Atmospheric Transport Model (ATM)

Input Required	Source
Geometry	Obtained from maps
Sampling point locations	
Emission source locations	
Micrometeorology	
Atmospheric stability class table	Pasquill
Maximum values of vertical dispersion	
Plume rise parameters	
Wind speed classes	
Stability wind rose data	Five-year averaged data for St. Louis
Washout and fallout weights	Computed from precipitation data
Source Characteristics	
Heights	K. Purushothaman, UMR
Pollutant emission rates	K. Purushothaman, UMR
Fallout deposition velocities	Laboratory experiments
Washout coefficients	Laboratory experiments

TABLE II. Lead Source Strength Input Data and Computed Deposition Rates for Wetfall and Dryfall for a Point Source and Two Area Sources

Point Sources:		
Acid plant stack		
Height, M	61	
Source strength, G/sec	0.587	
Area Sources:		
AMAX smelter plant		
	Vehicular Traffic	Windblown, resuspension
Area, M^2	8200	8200
Height, M	3	3
Source strength, G/sec·month	0.015	$10^{-5}-10^{-6}$
Deposition Rates at Centroid of Segment $MG/M^2 \cdot$month		
	Simulated	Measured
Wetfall	2	?
Dryfall	493	?
Total	495	250

point source. This will overestimate the point source contribution by probably 20% [5], since the emission rates are not continuous. The emission rate pattern has not been measured.

Table III shows the input required by the WHTM and where it was obtained. Most of the effort involved in applying the UTM to the Crooked Creek Watershed has gone toward getting the best possible values for the quantities listed here. Hourly precipitation data were obtained for Salem, Missouri, which lies 20 miles west of the watershed. This data should work well for winter and spring storms which generally affect large areas, but may be unsatisfactory for intense, local summer storms. Potential evapotranspiration data was gotten from pan evaporation data from two locations, 60 and 100 miles from the watershed. This data had to be normalized to give the correct annual evapotranspiration. Values for the fractions of impervious area and bare soil were obtained by W. Tranter [6] of UMR from aerial photographs. Initial values of Pb on the vegetation, on the soil surface, and in the theoretical ion exchange plates was gotten from data obtained by E. Bolter [6] of UMR. There is no data yet on the average channel dimensions or the observed flows. Channel dimensions were estimated on the basis of a visual inspection of the watershed. When no data were available for choosing a parameter value, a value was estimated based on experience from applying the model to the Walker Branch Watershed near ORNL. A value for the ion exchange distribution coefficient of 1000 was used for the simulation run.

The annual water budget for water year 1972 is shown in Table IV. Note that the sum of the total runoff and net ET exceeds the precipitation by about 10 inches. This is due to choosing too high an initial value for the lower zone storage. The best initial value for this storage has not been determined, though it is closer to 10 inches than the 20 inches used for the simulation run described here. This illustrates the importance of experience in helping to estimate some of the input values when they cannot be readily determined.

TABLE III. Input Required for the Wisconsin Hydrologic Transport Model (WHTM)

Input Required	Source
Precipitation	
Hourly precipitation values	Weather Bureau, Salem, Mo.
Wetfall deposition	ATM
Land Parameters and Initial Values	
Hydrologic:	
Climatologic	U.S. Forest Service, Salem, Mo.
Soil data	Dent County Soil Survey, S.C.S.
Land use data	Aerial photographs (W. Tranter, UMR)
Recession constants	Experience, R. J. Luxmoore
Topographic data	Topographic maps
Toxicant:	
Dryfall values	ATM
Initial values	Field measurements (E. Bolter, UMR)
Erosion parameters	Field measurements, experience
Ion-exchange, K_d	T. Tamura, E. A. Bondietti
Channel Characteristics	
Land segment areas	Topographic maps, aerial photographs
Channel network routing	Topographic maps, user's head
Channel geometry and dimensions	Field measurements (no values yet)
Observed Channel Output	Field measurements (no values yet)
Mean daily flows	
Hourly flows	
Mean daily toxicant flow	
Hourly toxicant flow	

TABLE IV. Annual Water Budget For Water Year 1972

Precipitation	36.04
Runoff	
Surface	5.81
Impervious	.79
Interflow	5.40
Base stream	1.74
Recharge	.00
Total	13.74
Evapotranspiration	
Net	29.05
Potential	31.84

The two components of lead transport to the stream by overland flow for water year 1972 are shown in Figure 6. During the fall,

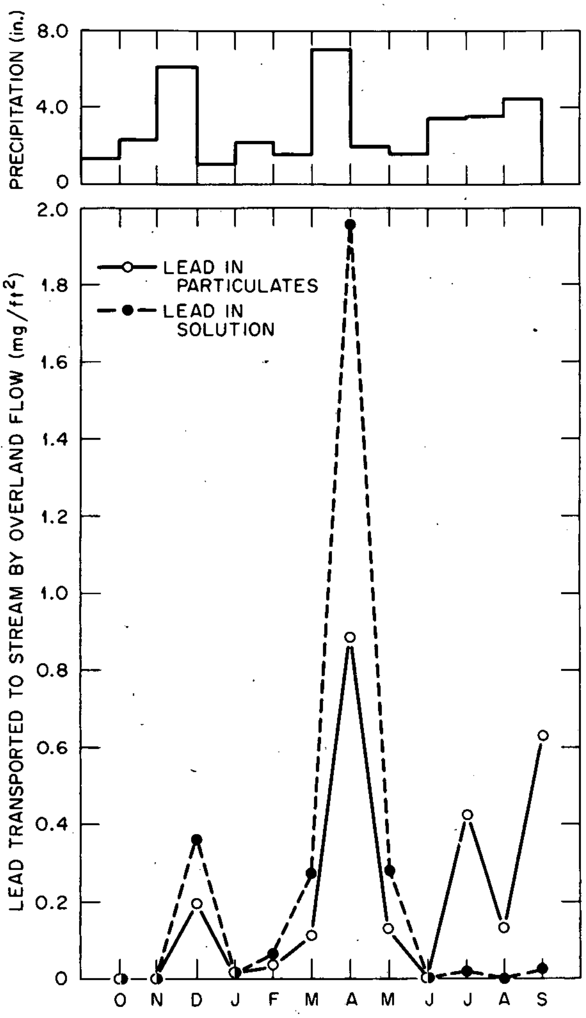

Figure 6. Simulated Components of Lead Transport from the Land Segment to the Channel on a Monthly Basis for Water Year 1972.

winter, and spring when the storms generally have long duration and low intensity, lead transported in solution phase exceeds that in particulate phase. Low intensity storms do not deliver enough power in a short period of time to erode much soil. The situation is quite different during the summer months when brief intense storms occur. Soil erosion becomes the dominant process for transporting Pb from the land segments to the streams. There is no data with which to compare these simulation results. The model also predicts a 12-fold increase of Pb at the soil surface for a period of a year if the initial value of Pb for this layer is based on the measured Pb concentration in the 0-1 soil layer. This is unreasonably high. The treatment of soil chemistry in the model at the soil surface needs to be modified or replaced.

The simulated flows from the stream are shown in Figure 7 for a series of successively more intense spring storms. No rain had occurred for several days, so the stream was almost dry at the beginning of the time period shown here. In between storms the flows are less than 1 cfs and die off to zero after a dry period of several weeks. The most interesting result of the simulation is the bottom curve showing the concentration of total Pb in the stream. The first order run indicates that the mobile Pb is flushed out of the land segment and that any measurement program should

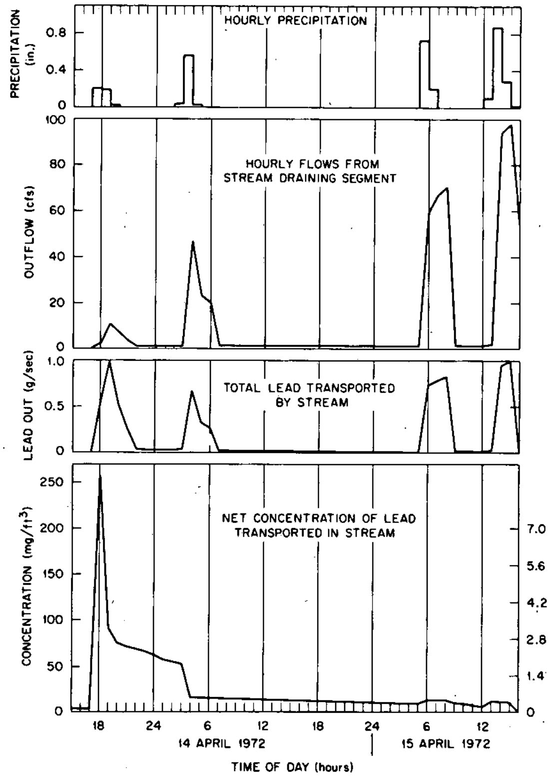

Figure 7. Simulated Hydrologic and Lead Flows from the Land Segment Studied for a Series of Spring Storms in Water Year 1972.

include sampling a storm immediately following a dry period and perhaps a series of successive storms for more information on how rapidly flushing occurs. This flushing is a consequence of the large difference between the dryfall and wetfall deposition rates, so is strongly tied into the results of the ATM simulation.

It is interesting, finally, to note that a sampling experiment carried out two miles further downstream on Crooked Creek by J. C. Jennett [6] of UMR indicated very small amounts of Pb being transported. Except for the most intense part of the storm, the concentrations bordered on the detection limit of 5.0 micrograms/liter. Jennett recently confirmed that the storm he sampled indeed followed soon after at least one respectable storm which could very well have flushed the mobile Pb from the watershed.

This illustrates the potential value of simulation models in showing how to design a more economical and efficient measurement program in ecological studies.

What is the next step in the modeling effort on Crooked Creek Watershed? D. E. Fields [7] has developed a submodel for simulating sediment transport and ion exchange in a stream channel. This submodel will be needed to model some of the watershed streams. R. J. Luxmoore and D. Huff [8] have developed an n-layered version of WHTM called the PROSPER version which treats the soil-plant-water relationships on a more physical basis. This version will hopefully be ready for application on Crooked Creek sometime during the coming year and will contain an improved model of the soil chemistry.

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Geochemical Effects of Lead Smelters on the Environment*

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Abstract

In 1968, two lead smelters started operating in Southeast Missouri, one in the "New Lead Belt" district and the other near the district. Both smelters are located in dense oak forests. Within the vicinities of the smelters, analyses of the leaf litter and soil samples for lead, zinc, copper, and cadmium indicate that pollution by lead occurs to a distance of up to 20 to 25 miles from one of the smelters and up to three to ten miles from the other. The concentrations of zinc, copper, and cadmium in the leaf litter are higher than the background concentrations for distances of up to 15 miles. The heavy metals are retained predominantly in the decaying leaf litter. Usually less than ten percent of the polluting heavy metals reach the underlying soil where they are retained in the top one inch of the soil layer. Field evidence and laboratory experiments indicate that the organic acids from decaying oak leaves dissolve the polluting heavy metal minerals to a significant extent. The dissolved metals, probably in a complexed form, appear to be removed from the leaf litter during periods of soaking rain.

Ongoing research concerning the influence of humic acids on the solubility and transport of heavy metals should add to the knowledge of metal mobility in nature.

Introduction

The development of the "New Lead Belt" of Southeast Missouri, which started around 1965, changed within a few years a sparsely populated, nonindustrialized area into the most productive lead mining district in the world. Industrial activity on such a scale obviously carries with it the danger of large scale pollution. This paper, in which the influence of lead smelting on the heavy metal content of soils is discussed, presents part of the results of an ongoing interdisciplinary research study. Other findings of the study are published elsewhere (1).

The "New Lead Belt", an area of approximately 5 x 25 miles, is located about 80 miles southwest of St. Louis in Iron and Reynolds Counties. The district, which contains seven active mines and mills and one smelter (Smelter A), is situated almost entirely within the boundaries of Clark National Forest. A second lead smelter (Smelter B) is located outside the mining district about 28 miles southeast of Smelter A. Except for scattered pastures, the area is heavily forested with oak trees. Both lead smelters started production in 1968.

Sampling and Analysis

Preliminary results indicated that the heavy metal fallout from the smelters is retained predominantly in the leaf litter (oak leaves) on the ground. Also, leaf litter samples of different age (partly decomposed and strongly decomposed) contain different heavy metal concentrations. Only a small fraction of the deposited heavy metals is found in the underlying soil.

The collected samples of leaves and leaf litter represent: (a) leaves from oak trees, (b) new leaf litter = "OL" horizon (collected in the fall only), (c) partly decomposed litter = "Of" horizon (collected several weeks to one year after being on the ground) and (d) well decomposed litter = "Oh" horizon. Underlying soil samples were collected from different depths.

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Both the leaf litter and soil samples were dried at 100 C. The soil samples were sieved through an 80-mesh sieve, and the less than 80-mesh fraction was analyzed. The leaf litter samples were prepared for analysis by wet-ashing in a mixture of 5:1 nitric to perchloric acid. The soil samples were digested with nitric acid. The samples were then analyzed by atomic adsorption spectrophotometry at the Environmental Trace Substances Research Center of the University of Missouri (Columbia, Missouri) and at the Geochemical Laboratory of the Department of Geology and Geophysics, University of Missouri-Rolla, Rolla, Missouri.

Distribution Patterns of Heavy Metals Near Smelters

Soil samples from 125 stations covering most of the "New Lead Belt" do not indicate the presence of naturally abnormal, heavy metal concentrations in the soils. The high concentrations can always be related to potential pollution sources. The background concentrations for leaf litter reported in Table 1 are estimates determined from samples collected at a distance of 25 to 30 miles from the smelters.

Several examples of the heavy metal distribution in the soil profiles from the vicinity of smelter A are shown in Tables 2 and 3. The data indicate the ability of leaf litter and moss cover to prevent the heavy metal fallout from reaching the underlying soil. The heavy metals which reach the soil remain concentrated in the top one inch layer of soil. Based on these data, the extent and intensity of heavy metal distribution patterns around the smelters were investigated mainly in the leaf litter horizons.

Smelter A. - Samples collected along six sampling lines radiating from Smelter A indicate that the lead concentrations in leaf litter and tree leaves reach background at a distance of 20 to 25 miles, as exemplified by the samples collected in the direction to the north northwest of the smelter (Fig. 1). High values for zinc are generally limited to a distance of about five miles. At a greater distance, the zinc values, while frequently somewhat higher than the estimated background, are erratic (Fig. 2). Copper and cadmium concentrations approach background at 10 to 15 miles distance respectively (Fig. 3). The area showing increased heavy metal concentrations is only slightly elongated in the northern and southern directions from the smelter with the direction of elongation coinciding with the predominant wind directions.

Smelter B. - The distribution pattern of heavy metals in the vicinity of Smelter B is different. To the north and south of the smelter (main wind directions) lead (Fig. 4), cadmium (Fig. 5), and copper reach background concentrations at a distance of eight to ten miles. Zinc concentrations are erratic but relatively low (Fig. 6). To the west and the east of the smelter, background values are reached at three to five miles distance. The elongated shape of the affected area is probably due to the location of the smelter in a north south running valley with the hills to the west and east reaching heights of 200-300 feet above the valley floor.

The Geochemical Mobility of the Heavy Metals in Soils

Deposition of the heavy metals in the soils appears to occur essentially in the form of particulate heavy metal compounds. The sources of the heavy metals are still under investigation. The presence of slag material that is found up to a distance of 0.5 mile from Smelter A in the soils and leaf litter indicates that fugitive sources, such as storage of ore concentrate and slag material, may be important contributors to the heavy metal content of the soils in the immediate vicinity of the smelters. However, a study of stack emission at Smelter A (1) and the great distances at which increased heavy metal concentrations are found suggest that stack emission is a major and probably the most important source. Baghouse dust can be considered to be chemically and mineralogically similar to the material emitted by the smelter stacks, although some size fractionation might occur. Chemical analyses of samples collected from the stack of Smelter A support this conclusion (1). Some typical data on baghouse dust are reported in Table 4.

An incomplete investigation of the mineralogy of baghouse dust by X-ray and reflective microscopy indicates the presence of PbS (25-50 percent), $PbSO_4$, elementary Pb, and probably $PbO \cdot PbSO_4$ in the baghouse dust of Smelter A. Only $PbSO_4$ and $PbO \cdot PbSO_4$ were found in the dust of Smelter B. Minor amounts of other compounds have not yet been identified.

Field data and laboratory experiments indicate that a significant fraction of the heavy metal compounds, which are deposited in the leaf litter near the smelters, is being dissolved and removed. For instance, a comparison of different litter horizons near Smelter A (e.g. Figs. 1 and 2) shows that the well decomposed leaf litter horizon, Oh, generally has higher heavy metal concentrations than the recent Of horizon. This should be expected, because the Oh layer should contain the heavy metal content deposited over several years. Also, the progressive decay of the leaf litter should reduce the weight of the matrix, which in turn should increase the concentration of heavy metals if there were no removal of these metals. It was expected, therefore, that the younger, Of leaf litter collected in June would have lower metal values, because the period of metal deposition on the trees and on the ground is much shorter. However, the data indicate that the difference in the heavy metal concentrations of the Oh and Of horizons is much too small if the relative length of time for deposition is considered. A fraction of the metal content in the older Oh horizon has to be removed to keep its concentration so near that of the Of horizon. Judging from the relatively low heavy metal concentrations in the underlying soil, which contains frequently less than 10 percent of the total lead in a unit area (e.g. one square meter), the mode of removal does not consist simply in having the lead particles washed downward into the soil.

The suggested removal of heavy metals from leaf litter becomes even more evident in the vicinity of Smelter B. The younger Of horizon partically always has much higher heavy metal concentrations than the underlying Oh horizon (Fig. 4 to 6). This can only be explained by the large scale mobilization of heavy metals from the older Oh horizon.

Because the heavy metals are removed mainly from the leaf litter, it appears reasonable to assume that organic acids, which are formed during the decay of the leaf litter, play an important role in dissolving the polluting particles. The organic acids also probably through the formation of organometallic complexes influence the subsequent mobility of the dissolved heavy metals in soils and water. Baker (2) reports that there is a sharp increase in the solubility of ore minerals in water containing 0.1 percent humic acid as compared to their solubility in water saturated with CO_2. The possibility that heavy metals are transported in aqueous systems in the form of fulvic or humic acid complexes has been pointed out by other researchers (3).

Laboratory experiments, although in a beginning stage, tend to confirm this. When one gram of baghouse dust from Smelter A was treated for 24 hours with distilled water, which had been circulated for 24 hours through uncontaminated leaf litter, 0.17 percent of the lead, 0.23 percent of the copper, 15.0 percent of the zinc, and 12.9 percent of the cadmium in the dust sample were dissolved. In a similar experiment by Dr. Bondietti at the Oak Ridge National Laboratory, deionized water leachates of smelter contaminated leaf litter from Smelter A appeared to contain significant amounts of organically complexed lead and copper. The zinc in the leachates appeared to be only slightly complexed, and cadmium was present largely in an uncomplexed form (4).

The influence of organic acids on the solubility of the heavy metal compounds, the degree and nature of organometallic complex formation, and the influence of complexing on the mobility of the heavy metals in soil and water are presently under investigation. Available data on runoff water indicate that part of the dissolved heavy metals are removed during periods of heavy runoff; however, most rains do not produce runoff. In cases of no runoff, the dissolved metals are transported into the underlying soil. Their chemical state (ionic or complexed) should have a strong influence on their geochemical mobility in the soil.

It may be of interest to consider in this context the differences in the extent of heavy metal distribution patterns around the two smelters. The area of heavy metal deposition around Smelter A is larger than the area around Smelter B. To some degree, this is probably caused by differences in production, morphology of the surrounding area, and stack height. However, it appears that the rate of removal of deposited heavy metals could also significantly affect the extent and intensity of the distribution patterns. If this is true, then the differences in the distribution patterns are strongly influenced by the mineralogy of the polluting particles. According to Baker (2), the presence of humic acids does increase the solubility of PbS. But the increases in the solubilities of such compounds as $PbSO_4$, elementary Pb, and probably $PbO \cdot PbSO_4$ under these conditions are very much higher than those of PbS. As has been pointed out above, the baghouse dust from Smelter A contains up to 50 percent PbS, whereas the baghouse dust from Smelter B is essentially free of PbS. Therefore, at Smelter B which emits only very soluble lead compounds, the rate of dissolution and removal would equal or surpass the rate of deposition at a closer distance than at Smelter A, which emits a more insoluble compound. The very high solubility of zinc compounds in baghouse dust would explain the short distance from the smelter at which it is found in high concentrations. It might also be argued that cadmium, which is equally soluble in baghouse dust, forms more pronounced distribution patterns than zinc, because cadmium appears to be, after dissolution, in an ionic, noncomplexed form which may be relatively immobile.

If these conjectures are essentially correct, then, in an organic rich environment, such as forests where dissolution and removal of polluting heavy metals is facilitated, the area which shows higher than background values is not the total area which receives pollutants but represents only the area where the rate of deposition exceeds the rate of removal. Also, estimates on the size of an area affected by several pollutants should be based on the element which is deposited in the most insoluble form.

Summary

1) Lead smelting activities were found to produce higher than background lead concentrations in leaf litter for distances up to 25 miles. Cadmium, copper, and zinc show less extensive distribution patterns.

2) In heavily forested areas, the deposited heavy metals are found mainly in leaf litter. The underlying soil shows relatively low heavy metal concentrations.

3) Field data and laboratory experiments indicate that a significant fraction of the deposited heavy metal compounds are dissolved, probably by the action of organic acids, and removed in complexed form.

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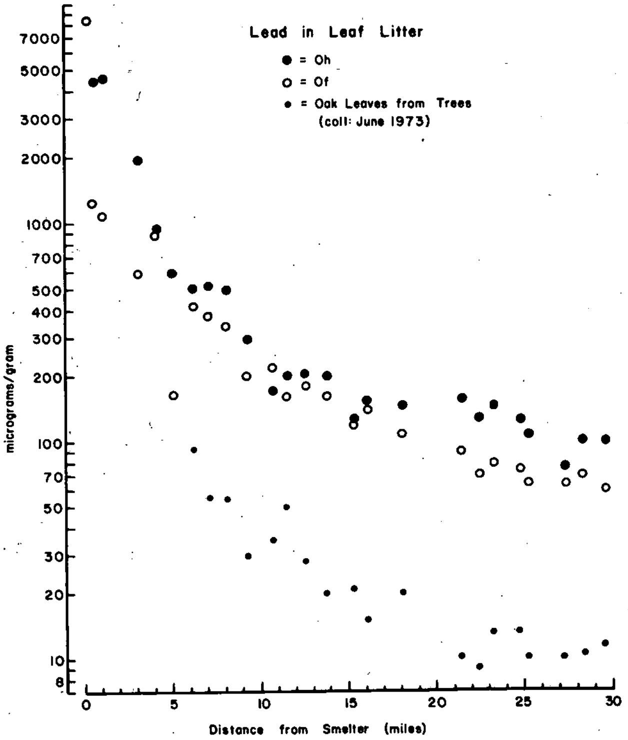

FIG. 1. LEAD IN LEAF LITTER NNW OF SMELTER A.

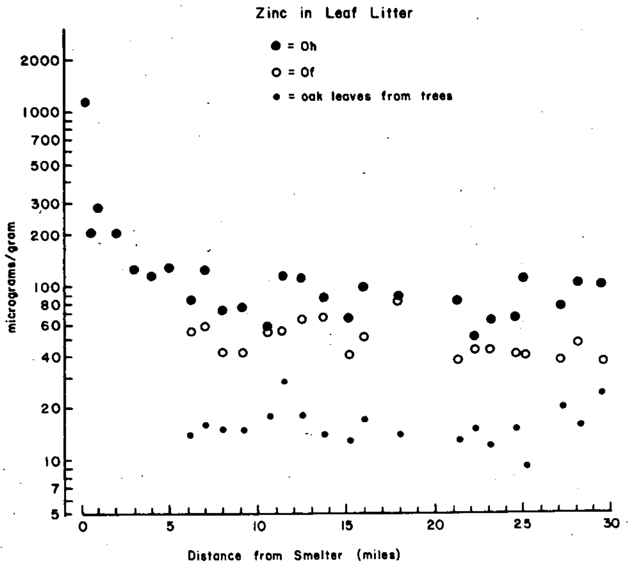

FIG. 2. ZINC IN LEAF LITTER NNW OF SMELTER A.

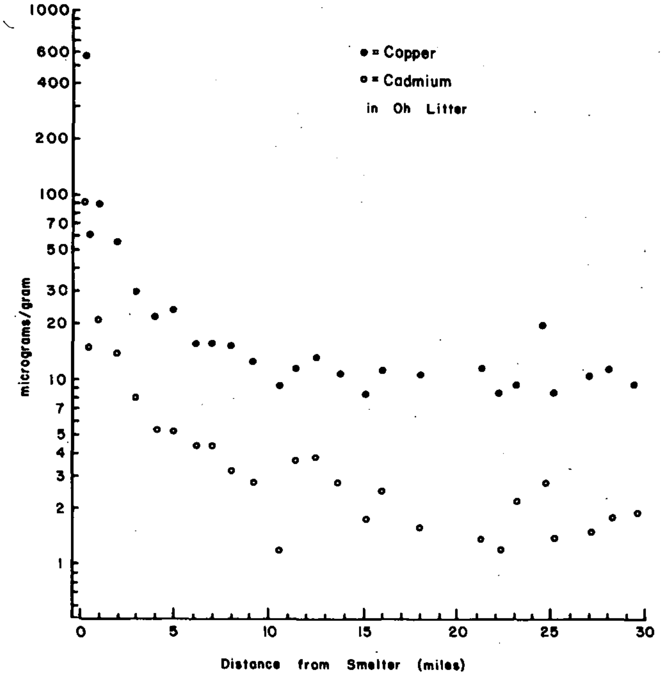

FIG. 3. COPPER AND CADMIUM IN LEAF LITTER NNW OF SMELTER A.

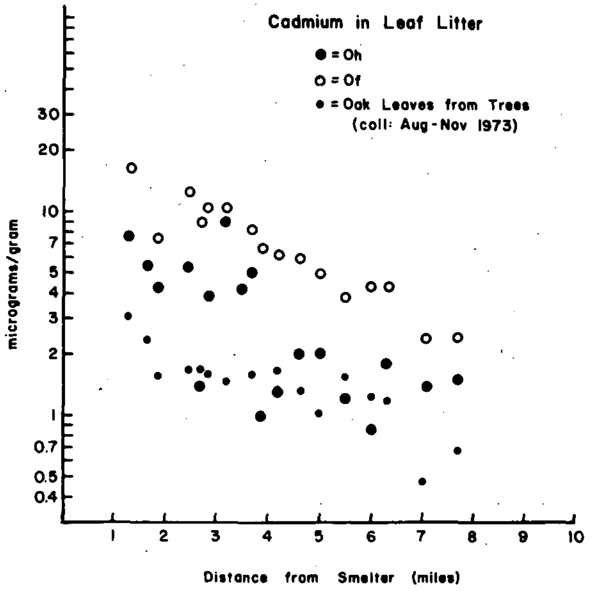

FIG. 5. CADMIUM IN LEAF LITTER NORTH OF SMELTER B.

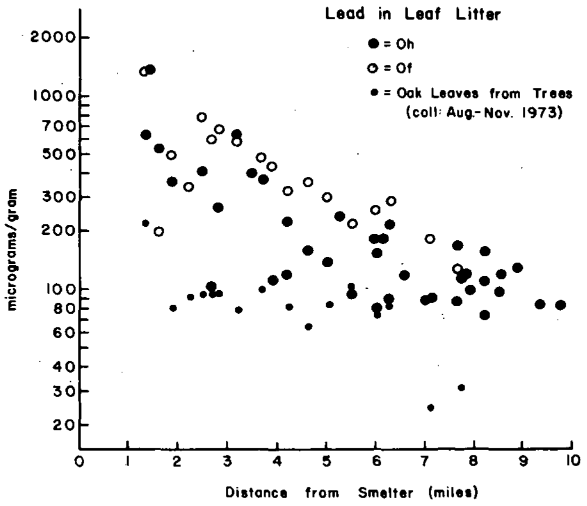

FIG. 4. LEAD IN LEAF LITTER NORTH OF SMELTER B.

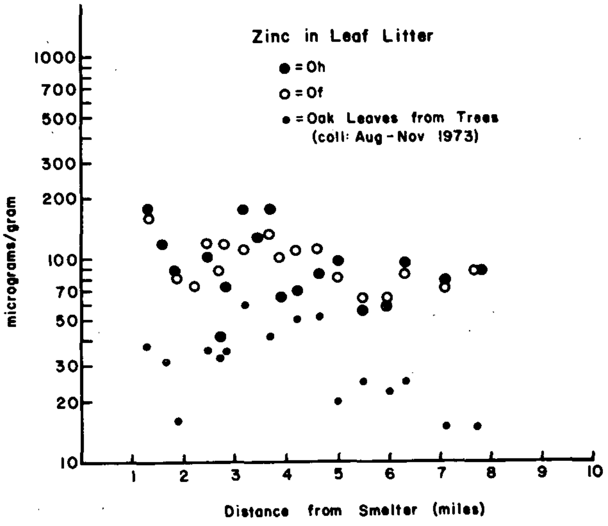

FIG. 6. ZINC IN LEAF LITTER NORTH OF SMELTER B.

Table 1. Background Concentrations

	Pb	Zn	Cu	Cd
		(micrograms/gram)		
Leaf litter, Of-horizon	40-70	35-50	6-8	0.7-1
Leaf litter, Oh-horizon	80-100	50-70	8-11	0.9-1.5
Soil (minus 80 mesh)	15-20	10-20	1.5-4	<0.5

Table 2. Heavy Metals in Soil Profile
(3/10 mile east of Smelter A)

	Pb	Zn	Cu
		(micrograms/gram)	
Total leaf litter (1/2 inch)	7500	330	150
0 - 0.25 inch soil	380	100	30
0.25 - 0.5 inch soil	80	60	10
0.5 - 1.0 inch soil	<20	50	<10
1 - 2 inches soil (minus 80 mesh)	<20	30	<10

Table 3. Heavy Metals in Soil Profile
(2/3 mile south of Smelter A)

	Pb	Zn	Cu
		(micrograms/gram)	
Moss cover (1/8 inch)	4700	480	140
0 - 0.25 inch soil	150	200	20
0.25 - 0.5 inch soil	<20	60	<10
0.5 - 1.0 inch soil	70	50	10
1 - 2 inches soil	70	50	<10
2 - 3 inches soil	20	30	<10
3 - 4 inches soil (minus 80 mesh)	20	50	<10

Table 4. Analysis of Baghouse Dust

	Pb	Zn	Cu	Cd
		Percent		
SMELTER A				
Flue Dust	18.5	1.73	0.25	0.568
Main Baghouse	42.2	4.3	0.37	1.58
Main Baghouse	34.8	6.3	0.145	1.59
SMELTER B				
Blast Furnace Dust	26.8	12.6	0.315	5.95
Sinter Plant Dust	27.2	1.248	1.31	3.07
Blast Furnace Dust	35.2	10.55	0.444	4.7
Sinter Plant Dust	24.8	1.19	0.73	3.2

A STATISTICAL STUDY OF CONTENT OF MOLYBDENUM IN STREAM SEDIMENT ADJACENT TO A MOLYBDENUM MILL*

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ABSTRACT

This work was concerned with the collection and reliability of grab samples of sediment in the study of a trace metal. The area of study was 50 km west of Denver, Colorado near a molybdenum mining and milling operation. Site 1 was on a stream draining the milling operation. Variation in the molybdenum concentration of this sediment was associated with the milling operation. Site 2 was a control stream located nearby. Variation in the molybdenum concentration of this sediment was not associated with the mining and milling operation. At each site five sources of variation were studied: 1) variation among a coarse, medium, and fine size fraction of the sediment; 2) variation among the six monthly sampling periods; 3) variation between winter and spring; 4) variation among samples; and 5) variation within the samples. A nested hierarchial sampling design and analysis of variance were used to examine the 300 samples.

The geochemical data were found to fit a log normal distribution. Therefore data were log transformed before statistical tests.

The concentrations of molybdenum in the three size fractions were different at each site and increased significantly with decreasing grain size.

Time of sampling was not important at the control site. The monthly sampling intervals contributed only a small part to the total variation. Variation between samples was the most important source of variation and contributed most to sampling error. At the Woods Creek site monthly sampling was an important source of variation to the total variation. Variance between the two localities was homogeneous. This suggests that the milling activity does affect the total concentration of molybdenum in the sediment but does not contribute significantly to the natural variation.

INTRODUCTION

Colorado contains numerous Mo deposits inincluding the largest reported deposit in the world at Climax, Colorado. Voegeli and King[1] establish at least 71 areas in Colorado where Mo mineralization can be found. This metal is a micronutrient, but in excess it can be harmful to cattle and other ruminants. With these facts in mind a study of Mo concentrations in stream sediment was begun in the major rivers of Colorado. As a preface to the study of concentrations of Mo in Colorado, a statistical investigation of the reliability of sampling stream sediment was undertaken.

The problem of representative sampling of stream sediment for Mo concentrations was examined with emphasis on five sources of variation. They include monthly variation, seasonal variation, between-sample variation at a sampling site, size-fraction variation, and within-sample variation. A comparison was made between a sampling site adjacent to a mining and milling operation, and a control site which was not influenced by the mining activity. One reason for choosing these two sites was to determine if the activities of man in mining and milling are reflected in the concentration and variability of Mo in the sediments.

The area chosen for study was near the Urad molybdenum mine and mill. This is situated 50 km west of Denver, Colorado in the igneous and metamorphic rocks of the Front Range. The mine operates on Red Mountain, a 12,000 foot peak on the Continental Divide. The ore, a Mo sulfide and Fe and Mo oxide, is transported several thousand feet down the mountain to a mill in the valley. A flotation process is used to separate the Mo from the finely crushed ore. The tailing is retained in disposal ponds and the tailing liquid is decanted to a mill process make-up water reservoir. The lower portion of Woods Creek receives the excess water discharge from the reservoir; for this reason it was chosen as one of the two sampling sites. A control site was chosen two km away on similar geologic terrain. Parameters such as size of stream, type of rock, altitude, and configuration of drainage basin were as homogeneous as possible.

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SAMPLE DESIGN AND STATISTICAL MODEL

The sampling design is a nested, hierarchial type using the analysis of variance. The design is similar to that advocated by Meisch[2] in a recent geochemical survey of Missouri. Figure 1 illustrates the nested levels.

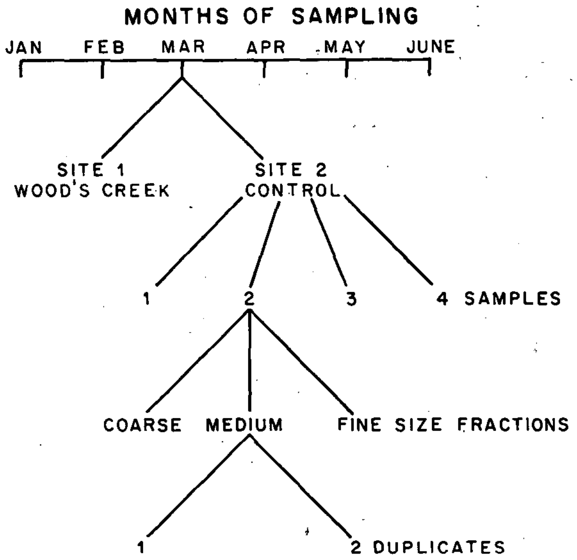

Figure 1. Nested hierarchial sampling design.

Four samples are taken each month with a random method from each site. These are split into coarse, medium, and fine size-fractions and analyzed for Mo in duplicate. Sampling began in January and continued through June 1974. Any seasonal changes associated with the spring run-off would be monitored with this time of sampling. The components of variance are used to determine variance associated with monthly sampling, between-sample variance, and within-sample variance. Formulae for analysis of variance and components of variance were taken from Krumbein and Graybill[3] and Olsen and Potter[4] and are shown in Table I.

The statistical model is represented in equation (1):

$$X_{ijk} = \mu + \alpha_i + \beta_{ij} + \gamma_{ijk} \qquad (1)$$

X_{ijk} is the structure of a single observation for Mo concentration in sediment taken from the i^th^ month, j^th^ sample, and k^th^ replicate. This value can be shown to be the sum of several factors. The first factor is μ, the grand mean of all samples in a size fraction; α_i is the contribution from the month of sampling. The term β_{ij} is the contribution associated with the sample, and γ_{ijk} is the contribution from the replicate. For point estimation α, β, and γ are assumed to be uncorrelated variables with mean zero and variances σ_α^2, σ_β^2, and σ_γ^2, respectively. The components of variance attribute a percentage variance to each of these three components. Equation (2) states that the total variance is the sum of independent variances of the components,

$$\sigma_T^2 = \sigma_\alpha^2 + \alpha_\beta^2 + \sigma_\gamma^2. \qquad (2)$$

The analysis of variance is used to compute these statistics. F-tests are used at each level of the nested sampling design to evaluate any differences.

Two important assumptions must be met to use the analysis of variance on a set of data. First, the distribution must be normal. Second, variation should be homogeneous. The

TABLE I. Equations for analysis of variance.

Source	Degrees of freedom	Sum of squares	Mean square	Expected mean square
Total	IJK - 1	$\sum\sum\sum_{ijk} Y^2_{ijk} - \frac{Y^2_{...}}{IJK}$		
Between A	I - 1	$\frac{\sum_i Y^2_{i..}}{JK} - \frac{Y^2_{...}}{IJK}$	MS_A	$\alpha_c^2 + K\alpha_b^2 + KJ\alpha_a^2$
Between B within A	I(J - 1)	$\frac{\sum\sum_{ij} Y_{ij.}^2}{K} - \frac{\sum_i Y_{i..}^2}{JK}$	MS_B	$\alpha_c^2 + K\alpha_b^2$
Between C within B within A	IJ(K - 1)	$\sum\sum\sum_{ijk} Y^2_{ijk} - \frac{\sum\sum_{ij} Y_{ij.}^2}{K}$	MS_C	α_c^2

data of this study were found to be lognormal in distribution. Figure 2 points out that a log-transform of data served to normalize the frequency curve. Thus all values were log-transformed before using the analysis of variance. The second assumption of homogeneity of the variance means that variances for the populations which are compared should be similar. The log-transform was needed for this requirement also. The term "robust" is used to describe the routine of the analysis of variance with respect to these two assumptions. This indicates that the statistic will still be valid or useful in spite of deviation from normality or homogeneity of the variance.[3]

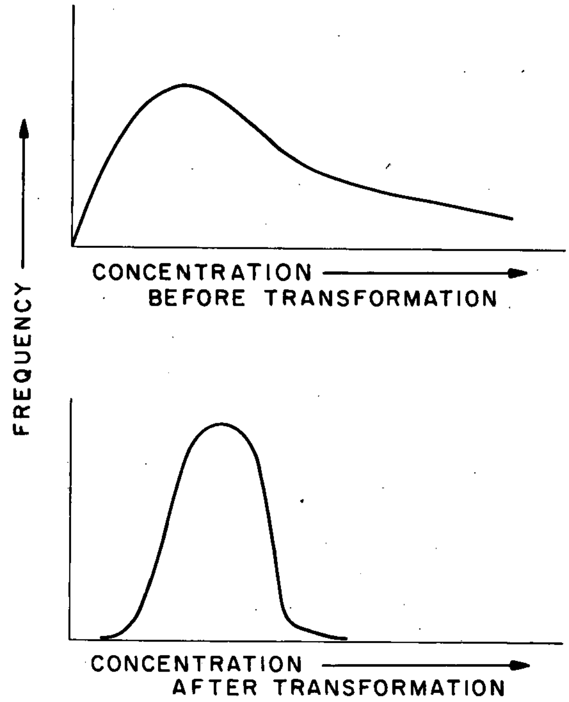

Figure 2. Effect of log transformation on geochemical data.

SAMPLE PREPARATION AND PRECISION

The sediments were air-dried, sieved, and the coarse and medium fractions were cleaned ultrasonically for five minutes. The ultrasonic cleaning was needed to remove silt and clay-size particles which adhered to larger grains and to the sieve. The sediments were then wet-sieved. A comparison of wet versus dry-sieving was done at the beginning of the study. Table II shows the mean concentrations of wet versus dry-sieving for both the control and Woods Creek sites. Using a F-test, significant differences were shown at p=0.05 level. Even without statistical tests obvious differences between wet and dry-sieving are seen. These differences in concentration of Mo are ascribed to finer fractions of sediment not being removed by dry-sieving. The finer fractions contain greater Mo concentrations.

TABLE II. Mo content of the wet versus dry-sieving in coarse size fraction. (Mean of 10 analyses)

	Wet	Dry
Woods Creek	100 ppm	250 ppm
Control Creek	2 ppm	5 ppm

After sieving, samples are oven-dried at 105°C to remove water and then weighed and fused with potassium pyrosulfate. The fusion mixture is dissolved with HCl. Mo is complexed with potassium thiocyanate, extracted into isoamyl alcohol, and determined colorimetrically at 465 nm on a Beckman DU-2 spectrophotometer.

The sensitivity of the determination of Mo in sediments was 0.5 ppm. Precision was ±10% above 10 ppm and ±2 ppm below that. Accuracy was ±10%, based on U.S.G.S. standards and Mo standards furnished by American Metal Climax, Inc. Blind standards were analyzed each month with the samples to monitor any significant monthly variation due to analytical error.

RESULTS

Significant differences were found for a all size fractions between the control site and the Woods Creek site. Table III shows the range of concentrations of Mo in the sediment. Normal background concentrations for Mo in river sediment in Colorado are approximately 2 ppm in -80 mesh size-fraction (medium size-fraction). The Woods Creek samples are two to three orders of magnitude above background. However, it is difficult to show that the mining and milling operation is responsible for these values. This is due to glaciation of the area and the exposure at the surface of the ore body. Another investigator, Dawn Brown of the Molybdenum Project (University of Colorado), is examining differences between tailings and glaciated sediment with electron microprobe in an attempt to determine the proportion of the total Mo which is natural and the proportion which has been introduced by man.

Differences were found for the three size fractions at each site. It can be seen from Table III that concentrations of Mo in the sediment increase with decreasing grain size. The size-fractions were split into smaller

TABLE III. Mo concentrations in sediment. Woods Creek versus Control Creek. (Each fraction is the mean of 75 analyses)

Size fraction	Woods Creek	Control Creek
Coarse	100 ppm	2 ppm
Medium	500 ppm	15 ppm
Fine	1200 ppm	45 ppm

intervals to investigate further the variation of concentration with size. Tables IVA and IVB show the Mo concentrations in the sediment from the 2.0 mm to 0.002 mm (coarse sand to clay-size particles). Mo concentrations increase with decreasing grain size at both Woods Creek and the control site. One plausible explanation for the increasing Mo concentration with decreasing grain size is the adsorption of Mo onto the smaller particles with increased surface area, but I have not verified this.

TABLE IVA. Mo concentrations of control site by size fractions.

Size interval	Concentration	Weight % of total sediment
Sand:		
2.0 - 1.0 mm	2. ppm	58
1.0 - 0.5 mm	2. ppm	29
0.5 - 0.25 mm	3. ppm	8
0.25 - 0.125 mm	5. ppm	1.4
0.125 - 0.063 mm	15. ppm	0.8
Silt:		
0.063 - 0.032 mm	40. ppm	0.8
0.032 - 0.016 mm	35. ppm	2
0.016 - 0.008 mm	35. ppm	
0.008 - 0.004 mm	40. ppm	
0.004 - 0.002 mm	50. ppm	
Clay:		
<0.002 mm	145. ppm	

TABLE IVB. Mo concentrations of Woods Creek by size fractions.

Size interval	Concentration	Weight % of total sediment
Sand:		
2.0 - 1.0 mm	120. ppm	71.3
1.0 - 0.5 mm	110. ppm	24.
0.5 - 0.25 mm	100. ppm	3.6
0.25 - 0.125 mm	300. ppm	0.55
0.125 - 0.063 mm	700. ppm	0.05
Silt:		
0.063 - 0.032 mm	850. ppm	0.5
0.032 - 0.016 mm	1750. ppm	
0.016 - 0.008 mm	1800. ppm	
0.008 - 0.004 mm	1850. ppm	
0.004 - 0.002 mm	1850. ppm	
Clay:		
<0.002 mm	1100. ppm	

The time of sampling was found to be of varying importance. At the control site, a F-test among months was not significant for the coarse and medium size-fractions. Table VA shows sum of squares, mean square, and F-values for the monthly tests; seasonal tests are shown in Table VB. The null hypothesis was accepted that there was no difference among months for the coarse and medium size-fraction of the control site, as shown in Table VA. The components of variance for these size fractions show that 11% and 0% of the total variance at the control site are associated with monthly sampling, respectively, as shown in Table VIA. Table VIA also shows that for the coarse fraction at the control site, replications are the major source of variation (89% of total variance). This is important in terms of the proposed program for determining background concentrations in Colorado. The time or season of sampling will not contribute significantly to the total variance, and multiple samples at a site will better illustrate the variance in concentrations of Mo in the stream sediment. The medium size-fraction at the control site has 42% of total variance between-samples and 58% within-samples.

The fine size-fraction at the control site did show a significant F-value, 3.16 (Table VA). As shown in Table VB, a seasonal test (i.e., combining January through March and testing against April through June) also showed significance.

Figures 3a and 3B show the monthly plots of the interval estimate of the mean for each month. There may be a slight increase in Mo concentrations in and during the spring run-off for the fine size-fraction at the control site (Figure 3a).

At the Woods Creek site all size fractions show significant F-values at the p=0.05 level when tested for monthly differences (Table VA). A seasonal test shows that the variation is significant only for the coarse and medium size fractions at Woods Creek (Figure 3b and Table VB).

In Figure 3b, the content of Mo in the coarse fraction in Woods Creek is seen to increase during the spring run-off, but the medium fraction (Figure 3b) decreases during the spring run-off. Interpretation here is difficult and several possibilities exist. First, the seasonal change could be an artifact, caused by the sample to sample variation

TABLE VA. Results of F-test for variations among months in Mo concentration in stream sediment. (Six month period. Total samples = 48)

Source	Size fraction	Sum of squares	Degrees of freedom	Mean square	F-value	Significance
Woods Creek	Coarse	SS_B = 2.0292	5	0.4058		
		SS_W = 1.0900	42	0.0259	15.6	.05
		SS_T = 3.1192	47			
	Medium	SS_B = 2.6235	5	0.5247		
		SS_W = 3.7413	42	0.0891	5.90	.05
		SS_T = 6.3648	47			
	Fine	SS_B = 0.3695	5	0.0739		
		SS_W = 0.9813	42	0.0234	3.16	.05
		SS_T = 1.3508	47			
Control	Coarse	SS_B = 0.4238	5	0.0848		
		SS_W = 2.2542	42	0.0537	1.58	N.S.
		SS_T = 2.6780	47			
	Medium	SS_B = 0.2769	5	0.0554		
		SS_W = 3.1162	42	0.0742	0.7	N.S.
		SS_T = 3.3931	47			
	Fine	SS_B = 0.8335	5	0.1667		
		SS_W = 1.8213	42	0.0434	3.84	.05
		SS_T = 2.6548	47			

SS_B = Sum of the squares between
SS_W = Sum of the squares within
SS_T = Sum of the squares total

N.S. = Not significant

$F_{p = .05;\ 5,\ 42} = 2.44$

at the sampling site. The evidence for this possibility is suggested by the fine fraction which should be the most likely to show monthly change and in fact does not appear to change (Figure 3b and seasonal test fine fraction Table VB). The fine fraction should be most easily carried by increased water flow and has considerably more surface area for adsorption or desorption of Mo. Second, the seasonal change could be real and could represent adsorption or desorption onto the larger grains from the increased Mo concentration in the water during spring flow from the tailings pond on Woods Creek. However, the medium size-fraction is seen to decrease during spring run-off (Figure 3b), which is contrary to what would be expected on the basis of its greater surface area than the coarse size-fraction. The program of monthly sampling will continue throughout the summer of 1974 to further test the reality of the monthly variations.

Other investigators have found monthly variation in the content of heavy metals in stream sediment. Govett[5] in northern Rhodesia found variation in Cu content from two to four fold during the rainy season. Malmqvist[6] in Sweden has found seasonal changes at the end of spring for Mo in sediment, but the changes are slight, with most variation associated with the sampling site. Gawron[7] found that time of sampling could be important in collection of sediment for a series of trace

TABLE VB. Results of F-tests for variation between seasons (winter vs spring) of the Mo content of stream sediment using analysis of variance for significant size fractions from monthly tests (Table VA). (Six month period. Total samples = 48)

Source	Size fraction	Sum of squares	Degrees of freedom	Mean square	F-value	Significance
Woods Creek	Coarse	$SS_B = 1.68750$	1	1.68750		
		$SS_W = 1.38350$	46	0.03010	56.	.05
		$SS_T = 3.07100$	47			
	Medium	$SS_B = 0.96330$	1	0.96330		
		$SS_W = 5.37330$	46	0.11680	8.2	.05
		$SS_T = 6.33660$	47			
	Fine	$SS_B = 0.00333$	1	0.00333		
		$SS_W = 1.37583$	46	0.02990	0.1	N.S.
		$SS_T = 1.37916$	47			
Control Creek	Fine	$SS_B = 0.42188$	1	0.42188		
		$SS_W = 2.23291$	46	0.04854	8.7	.05
		$SS_T = 2.65479$	47			

SS_B = Sum of the squares between

SS_W = Sum of the squares within

SS_T = Sum of the squares total

N.S. = Not significant

$F_{p = .05;\ 1,\ 46} = 4.06$

elements in Ontario, Canada. However, his sampling period was only from October to December. Barr and Hawkes[8] found that time of sampling was not important in British Columbia when sampling for trace metals. Their sampling period was from June to September and did include the high water season.

The conclusion reached to date is that background concentrations of Mo do not seem to vary with season. However, anomalous values of Mo do change with time of sampling, at least in the situation affected by mining and milling. Anomlaous values are those above about 25 ppm in the sediment. An exception to this temporal variation may occur in the very fine size-fraction at Woods Creek.

Water samples were also taken each month at Woods Creek and the control site. These data are presented in Table VII. The water from the control sites contain 0-5 μg/ℓ Mo which is background for natural river water. Woods Creek contains two to three orders of magnitude more Mo than background and is found to change seasonally. During the spring runoff Mo concentrations increased 20 fold, contrary to what might be expected due to the five to ten fold increase in volume of water. This same phenomenon is seen below a tailings pond at another Mo mine west of Urad and is probably associated with release of excess water from the tailings ponds during the influx of meltwater from snow. The concentrations of Mo in the water were analyzed both before and after filtering through a 0.45μ membrane filter, and no difference was found in concentration.

It is interesting to note that the sediment at Woods Creek during the time that the high concentrations of Mo existed in the water apparently responded in different ways depending on size fraction. The coarse fraction went up in Mo concentration, the medium went down, and the fine fraction did not change. It seems that interactions between water and sediment could be important during these times, but more study is obviously needed on the capacity of sediments for adsorption of Mo.

Three different chemical extractions were performed on the fine fraction at Woods Creek

TABLES VIA AND VIB. Components of variance for control site and Woods Creek.

Size fraction		Degrees of freedom	Sum of squares	Mean square	Expected mean square	% total variance
TABLE VIA. Control Site						
Coarse	Total	47	2.672			
	Between months	5	0.442	0.0084	$\alpha_m^2+4\alpha_S^2+6\alpha_M^2$ *	$\alpha_M^2 = 11\%$
	Between samples within months	18	0.845	0.0469	$\alpha_m^2+4\alpha_S^2$	$\alpha_S^2 = 0\%$
	Between measurements within samples within months	24	1.385	0.0577	α_m^2	$\alpha_m^2 = 89\%$
Medium	Total	47	3.393			
	Months	5	0.296	0.0592		$\alpha_M^2 = 0\%$
	Samples	18	2.320	0.1290		$\alpha_S^2 = 42\%$
	Measurements	24	0.777	0.0324		$\alpha_m^2 = 58\%$
Fine	Total	47	2.622			
	Months	5	0.808	0.1616		$\alpha_M^2 = 31\%$
	Samples	18	1.127	0.0626		$\alpha_S^2 = 16\%$
	Measurements	24	0.687	0.0286		$\alpha_m^2 = 53\%$
TABLE VIB. Woods Creek						
Coarse	Total	47	3.216			
	Months	5	2.129	0.4258		$\alpha_M^2 = 77\%$
	Samples	18	0.842	0.0468		$\alpha_S^2 = 11\%$
	Measurements	24	0.245	0.0102		$\alpha_m^2 = 12\%$
Medium	Total	47	6.447			
	Months	5	2.732	0.5464		$\alpha_M^2 = 51\%$
	Samples	18	3.342	0.1857		$\alpha_S^2 = 36\%$
	Measurements	24	0.373	0.0155		$\alpha_m^2 = 13\%$
Fine	Total	47	1.418			
	Months	5	0.375	0.0750		$\alpha_M^2 = 23\%$
	Samples	18	0.700	0.0389		$\alpha_S^2 = 23\%$
	Measurements	24	0.343	0.0143		$\alpha_m^2 = 54\%$

*m = measurements; S = samples; M = months.

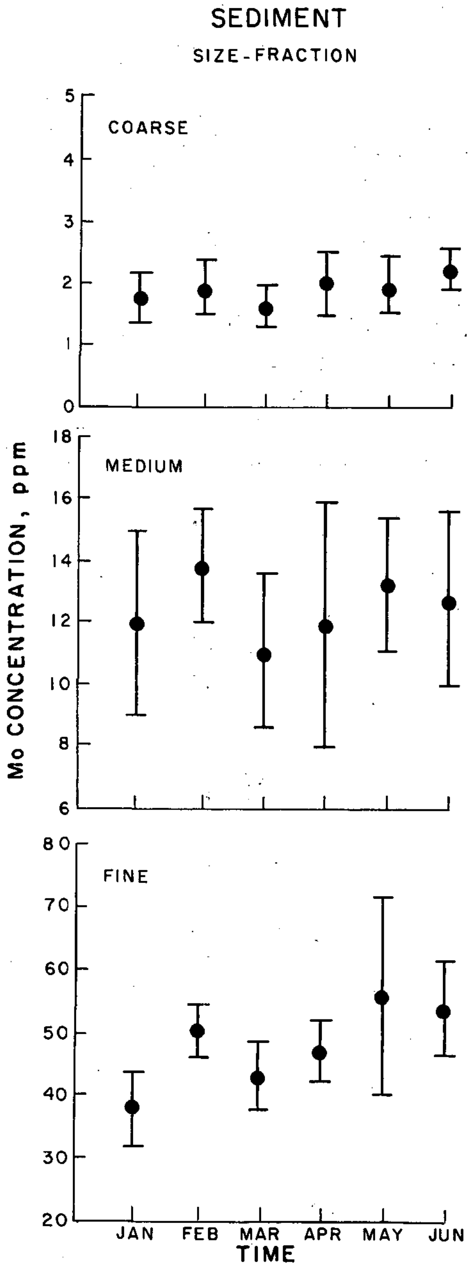

Figure 3a. Results of interval estimates of the mean at the 95% confidence limits for a six month period at the control site.

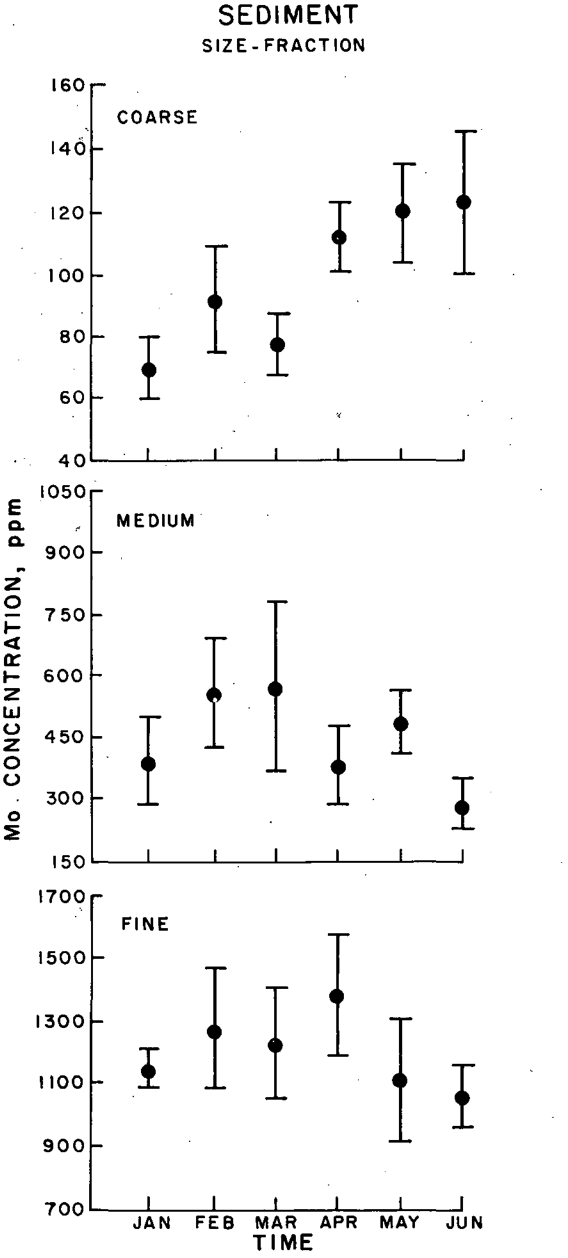

Figure 3b. Results of interval estimates of the mean at the 95% confidence limits for a six month period at the Woods Creek site.

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to learn something about the location and form of the Mo in the sediment. It was found that some Mo was easily exchangeable, some was bound in organic matter, and some was bound in Fe and Mn oxyhydroxides. Table VIII shows the extractants used and the percent of the total Mo extracted from the sediment.

Sodium sulfate (0.1 M) extracted 35% of the total Mo, presumably only representing the amount of Mo that is ion-exchangeable. Sodium hypochlorite (5 percent, v/v) was used to dissolve the organic matter, thus removing another 30% of the total Mo. Finally, a 25% acetic acid treatment was used to remove Mo loosely associated with the Fe and Mn

TABLE VII. Monthly water monitoring, 1974. (Mo content in mg/ℓ)

Month	Woods Creek	Control Creek
January	5	< 0.005
February	2	< 0.005
March	35	< 0.005
April	35	< 0.005
May	5	< 0.005
June	5	< 0.005

TABLE VIII. Percent of Mo extracted by three reagents from Woods Creek sediment.

Sample number	Sodium sulfate 0.1 M	Sodium hypochlorite 5%	Acetic acid 25%
1	25	35	0
2	35	35	0
3	30	40	0

oxyhydroxides. No Mo was recovered from this extraction. In retrospect, this extraction was probably not sufficiently severe to dissolve all of the Fe and should be repeated. However, there is evidence that the sulfate and hypochlorite treatments could have removed Mo adsorbed on the ferric hydroxide; the acetic acid did partially dissolved the Fe hydroxides but no Mo was found. In summary, although these extractions represent only preliminary work, the results do suggest that approximately 50% of Mo in fine fraction at Woods Creek is loosely bound as adsorbed ions on fine particles or organic matter.

CONCLUSIONS

The conclusions drawn from this work are: 1) monthly variation or seasonal variation is not significant at background levels of Mo concentration in sediment, especially in comparison to the variation associated with the sampling site or with replication; 2) Mo concentrations increase with decreasing grain size - this could be an adsorption process because surface area increases with decreasing grain size; 3) the most important source of variation in a background study for Mo in stream sediment is the within-sample variation; 4) Mo concentrations in stream sediment are log-normally distributed; 5) wet-sieving is necessary to remove silt and clay from the coarse size-fractions; 6) water-sediment interactions are complex, and it is not readily apparent whether adsorption or desorption is taking place between the Mo-rich sediments and the water of Woods Creek; 7) in spite of large differences in mean values between the control site and the Woods Creek site, the variation about the mean in log units was the same which suggests that the variation is about the same in the man-distributed site and the control site; and 8) about 50% of the Mo is easily extractable from the Woods Creek sediment.

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MODIFICATION OF THE UNIFIED TRANSPORT MODEL TO ALLOW FOR SEDIMENT TRANSPORT AND CHEMICAL EXCHANGE*

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We have developed a process model of trace contaminant transport through a stream channel system. Dissolved contaminant is controlled by the flow routing of the system while the adsorbed fraction is controlled by sediment transport dynamics governed by bed load and suspended load transport. The dynamic partitioning of the contaminant between water and particulate is considered. Our sediment transport formulation is an extension of an approach described by R. A. Bagnold in 1966, and includes Manning's equations and modifications to Stoke's law allowing calculation of particle fall velocity in both the viscous and inertial particle settling regions. Sediment is separated conceptually into three components, that resident in the stream bed, that in transit as bed load, and that in transit as suspended load. Each of these components is partitioned into twelve size classes of logarithmically varying size ranges. Required input parameters are exchange constant and, for each such class, particle density, diameter, void fraction, and angle of repose. For a non-homogeneous channel made up of several reaches, each reach is specified according to slope, width, length, and roughness, as characterized by Manning's "n" coefficient. The magnitudes of bed and suspended load for each size class and the net contaminant flux out of the reach are computed. Initial results are presented, and comparisons are made of nineteen simulated and measured values.

You will hear three talks today dealing with the Unified Transport Model. John Munro has told you of our application of the model to the Crooked Creek Watershed near Rolla, Missouri, while Dick Raridon has described simulations of the transport of potassium and cadmium on Walker Branch Watershed in East Tennessee.

I would like to describe to you in this talk some recent refinements of the model. We have merged the Unified Transport Model (UTM) with CHNSED (Channel Sediment Transport Model) and have implemented algorithms for chemical exchange between the sediment and the water in the channel system. The flow of hydrologic and pollutant information in the UTM/CHNSED model is as follows: The Atmosphere Transport Model (ATM) computes, given source-related information, the wet and dry deposition rates to be used in the subsequent portion of the model. Next, the PRECIP section accepts this information and distributes these input quantities for the desired simulation period to the LAND section. The LAND section distributes quantities from the PRECIP section and includes algorithms to simulate subsurface and surface transport-associated processes for the response of a unit area of landscape. The CHANNL section (where most of the changes I will be describing have been implemented) routes the water, pollutant, and sediment provided by the LAND section

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through a system of reaches. Mechanisms simulated here include sediment transport and chemical exchange.

Some of the terms we will be using during this discussion are reach, bed load, and suspended load. A "reach" is a nominally homogeneous segment of a stream-reservoir system; it has the same slope and bed friction coefficient along its entire length. We use the term "suspended load" to describe that fraction of transported sediment load supported primarily by fluid-transmitted stresses, and we describe by bed load that fraction supported primarily by solid-transmitted stresses.

First I'd like to describe in general terms the CHNSED model, and then I'll discuss what the combined UTM/CHNSED model does and how it operates. If we assume for the moment that we have one single type of sediment, we can say that bed load transport occurs when

$$T/P = \tan\alpha ,$$

where T is the shear force, P the normal force on a particle, and α is the angle of repose for that sediment type. The bed load work rate then can be shown to be the product of i_b, the wet mass transport rate per unit width for the bed load times the tangent of α. The suspended load work rate can be shown to be the product of the wet mass transport rate for suspended load per unit width times the ratio of V_F, the sediment fall velocity (settling velocity) to the average stream velocity $\overline{u}_s$.

Thus we have relationships between the mass transport rates per unit width and the work rates for bed load and suspended load transport. R. A. Bagnold in 1966 described a procedure for calculating sediment transport rates based upon, as starting points, bed load and suspended load work rates. He showed that one could relate these work rates to the available stream power by appropriate efficiency factors. The available stream power, ω, is dissipated by several work-rate mechanisms, among these the bed load transport work rate and the suspended load work rate. The bed load work rate is defined as the product of the available stream power, ω, and e_b, the efficiency factor for bed load transport. Similarly, the product of the available stream power and the efficiency factor e_s is the suspended load work rate. Thus we can relate the available stream power, ω, which arises from the fall of water through a gravitational potential to the bed load and suspended load work rates. Bagnold showed through a combination of theoretical arguments and flume experiments that one could determine the factors e_b and e_s--I'm going to go very rapidly here and come back if there are any questions. The factor e_b can be shown to lie between .11 and .15, whereas e_s is approximately .016. In conclusion, if the shear stress at the boundary is sufficient to cause bed load transport to occur, the bed load transport rate is given by the formula

$$i_b = e_b \omega / \tan\alpha$$

and if the suspended load criteria is satisfied, i.e., if the RMS vertical component of the velocity is sufficient to support the sediment against the gravitational force attempting to cause it to settle out, the suspended load transport rate is given by

$$i_s = e_s \omega (1-e_b) \overline{u}_s / V_{fall}$$

Thus far we have assumed that we have a single homogeneous reach and that we have a single type of sediment having a known density, diameter, packing fraction, and angle of repose. Our real world model is somewhat more complex. We have implemented a multireach approach that accepts a realistic distribution of sediment sizes and properties. The suspended load, as well as the bed load, has been computed from the distribution of sediment on the channel bed. We have defined the sediment by specifying its fractional distribution into 12 different size classes, spanning the range from a micron to a centimeter. Applying this characterization process in Figure 1, we see the fractional mass contribution of each of the twelve size classes to the total bed sediment on the Rio Grande River near Bernalillo, New Mexico. The abscissa shows the size class and the ordinate the fractional contribution of that class. Plotted also along the abscissa is the particle size in millimeters.

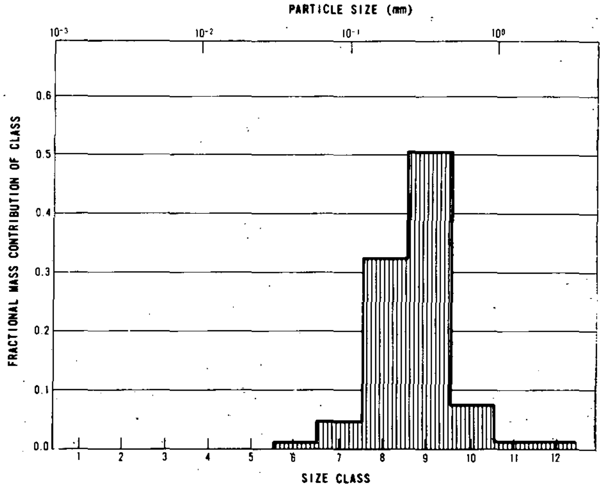

Figure 1: Average fractional sediment mass contribution vs. particle size for each of twelve size classes on bed; flow rate = 10100 ft /sec.

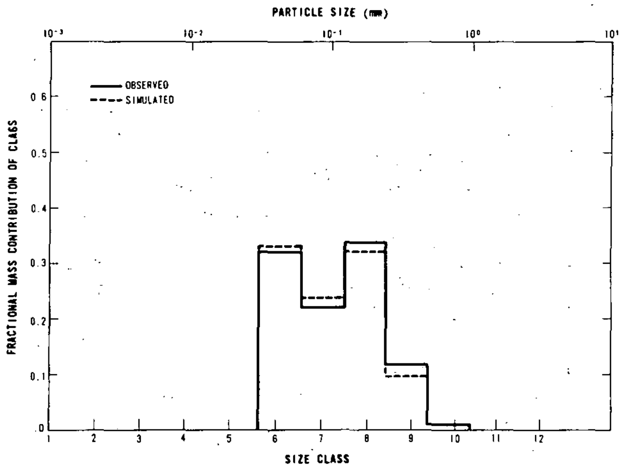

Figure 2: Simulated (dashed) and observed (solid line) particle size distribution in suspended load; flow rate = 10100 ft /sec.

Figure 2 shows the simulated (dashed line) and observed (solid line) particle size distribution of the suspended load. In Figure 3 we see that the suspended load distribution is doubly peaked on the lower side as a result of the increasing tendency of the smaller sediment particles to be suspended and on the higher side as a result of the increased available sediment present in the higher classes.

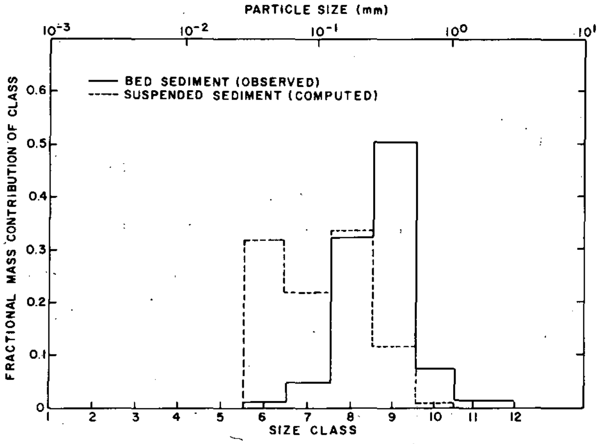

Figure 3: Size distribution observed for resident bed sediment (solid lines) and computed for suspended sediment (dotted lines) for flow rate = 10100 ft /sec.

Staying with this same test site--and at this point using data published by R. A. Bagnold and by F. B. Toffaleti--we plot in Figure 4 the observed (solid line) and simulated (x and broken line) total transport rate in tons per day via bed load and suspended load. These transport rates are plotted against the measured mean flow velocity in feet per second. The points denoted by X and connected by a dashed line resulted from the following process: For the simulation for April 25, 1952, we adjusted the bed friction coefficient (which is Manning's n, for those of you familiar with this parameter) so that the simulated mean flow velocity agreed with the measured mean flow velocity; for the other points on this curve we preserved this value of the friction coefficient. For each of these runs we input the size distribution characterizing bottom sediment and the measured slope of the water surface (necessary for the computation of available stream power).

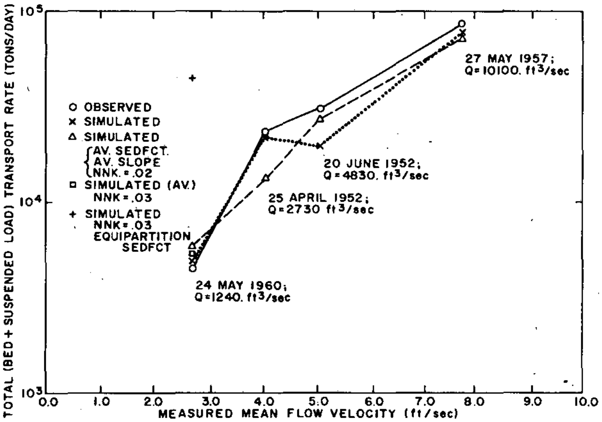

Figure 4: Observed and simulated sediment transport rate (bed load + suspended load) vs. measured flow velocity for Rio Grande River, Bernalillo, New Mexico.

The next series of runs were made by keeping the distribution of sediment sizes on the bottom at an average value and by keeping also constant the parameters average slope and bed friction coefficient. We obtained the simulations denoted by the triangles and connected by dotted lines, which again exhibit reasonable agreement with the observed values. Next, a single simulation, denoted by the square, was carried out, changing from the previous values only the bed friction coefficient. The original value was 0.02, the new value 0.03. We see that the bed friction coefficient is not a sensitive determinant of computed transport rate. A single run, denoted by +, was then made with the average sediment distribution function replaced by an equapartition distribution function, i.e., with the same mass in each of the twelve size classes; we see that this simulation is in poor agreement with the experimentally determined transport rate, indicating the importance of measuring the distribution of sediment sizes on the bed.

We then went back to average parameters and made several more simulations to insure that we hadn't accidentally picked four that seemed to give reasonable results. The results for these runs are shown in Figure 5, which bears out our original conclusion that the model seems to be working as hoped.

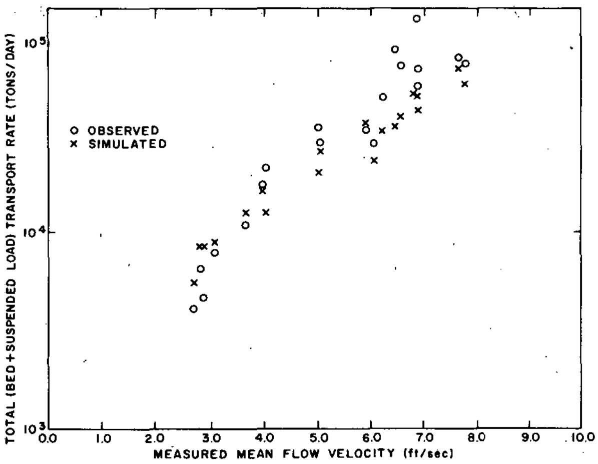

Figure 5: Observed and simulated sediment transport rate (bed load + suspended load) vs. measured flow velocity for Rio Grande River, Bernalillo, New Mexico. Average channel slope and sediment parameters have been used.

This concludes the discussion of the CHNSED portion of the model. I would like to now describe the operation of the merged UTM/CHNSED model.

Figure 6 shows the sediment routing scheme used in the current UTM/CHNSED model. For clarity we show only one reach. Input sediment is tracked as suspended load input and bed load input. Whereas the bed load input, for computational purposes, is assumed to immediately become part of the sediment resident on the reach bed, the suspended load input is split into two parts, that part which settles out as the suspended load migrates through the reach and that portion which remains in suspension. At the reach output, to that unsettled suspended load portion is added the suspended load contribution from the reach bed. The suspended load out is computed by bearing in mind the actual distribution of settlement sizes on the reach bed and that computed to be in suspension. The bed load output is assumed to have a composition identical to that of the sediment resident on the reach bed.

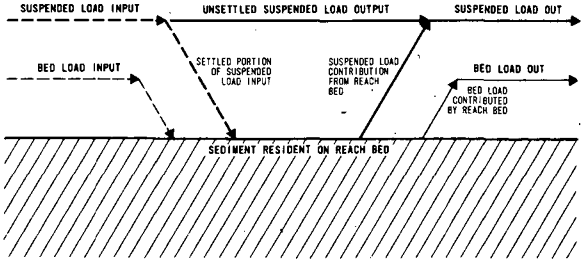

Figure 6: Sediment routing in current UTM/CHNSED model (one reach shown for clarity).

In this version of the UTM/CHNSED model, chemical exchange is assumed to occur between the sediment and the reach water at two points. These points are the input to the reach where exchange occurs between total input sediment and the input water and at the output of the reach where exchange is considered to occur between the total sediment output and the water output. The pollutant is assumed, in this very simple model, to equilibrate between the sediment and water with the equilibrium pollutant distribution subsequent to exchange governed by the following equations. We describe the ratio of the concentration of pollutant in the solid phase to the concentration of pollutant in the water by the chemical distribution coefficient k_d, which we here denote by KD. The exchange at the reach input leads to the distribution of pollutant shown in the following equations:

$$\mathrm{PWAIN} = \frac{\mathrm{POLIN} * \mathrm{WATMAS}}{(\mathrm{SEDINT} * \mathrm{KD}) + \mathrm{WATMAS}}$$

$$\mathrm{PSEIN} = \frac{\mathrm{POLIN} * \mathrm{KD} * \mathrm{SEDINT}}{(\mathrm{SEDINT} * \mathrm{KD}) + \mathrm{WATMAS}}$$

Here POLIN is the total available pollutant, WATMAS and SEDINT are the water mass and sediment mass available to exchange the pollutant, and PSEIN and PWAIN represent the quantity of pollutant associated with sediment and with water following the chemical exchange. A completely analogous pair of equations describes the concentration in the water and in the sediment after exchange at the reach output.

Figure 7 diagrams pollutant routing in the UTM/CHNSED model. We see schematically on the left the input pollutant routing, then the intra-reach simulation, and on the right the output pollutant routing. The water-associated input consists of contributions from the LAND segments and inputs from higher reaches. The sediment-associated pollutant input consists of sediment input from the LAND segments plus sediment input from the higher reaches. Following chemical exchange between these inputs the water-borne pollutant is routed through the reach along with the water, and the sediment input is assumed to combine with the resident bed sediment. Following computation of sediment output, and thus pollutant output associated with the sediment, this sediment combines with the output water and the water-associated pollutant. Following exchange at the output of the reach, the pollutant is tallied as water-associated pollutant output and sediment-associated pollutant output.

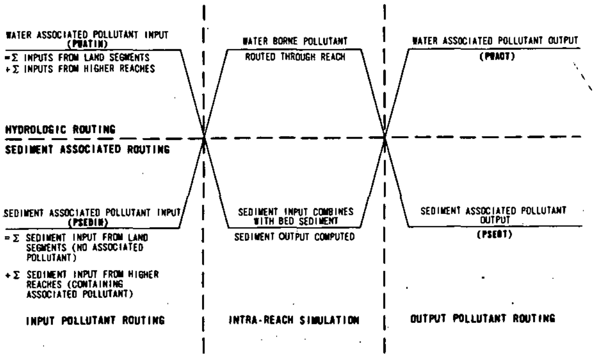

Figure 7: Pollutant routing showing current UTM/CHNSED approach to water-sediment pollutant exchange (one reach shown for clarity).

Finally, I should mention required UTM/CHNSED input parameters. First, we need all UTM parameters. The additional CHNSED parameters required relate mostly to sediment data where we need, for each size class, the density, the packing fraction, and the angle of repose. We also need the distribution function of the sediment resident on the bed, and we need some measured or assigned k_d for the pollutant of interest.

TRANSPORT OF POTASSIUM AND CADMIUM ON WALKER BRANCH WATERSHED*

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Abstract

A modified version of the Wisconsin Hydrologic Transport Model has been used to simulate the movement of potassium and cadmium through the Walker Branch Watershed, a highly instrumented area of 250 acres situated near Oak Ridge National Laboratory (ORNL). Weekly measurements of trace materials in rainfall and dustfall, together with hourly rainfall data, provided the input for the computer program. The calculated amounts of potassium and cadmium in the stream exiting the watershed show reasonable agreement with the observed values. Some potassium appears to be leached from the soil since the output on an annual basis, _ca_. 5 kg per hectare, is approximately twice the input. In contrast, preliminary observations indicate that over 90% of the input of cadmium is retained by the watershed.

One of the projects in the NSF Sponsored Ecology and Analysis of Trace Contaminants Program at Oak Ridge is the development of a computer model to follow the pathways of trace contaminants in the environment. Figure 1 shows a block diagram of the Unified Transport Model which was described by M. R. Patterson at last year's trace contaminants conference [1]. Precipitation data, together with an air transport model, provide both rainfall and contaminant deposition to the land surface of a watershed. Alternately, monthly deposition values can serve as input directly without using ATM. The hydrologic portion of the model, from PRECIP, through LAND, and into CHANL, is based on the Stanford Watershed Model [2]. It was modified by Dale Huff [3] to include material transport through an ion exchange mechanism. I have been concerned with attempting to validate the hydrologic and transport portion of the UTM using data collected on the Walker Branch Watershed.

Figure 2 shows the hydrologic flow through a land area segment of a watershed. Part of the input data is hourly precipitation. A subroutine calculates the evapotranspiration given the input of wind speed, solar radiation, and daily temperature variations. There are 20 land surface parameters, including the initial values for the storage terms, which govern the rate and volume of water flow through the

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**Prime contractor for the U. S. Atomic Energy Commission.

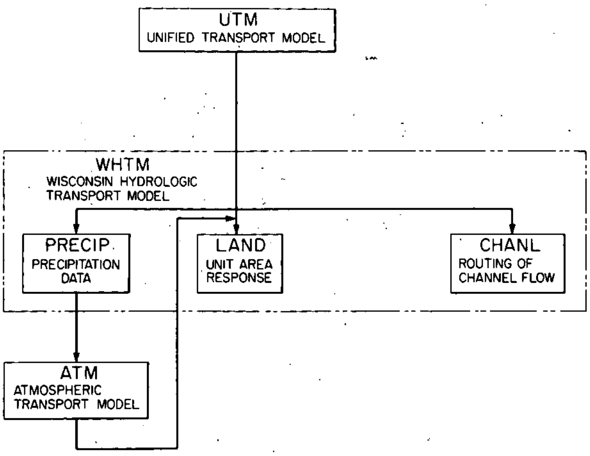

Fig. 1. Structure of the Unified Transport Model.

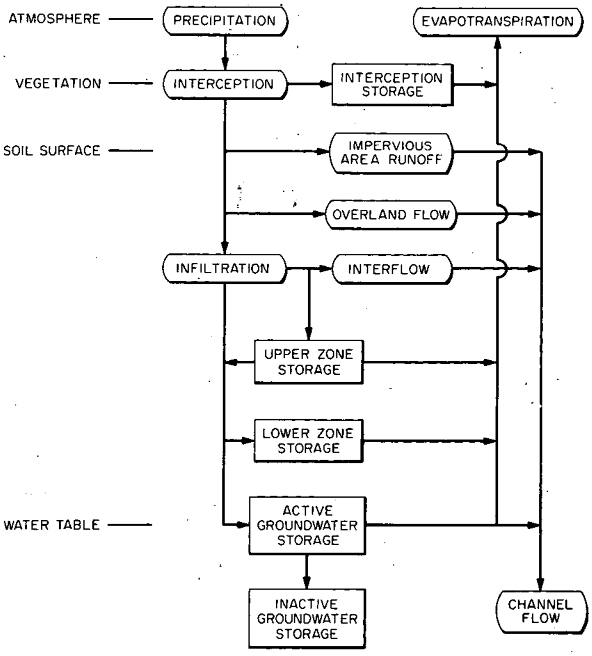

Fig. 2. Hydrologic Flow in a Land Area Segment.

various pathways to the channel. Some of these parameters, such as surface slope and average distance to the stream, can be determined from topographic maps of a watershed. Other parameters can only be estimated or evaluated using experience with Crawford and Linsley's recommendations [2] or calibrations with observed channel flows.

Figure 3 shows the corresponding material transport through a land segment. Wetfall deposition refers to that which comes down while it is raining, while dryfall is dust fall. Once the material reaches the surface, there are three paths by which it can travel to the stream, other than direct deposition into the stream, which is generally only a small portion of the total.

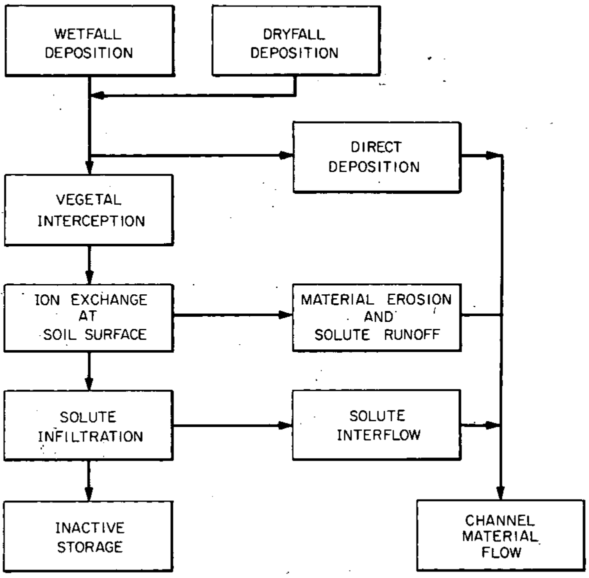

Fig. 3. Material Flow in a Land Area Segment.

If the rainfall is so intense that surface runoff occurs, the material may be transported overland as a solute or adsorbed on soil particles which are being eroded. Material which makes contact with the top layer of soil may be adsorbed and later carried to lower layers. This downward migration is simulated by assuming that the top layers of soil are plates in an ion exchange column. With an appropriate distribution coefficient and other soil parameters related to material transport, the amount of material reaching the stream by underground pathways can be computed. There are a total of 15 parameters related to material transport including the initial concentration in each of the four theoretical plates. Some of these can be measured directly, while several must be adjusted to fit observed conditions.

The Walker Branch Watershed, which we have been studying, is within the AEC reservation at Oak Ridge, about 2 miles east of ORNL. It is approximately 241 acres or 98 hectares, consisting of 2 segments of 146 and 95 acres, respectively. The streamflow from each segment is monitored continuously and samples from each stream are analyzed weekly for various constituents. There are five rain gauges on the watershed which give hourly readings. The rainfall at each gauge is analyzed weekly, together with dustfall in Wong sample buckets which are automatically covered during periods of precipitation to separate wet- and dryfall deposition.

Figure 4 shows average precipitation and evapotranspiration data for the Oak Ridge area. The average yearly total precipitation is about 55 inches, while the average ET is about half of this amount. As can be seen, the precipitation is generally lowest in the spring and fall with a peak in July and a broad peak during the winter. During the period May through October, the runoff is generally less than one inch per month.

The International Biological Program (IBP) has financed the collection of data on Walker Branch since 1969 with emphasis on the nutrients Na, K, Mg, Ca, P, and N. Table I shows some of the chemical budgets with each year representing the sum of 52 weekly analyses. Over the period of study there have been net losses for K and Ca and a net gain for Na. In June, 1973, analyses of rainfall and stream samples were also started under NSF-RANN funding for a number of trace materials, including Cd, Cr, Cu, Ni, Pb, and Zn. Today I plan to show the results of some of our simulation studies for potassium and cadmium. We began working with potassium while waiting for the trace element data to become available.

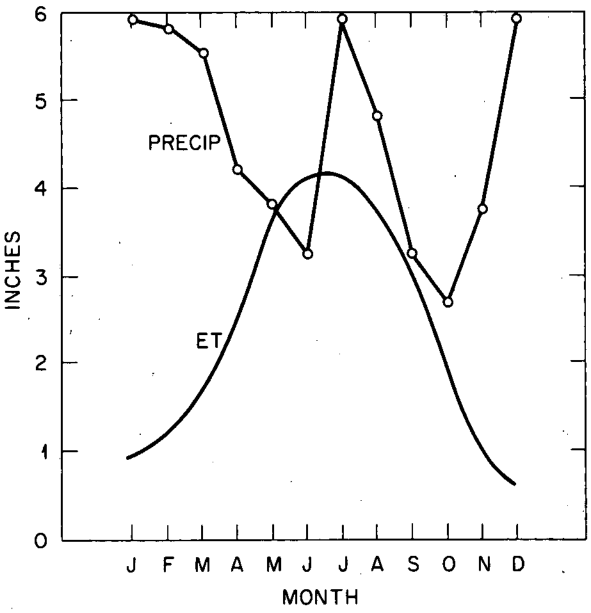

Fig. 4. Average Precipitation and Evapotranspiration Data for the Oak Ridge, Tennessee, Area.

Table I. Walker Branch Watershed Nutrient Balance (kg)

Year	In	Out	Net
	Potassium		
1969	590	300	+290
1970	470	650	-180
1971	380	490	-110
1972	450	650	-200
	Sodium		
1969	660	220	+440
1970	970	500	+470
1971	1000	420	+580
1972	1450	800	+650
	Calcium		
1969	1900	8600	-6700
1970	1400	12700	-11300
1971	1800	11000	-9200
1972	1800	15000	-13200

We were able to use the IBP data on Walker Branch soils to estimate a distribution coefficient for K and the concentration of the element in the upper layers of soil. In general, we tried to evaluate non-measurable parameters, either by making individual computer runs and changing the parameters slightly or with an optimization routine, which would give a satisfactory water simulation first. Then we concentrated on the parameters related to material transport.

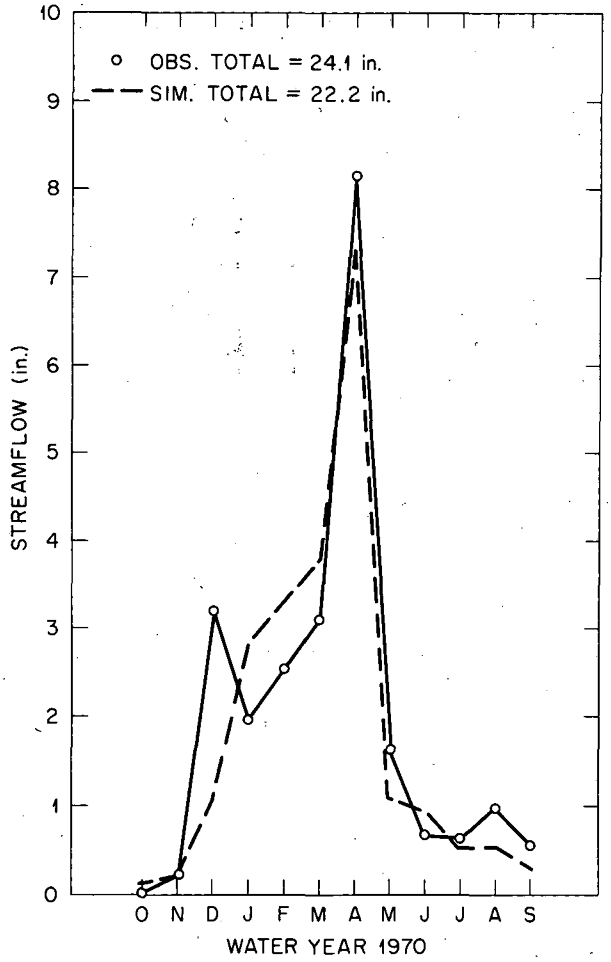

Fig. 5. Walker Branch Watershed, East Fork Runoff WY70.

Figure 5 shows a comparison of observed and simulated monthly flows for the east fork for Walker Branch for water year 1970. The simulation is fairly good, considering the larger-than-average rainfall during April. The program will compute daily runoff values, but since chemical analyses are only available on a weekly basis, it seemed reasonable to look first at monthly and yearly totals.

Figure 6 shows the corresponding potassium simulation. Since the potassium concentration in the stream is generally in the narrow range of 0.6 to 1.0 mg/liter, the magnitude of the observed values closely parallels the water volumes. As has been observed at Hubbard Brook, the concentration of potassium in the stream is an inverse function of the flow volume.

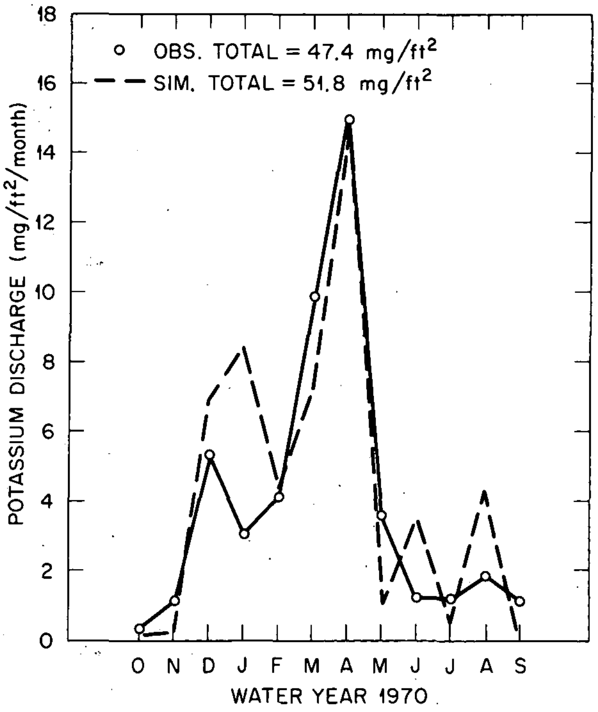

Fig. 6. Walker Branch Watershed, East Fork Potassium Discharge WY70.

It has proven somewhat difficult to obtain a proper set of parameters to simulate the water and material transport simultaneously. We are considering replacing the ion exchange portion of the model with another soil model such as the Dutt Model [4] or Jurinak Model [5].

During the last 7 months of 1973 the monthly accumulations of Cd in the rainfall ranged from 140 to 2200 grams, roughly a factor of 50 lower than the potassium deposition. The dryfall was not analyzed, but recent observations indicate that the amount of Cd in dryfall is no greater than 10% of that in wetfall. In contrast to potassium, where there was a net loss in the watershed, the 7-month total for Cd in the stream was a factor of 15 lower than the deposition. Thus over 90% of the Cd deposited in this 7-month period remained on the watershed. These data are for dissolved Cd in the stream. Recent measurements, however, indicate that not more than about 6% of the Cd in the stream is associated with particulates.

Figure 7 shows the water balance for this period, including the rainfall which was exceedingly heavy for the last 2 months. The simulation is very good for the entire period. With the same set of land parameters, the Cd discharge is shown in Figure 8. The agreement between observed and simulated values is reasonable except for December. This may be due to some overland flow simulated but generally not observed on the heavily forested watershed. For comparison, Figure 9 shows the potassium discharge for the same period. The simulation is good, even for the months with large flows. The parameters that are significantly different for the Cd vs. K simulations are the distribution coefficient, the concentrations in the theoretical plates, and FIXM, which is the mass of stationary soil at the land surface that is available for exchange. Dale Huff [3] states that the optimum value for FIXM depends upon its empirical adjustment to reproduce the observed contaminant hydrograph. The value of FIXM necessary to reproduce the Cd data was over two orders of magnitude greater than that used for potassium. It is not clear at this time why this should be the case. We will soon have Cd data for 1974 available that may help answer this question.

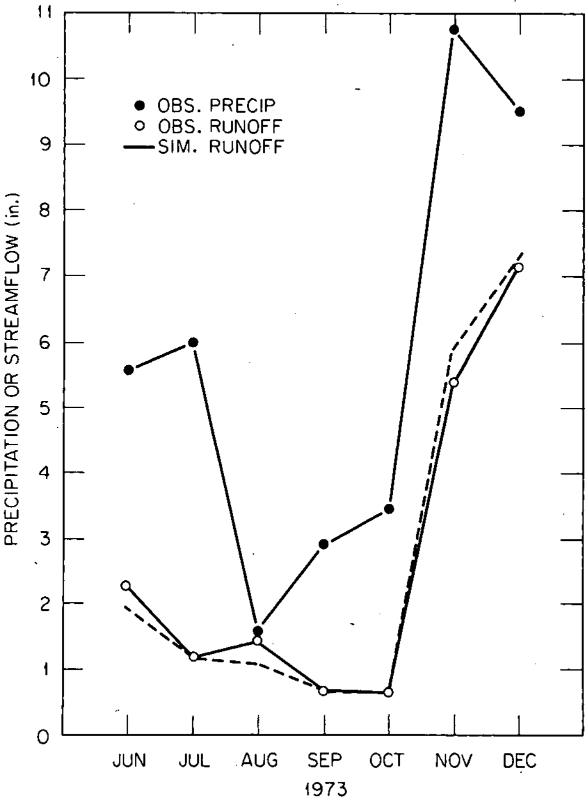

Fig. 7. Walker Branch Watershed Water Budget June-December 1973.

Thus we have demonstrated the ability of the model to satisfactorily simulate observed streamflows on Walker Branch Watershed and to at least approximate the material transport of Cd and K. We are continuing validation studies on this watershed in addition to several others with larger areas to better determine the range of application of the model.

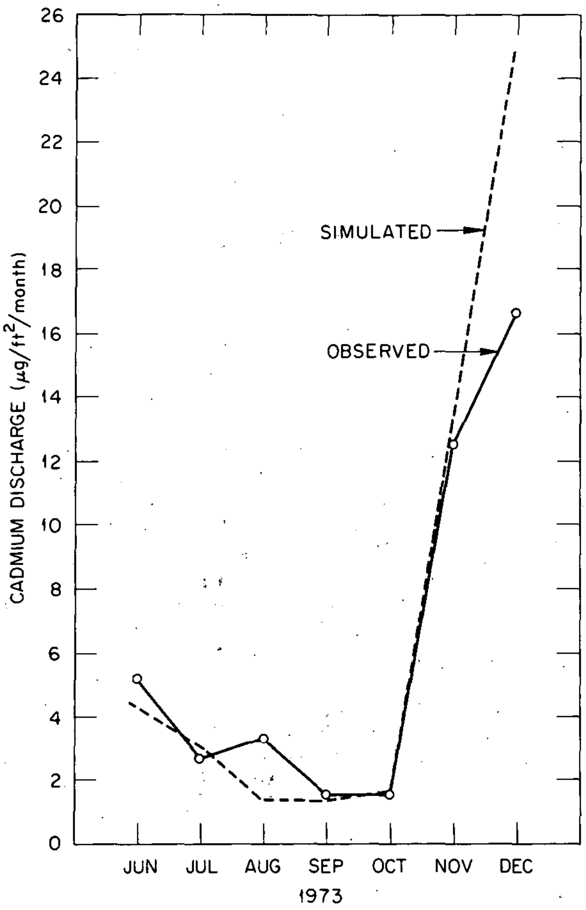

Fig. 8. Walker Branch Watershed, Cadmium Discharge June-December 1973.

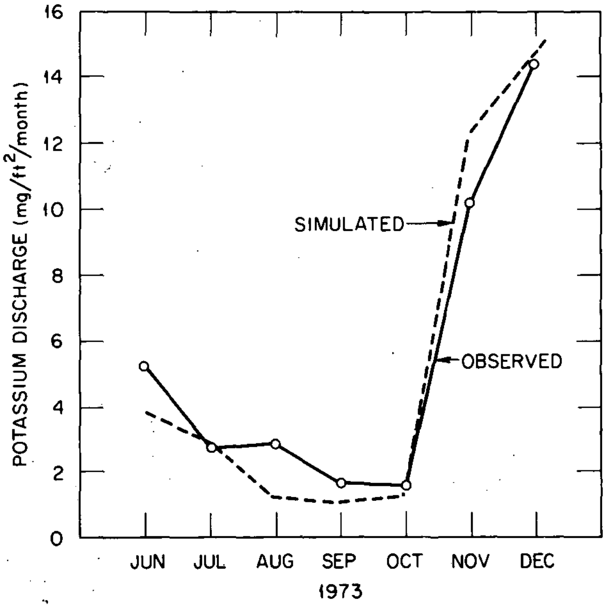

Fig. 9. Walker Branch Watershed, Potassium Discharge June-December 1973.

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THE ABILITY OF SELECTED SOILS TO REMOVE MOLYBDENUM FROM INDUSTRIAL WASTEWATERS*

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ABSTRACT

The aqueous effluents of many metallurgical milling operations in the western U.S. contain molybdenum as an abundant dissolved metal. These wastewaters may enter and percolate through the soil environment. This could result in contamination of groundwater reservoirs. The ability of soils adjacent to these milling operations to remove molybdenum from infiltrating effluents should be well documented.

The maximum amount of molybdenum sorbed by desert, agricultural, and alpine soils was investigated. The following soil properties were examined in order to determine which properties have the greatest control on the sorption of molybdenum: 1) pH, 2) amount of organic matter, 3) amount of clay, 4) clay mineralogy, and 5) amount of extractable iron and aluminum oxyhydroxides.

The average maximum sorption value for molybdenum was 9.5 μg Mo/g soil by desert soils and 50 μg Mo/g by the agricultural soil. The alpine soils showed an average sorption value of 160 μg Mo/g soil. These three types of soils do not differ significantly in their clay mineralogy, content of clay minerals, and amount of extractable iron oxides. Therefore these properties cannot account for the large observed differences in the molybdenum sorption capacities. The mountain soils showed significantly higher extractable aluminum. Low soil slurry pH values (pH 5.0-6.0) with high percentages (10-14%) of organic matter were also observed for the alpine soils. The desert and agricultural soils have almost no organic matter and show high soil slurry pH values (7.8-8.2).

This study has demonstrated that soils with higher pH values, with correspondingly lower amounts of organic matter and lower contents of extractable aluminum are much less effective in removing molybdenum from milling water solutions than soils which contain higher amounts of organic matter, aluminum oxyhydroxides, and which are acidic. These findings are consistent with previously published data.

INTRODUCTION

In the western U.S., Mo is the most abundant dissolved metal in the aqueous effluents of many metallurgical milling operations. Such industrial wastewaters may escape into the subsurface and may percolate through various soils. The ability of soils adjacent to these milling operations to remove Mo from infiltrating solutions should be documented. The contamination of potential groundwater reservoirs may be prevented by soils which sorb contaminants from infiltrating waters.

In order to investigate the capacity of desert, agricultural, and alpine soils for removal of Mo, two types of studies were performed. The first set of experiments involved time-equilibration studies, whereas the second set consisted of the determination of sorption isotherms. The time-equilibration studies yielded K_d values which gave the equilibrium ratio of the amount of Mo in the solid (soil) phase relative to the amount of Mo in the liquid phase. The isotherm work predicted the maximum amount of Mo sorption by the different soils by means of Langmuir adsorption isotherms. One form of the Langmuir equation is $X/m = KbC_{eq}/1 + KC_{eq}$ where X/m = μg Mo sorbed per g of soil; b = the adsorption maximum in μg/g; C_{eq} = equilibrium concentration in μg/mℓ; and K = a constant. In linear form this equation becomes $C_{eq}/X/m = C_{eq}/b + 1/Kb$ where the slope = $1/b$ and the intercept = $1/Kb$. Predicted adsorption maxima (b) have been calculated using the Langmuir equation for many different soils and anions.[1,2,3,4,5,6,7,8]

The soils chosen for study represent those found near three metallurgical milling operations. The soils from Arizona were collected near copper mines and mills, and those from Canon City, Colorado were collected near a uranium mill. The alpine soils were collected from Mt. Aetna in southcentral Colorado and represent the type of soil found in a similar alpine environment near a molybdenum mine and mill farther to the north in Colorado.

Five soil properties were measured in order to determine which soil parameters have the greatest control in the capacity for removal of Mo. These soils properties include: 1) pH, 2) amount of organic matter, 3) soil

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texture, 4) clay mineralogy, and 5) amount of extractable iron and aluminum oxyhydroxides.

MATERIALS AND METHODS

Soils. Bulk samples were collected of two desert soils from southern Arizona, two agricultural soils from Canon City, Colorado, and two alpine soils from Mt. Aetna in southcentral Colorado (12,500 feet elevation). The soils were air-dried and passed through a 4.8 mm sieve. Arizona Soil 4 is a composite sample collected over an interval from the surface to a depth of about 24 inches. Arizona Soil 5 also represents a composite sample of the upper two feet of the desert soil profile, collected a few miles from sample 4. Both soils are located immediately adjacent to areas of copper mining and milling, but neither has been contaminated. Canon City Soil 25 is a composite sample collected over an interval of about eight inches from a depth of two to ten inches below the surface. The site of this sample is located up-gradient from a uranium mill. Canon City Soil 1 also represents a composite sample collected over an interval from two to twelve inches in depth. This agricultural soil is located a mile and a half down gradient from the uranium mill and has been irrigated for the past eight years with contaminated groundwater containing Mo concentrations as high as 50-60 mg/ℓ, high T.D.S., and high radioactivity.

Chemical analyses. Mo was determined by the thiocyanate-stannous chloride procedure of Johnson and Arkley[9] as modified by Meglen.[10] A Leeds and Northrup pH meter with a combination glass electrode was employed to measure the pH of the 1:2 (soil:water) slurries. An Instrumentation Laboratories Model 353 Atomic Absorption Spectrophotometer was used to determine the amounts of Fe and Al present in the dithionite-citrate extraction solutions.

Time of equilibration and isotherm studies. The amount of time required by the soils for equilibration with dissolved Mo and the procedure for the Langmuir isotherm studies were described by Katz and Runnells.[11] Briefly, shaker-type experiments showed that the desert and agricultural soils reached equilibrium with dissolved Mo in about 18 to 24 hours and four to six hours, respectively. The alpine soils needed only one to two hours to reach equilibrium with dissolved Mo.

Percent organic matter. The percent organic matter was determined by two different methods. The first method consisted of an ashing technique as described by Davies.[12] This procedure involved ashing 25 to 30 g of soil at 430°C for 24 hours. Loss of interlayer water from clay minerals was taken into account and corrected by calculation. The second method involved a hydrogen peroxide digestion as described by Jackson.[13]

Soil texture analysis. The distribution of particle sizes of sand, silt, and clay for each soil was determined by the settling-pipette method of Markos.[14] This method uses a 25 g sample of soil and sodium hexametaphosphate as the dispersing agent, with the sizes determined by the usual Stokes equation[13] for time of settling.

Clay mineralogical analysis. The clay fraction of each soil was washed with sodium acetate (pH 5 buffer) in order to remove all Ca^{2+} ions from interlayer positions and all $CaCO_3$ from the sample.[13] Oriented specimens of the washed clays were mounted on heated porcelain tiles for x-ray diffraction analysis. Three different diffraction patterns were obtained from the untreated, glycolated, and heated (550°C) clays. The specimens were mounted again after treatment with 1N HCl at 90°C for one hour and a fourth diffraction pattern was obtained. A Philips-Norelco X-ray Diffractometer was employed with Cu-K_α radiation for all x-ray diffraction analyses.

Extractable Fe and Al oxyhydroxides. The amount of extractable Fe and Al oxyhydroxides was determined by the citrate-dithionite procedure of Mehra and Jackson.[15] This method involves buffering the system at pH 7.3; it has almost no destructive effect on iron silicates or clay minerals. Fe and Al were determined by atomic absorption.

PREVIOUS STUDIES

Davies[16], in summarizing the research of others on the reactions of molybdate with soils and clays, concludes: 1) the amount of Mo sorbed by soils and clays decreases with increasing pH to about 7.5, above which virtually no sorption of Mo takes place and 2) the sorption of molybdate ions by soil colloids results in an increase in pH of the system. He suggested that one mechanism of sorption of Mo is through replacement of exchangeable hydroxyl ions.

Reisenauer and others[17] conclude that the solubility of Mo in soil and hydrous oxide systems is controlled by the percentage Mo saturation and the pH of the system. The strong effect of pH, with adsorption decreasing with rising pH, has been confirmed by other workers.[8,16,18]

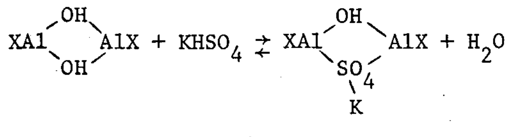
Another major soil property controlling sorption of Mo in soils is the amount of organic matter. Bloomfield and Kelso[19] have found that mobilized Mo is fixed by organic colloidal decomposition products and that the maximum retention of Mo is at pH 1.5. Szilagyi[20] reports that a peat preparation enriched in humic acid reduces molybdate ions at low pH to yield Mo(V) which in cationic form is readily bound by humic acids. Harward and others[21] postulate that the positive charge possessed by some amphoteric organic compounds may account for the sorption of anions.

Grim[22] in his research with clay minerals, states that anions such as phosphate and arsenate which have the same size and geometry as the silica tetrahedron, may be adsorbed by becoming attached onto the edges of silica tetrahedral sheets. Molybdate ion may behave in similar fashion.

Grim[22] also states the importance of particular clay minerals in anion exchange. For clay minerals such as kaolinite, in which cation exchange is due to broken bonds, the cation- and anion-exchange capacities would be almost equivalent. In other minerals such as smectite and vermiculite, the anion exchange capacity would be only a small percentage of the cation exchange capacity. This is because in smectite and vermiculite clay minerals, cation exchange is the result of lattice substitutions. Illite and chlorite clay minerals should also have anion exchange capacities lower than their cation exchange capacities.[22]

The presence of Fe and Al oxides and oxyhydroxides is an important property of soils in terms of removal of dissolved Mo. Reyes and Jurinak[8] found that approximately five times as much Mo was adsorbed by α-hematite (Fe_2O_3) near saturation at pH 4.0 than at pH 7.8. They postulate two different adsorption sites. The first is a fixed site, whereas the second involves weaker positive sites which should be neutralized as the surface is exposed to a basic solution. This neutralization of positive sites lowers the sorption capacity at higher pH values.

Jackson[23] states that anions such as Cl^-, SO_4^{2-}, and PO_4^{3-} are held in a hydroxy-alumina structure (X) through the substitutions for OH^-:



$$\mathrm{XAl}\overset{\mathrm{OH}}{\underset{\mathrm{OH}}{}}\mathrm{AlX} + \mathrm{KHSO_4} \rightleftarrows \mathrm{XAl}\overset{\mathrm{OH}}{\underset{\underset{\mathrm{K}}{\mathrm{SO_4}}}{}}\mathrm{AlX} + \mathrm{H_2O}$$

At lower pH values, SO_4^{2-} exchange is favored. The molybdate ion (MoO_4^{2-}) may be retained in a similar fashion in a hydroxy alumina structure.

Runnells and others[18] have found that solutions containing oxyhydroxides of Fe and Al can be extremely effective in removing dissolved Mo. The optimum pH for 98% removal of Mo by Fe oxyhydroxides was found to be 3.2 for particular waters studied. The Fe:Mo ratio in solution was approximately 25:1. Using an Al:Mo ratio of approximately 440:1 the most effective pH for removal of 75% dissolved Mo was 4.8.

RESULTS AND DISCUSSION

Table I shows the predicted maximum amount of Mo which can be sorbed by the six soils as obtained from the modified Langmuir adsorption isotherm equation. The adsorption isotherm plots for these soils were described by Katz and Runnells.[11] From Table I it is seen that the maximum sorption values "b" for Mo for the acidic alpine soils are approximately 20 to 30 times larger than those for the alkaline desert and agricultural soils.

TABLE I. Results of isotherm experiments.

Soil sample	1:2 soil:water slurry pH	Predicted max. Mo sorption "b" ± 30% (μg/g)	Other major waste-water components
Arizona Soil 4	8.0	10	Ca-Mg-SO_4 pH 7.0
Arizona Soil 5	8.2	9	Ca-Mg-SO_4 pH 7.1
Canon City Soil 1	8.0	Released Mo	Na-Ca-Mg-SO_4 HCO_3-Cl pH 7.0
Cánon City Soil 25	7.8	50	Na-Ca-Mg-SO_4 HCO_3-Cl pH 7.0
Mt. Aetna Soil "A"	5.6	140	Ca-SO_4-Cl pH 6.5
Mt. Aetna Soil "B"	5.1	180	Ca-SO_4-Cl pH 6.5

For Canon City Soil 1, a sorption maximum ("b") for Mo could not be predicted. This soil, located down-gradient from the uranium mill, has been irrigated periodically with contaminated well water for the past eight years. The water contains approximately 50 mg/ℓ dissolved Mo, presumably due to leakage from the mill ponds. During the experiments, this soil was found to be already saturated with exchangeable Mo and actually released Mo to our test solutions.

The amount of organic matter in each soil sample is shown in Table II. As described earlier, the percent organic matter was estimated by two different methods. There is a close correlation between the two methods when the interlayer water loss from the clay minerals is taken into account in the ashing procedure by Davies.[12] The alpine soils which contain 4-13% organic matter are much more effective in removing Mo from the milling solutions. The alkaline soils from Canon City and southern Arizona contain almost no organic matter (less than one percent) and have a much lower capacity for Mo removal.

TABLE II. Precent by weight of organic matter.

Soil sample	% organic matter Ashing (%)	H_2O_2 digestion
Arizona Soil 4	0.3	0
Arizona Soil 5	0.2	0.3
Canon City Soil 1	0.8	0.2
Canon City Soil 25	0.8	0.2
Mt. Aetna Soil "A"	10.	13
Mt. Aetna Soil "B"	4.1	2.1

The texture of the soil is a property which may also partially control the amount of Mo which can be removed by a given soil. Many researchers have stated that the important chemical reactions going on in soils take place within the clay-size fraction. Table III lists the particle size distribution for each soil sample in weight percent.

TABLE III. Particle size distribution in weight percent. (By settling)

Soil sample	Particle sizes 4.8-2.0 mm	 2.0-0.05 mm	 0.05-2μ	 <2μ clay size
Arizona Soil 4	12	67	10	7
Arizona Soil 5	12	48	15	22
Canon City Soil 1	1	42	33	18
Canon City Soil 25	2	66	17	10
Mt. Aetna Soil "A"	10	60	18	8
Mt. Aetna Soil "B"	23	61	6	6

Both the Arizona soils and the Canon City soils contain twice as much clay-size material as the Mt. Aetna (alpine) soil samples. However, the alpine soils are 20 times more effective in removing Mo than the Arizona soils and have four times the capacity for removal of Mo as Canon City Soil 25 (Table I).

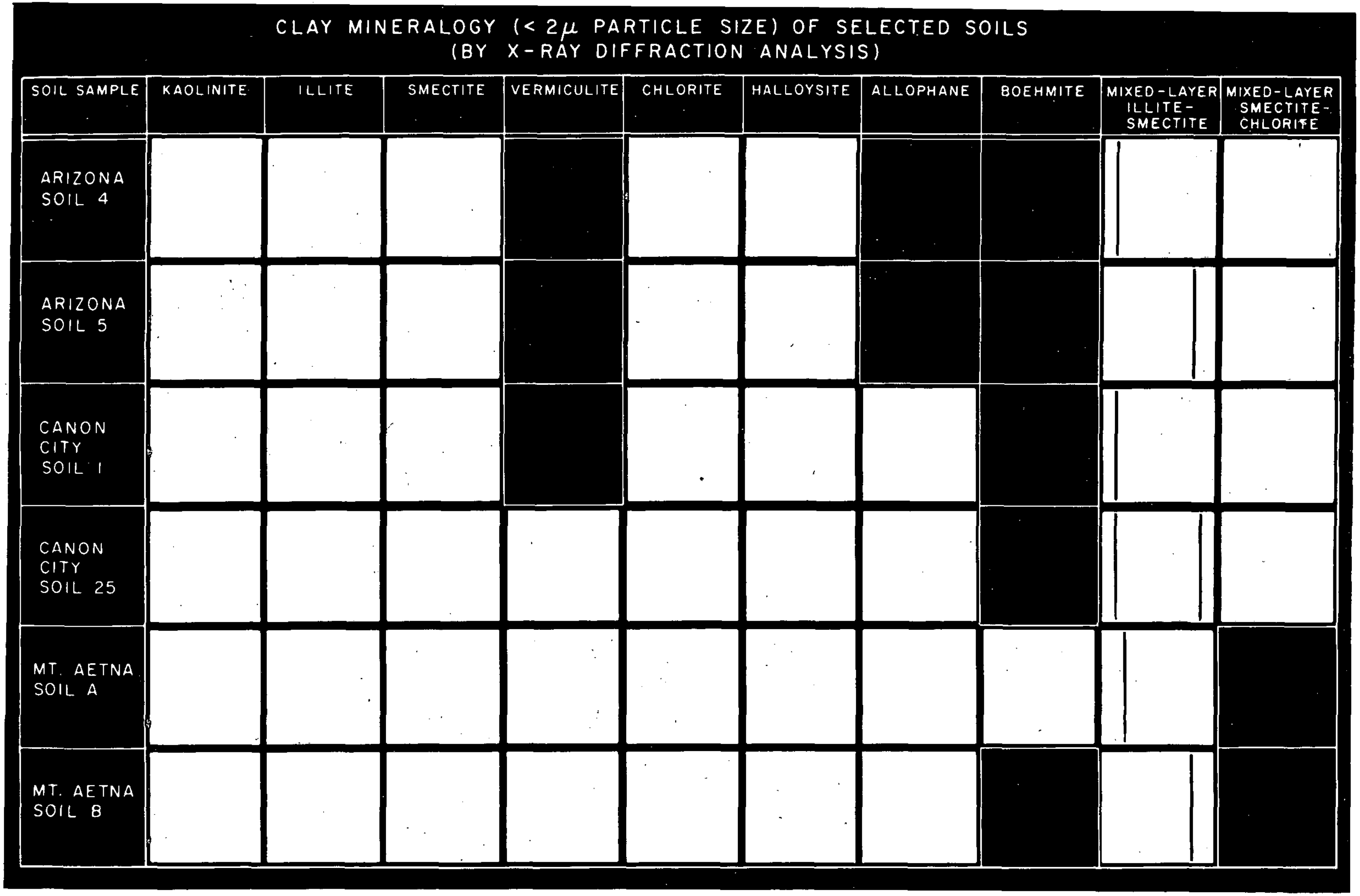
This apparent contradiction could possibly be caused by gross differences in the clay mineralogy of each soil. However, closer examination of Figure 1 reveals that all six soils are remarkably similar in the types of clays present, as determined from the analysis of the x-ray diffraction patterns.[4,24,25,26,27] All three types of soils are predominantly composed of illite-smectite mixed-layer clay minerals, with the following randomly stratified composition: 80-90% illite - 10-20% smectite and 10-20% illite - 80-90% smectite. All six soils contain kaolinite, chlorite, smectite, and illite. One of the major differences in the mineralogy of the clays appears in Mt. Aetna Soil "A". This soil contains boehmite (AlOOH). This mineral was previously thought to occur only in tropical lateritic environments, but the occurrence of boehmite has now been documented in the alpine environment.[28] The alpine soils show weaker peaks for allophane and vermiculite in the "A" sample than in the deep "B" sample.

Although the clay minerals most likely occur in different proportions in each of the soils studied, the small differences in types of clay cannot be a major factor controlling the large observed differences in the maximum sorption values for Mo. We were not able to determine proportions of each clay mineral from our data.

The amount of hydrous oxides of Fe and Al is another soil property which must be considered in attempting to explain removal of Mo by soils. Bar graphs of the percent of extractable free Fe and Al oxyhydroxides for each soil sample appear in Figures 2a and 2b, respectively. The graph in Figure 2a shows that all six soil samples contain the same amount of extractable free Fe oxides, within analytical and experimental error. Thus the extractable Fe values, or the equivalent contents of Fe oxyhydroxides, cannot account for the large observed differences in maximum Mo sorption.

The amounts of extractable Al oxyhydroxides, however, are quite different. The Mt. Aetna soil samples (Figure 2b) contain 0.25% Al oxyhydroxides, whereas the Arizona and Canon City soils show average values of 0.04% and 0.05%, respectively. This higher content of extractable Al offers a plausible basis for the observed differences in sorption.

To eliminate possible interference by organic matter in the extraction procedures, the organic matter in triplicate samples of Mt. Aetna soils was removed by a H_2O_2 digestion.



CLAY MINERALOGY (< 2μ PARTICLE SIZE) OF SELECTED SOILS
(BY X-RAY DIFFRACTION ANALYSIS)

SOIL SAMPLE	KAOLINITE	ILLITE	SMECTITE	VERMICULITE	CHLORITE	HALLOYSITE	ALLOPHANE	BOEHMITE	MIXED-LAYER ILLITE-SMECTITE	MIXED-LAYER SMECTITE-CHLORITE
ARIZONA SOIL 4	⬜	⬜	⬜	⬛	⬜	⬜	⬛	⬛	⬜	⬜
ARIZONA SOIL 5	⬜	⬜	⬜	⬛	⬜	⬜	⬛	⬛	⬜	⬜
CANON CITY SOIL 1	⬜	⬜	⬜	⬛	⬜	⬜	⬜	⬛	⬜	⬜
CANON CITY SOIL 25	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬛	⬜	⬜
MT. AETNA SOIL A	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬛
MT. AETNA SOIL B	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬛	⬜	⬛

Figure 1. Clay mineralogy of selected soils. The presence of a particular clay mineral is indicated by the white squares. The relative percentages of randomly stratified illite-smectite components within the mixed layer clays are shown by the position of the solid black line in the illite-smectite mixed layer clay column.

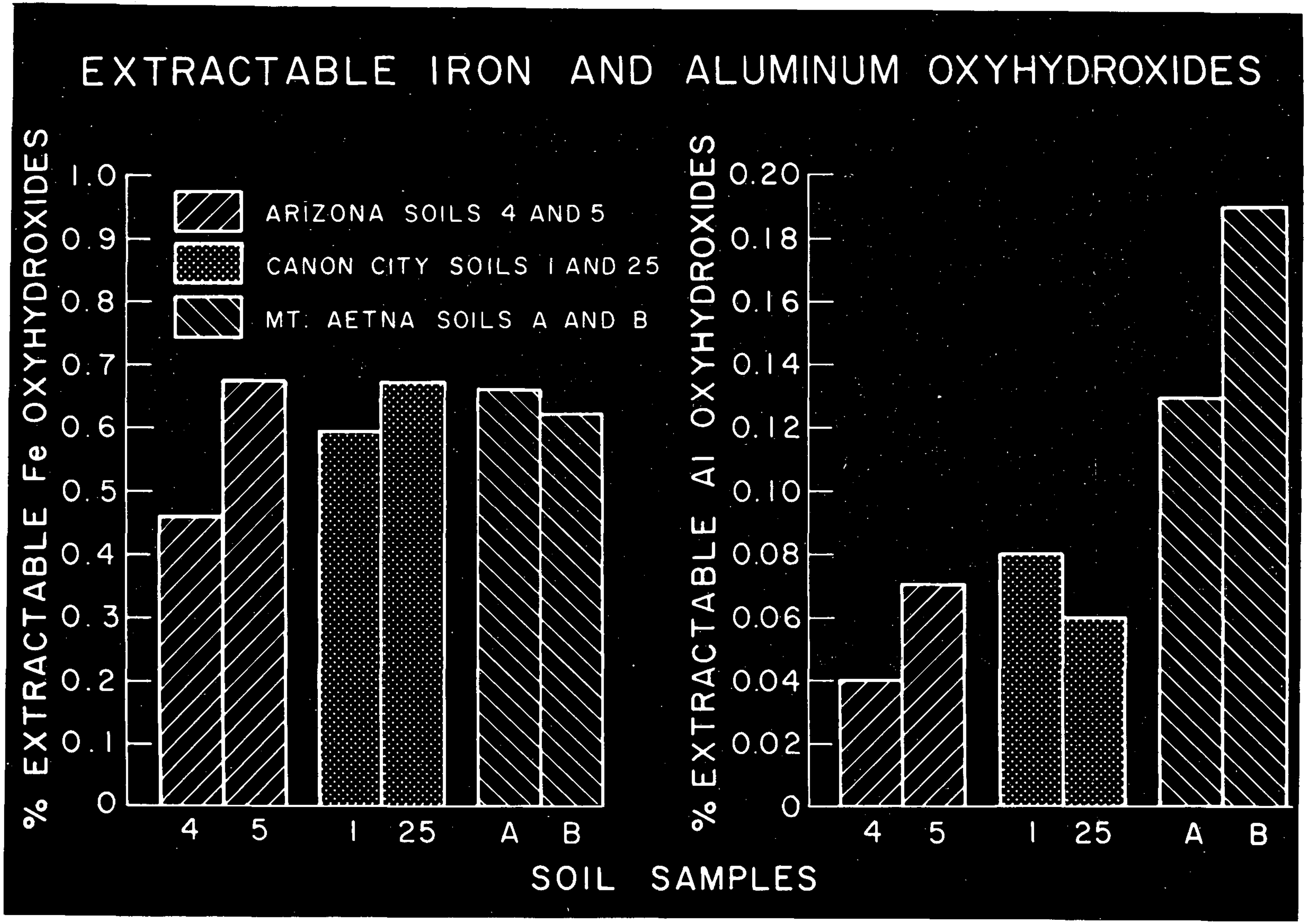


Figure 2a. Extractable iron oxyhydroxides.

Figure 2b. Extractable aluminum oxyhydroxides.

(without removal of organics)

The amounts of extractable Fe and Al were then redetermined. Table IV shows the percentages of Fe and Al oxyhydroxides extracted from Mt. Aetna soil samples "A" and "B" after removal of organic matter. The results show surprisingly good precision, and the results for the "B" sample for Fe compare very well with the extractions done prior to removal of organics. However, the results for Al and Fe in the "A" sample and Al in the "B" sample indicate that a considerable portion of the Fe and Al was bound up with the organic matter. This organically bound Fe and Al gave results which were not consistent from sample to sample without prior digestion. When the organic matter was removed by H_2O_2 digestion reproducible results were attained.

TABLE IV. Extractable Fe and Al oxyhydroxides.

Soil sample	% Fe oxyhydroxides		% Al oxyhydroxides	
	organics not removed	organics removed	organics not removed	organics removed
Mt. Aetna Soil "A"	0.67	0.81	0.13	0.25
		0.82		0.25
		0.83		0.25
Mt. Aetna Soil "B"	0.63	0.69	0.19	0.26
		0.64		0.18
		0.64		0.24

It is evident from Table IV and Figures 2a and 2b that the alpine soils contain approximately five times as much extractable Al oxyhydroxides as the other two types of soil.

INTERPRETATION

The pH of a soil system is a major factor in controlling the amount of Mo that can be sorbed by various types of soils. The acidic alpine soils show a much greater capacity for sorbing Mo from metallurgical wastewaters than do the alkaline desert and agricultural soils. This is shown well by comparing the results (Table I) for the acidic alpine soils with the two alkaline soils from Canon City and Arizona. Table I shows that from isotherm studies, the predicted maximum sorption capacities for Mo for the alpine soils are approximately 20 times larger than those obtained for the desert soils and three to four times larger than those obtained for the agricultural soil.

The alkaline soils of this study, which are generally located in oxidizing environments, contain only small amounts of organic matter. The alpine soils, on the other hand, contain up to 11% combustible organic matter.[12] The larger amounts of organic matter present in the alpine soils may contributed to the observed higher values for sorption of Mo.

The acidic alpine soils also contain approximately five times the amount of Al oxyhydroxides than the alkaline soils from southern Arizona and Canon City. From the results obtained by Runnells and others,[18] it can be concluded that these higher amounts of Al oxyhydroxides in the alpine soils may contribute to the observed higher Mo sorption values at low values of pH.

The higher clay mineral content of the alkaline soils as compared to the alpine soils is not an important control on the amount of Mo that can be sorbed. The types of clays of all three types of soils are so similar that differences in clay mineralogy cannot account for the large observed differences in the amount of Mo sorbed. It is possible that differences in proportions of clays, which we did not determine, could influence the sorption.

In documenting the effective capacity of particular soils for removing Mo from industrial wastewaters, one should investigate at least three soil properties. These are the 1) pH, 2) amount of organic matter, and 3) amount of extractable free Al oxyhydroxides. From our work it is clear that acidic mountain soils offer far more protection to groundwater from infiltrating wastewaters containing Mo than do alkaline desert and agricultural soils.

ACKNOWLEDGMENTS

Appreciation is extended to Robert Meglen and Michael Glaze for help with analytical determinations, to Gergely Markos for help with x-ray and particle size distribution analyses, and to Kathy Petersen for clerical work.

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RAPPORTEUR'S REPORT OF THE SESSION ON WATER AND SOIL

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I don't know whether I can follow Harry Edward's excellent example, but I will try to report something of what I heard and something of what I thought was the significance of what I heard. Of course, I can't hope to give any sort of a complete or comprehensive report; but maybe I can give you a flavor of the session. I am not going to review the invited paper in this area by John Lagerwerff because you all heard it, but I would remind you of three of his admonitions to us which are:

1. Each pollution case is different,
2. Avoid oversimplification (synergisms, etc.), and
3. Consider metal-organic material interactions more carefully.

The third item was a major emphasis in the Session 2 deliberations, and I think that in that area we're going to find the crux of the explanation for accumulation of trace contaminants in certain compartments in ecosystems as well for mobilization of trace elements through chelation. The first two admonitions are true, but what we would still like to be able to do is to develop some unifying hypotheses in this very complicated area of soil-water interactions. I think I saw some bits of hypotheses being developed in Session 2. As a matter of fact, people were even adventurous enough to presume to model some of these interactions and to model transport.

Illustration #1

Soil-Water	No. of Papers
Transport	
Deposition-Evaporation-Resuspension	
Transformation (Chemical and Biological) Movement with Water	5
Input-Output and Ecosystem Budgets	5
Mathematical Simulation Models	3
Sampling, Measurement and Monitoring	
Sampling Strategy	2
Analytical Methods	3
Monitoring (Ecosystem Health)	1
Trace Contaminants	
Elemental (Pb, Cd, Cu, Zn, Mo, As)	18
Organic	1

The papers that we heard can more or less be categorized as shown in Illustration #1. The major areas were (1) transport and (2) sampling strategy and measurement and monitoring techniques. One important aspect of transport, which concerns how the contaminant in question is deposited, was not addressed specifically; however, there were at least two papers that dealt with input-output balances or budgets for equatic systems where deposition was measured for the simple case of a water surface. Evaporation, resuspension, were really not considered at all, except in the case of mathematical models. I would say that deposition is an area of considerable importance; I'd like to see some more emphasis there. In the second area under transport the papers dealt with the transformation of pollutants--chemical and biological transformation--and with the movement of pollutants in water. We heard some very important papers. However, I should mention that there was something missing. We didn't have any papers on plant uptake in the session; I understand that Dr. Van Hook will review at least two papers on plant uptake that were given in the biological section. Obviously, the work done to study transformations and water movement certainly has relevance to the question of plant uptake.

Of the five papers in this area two concerned the New Lead Belt in Southeast Missouri--one by E. A. Bondietti and E. Bolter, and the other by E. Bolter alone. The evidence indicated the formation of copper, cadmium, zinc, and lead soluble organic complexes in soil and litter material. Lead which turns out to be the least soluble shows litter-layer concentration anomolies to greater distances from two

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*Operated by the Union Carbide Corporation for the U. S. Atomic Energy Commission.

lead smelters studied than did the other elements. Presumably the explanation is that lead undergoes slower subsequent movement with water after deposition. Three papers were concerned with sorption of metal onto soils. R. L. Zimdahl reported that lead sorption on various soil types obeyed a Langmuir type isotherm, and, furthermore, that the Langmuir constant could be correlated with the ion exchange capacity of the soil, the organic matter content, and pH. Similarly, B. Katz and D. D. Runnells showed that a Langmuir type isotherm was obeyed for sorption of molybdenum on various soils, again with the important parameters being pH and organic content of the soil; but the aluminum oxy-hydroxide content of the soil was found to be important as well. The importance of iron, magnesium, and aluminum oxide as the hydrated species for influencing the sorption was emphasized by R. M. Jordan, and he pointed out the importance of pH and the age or history of the hydroxide relative surface reactivity. Incidentally, R. Carpenter and E. A. Crecelius, who reported one of the input-output studies, found that iron oxy-hydroxides were important in the precipitation of arsenic from Lake Washington.

I don't understand why Langmuir's isotherm should be obeyed for all of these very complicated systems. Langmuir, whose theoretical development was quite simple, assumed one type of active site on a surface, and I don't really understand why such a simple model should be obeyed in such complex systems. I think this may be one of the areas (my naivete is showing I'm sure) where we may identify some general principles that lead to a more fundamental understanding of what is going on. At least a useful empiricism may develop that can be applied in models.

There were five very good papers on input-output measurements around ecosystems or parts of ecosystems. Three of these dealt with watersheds and two with the predominantly aquatic systems; R. I. Van Hook, my ORNL colleague, reported detailed budgets of lead, zinc, cadmium, and copper, for a highly instrumented watershed, the Walker Branch Watershed at Oak Ridge. This is a relatively uncontaminated system (if you consider three power plants not sources of pollutants). The information, and, I hope, the experience gained at the Walker Branch Watershed can be applied in various contaminated areas, more contaminated areas (I should say). We are studying such an area, the New Lead Belt area, with the University of Missouri-Rolla. For both uncontaminated and contaminated areas there is accumulation of toxic elements in litter material. Some important differences in accumulation by various tree species was evident at Walker Branch Watershed. E. Bolter in his work at the New Lead Belt showed some very interesting data (as mentioned above) on accumulation of lead, cadmium, copper, and zinc in the O_1 and O_2 litter layer around two smelters. The pattern of concentration anomalies are strikingly different around the two smelters, and the implication is that the difference in pattern is related to differences in chemical species emitted by the two plants. Bolter's report was in the nature of a progress report, and I trust that this phenomenon will be better elucidated. J. C. Jennett and M. G. Hardie, in studying some of the watersheds in the New Lead Belt area, concluded that surface water quality has not been impaired seriously by heavy metals. There may be some buildup of heavy metals in sediments in reservoirs downstream.

A. W. McIntosh and T. Peyton, reported on the input-output budgets for a borrow pit (a pit you dig nextdoor to a highway when you're stealing dirt) in Gary, Indiana. The input to this pit is mostly via atmospheric fallout and it roughly matched the measured accumulation of lead, zinc, cadmium, and iron in the sediments of the pit which had been subject to this fallout for some twenty years. No appreciable food chain accumulations were observed. The pit had fairly elaborate aquatic food chain, all the way up to bass.

On a much larger scale and in somewhat the same vein, E. A. Crecelius worked on an arsenic balance for Puget Sound and Lake Washington, and, I thought, did a very commendable job on this difficult task. He showed that the the accumulation of arsenic in the sediments in Lake Washington could be attributed to the input from a copper smelter. The smelter was some 25 kilometers away and had been in operation for sixty or seventy years. This result was interesting to me because it showed an appreciable accumulation effect on a regional scale (i.e., at quite a distance from the source). Incidentally, the arsenic accumulates in the sediments or is washed out to sea, and the conclusion was that there was no great harm that had been done to the aquatic system.

Three papers were presented on mathematical simulation models for the transport of contaminants in the soil-water system. Since all three of these papers came from my shop, I can, I guess, be critical of the effort. R. J. Raridon and J. K. Munro presented results of our first attempts, to apply a unified air-water transport model to two watersheds – the Walker Branch Watershed at ORNL and Crooked Creek in the New Lead Belt. Raridon and co-workers were able to simulate the outflow of cadmium and potassium from Walker Branch Watershed in a very reasonable way. It remains to be seen whether extrapoloation in time can be made using this model. Can the model be transferred to other situations which are perhaps a little less well defined? Walker Branch Watershed has had several million dollars of research money poured into it. J. K. Munro and B. G. Wixson reported on our simulation for the Crooked Creek Watershed in the New Lead Belt, which is just such a less well defined situation. This was a very rough first attempt, and the validation awaits the further work by the ORNL and Rolla groups. I guess I remain sort of cautiously optimistic that we can do watershed transport modeling which will be useful if it is backed up by at least a minimum amount of monitoring data. Finally, D. E. Fields reported on his work to develop a sediment transport model. Sediment transport may be very important in some river pollution situations. The model provided a good simulation of observed bedload and suspended sediment transport in the Rio Grande River and of the particle size distribution of suspended sediments.

Turning now to the sampling, measurement, and monitoring area, the papers presented were excellent, but they were rather mixed. They were a collage, if you will permit me to say so. The first two were on the important, and, I think, generally neglected area of sampling strategy. W. Tranter and J. L. Sandvos showed a scheme for determining the optimum sampling locations and sample numbers for soil and vegetation for the case where there is a point source which is the "forcing function". He described the application of the principle of "getting more samples where things are happening" to the experience of the Rolla group with litter measurements in the New Lead Belt. E. M. Thurman and D. D. Runnells discussed results of a study of stream sediment samplings in Colorado. He found it necessary to obtain a number of samples at each stream location to avoid missing important effects. He showed some interesting results illustrating how one sediment sample could be used to gain a good deal of information by fractionating that sample relative to particulate size.

There were four papers on analytical methods. F. P. Brady and S. K. Perry reported on very highly automated multi-element x-ray fluorescence method for determining the elemental composition of suspended particulates from water samples around the world. This is a very elegant technique, and it is an interesting contrast to the oven-ring method described by F. K. West and P. W. West. West showed the oven-ring method can give quite sensitive and reproduceable results on many elements. One method requires a many kilobuck capital investment, the other only a few hundred dollars. Both methods have their place.

J. A. Carter described a method for rapid determination of total nitrogen and nitrogen isotopes in a variety of environmental samples. This paper probably should have been given in the Biological Session along with other nitrogen and nitrate papers, but the technique works well and was applied to some of the environmental samples from the University of California at Davis. The work of the Davis group was reported in the Biological Session.

Only one paper in the session concerned organic contaminants. This was an immuno assay method reported by Williams. This is, I understand, a fairly old technique, but it has been made highly sensitive and specific for a number of rather complicated pesticides. The trick apparently is to label the contaminant about which you are concerned with a fluorescent marker. This is a very neat method. I guess, if I had to make a prediction, it would be that the next few years will see the emphasis of this conference change from elemental contaminants to organic contaminants. This is not because we have done everything in the elemental contaminant area, but because the research money is changing to the organics. The reason, of course, is that we are committed to Project Independence. Thus, we will be concerned with coal conversion technology and oil shale technology. One of the difficulties, of course, is to find adequate analytical methodology. I understand from the people that I talk to in our Analytical Chemistry Division that they can analyze anything at any level for enough money, and that they will be glad to analyze a coal liquid for us if we'll give them three years and a million dollars. It's got to be done for less than that.

The last paper that I should mention -- certainly not the least -- is the work reported on monitoring ecosystem health. J. Cairns and co-workers reported using a laser interferometer or holographic method to automatically monitor one measure of aquatic ecosystem health, namely, the population distribution of diatoms. Now this really sounds way out, but it is an intriguing idea, and they have come a long way towards implementing this idea. If it works it is going to be quite significant relative to monitoring subtle effects of contaminants.

Well, I really should sum-up and give some wise words of advice and thoughts for future research directions, but I think that the better thing would be for us all to read the papers.

DETERMINATION OF TRACE METALS IN WATER BY MEANS OF THE RING OVEN TECHNIQUE. I. DETERMINATION OF COPPER, CADMIUM, ZINC, NICKEL, AND COBALT

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Abstract

An analytical scheme for the separation and concentration of copper, cadmium, and zinc from waters has been developed. The final concentration step and the measurement of the isolated species is made using the ring oven technique. Detection of concentrations of these metals well below the maximum permissible concentrations is possible. It is anticipated that this procedure will be useful in field studies and by water laboratories having limited equipment and personnel. Water samples are extracted by the use of ammonium pyrrolidine dithiocarbamate to chelate the metals and methyl isobutyl ketone to extract the metal species from the aqueous samples. The organic layer is back extracted with a dilute potassium cyanide solution. The volumetric ratio of KCN to MIBK is 1:10. Concentrated HCl and HNO_3 are added to the final extract and the sample is oven dried. One to 10 milliliter of dilute KCN are used to dissolve the final residue containing the metallic species. This permits concentration factors of 1000:1, 100:1, etc., as required. Suitable aliquots of the concentrated samples are added to the filter paper on the ring oven. Appropriate reagents are added to move the metallic species from the center of the filter paper out to the heated ring zone for concentration and development of a specific colored ring for each metal. Standard rings are used for quantification.

TRACE ELEMENT REMOVAL FROM AQUEOUS SOLUTION BY HYDROUS METAL OXIDES

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Abstract

The hydrous metal oxides of iron, manganese and aluminum exhibit solubility, and surface charge dependence as a function of pH. They are also known to incorporate a wide variety of elements and chemical species (both cationic and anionic) into their solid phase from aqueous solution. The intensity of incorporation is likewise strongly pH dependent but the patterns vary widely with element and chemical species identity. In environments where the hydrous metal oxides exhibit a significant interfacial concentration with water they may play a pronounced role in controlling the chemical phase and thus transport of a large number of chemical species. This phenomena is thus of interest in a number of disciplines, e.g., soils, limnology, oceanography, geochemistry, metallurgy, and analytical chemistry. This paper deals with the general nature of the phenomena for the purpose of defining its role and application in the removal of a variety of trace elements from aqueous solution. Specific reference is made to Fe(III)-Mo(VI) interactions.

RAPID MEASUREMENT OF TOTAL NITROGEN AND NITROGEN 15 IN SOIL GROUNDWATER AND PLANT TISSUES USING REDUCTIVE PYROLYSIS COUPLED WITH MASS SPECTROSCOPY

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Abstract

The introduction of isotopic materials has given scientists a powerful method for research. Research on the environmental behavior of nitrogenous materials with the aid of nitrogen isotopes include: (1) the sources of nitrate contamination of ground water, (2) role of nitrogen in eutrophication, (3) dynamics of nitrogen fertilizers, (4) nitrification and/or denitrification processes, (5) rates of biochemical cycling, (6) fate of nitrogen oxides from internal combustion engines. Research of this nature requires the use of the stable nuclides of nitrogen, nitrogen 14 and nitrogen 15 as tracers. The great advantage of stable isotopes is their permanency; they are invaluable for experiments which require considerable time for completion. Fortunately, the enriched isotopes of nitrogen are now available in large quantities. An analytical system for measuring total nitrogen and its isotopic abundance in a variety of environmental samples has been developed. A reductive pyrolysis system and a directional focusing 6-inch gas mass spectrometer were combined into the analytical system. In the pyrolysis part of the system, nitrogen species are converted to ammonia with an atmosphere of hydrogen in the presence of a heated nickel catalyst. Five percent of the gas stream is split away for measuring total nitrogen by a conductivity detector. The ammonia is removed from the gas stream employing a cold finger reaction vessel. The hydrogen-free ammonia is decomposed thermally to nitrogen and hydrogen at 1000 degrees C employing a hot rhenium filament. The N2 produced from the decomposition is used for measuring the abundance of masses 28 and 29 by mass spectrometry. From this ratio, the nitrogen 15 atom fraction is calculated. Standard samples of nitrogen 2, ammonia, orchard leaves and urea have been successfully analyzed to determine isotopic compositions. Samples containing as little as 20 microgram of total nitrogen can be analyzed by this system. Three samples may be completed per hour using three reaction vessels.

LEAD-TANNIN COMPLEXES LEACHING FROM A SMELTER CONTAMINATED FORESTED WATERSHED

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Abstract

Delineating trace contaminant chemistry in soils is of importance in understanding the abiotic transfers of contaminants in ecosystems. Water-soluble organic acids and polyphenols have been implicated in the mobilization and transport of iron and aluminum in soils developing under forest-type vegetation. Oak species have been particularly noted as a source of water-soluble complexing agents which enhance transition metal mobility in soils. Consequently, such organo-metallic complexes appeared likely to be important in the transport of the trace metal contamination of a predominantly oak-pine watershed located in southeastern Missouri by a lead smelter operation. Laboratory studies under way at ORNL and the University of Missouri, Rolla, have shown that deionized water leachates of smelter-contaminated litter (3700 ppm lead) contain significant amounts of organically complexed lead (0.2-0.8 milligrams per liter) and copper (0.1-0.2 milligrams per liter). Zinc is only slightly complexed by the tannin-like substances leachable from the contaminated litter. Cadmium appears present largely in uncomplexed forms. Specific-ion electrodes, synthetic ion exchange, and chelating resins, as well as soil collected from the contaminated watershed, were used to study the nature of the complexed metals. Copper appears to be the most mobile, followed by lead. Because of the low soil pH (4.4), zinc and cadmium appear to behave largely as uncomplexed cations when the leachates were equilibrated with soil. Treatment of the litter leachates with H202 destroys the mobile nature of copper and lead. Saturation extracts of soil taken about 1 mile from the smelter contain appreciable quantities of the yellow-colored organic acids. These extracts from complexes with copper and lead, verifying the presence in both soil and litter, of potential lead and copper carriers. The importance of these substances in lead mobility in the watershed requires further onsite evaluation, but it appears that soil adsorption parameters required for application of a "unified transport model" simulation for trace elements to this ecosystem may be quite different from that predicted based on simple cation-soil interactions.

THE DISTRIBUTION AND DYNAMICS OF TRACE ELEMENTS FROM URBAN INDUSTRIAL FALLOUT IN A CLOSED AQUATIC ECOSYSTEM

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Abstract

Abstract

Distribution of aerially-deposited trace metals, including cadmium, lead, zinc, and iron, was investigated in a man-made aquatic ecosystem. The site, a borrow pit formed in Gary, Indiana during construction of the Indiana Toll Road in 1954, is ideally situated to receive both automotive and industrial emissions. A control pond was located in a rural area 90 miles south of the borrow pit. Floating funnel traps were placed onto the surfaces of both systems to collect aerially-deposited substances. Metal deposition rates (mg/m squared/mo) were significantly greater at the urban site. Estimates of the weight of metals deposited over the 19-year life of the borrow pit ranged from 0.91 kg cadmium to 6437 kg of iron. Elevated sediment metal concentrations were noted in the borrow pit. Average levels in the upper 5 cm of core samples (dry-weight basis) were 1.82 ppm cadmium; 354 ppm lead, 481 ppm zinc, and 40,500 ppm iron; corresponding concentrations in the control pond were less than 0.2 ppm cadmium, 5 ppm lead, 25 ppm zinc, and 6,300 ppm iron. Vertical distribution of metals within the sediment was fairly uniform throughout the top 5 cm; then decreases with depth occurred until the sediment-sand interface was reached. Metal levels in water samples were low; cadmium concentrations were generally less than 1 ppb. Significant release of all metals from sediment into overlying waters occurred during summer stagnation. It is doubtful that these metals were available for biological uptake. Biological samples contained background or only moderately elevated metal levels. Concentrations noted in fish muscle tissue (wet-weight basis) were 0.037 ppm cadmium and 0.103 ppm lead for bluegills and 0.025 ppm cadmium and 0.116 ppm lead for largemouth bass.

GEOCHEMICAL CYCLES AND BUDGETS OF ARSENIC IN PUGET SOUND AND LAKE WASHINGTON

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Abstract

Abstract

A first order budget of arsenic fluxes through Puget Sound has been constructed by estimating arsenic input rates from the incoming sea water, river water, atmospheric precipitation, the liquid effluent of the Tacoma smelter, and the sewage and industrial discharges of Seattle. Arsenic removal rates due to sedimentation and to discharge of surface sea waters flowing out of the Sound have also been estimated. The aim is to determine the rate of movement of arsenic through the four Puget Sound subregions and the ultimate fate of both natural and anthropogenic arsenic introduced into Puget Sound. This information is needed to be able to predict the concentrations of arsenic with time in different parts of Puget Sound, given various natural and anthropogenic inputs at different places around the Sound. The natural distribution of arsenic in the sediments and waters of Puget Sound is modified by a large copper smelter which releases approximately 300 tons per year of arsenic to the atmosphere in stack dust. A budget of arsenic fluxes for Lake Washington shows that this smelter stack dust is a major contributor of arsenic to the lake, located some 35 kilometers downwind. A major removal mechanism for arsenic in Lake Washington is by coprecipitation with an unusual hydrous iron/manganese oxide solid which forms during summer by either bacterial or inorganic processes.

IV. BIOLOGICAL SYSTEMS

EFFECTS OF MOISTURE AND MANURE UPON GASEOUS CONCENTRATIONS OF NITROUS OXIDE IN SOILS*

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Abstract

Nitrous oxide concentrations in soil gases were sampled at 20, 30, 60, and 80 cm depths over a 70 day period following an irrigation. Four plots from a Holtville clay had previously been treated with manure over a three year period as follows: 1) untreated, 2) 45 metric tons/hectare/year for 3 years, 3) 180 T/ha/yr for 3 years, 4) 360 T/ha/yr for the first year and none thereafter. Nitrous oxide concentrations were greatest about one to two weeks after irrigation, following about a one week lag period after the soils had been saturated and began to drain. Nitrous oxide concentrations in all the plots were the highest at all depths when the soil moisture was between 5-20 cbar. Low concentrations of N_2O (near ambient) at saturation were attributed to a faster rate of reduction of N_2O to N_2 by bacterial action, while low concentrations beyond 20 centibar (cb) were attributed to inhibition of denitrification by diffusion of oxygen. Nitrous oxide and CO_2 concentrations were highest in the two treatments receiving manure for a 3 year period. Gaseous oxygen concentrations never fell below 14% in any of the samples despite the occurrence of denitrification. This finding supports the soil microsite concept that aerobic and anaerobic reactions can occur in very close proximity to one another.

Introduction

The occurrence of nitrous oxide in soils is qualitative proof for the occurrence of bacterial denitrification. Quantitatively, the significance of N_2O remains obscure largely because it may be further reduced to N_2. Thus, low concentrations of nitrous oxide may be indicative of either slow reduction of nitrate or rapid reduction of N_2O during denitrification. Nommik (1) and Wijler and Delwiche (2) observed that N_2O concentrations were lowest in soils amended with exogenous organic matter even though denitrification rates were highest. Focht (3) postulated that available carbon had a proportionally greater effect upon the rate of N_2O oxide reduction than upon its rate of formation from NO_3^-. Burford and Stefanson (4) concluded that the diffusive loss of N_2O from soil was related directly to the soil-water status, yet were unable to accurately measure losses of N_2O because of insufficient data relating to diffusion coefficients and solubility changes with pH and temperature. Stefanson (5) showed that the ratio of N_2:N_2O gases evolved from $^{15}NO_3^-$ varied from 0.06:1 to 6:1 depending on the soil water potential. The study which follows was undertaken to determine the effects of soil-water suction and organic nitrogen additions upon the gaseous concentration of N_2O at various depths in the soil.

Method and Materials

The plots used in this study (12.2 m by 12.2 m each) were situated on a calcareous Holtville clay located at the Imperial Valley Conservation Research Center in Brawley, California. The four plots under study had the following three year history of manure additions: (1) none, (2) 45 metric tons per hectare per year, (3) 180 T/ha/yr, (4) 360 T/ha/yr added the first year with no additions the following two years. The plots were instrumented at the end of the 3rd year, after the growing season, with probes for collection of gas samples (6) and with tensiometers to measure soil suction. Samples and tensiometer readings were taken four days prior to irrigation and at 2,4,9,17,23,37,43, 52,57, and 70 days thereafter. Gas samples were withdrawn in 5 ml gas-tight syringes, and the needles were plunged into rubber stoppers to eliminate gas leakage. N_2O was

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*Work supported by the National Science Foundation, RANN Project GI-34733.

sampled separately from CO_2 and O_2. Samples for N_2O analyses were drawn through a 2.5 ml cartridge containing Ascarite to eliminate interference of CO_2. Partial pressure changes resulting from CO_2 removal were insignificant in calculating N_2O concentrations. The gases were transported 100 miles to Riverside where they were analyzed the following day for N_2O, CO_2, and O_2 on a Finnigan 3100 gas chromatograph-mass spectrometer. Each of the three gases was determined separately by injecting the entire 5 ml for N_2O determination and half (2.5 ml) from the syringe for CO_2 and O_2 through a septum into a gas sampling valve equipped with a 2 ml sample loop. A stainless steel column (54.5 x 0.318 cm) packed with Porapack Q (50-80 mesh) was used for analysis of N_2O and CO_2 and was maintained at a temperature of 25 C and a helium carrier gas flow rate of 35 ml/min. The retention times of CO_2 and N_2O under these conditions were approximately 6 and 8 minutes, respectively. Samples were compared with known standards and calculated by integrating the peak area response on a chart recorder with a planimeter. The total ion current produced in the mass spectrometer at m/e 44, the parent ion for N_2O and CO_2, was used as the detector. Nitrous oxide concentrations as low as 0.1 ppm (v/v) could be detected by this method. O_2 concentrations were determined from the other half of the remaining gas sample used for CO_2 analysis. G.C.-M.S. conditions described previously were used except that the total ion current was monitored at m/e 32, and a column packed with 50-80 mesh 5-A molecular sieve was used.

Results

A representative sequence of events is shown in Fig. 1 for the 60 cm depth in the control and in the 45 T/ha/yr manure treatment. A rapid drop in suction occurred within 2 days after irrigation. Nitrous oxide concentrations, however, did not reach a peak until about one to two weeks from the onset of irrigation, at which time, soil suction increased. Oxygen concentrations remained high throughout the experiment and never fell below 14%. This sequence was similar in the 180 T/ha/yr and in the 360 T/ha/yr treatments except that CO_2 concentrations were higher than all treatments in the former, while they were not much higher than the control in the latter.

When all of the N_2O concentrations are plotted separately for each treatment and distinguished for each depth as a function of suction (Fig. 2), it is apparent that N_2O concentrations are highest between 5-20 cbar. The highest concentrations were observed at 60 and 80 cm and in the two plots receiving yearly additions of manure.

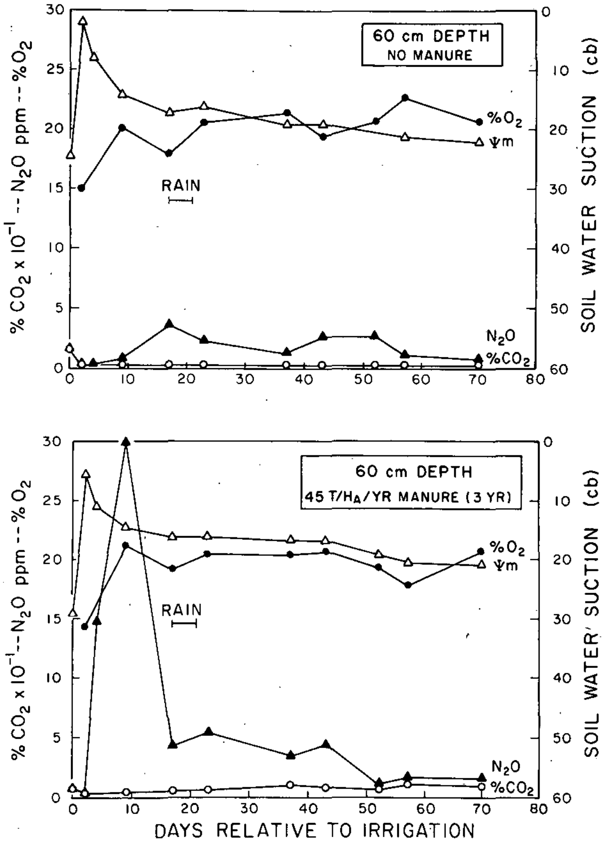

FIG. 1. Changes in O_2, CO_2, N_2O and suction at 60 cm depths with time in an untreated soil and in one receiving 45 T/ha/yr.

Discussion

The higher N_2O concentrations observed in the 45 and 180 T/ha/yr treatments would be expected as a result of vigorous microbial activity which is indicated by high CO_2 concentrations and high levels of soluble carbon (B. D. Meeks, unpublished data). The low concentrations of N_2O observed above 20 cb reflects inhibition of denitrification. In laboratory studies, Pilot and Patrick (7) found that denitrification ceased between 20 and 40 cb, depending on the soil type. As the aerated pore space increased, diffusion of oxygen into the soil plays a major role in inhibiting denitrification.

Under saturated conditions (near 0 cb),

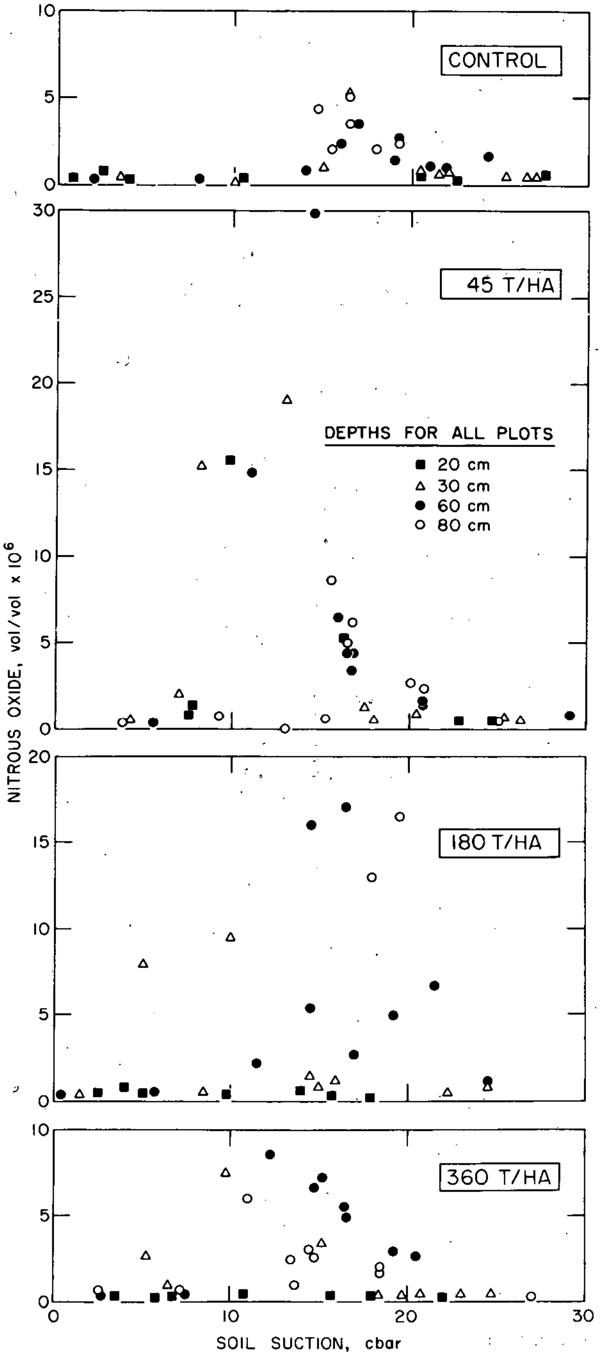

FIG. 2. Gaseous N_2O concentrations as a function of suction in four plots at four depths each.

maximum denitrification should occur since diffusion of oxygen would be most restricted. However, an examination of Figure 2 shows low concentrations of N_2O at high levels of soil moisture. This apparent anomaly is probably the result of the N_2O being dissolved in the soil water and resulting in low concentrations in the soil gas. The low initial concentrations of N_2O may also result from a larger fraction of nitrate being converted to N_2 under the anaerobic conditions of high soil moisture and high liquid phase N_2O concentrations.

These data appear to support a model proposed by Focht (3) that N_2O concentrations in the soil gas phase would be greatest at about 12% (approx. 5-10 cb) of the total pore space. Diffusion coefficients for N_2O and rate constants for the microbial reduction of nitrate to N_2 will have to be determined, in lieu of ^{15}N tracer studies, before an estimate can be made of the gaseous losses of nitrogen from soil.

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NITRATE MOVEMENT AND PLANT UPTAKE OF N IN A FIELD SOIL RECEIVING ^{15}N-ENRICHED FERTILIZER*

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Abstract

A plot of 13.9 m^2 on Yolo fine sandy loam was fertilized with $(NH_4)_2SO_4$ containing 8.04 atom % excess ^{15}N at the rate of 112 kg N/hectare and planted first to wheat and then to corn. The plot was surrounded by a buffer zone of 405 m^2 which was treated in identical fashion except that unlabeled fertilizer was used. Porous ceramic probes for measuring soil moisture tension and for extraction of soil solution were installed depths from 15 to 180 cm. Harvested crops were analyzed for ^{15}N as were soil cores taken after crop harvest.

Nitrate-N concentrations in the soil solution at 15 cm ranged from a maximum in March of 70 ppm, of which 39 ppm was derived from fertilizer, to a minimum of 0.2 ppm in July. The largest amount of fertilizer-derived NO_3-N at 180 cm was 0.28% of that applied, conttributing 0.36 ppm to the concentration at that depth.

The wheat crop removed 32.3% of the fertilizer N and the corn crop utilized 22.8%. Organic and inorganic N remaining in the soil after cropping represented 32.9% of the applied N, leaving 12.0% unaccounted for. The consistently low nitrate concentrations at 180 cm suggest that this deficit was not due to leaching, and should be attributed to denitrification.

Introduction

In dealing with the question of nitrate as a trace contaminant it is important to determine the origin of nitrate which moves downward in soil profiles and which potentially may contaminate ground or surface waters. That quantity of nitrate derived from added fertilizer which escapes the root zone is in principle subject to some degree of control by fertilizer management. On the other hand, nitrate resulting from decomposition of soil organic matter is much less subject to regulation by management practices.

Although nitrate is the end product of a complex and interrelated series of biochemical transformations in soils, it is possible to determine its origin by use of fertilizer materials labeled with the ^{15}N isotope. If it is assumed that labeled nitrogen will be added at levels on the order of 100 kg/hectare to soil with an initial nitrogen content of 0.1%, complete equilibration of the labeled N with soil N would result in an isotopic composition of about 0.41% ^{15}N. This value is sufficiently different from the normal value of about 0.36% to ensure two significant figures in calculations based upon the difference. In fact, ^{15}N in crops fertilized with labeled N and in nitrate found in the soil solution is usually much higher than would be expected if complete equilibration had occurred. Earlier work (1) has shown that interchange between organic and inorganic N in soils is relatively slow.

An additional advantage of the tracer procedure is the improved accuracy in accounting for gains and losses in the soil system. Since conventional analytical procedures are not sufficiently accurate to account for changes smaller than 50 to 100 kg/ha, field estimates of denitrification losses are not attainable by these techniques. However, an accounting of ^{15}N-labeled fertilizer added to the soil can be made within about 5 kg/ha, so that reasonable estimates of denitrification losses are possible.

Procedure

A plot of 13.9 m^2 area on Yolo fine sandy loam was instrumented by placing porous ceramic suction probes at depths 15, 30, 60, 90, 120, 150 and 180 cm. These were connected to collection vials by means of fine diameter plastic tubing and were used for extraction of samples of soil solution by application of vacuum. After collection samples were analyzed for ammonium and nitrate N and their isotopic composition determined in a mass spectrometer. Additional probes of identical design were connected to mercury manometers for measurement of soil moisture tension. It was assumed that the measured tension was representative of the soil 15 cm above and 15 cm below the probe. On the basis of calibration

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*Work supported by National Science Foundation Grant GI-34733X curves of soil moisture tension vs. moisture content prepared by LaRue (2) it was possible to monitor the water content of the soil down to 195 cm throughout the growing season.

The plot was fertilized with $(NH_4)_2SO_4$ containing 8.04 atom % excess ^{15}N at a rate equivalent to 112 kg/ha. The fertilizer was worked into the soil surface and a crop of wheat planted immediately thereafter. The crop was irrigated by means of a sprinkler system which was turned on whenever the soil moisture tension at any depth reached 0.85 bar. The wheat was planted February 23, 1973 and harvested May 2 prior to complete maturity. After harvest soil core samples were taken at 15 cm intervals down to 180 cm and analyzed for organic and inorganic N and the ^{15}N content determined. A corn crop was planted May 5 without additional fertilizer and harvested August 24. Another series of soil cores were obtained after corn harvest.

Results and Discussion

Nitrate in the Soil Solution: Concentrations of nitrate in samples of soil solution taken at various depths during the period of crop growth are shown in Figures 1 and 2.

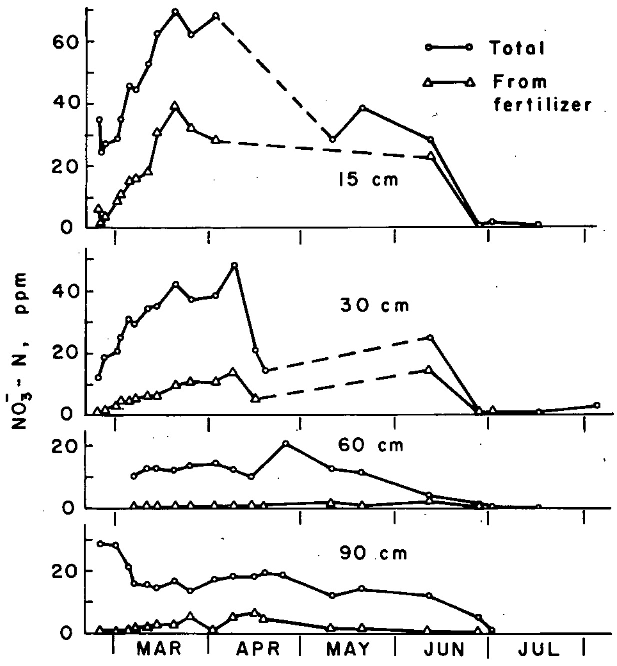

FIG. 1. Nitrate concentrations in soil solution samples at depths 15 to 90 cm during the growing season.

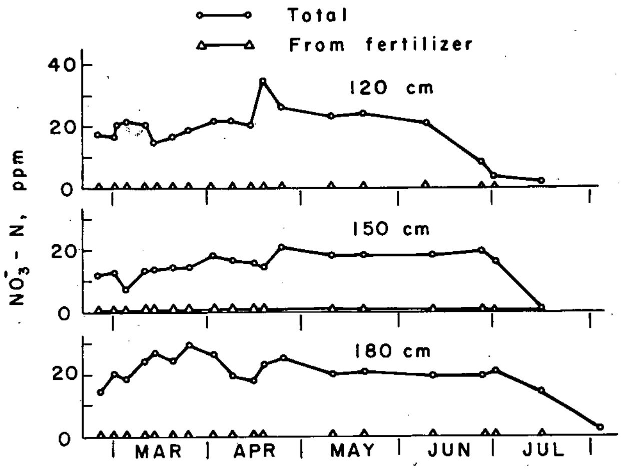

FIG. 2. Nitrate concentrations in soil solution samples at depths 120 to 180 cm during the growing season.

As expected, relatively high concentrations were observed at 15 and 30 cm depths early in the season, with labeled N from the added fertilizer contributing significantly to these concentrations. The dashed lines at these two depths indicate a period when the moisture content of the soil was too low to obtain a sample of soil solution. Nitrate concentrations declined sharply during June, a period of rapid corn growth, at all depths above 150 cm and in July a similar trend at 150 and 180 cm indicated extension of the root system into these layers of soil. At 120 cm and below the concentration of fertilizer-derived nitrate was barely detectable, indicating very little leaching within the profile. It will be noted that the total nitrate concentration at these depths was near or above the 20 ppm level considered hazardous for drinking water during much of the season, but the potential for contamination of groundwater was eliminated by the presence of a deep-rooted crop. After harvest, however, these nitrate levels could easily be regained by mineralization of organic nitrogen.

Distribution of fertilizer-derived nitrate as a function of depth, expressed as a percentage of the total applied, is shown in Figures 3 and 4. For a short period in March about 28% of the labeled N was present in the 0-22.5 cm layer of soil, falling to about half this amount in April. At no time did a significant quantity of this nitrogen reach the 45-75 cm layer. A small pulse of labeled N was observed at 75-105 cm (note the expanded scale in Figure 4) but only negligible values were found below this depth. Data are shown only down to 135 cm.

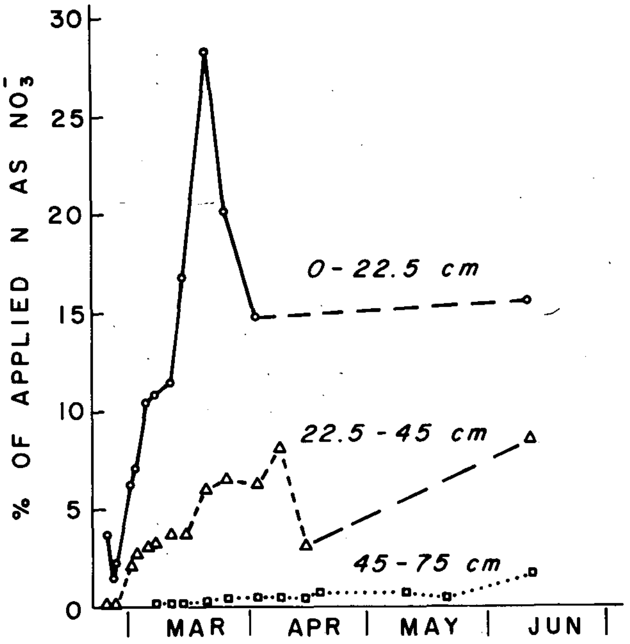

FIG. 3. Distribution of fertilizer-derived nitrate as a function of depth, 0-75 cm.

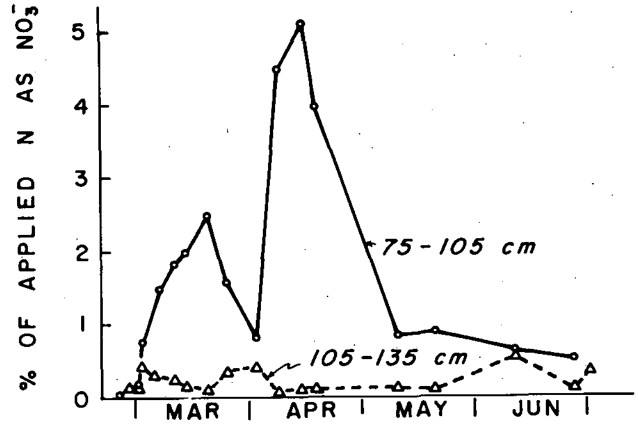

FIG. 4. Distribution of fertilizer-derived nitrate as a function of depth, 75-135 cm.

Crop Removal: Yield and nitrogen uptake of the two crops are shown in Table 1. Fertilizer utilization efficiency of the combined crops, 55.1%, is within the normal range as shown by comparison with other reports (3, 4). Of the remaining 45% relatively little was in a form subject to leaching as evidenced by the very low nitrate concentrations in the soil solution discussed previously.

TABLE 1. Crop yield and uptake of fertilizer nitrogen.

Crop	Yield, kg/ha	% of fertilizer N in crop
Wheat	2818	32.3
Corn	16358	22.8

Residual Soil Nitrogen: A substantial part of the labeled N was present in the soil organic fraction of the upper 30 cm of soil at the time the wheat crop was removed (Figure 5), with 2-3% of the applied N remaining in the inorganic form.

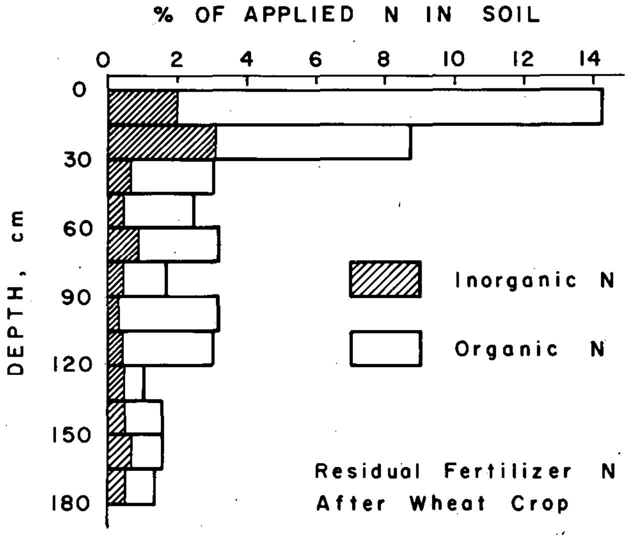

FIG. 5. Distribution of organic and inorganic N derived from added fertilizer at the time of wheat harvest.

Presumably much of the organic N was present in the form of roots. After the corn harvest the residual inorganic N had largely disappeared (Figure 6), but a considerable quantity of organic N remained. Remineralization of this nitrogen has been shown to be a slow process, with progressive stabilization over a long period of time (5). The presence of 29.6% of the fertilizer N in the organic form at the end of the growing season illustrates the difficulty of relating fertilizer inputs to the concentration of nitrate deep in the soil profile. Since much of the input N is converted to a stable organic form a long time, possibly several decades, may elapse before this reappears in the form of nitrate.

Denitrification Losses: An accounting of labeled nitrogen given in Table 2 shows a deficit of 12.0% which is attributed to denitrification in the absence of any evidence of leaching.

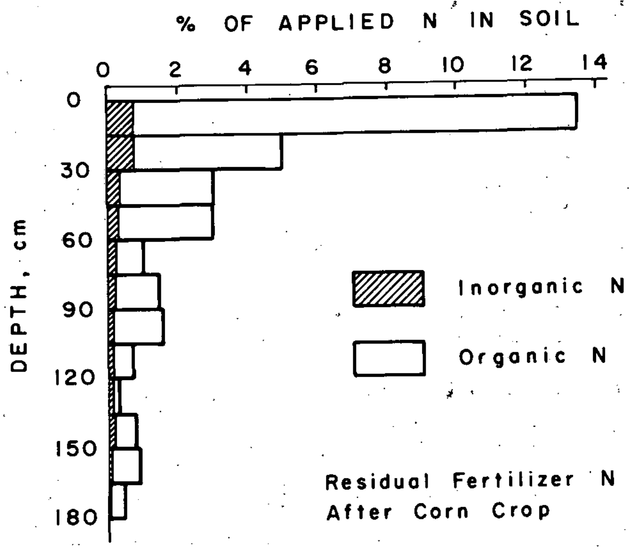

FIG. 6. Distribution of organic and inorganic N derived from added fertilizer at the time of corn harvest.

TABLE 2. Balance sheet of labeled N at end of crop season

	% of N Applied
Removed in wheat crop	32.3
Removed in corn crop	22.8
Inorganic N in soil	3.3
Organic N in soil	29.6
Not accounted for	12.0

losses. This estimate is comparable to values reported in tracer experiments conducted in greenhouse pots or small lysimeters (6, 7). Careful watering procedure to avoid excess water probably minimized the denitrification loss. However it is significant that some denitrification occurred even with careful management. At the present time the use of ^{15}N-enriched fertilizer is the most accurate procedure for estimating such losses in field experiments.

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POLICY IMPLICATIONS OF THE RELATIONSHIP BETWEEN NITRATE POLLUTION IN SURFACE WATERS AND USE OF NITROGEN FERTILIZER*

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Abstract

Two Studies investigate the relationship between the rate of application of nitrogen fertilizer and nitrate concentration in agricultural drainage water in Illinois to illuminate the consequences of policies aimed at controlling the movement of nitrate from the soil to water. The first uses watersheds of Illinois as the unit of analysis and finds limits on the application rate of nitrogen fertilizer to corn that will meet the 10 ppm Public Health Service standard in the spring for various probabilities of exceeding the water quality standard. Controls would be required for some areas of northern and central Illinois. No controls are necessary in southern Illinois. The controls result in relatively small decreases in corn production and gross farm income. The second study is in progress and investigates the nitrogen fertilizer-water quality relationship across tributaries of one Illinois watershed in the east central region. Estimates of the economic efficiency of nitrogen fertilizer use will be made as a means of assessing the potential for policy that would persuade farmers using greater than optimal applications to decrease their use of fertilizer.

Introduction

We have engaged in two studies to test the relationship between the rate of application of nitrogen fertilizer and nitrate concentrations in agricultural drainage water in Illinois for the purpose of investigating some policies that might be used to reduce the nitrate in surface waters of the Corn Belt. The first estimates a relationship between fertilizer use and water quality using watersheds of Illinois as the unit of analysis. The relationship is used to estimate limits on nitrogen applications to corn that will meet a 10 ppm nitrate nitrogen standard and some economic effects of controls. The second study is in progress and uses survey data on nitrogen fertilizer use in tributaries of the Sangamon watershed of Illinois to test the relationship between fertilizer use and water quality. We will also investigate the economic efficiency of nitrogen use as a means of analyzing the potential for a policy of persuasion that would lead farmers applying nitrogen at rates above the economic optimum to reduce their use.

A number of tests have been conducted of the relationship between nitrogen fertilizer use and nitrates in drainage water (see reference (1) for a survey of the literature), but only one study is based on historical data similar to those used in the first project discussed below (3). The work reported here utilizes improved estimates of nitrogen fertilizer use and a more accurate specification of the relationship between nitrate in drainage water and various explanatory variables. It is also the first study to encorporate uncertainty in the relationship between the nitrogen fertilizer use and nitrate concentrations in drainage water into a formulation of policy measures for control.

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The first study was conducted for the Illinois Institute for Environmental Quality (1). It uses multiple regression as the primary tool of analysis with watersheds as the unit of observation in order to find a relationship between nitrogen fertilizer applications and nitrate nitrogen concentrations in surface waters. The study relies entirely on historical data -- that is, data collected by various federal, state, and private organizations in the past. Consequently, the data limit to some extent the questions addressed, the choice of analytical techniques, and occasionally the confidence in conclusions.

We used observations on nitrate nitrogen concentration in Illinois streams in the April-June period as the dependent variable. The April-June period was chosen because it is the time of elevated nitrate concentrations in Illinois streams.

Data were collected for direct and indirect measures of major sources of nitrate

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*Work supported by RANN and the Illinois Institute for Environmental Qaulity.

in Illinois streams. Estimates of nitrogen fertilizer use were made for watersheds of Illinois. The fraction of watershed acreage planted to row crops (corn and soybeans) was used as a proxy variable for soil organic sources of nitrate since the net breakdown of soil organic nitrogen is greater under the soil conditions associated with row crops. Population variables were used as proxies for nitrates arising from industrial and human wastes, and livestock inventories served as a proxy for this source of nitrate.

We also tested the explanatory power of environmental variables that might affect the movement of nitrate from the soil to water. These included measures of various characteristics of topography, artificial drainage, and hydrology such as the slope of the land, the fraction of cropped acreage drained by tiles or ditches, and stream flow.

A statistical test was conducted of the relative explanatory power of two alternative hypotheses for variations in nitrates in surface waters of the Corn Belt. One is that nitrate originates chiefly from applied fertilizer. The other is that nitrate derives largely from the mineralization of soil organic matter which is increased when land is planted to row crops. Due to multicollinearity problems that result from intercorrelation of the fertilizer use and the soil nitrogen proxy variable, the results are somewhat ambiguous. But the fertilizer variable does have greater predictive power than the soil nitrogen proxy variable in recent years, 1968 through 1972. From this result we proceeded by using the fertilizer variable as the primary agricultural source of nitrates in Illinois streams in our analysis.

The following predictive equation for nitrate concentrations in Illinois watersheds was estimated using multiple regression on pooled cross section data for 1969, 1970, and 1971 (time series analysis is possible for only a few watersheds):

$$(1)\quad WQ = 0.33 + \underset{(0.66\mathrm{x}10^{-5})}{5.49\mathrm{x}10^{-5} * NF^3} + \underset{(0.20\mathrm{x}10^{-5})}{1.19\mathrm{x}10^{-5} * NF^3} \cdot FLO + \underset{(0.0022)}{0.0046 *}\ UPOP$$

$$R^2 = 0.59 \qquad n = 198$$

where WQ is observations on nitrate nitrogen concentrations in the April-June period, NF is estimated nitrogen fertilizer application per watershed acre in the previous crop year, FLO is the average daily discharge rate for the April-June period divided by a yearly average daily discharge rate over 10 to 30 past years, and UPOP is urban population per square mile in 1969. The numbers in parentheses are standard errors, and the asterisks denote coefficients significant at the 5% level. A nonlinear functional form corresponds with our apriori expectations -- the deminishing yield response of corn to nitrogen suggests that more nitrate is available for leaching at higher nitrogen fertilizer application rates, and corn and soybeans (row crops) are planted on better land with higher soil organic content and, therefore, higher potential for mineralization and leaching of nitrate which also suggests a nonlinear relationship. Livestock inventory variables which were used as proxies for animal sources of nitrate were not included in the predictive equation after performing poorly in other regression equations.

Controls in the form of limits on nitrogen fertilizer applications to corn were estimated in the following way. First equation (1) and an equation for the upper bound of the confidence interval for predictions based on equation (1) were solved simultaneously for the average application of nitrogen fertilizer per watershed acre and the average nitrate nitrogen concentration given: (a) the upper bound on the confidence interval equal to 10 ppm, the Public Health Service standard, (b) a relative stream flow of 1.5 which is the long term (1946-1971) mean for all the watersheds entering our analysis, (c) urban population density of 25 per square mile which is the 1969 median for the watersheds on which the 1969-71 regressions were run, and (d) an arbitrary value for the probability that 10 ppm will be exceeded. We assumed that all nitrogen fertilizer is applied to corn (about 90% is applied to corn in Illinois). Then, average nitrogen fertilizer use per watershed acre was converted to average nitrogen fertilizer use per corn acre by means of the ratio of corn acreage to watershed acreage in any given area. Finally, with 1971 data on the estimated distribution of nitrogen fertilizer application rates to corn for five regions of Illinois from the Doane Agricultural Service and the assumption that farmers applying nitrogen at rates above the limit move to the limit and those below the limit do not change their practice, we determined the limit on nitrogen use per corn acre that would bring average use to the desired level in each of the five regions of the state. This procedure was repeated for a range of probabilities of exceeding 10 ppm. See Table 1. As one would expect, controls in each region become considerably more restrictive the lower the probability that the 10 ppm standard will be exceeded.

Only east central Illinois requires controls at the fraction of land area planted to corn in 1971 if controls are differentiated by regions. The fraction of land planted to corn was 31% in the north, 36% in the west central region, 29% in east central Illinois, 21% in the southwest, and 16% in the southeast.

However, if one is willing to assume that the distribution of nitrogen fertilizer application rates for a region holds for smaller areas within that region, then a number of areas in the northern and both central regions would require controls if controls are differentiated by watersheds or counties. Since controls are not indicated for the southern regions or watersheds and counties within them, data for these regions are not reported in the remainder of this paper.

We have estimated several dimensions of the economic effects of the limits on nitrogen fertilizer use shown in Table 1. We deal only with private costs to farmers; our analysis does not include the enforcement or administrative costs of controls. The estimates are based on the 1971 distribution of nitrogen fertilizer use rates, 1971 corn and fertilizer prices, and the strong assumption of unchanging corn acreage and price under controls. The latter assumptions are made tenable by the recent work of Taylor and Swanson whose spatial linear programming analysis of statewide controls on nitrogen use in Illinois shows little change in corn acreage and price for controls down to and including 100 pounds per acre (4).

Table 2 shows the percentage of farms affected by the estimated limits for the north, west central, and east central regions of Illinois. The estimated percentage changes in corn output for the three regions are presented in Table 3.

Table 4 shows the estimated percentage decrease in nitrogen fertilizer use by regions for north, west central, and east central Illinois. The percentage decrease in corn output for any given cell of Table 3 is considerably less than the decrease in nitrogen use in the corresponding cell of Table 4. This results from the marginally diminishing yield response of corn to nitrogen and the fact that limits on nitrogen use in this analysis are at relatively high levels of nitrogen application. Hence, the change in yield response is small.

The estimated percentage decrease in gross farm income per affected farm, due to limits on nitrogen fertilizer use for the three regions of Illinois, are presented in Table 5.

Finally, Table 6 presents crude estimates of the change in net farm income per affected farm which is the change in gross farm income per affected farm less the product of the change in nitrogen fertilizer use per affected farm and the 1971 price of nitrogen (five cents per pound). At the right hand margins of the table which correspond to relatively high values for the limit, the estimated change in net income is frequently positive which suggests that some farmers using high nitrogen application rates were inefficient in their use of nitrogen fertilizer at the prices for corn and nitrogen prevailing in 1971.

II

The second study is in progress, and only the outline of the work will be dealt with here. It is based on survey data collected from farmers in the upper Sangamon watershed in east central Illinois in the spring of 1974. Nitrate nitrogen concentrations regularly exceed 10 ppm in the Sangamon in the spring, and it is the source of drinking water for a city of 100,000 people, Decatur.

There are two major objectives in this work. The first is to test the relationship between fertilizer use and nitrate in surface waters using data not subject to the problems of the historical data in the study described above. The upper Sangamon is a relatively homogeneous area in terms of soil type and hydrology and has low concentrations of urban population and industry. At the same time there is considerable variation in the nitrate concentrations of its tributaries in the spring.

The survey gathered data on agricultural practices including the use of nitrogeneous fertilizers for three crop years from 323 farms in 16 subwatersheds which are tributaries of the Sangamon. Nitrate concentration data are available for most of these streams on a monthly basis going back to January 1971. We will test the relationship between nitrogen fertilizer use and water quality across subwatersheds of the Sangamon.

The second purpose of the study is to determine if farmers are using nitrogen fertilizer efficiently in an economic sense. There is some evidence of excessive use in the study discussed above, and there is similar evidence from other sources (3). We will investigate the extent of excessive use, if any, and the likely impact that a change to optimal use would have on water quality. Obviously, evidence of considerable non-optimal use of nitrogen by farmers suggests a policy of education and persuasion of farmers that is in their own self interests and, hence, relatively painless.

The economic efficiency study will be accomplished by estimating a production function for corn based on the survey data, deriving a demand function for nitrogen fertilizer from the production function and a profit equation, and then using the price of corn and nitrogen fertilizer to determine optimal nitrogen fertilizer application rates.

If the analysis shows farmers are deviating from optimum use rates, we will test for the shouces of this behavior in the demographic characteristics of farmers, farm size, and the sources of information farmers rely on for best fertilizer practice.

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TABLE 1

Estimates of Limits on Nitrogen Fertilizer Applications to Corn in Order to Meet a 10 ppm Nitrate Nitrogen Water Quality Standard with Various Probabilities of Exceeding the Standard for Regions of Illinois

Region	Fraction of Land in Corn	Probability that 10 ppm will be exceeded							
		.01	.02	.05	.10	.20	.30	.40	.50
North	.45	110	110	130	140	170	240		
	.40	120	130	170	unregulated				
	.35	160							
West Central	.45	120	130	160	300				
	.40	150	190		unregulated				
East Central	.45	90	100	110	120	130	130	140	150
	.40	110	110	130	140	160	170	210	260
	.35	120	140	170	260				
	.30	170	300						
South West	.40	120	130	160	240				
	.35	160	220						
	.30								
South East	.40	150	200						
	.35	unregulated							
	.30								

TABLE 2

The Percentage of Farms Affected by the Nitrogen Fertilizer Limits for the 10 ppm Nitrate-Nitrogen Standard Regions of Illinois

Region	Fraction of Land in Corn	Probability that 10 ppm will be exceeded							
		.01	.02	.05	.10	.20	.30	.40	.50
North	.45	51	51	23	17	5	1		
	.40	37	23	5					
	.35	8							
West Central	.45	29	24	6	1				
	.40	14	2						
East Central	.45	71	66	59	52	37	37	29	22
	.40	59	59	37	29	18	12	3	1
	.35	52	29	12	1				
	.30	12	1						

TABLE 3

The Percentage Decrease in Corn Output Due to the Nitrogen Fertilizer Limits for the 10 ppm Nitrate-Nitrogen Standard by Regions of Illinois

Region	Fraction of Land in Corn	Probability that 10 ppm will be exceeded							
		.01	.02	.05	.10	.20	.30	.40	.50
North	.45	1.7	1.7	0.6	0.3	<0.05	0		
	.40	1.0	0.6	<0.05					
	.35	0.1							
West Central	.45	1.3	0.7	0.1	0				
	.40	0.2	0						
East Central	.45	6.3	4.3	2.9	1.8	1.1	1.1	0.7	0.4
	.40	2.9	2.9	1.1	0.7	0.2	0.1	0	0
	.35	1.8	0.7	0.1	0				
	.30	0.1	0						

TABLE 4

The Percentage Decrease in Nitrogen Fertilizer Use Due to the Nitrogen Fertilizer Limits for the 10 ppm Nitrate-Nitrogen Standard by Regions of Illinois

Region	Fraction of Land in Corn	Probability that 10 ppm will be exceeded							
		.01	.02	.05	.10	.20	.30	.40	.50
North	.45	21	21	11	8	3	<0.5		
	.40	15	11	3					
	.35	4							
West Central	.45	16	13	5	1				
	.40	7	2						
East Central	.45	36	30	25	19	15	15	12	10
	.40	25	25	15	12	8	6	3	1
	.35	19	12	6	2				
	.30	6	1						

TABLE 5

The Percentage Decrease in Gross Farm Income per Farm for Farms Affected by the Nitrogen Fertilizer Limits for the 10 ppm Nitrate-Nitrogen Standard by Regions of Illinois

Region	Fraction of Land in Corn	Probability that 10 ppm will be exceeded							
		.01	.02	.05	.10	.20	.30	.40	.50
North	.45	1.7	1.7	1.3	0.9	0.2	0		
	.40	1.3	1.3	0.2					
	.35	0.4							
West Central	.45	2.2	1.5	0.5	0				
	.40	0.6	0						
East Central	.45	5.0	3.7	2.7	2.0	1.7	1.7	1.4	1.0
	.40	2.7	2.7	1.7	1.4	0.6	0.4	0	0
	.35	2.0	1.4	0.4	0				
	.30	0.4	0						

TABLE 6

The Change in Net Income (in Dollars) per Farm for Farms Affected by the Nitrogen Limits for the 10 ppm Nitrate-Nitrogen Standard by Regions of Illinois

Region	Fraction of Land in Corn	Probability that 10 ppm will be exceeded							
		.01	.02	.05	.10	.20	.30	.40	.50
North	.45	-278	-278	-100	+11	+378	+243		
	.40	-146	-100	+378					
	.35	+254							
West Central	.45	-329	-127	+331	+530				
	.40	+120	+745						
East Central	.45	-1176	-797	-532	-319	-186	-186	-92	+51
	.40	-532	-532	-186	-92	+180	+318	+836	+1072
	.35	-319	-92	+318	+1210				
	.30	+318	+1072						

TRACE-ELEMENT CONTENT OF HAIR: VARIATION ALONG STRANDS AND AS A FUNCTION OF HAIR-WASH FREQUENCY

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Abstract

Although a number of factors could influence the measured trace-element content of head hair, it appears that distance from the scalp and frequency of hair washing are two especially important variables that must be considered when utilizing hair analysis data to evaluate the human exposure to trace elements.

For all elements tested, the hair content, in general, increases in progressing outward from the scalp; the concentrations in the extreme distal portions of hair for some persons were observed to be up to 10 times and occasionally up to 50 times greater than more proximal segments of hair. Some trace elements, and sodium and chlorine in particular, exhibit length-content variation patterns which strongly implicate eccrine sweat as a contributor to this variation. This hypothesis is further supported by hair analysis data for samples of hair from two sets of individuals whose hair-washing frequency differ by more than a factor of 10. The hair of infrequent hair washers have statistically significant larger trace-element contents, with two important exceptions: Mg and Ca, trace elements that would be "precipitated" from water during hair washing.

These combined observations suggest that our initial analysis data for historical hair samples, which generally showed equal or higher contents for older hair, should have been expected because of the lesser frequency of hair washing 50-200 years ago and the fact that the historical samples frequently represent clippings of distal segments of hair. A qualitative reevaluation of these historical hair sample data, when compensated for these effects, would imply that the present day human exposure to many trace elements may exceed that of a century ago.

Introduction

There are three major goals of this study of the trace-element content of human scalp hair:

I. To determine which factors and variables such as age, sex, hair color and physical characteristics must be taken into account in evaluating the measured trace-element content of hair.

II. To establish a present-day baseline for the trace-element content of hair for the U.S. population.

III. To determine the degree to which those who lived 50-200 years ago differed from those living today in their exposure to trace elements.

We have previously described methods (neutron activation and flameless atomic absorption) used to analyse 10-20 mg samples of hair for up to 40 trace elements (1-3). Various data have also been given in these reports for the hair contents of selected homogeneous population groups: young men at the U.S. Naval and Air Force Academies and University of Michigan male freshmen.

Presented in this paper are data we have recently obtained for two of the variables which appear to be especially important in affecting the measured trace-element content of hair: frequency of hair washing and the variation of trace-element concentrations as a function of the distance from the scalp. Information on these two variables is used to evaluate the significance of preliminary data for 48 historical hair samples dating between 1850 and 1935.

Frequency of Hair Washing

Since the mid-60's, when considerable research was performed to assess the degree to which trace-element analysis of hair can serve in forensic identification, it has been known that the simple act of washing a hair sample, even using distilled water, resulted in a decrease in the content of some of the elements. This was particularly true for the so-called labile elements: Na, K, Cl, Br, etc. The contents of many other elements appeared only slightly affected, if at all, by any pre-analysis washing. Presumably, the keratin structure of hair, with its high sulfur content, was able to bind the heavier metals, almost all of which form very insoluble sulfides.

It appeared to us that the hair donor's personal hair washing habits could be an important factor in affecting the measured trace element content of hair. The use of certain shampoos which contain Zn or Se compounds as active ingredients could (and does) result in enhanced measured levels of these elements (1-3). Equally important, it seemed, would be the frequency of hair washing and its possible relationship in reducing the trace-element content of hair. Therefore, questions relating to hair washing frequency, shampoos used and frequency of use, as well as frequency of swimming were asked of all present-day hair donors.

Among the 1300 hair clippings we collected in 1971 from male University of Michigan freshmen were some whose donors indicated on our questionnaire that they washed their hair twice a month or less. The majority of the donors noted a hair-washing frequency of at least 20 times a month. Two groups of 12 hair samples each from these two extremes in hair-washing frequency were selected for analysis and those who stated that they washed their hair infrequently were contacted to verify their questionnaire reply. The hair samples were trimmed to remove approximately the last two cm of hair since, as noted in the next section, the distal segments frequently show much higher contents of almost all trace elements.

Table I. Geometric means[a] and analysis of variance comparison of trace-element contents of 12 frequent[b] and 12 infrequent[c] hair washers.

Element	Geometric Mean (μg/g) Frequent	Geometric Mean (μg/g) Infrequent	ANOVA +/-	ANOVA P[d]
Na	22	66	-	0.001
Mg	117	74	+	0.04
Al	5.9	13.8	-	0.0002
Cl	400	1350	-	0.0003
Ca	1100	500	+	0.006
Ti	3.1	5.7	-	0.02
V	0.036	0.094	-	0.002
Mn	0.44	0.37		N.S.
Co	0.19	0.13		N.S.
Cu	24	32		N.S.
Zn	167	183		N.S.
Ga	2.8	5.7	-	0.003
As	0.21	0.35	-	0.04
Se	0.76	0.80		N.S.[e]
Br	4.5	11.3		N.S.
Sr	2.2	2.5		N.S.
Cd	1.2	1.4		N.S.
I	0.71	1.2	-	0.02
Ba	1.3	2.1	-	0.02
Hg	2.1	3.1		N.S.
Pb	3.1	7.7	-	0.002

[a] The geometric mean is the antilog of the log-mean.

[b] 20 or more times a month.

[c] Twice a month or less.

[d] Probability of the correlation being due to chance; e.g. 0.02 is 1 chance in 50. N.S. = not significant and is given for $P > 0.05$.

[e] P = 0.0005 (negative correlation) if data are excluded for students who recently swam in a brominated pool.

Summarized in Table I are data obtained in the analysis of these two sets of samples (4). For 11 of the 21 elements, statistically significant higher contents were found for those who washed their hair less than twice a month. In addition, for the eight trace elements not showing a statistically significant difference, infrequent washers still had higher log-mean hair contents for six of these elements. Two important exceptions to this general trend are apparent: Ca and Mg, both of which are found in significantly higher amounts in clippings from those who wash their hair 20 times a month or more. Apparently these two trace elements, which contribute to water hardness, are precipitated onto the hair by soaps and shampoos.

Variation with Distance from Scalp

When single strands or bundles of 200 strands of hair are cut into segments and analysed, the general pattern of variation in content with distance from the scalp is one showing an increase, especially toward the distal segments. Examples of some of the more pronounced variations are shown in Fig. 1.

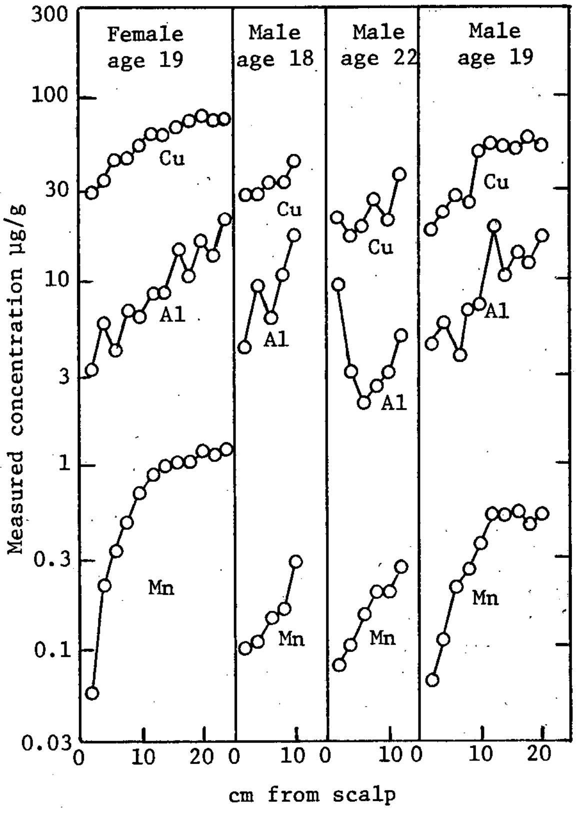

Fig. 1. Variation in 2 cm segment bundles of about 200 hair strands from four University of Michigan students.

The length-content variation patterns for Na and Cl, which are prominent components in eccrine sweat, are particularly interesting since most show a behavior similar to that of Fig. 2. High contents are frequently observed in both the proximal and distal segments; the intermediate, medial segments usually exhibit a decline and then a rise in content in progressing outward from the scalp. Normal hair

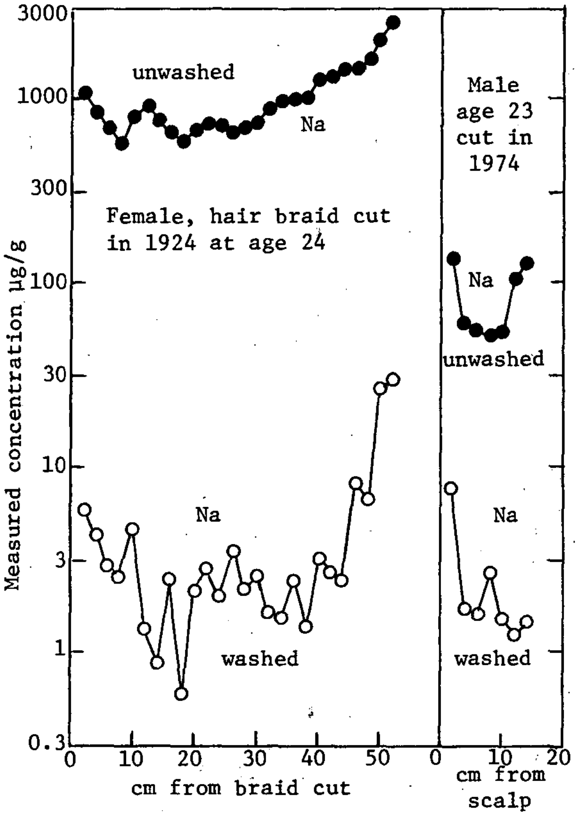

Fig. 2. Variation in Na content in 2 cm segment bundles of about 200 hair strands for historical hair sample and clippings from University of Michigan student.

washing and shampooing apparently extract some, but not all, of the Na and Cl and these medial segments probably represent sets of equilibrium states between sweat production and hair washing extraction. However, this equilibrium would be at least partially altered for the more distal segments which usually show a fair degree of mechanical damage in the form of cuticle loss, splitting of the hair strands, etc., thus allowing greater exposure of sweat (as well as exogeneous contaminants) to the internal structure of the hair.

Although external, air-borne contamination could produce a length-content variation in hair of the type seen in Fig. 1, it appears from the various data we have obtained that sweat (and sebaceous oils) probably plays an important, if not prominant role in this observed variation. As a result, during this last year we have asked present-day hair donors to provide us with their own estimate of their degree of scalp sweating as well as an assessment of the oiliness or dryness of their hair. To investigate further the effects of sweat on hair content, we are performing experiments whereby the proximal portions of hair bundles are immersed for a few hours in approximately 1 ml of scalp sweat from the hair donor. Analysis of 2 cm segments of washed and unwashed hair of both untreated and sweat-immersed hair samples from the same individuals should allow assessing the degree to which sweat and sebaceous oils contribute to the measured trace-element content of hair. In addition we are also performing direct analyses of the trace-element contents of sweat samples.

Although very few analyses for trace elements in sweat are reported in the literature, and these papers are mostly concerned with the "electrolyte" content (mainly Na$^+$ and Cl$^-$), it is safe to assume that sweat can serve as one, perhaps important, route whereby trace elements are given off by the body. However, we know of only two reports that provide direct information on sweat-hair content relationships for humans. In a study of the arsenic content of hair and nails in acute arsenical poisoning, the authors stress that arsenic appears in sweat soon after ingestion and that the sweat can carry the dissolved poison along the hair shafts where the arsenic can bind with the sulfur in hair (5). The other study reports that within a few days after administration of clinical doses of ^{131}I to patients with malfunctioning thyroids, detectable amounts of radioactive iodine were found adsorbed onto scalp hair and that a non-ionic detergent wash was incapable of removing more than 60-70% of this ^{131}I (6).

Historical Hair Samples

A majority of the more than 2000 documented historical hair samples we have collected over the past few years are clippings from females. Since male and female hair may show important differences in the levels of some elements, it is best to compare data on the basis of at least matched age and sex. Data for hair samples collected from 41 University of Michigan coeds served as an approximation of the present-day levels. As part of a preliminary study of historical hair, we preferentially selected for analysis 48 samples of hair from females aged 12-40.

Log-means (and standard deviations) were calculated for these data for 24 elements and are given in Table II. As noted before (2,3), many of the historical hair contents are higher than those of modern hair. However, it must be stressed that hair washing was less frequent 50-100 years ago than it is today. In addition, many of the historical hair samples analysed in this preliminary study are clippings of distal segments of hair, which usually have higher contents than other parts of the hair shafts.

Both effects could easily account for the Na, K, Cr, Fe, As, Br, Ag, Sb, I, La, Au, and Hg data. The higher Mg and Ca data in modern

Table II. Geometric mean[a] contents in μg/g[b] for 24 trace elements in female[c] scalp hair.

Date when cut	Na	Mg	Al	Cl	K	Ca	Sc	Ti	V	Cr	Fe	Co
U of M-1972 (N = 41)	16	298	20	238	9	2900	2.7	9.0	54	1.4	24	106
1910-1935 (N = 27)	84	112	22	110	87	303	8.9	3.1	16	3.9	67	54
1890-1910 (N = 11)	119	88	39	466	117	---	15.3	3.6	20	3.8	73	69
Before 1890 (N = 10)	145	73	18	334	127	---	10.5	4.3	14	2.4	196	125

Date when cut	Ni	Cu	Zn	As	Se	Br	Ag	Sb	I	La	Au	Hg
U of M-1972 (N = 41)	6.3	21	148	0.04	0.54	2.2	0.7	84	0.6	43	41	2.8
1910-1935 (N = 27)	4.0	11	216	1.2	0.62	2.9	0.7	507	1.4	380	120	1.6
1890-1910 (N = 11)	2.5	12	141	1.5	0.47	---	2.6	779	1.9	530	220	1.8
Before 1890 (N = 10)	3.1	13	109	2.5	0.62	14.8	5.4	476	1.3	580	120	3.5

[a] The geometric mean is the antilog of the log-mean. Typical standard deviations of the ln-means are ± 0.7-1.1.

[b] Except for Sc, V, Co, Sb, La, and Au which are in units of ng/g.

[c] Ages when hair was clipped: U of M, 18-22; others, 12-40 years old.

hair is probably a result of the precipitation of these elements onto hair during frequent hair washing. The higher Cl content of modern hair, at least in comparison with hair clipped between 1910 and 1935, is probably due to the U-M coeds swimming in chlorinated pools. In those other cases where modern hair has higher contents: Ti, V, Ni, and Cu, there probably havebeen actual increases in the human exposure to these elements. Even for those elements that show little difference between modern and historical hair, there probably have also been increases in exposure during the last 50-100 years since, as noted above, many of the historical hair samples are distal clippings which have aberrant, high contents. As a result, it may be that the Cr, Co, Zn, Se, and Hg exposures are also higher today and the same may also apply to many of the other elements. As more data are obtained on the significance of other variables that could affect the measured hair contents, and as further length-content variation data are obtained for additional samples and elements, it should be possible to suggest with more certainty the degree to which the human exposure to trace elements has actually increased in the last two centuries.

Acknowledgments

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ISOTOPE SHIFT ZEEMAN TECHNIQUE FOR DETECTION OF ATOMS AND MOLECULES*

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Abstract

About 4 years ago, researchers at the Lawrence Berkeley Laboratory were encouraged to go into environmental research. As a result, many methods, based on techniques previously developed, evolved that are proven to be of considerable value to environmental monitoring. Isotope shift Zeeman technique is only one of such developments at the Lawrence Berkeley Laboratory. This technique is basically an atomic absorption spectroscopy method. However, there is one basic difference which is unique to this invention. IZAA (Isotope shift Zeeman effect Atomic Absorption) technique is capable of detection of atomic elements directly from the host material without prior chemical treatment. A typical measurement time for most samples is 15 seconds and very seldom exceeds a minute. A brief explanation of the principle of IZAA and the operating characteristics will be presented.

The optical absorption cross section for the resonance absorption cross section for the resonance absorption by atoms is proportional to the square of the wavelength. Because of the long wavelength in the optical region, say from 2000 to 10 000 Å, the absorption cross section is on the order of 10^{-10} cm^2. Thus, it is evident that the atomic absorption technique is extremely sensitive compared with other techniques such as x-ray fluorescence and neutron activation. However, the conventional atomic absorption technique is extremely susceptible to the background interference. Many attempts were made in the past to overcome this difficulty. The standard background correction is made by means of dual light beams; one of them is usually a selected portion of the continuum from a deuterium light source and the other from a spectral line source such as a hollow cathode. However, the very fact that two independent light sources were used implies that it is not possible to have the same intensity for extended periods of time. Thus, when high sensitivity is required, it is not possible to accurately balance the light intensity from the two sources (whether the intensity is to be balanced before the optical detector or after the detector by electrical means). The problem gets even more serious when a mechanical chopper is used to alternately allow one or the other beam into the photodetector since it is very difficult to keep the shape and direction of the two beams the same. In the case of IZAA, two groups of wavelengths, one to monitor the atomic vapor and the other to monitor the background, are generated from the same light source and truly a single light beam containing two groups of wavelengths is used. Thus, this technique offers just about the best possible condition for the background correction. Figure 1 illustrates the operating principle of Zeeman effect atomic absorption spectroscopy technique.[1] Figure 2 shows the relationship between the absorption profile of naturally occurring mercury in one atmosphere of nitrogen (STP) and Zeeman triplets of mercury isotope 204 at 2537 Å. The mercury spectral line is generated from the low pressure mercury electrodeless discharge in the magnetic field with almost no self-reversal. The π component is not shifted and is polarized parallel to the magnetic field while the σ components are shifted by the Zeeman effect by ± $g_J\beta H/\eta$ from the π component and both are polarized perpendicular to the magnetic field. Thus, the π component is used to monitor the density of atomic vapor while the two σ components are used to monitor the background due to scattering from particulates (smoke) and absorption by molecular absorption band. Because of the polarization property associated with these Zeeman components, the π and σ components can be selected by a linear polarizer. At $H = 15$ kG, the shift in the wavelength is 0.065 Å so that the background attenuation applies equally to all the Zeeman triplet. However, only the π component gets absorbed by mercury vapor. Thus, by means of automatic gain control set in such a way that the output of the photodetector for the sigma components is always constant, the accurate amount of mercury can be determined, since errors arising from scattering and molecular absorption can be accurately corrected.[2,3]

In the actual instrument, polarization selection, hence, the wavelength selection, was made periodically by means of a magnetically actuated variable-phase retardation plate based on the photoelastic effect.[3] Figure 3 shows the operating principle of the instrument with the electro-optical wavelength selection. The host material (sample) is vaporized thermally in the high temperature furnace in presence of oxygen. The instrumental development went through the usual evolutionary steps. Figure 4 shows the original mercury detector used for illustrating the principle of operation; it is currently used by the Environmental Protection Agency in Las Vegas (NERC), Nevada. Figure 5 shows the more recent engineering prototype unit for field use. We have used mercury detection as an example. This principle can be used for almost any element.

So far, we have described the ability of the IZAA technique to correct for background interference. This is not sufficient to measure the amount of trace element accurately. In order to measure trace elements accurately, detection must be independent of matrix effect. This means we must be able to detect the amount of the trace elements of interest, regardless of the nature of the host material. Thus, whether one is measuring from host materials which are solids, liquids, biological samples, or gaseous samples, the amount of trace elements detected must be independent of the type of host material. This is accomplished by the design of the absorption furnace. Figure 6 shows the basic configuration of the the furnace used. A detailed mathematical model describing the operation of the furnace was made. With the configuration of the furnace shown in Fig. 6, it is evident that as long as the additional flow rate due to the sample evaporation does not vary the flow rate of the carrier gas (usually oxygen), matrix effects do not exist. This condition is easily satisfied by flowing a sufficient amount of carrier gas. The matrix independence was tested by intercomparison of the measurements made by IZAA with other methods such as wet chemistry, neutron activation, and x-ray fluorescence. This is shown in Table I for mercury.

Figure 7 shows the lineality and the range of the instrument for Hg. Figure 8 shows the reproducibility for various type of samples. Figure 9 illustrates the capability of the instrument for detection of mercury in human hair, urine, soil, and fish meat. The IZAA instrument in the latest form is capable of detecting Hg, Pb, Cd, and As. The very same instrument should be capable of detecting Sn, Bi, Se. The main limitation for other elements is the temperature range of the present furnace, which goes up to only 1700°C. However, with development of a higher temperature furnace, most elements should be detectable. Also, a graphite rod atomizer which is commercially available can be used until a more satisfactory furnace is developed in the near future.

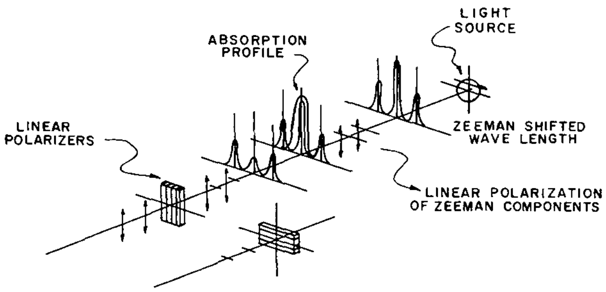
We shall briefly describe the use of the IZAA technique for detection of molecules. Because of the complex absorption spectra of molecules in the ultraviolet region, most molecular detections are made in the infrared region. However, the photodetection problem in the infrared region is extremely severe because of low quantum efficiency and the thermal noise. It is evident that if we could find a way to detect molecules in the ultraviolet region, the detection problem could be greatly simplified. In order to detect molecules in the ultraviolet region by using the IZAA technique, we have treated the vibration band associated with the optical transition in the same way as the absorption line of atoms. In order to achieve a similar background correction scheme used in atomic detection by IZAA, we used the self-reversal effect of the light source at the resonance lines. Consider, e.g. the 2980 Å resonance line of Cd in a magnetic field. Similar to the mercury resonance line, we again have the Zeeman triplet for the even isotopes of Cd. If we let such a line pass through a Cd absorption cell in zero magnetic field, the unshifted π component is completely absorbed while all the σ component pass through, provided the magnetic field in the light source is sufficiently high. On the other hand, all of the non-resonant lines pass through the Cd vapor cell. It so happens that the 2980 Å line of Cd coincides almost exactly with one of the optical vibration band heads of SO_2 and the nonresonant 3080 line lies between absorption bands of SO_2. Thus, by switching σ components of Cd at 2980 Å on and off by an electro-optical switch and using the 3080 line as a reference monitor, we have exactly the same condition as atomic detection using the IZAA technique. There are many similar coincidences with other resonance lines of Cd as well as other resonance lines of Pb and As. By this technique and by the use of a folded mirror configuration to achieve a path length of about 10 meters, about 10 ppb of SO_2 can be detected. Also, this technique is not limited to SO_2 but other molecules can be detected in a similar way. At present, we are concentrating our efforts on the detection of SO_2, CO, CO_2 and the identification of sulfates and nitrates.

We believe that our research, which led to the development of IZAA, has demonstrated that this technique could be quite universally used for the detection of many elements directly from the host material without the usual requirement of chemical pretreatment. We also believe that we have just touched the surface of the capability of this type of technique. As time progresses, it is possible that many exciting developments for the detection and identification of molecules will result from this work.

TABLE I. Comparison of isotope-shifted Zeeman-effect technique to other conventional methods.

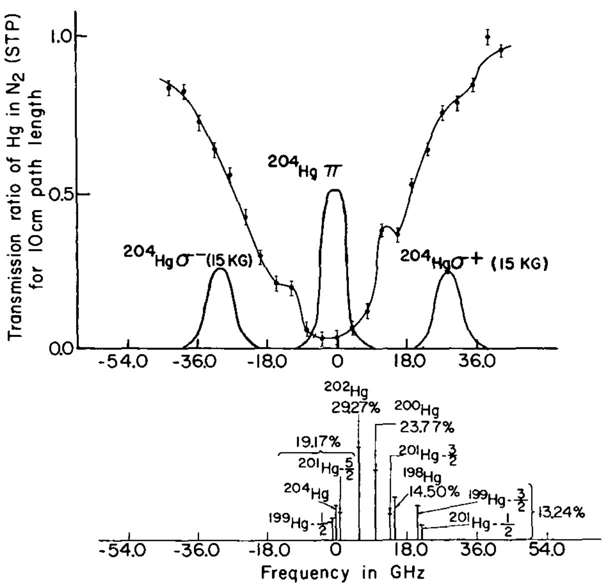
Sample source and identification	Lab where tested	Method used	Their results (ppm)	Our results in ~ 10 sec (ppm)
National Bureau of Standards Reference No. 1571 (orchard leaves)	NBS	Spark source mass spectrometer, neutron activation, chemical analysis with atomic absorption	0.155 ± 0.015	0.149[a] 0.141[a]
National Marine Fisheries Service Seattle, Washington Sample No. 614-1200 (fish protein concentrate)	NMFS	Wet chemistry	0.72	0.72 ± 0.05
Sample No. 628-0400 (fish protein concentrate)	NMFS	Wet chemistry	0.59	0.53 ± 0.01
Sample No. S-433 (wet cod)	Phoenix Member	Neutron activation	0.49	
	Gulf Atomic	Neutron activation	0.48	0.14 ± 0.02
	NMFS	FDA method (wet chemistry)	0.48, 0.45, 0.58	
Sample No. S-430 (wet halibut)	Phoenix Member	Neutron activation	0.12	
	Gulf Atomic	Neutron activation	0.13	
	NMFS	FDA method (wet chemistry)	0.10, 0.14, 0.09	
National Canners Association Aceton powder tuna (white meat)	NCA	Wet chemistry	2.48	2.08 ± 0.02
University of California at Davis UCD control mare liver	LBL	x-ray fluorescence	12.0 ± 2.0	10.0 ± 0.3
	LBL	Neutron activation	11.0, 14.0	

[a] V. Andarline, private communication. The 0.149 result was obtained with freeze-dried sample.



XBL 748-1306

Fig. 1



XBL 731-105

Fig. 2

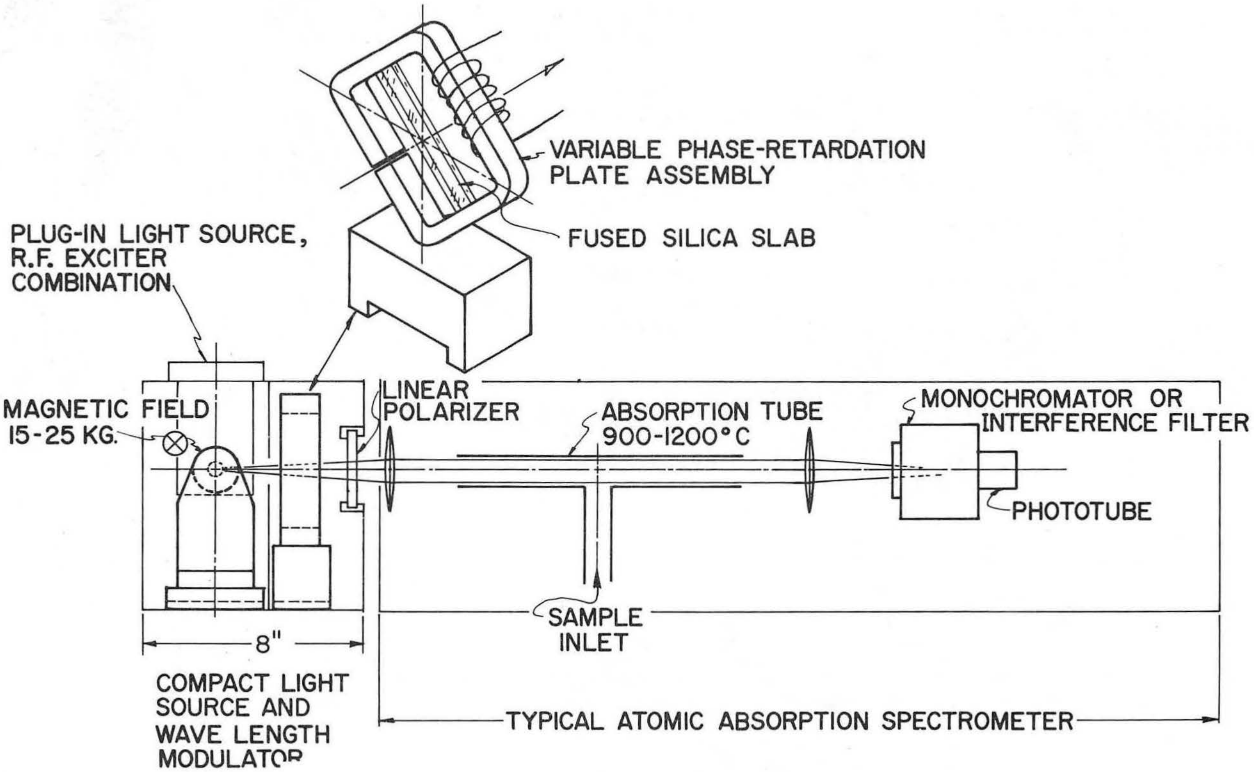


Fig. 3

XBL 731-104

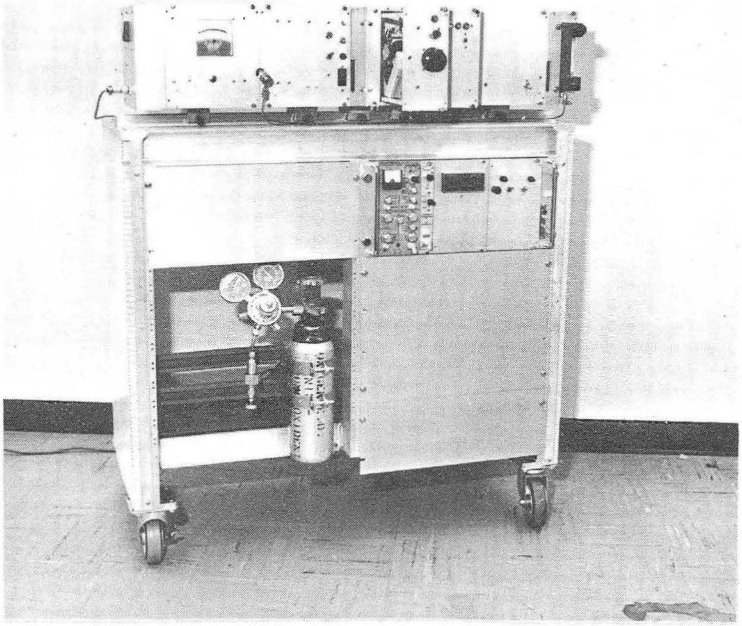


Fig. 4

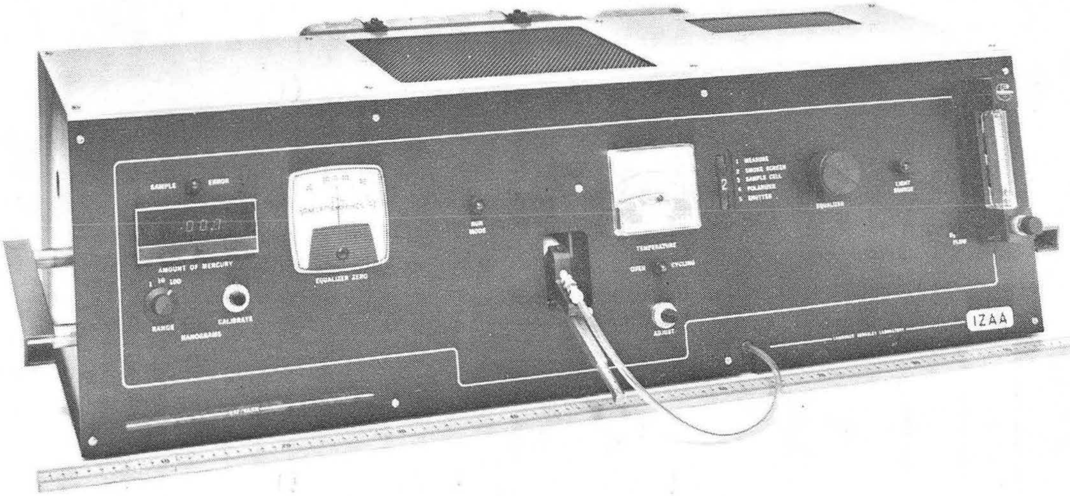
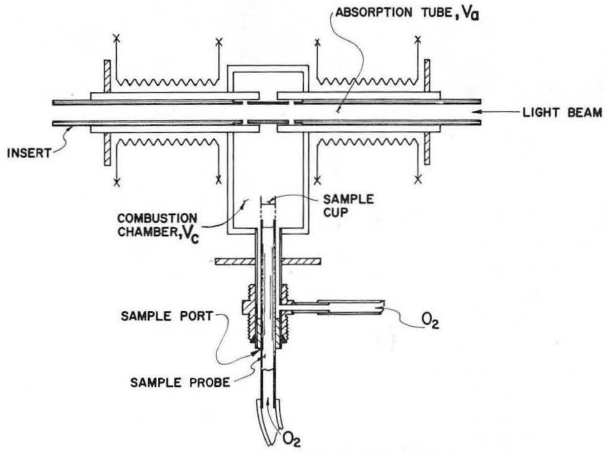
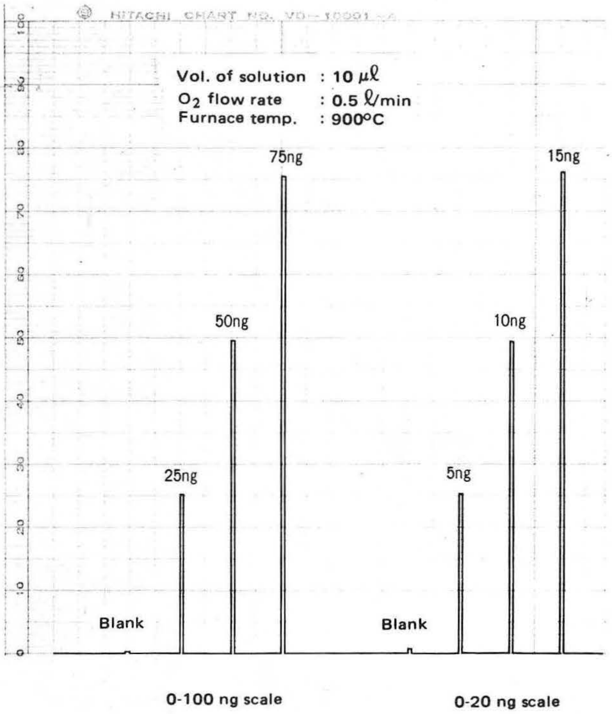


Fig. 5



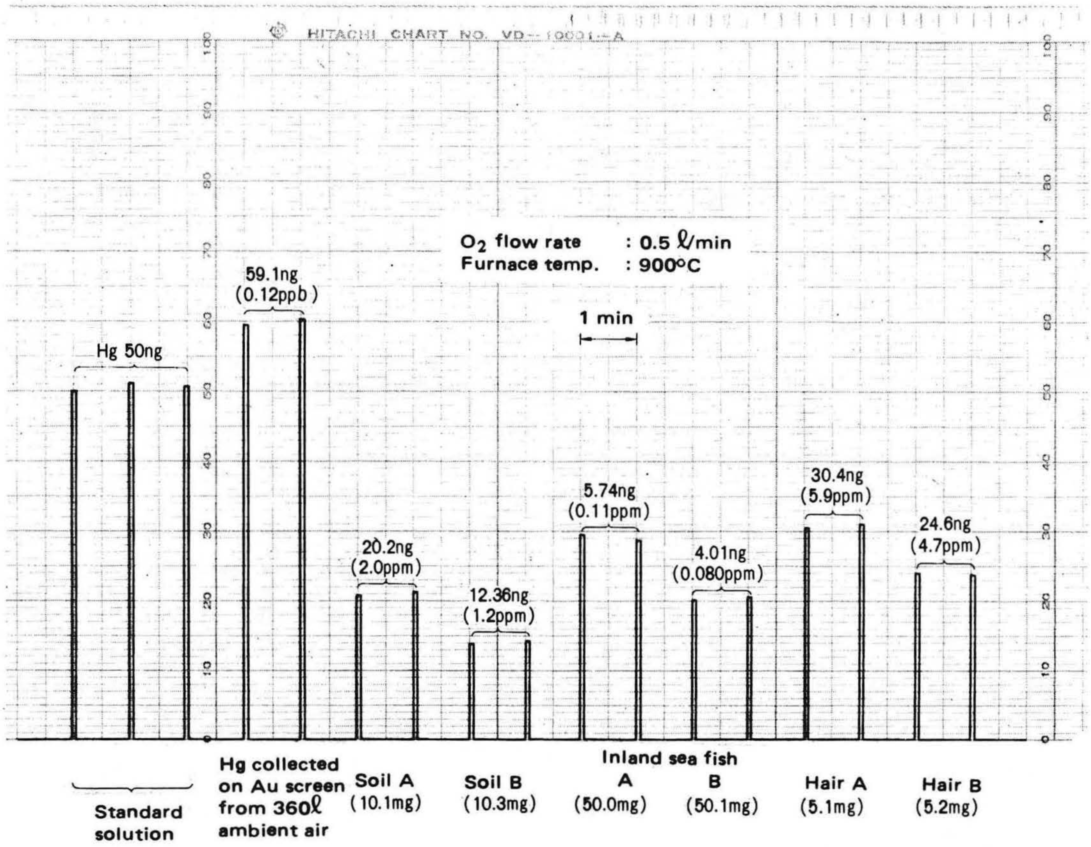
XBL 736-858

Fig. 6



XBL 748-1304

Fig. 7



XBL 748-1305

Fig. 8

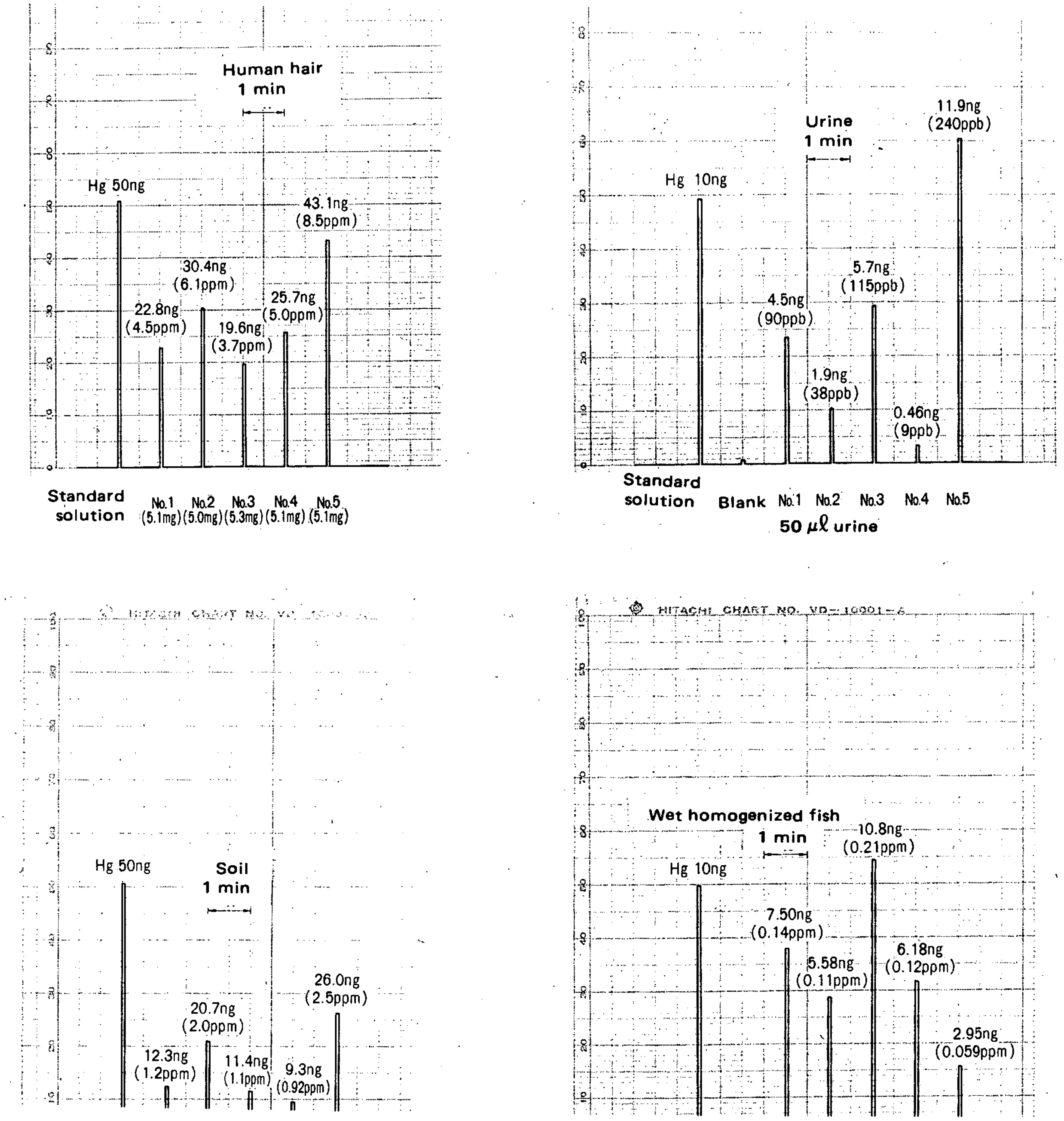

Human hair
1 min
Hg 50ng
22.8ng (4.5ppm)
30.4ng (6.1ppm)
19.6ng (3.7ppm)
25.7ng (5.0ppm)
43.1ng (8.5ppm)
Standard solution
No.1 (5.1mg)
No.2 (5.0mg)
No.3 (5.3mg)
No.4 (5.1mg)
No.5 (5.1mg)
Urine
1 min
Hg 10ng
4.5ng (90ppb)
1.9ng (38ppb)
5.7ng (115ppb)
0.46ng (9ppb)
11.9ng (240ppb)
Standard solution
Blank
No.1
No.2
No.3
No.4
No.5
50 μℓ urine
Hg 50ng
Soil
1 min
12.3ng (1.2ppm)
20.7ng (2.0ppm)
11.4ng (1.1ppm)
9.3ng (0.92ppm)
26.0ng (2.5ppm)
HITACHI CHART NO. VD-10001-6
Wet homogenized fish
1 min
Hg 10ng
7.50ng (0.14ppm)
5.58ng (0.11ppm)
10.8ng (0.21ppm)
6.18ng (0.12ppm)
2.95ng (0.059ppm)

Fig. 9

A STATISTICAL ANALYSIS AND COMPUTER DISPLAY OF THE DISTRIBUTION OF MOLYBDENUM BETWEEN ALPINE SOILS AND PLANTS*

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ABSTRACT

Mining and milling of molybdenum takes place on a large scale in the mountains of central Colorado. It is difficult to assess the impact of these activities on the ecosystem. One especially difficult problem is that of establishing natural background levels in a region after mining and milling have begun. As one appraoch to this problem, we have studied a mineralized, undisturbed molybdenum deposit in the alpine environment of south-central Colorado.

We have investigated the transfer of molybdenum from the soils above an undisturbed deposit of molybdenum to the plants which grow on those soils. Samples of soils and plants were collected at the intersection of 100-foot grid intervals. A total of 1080 data points were accumulated, each representing the content of molybdenum in a particular type of plant, together with either the total or extractable molybdenum from one of two depths in the soil.

Statistical correlations were made for content of molybdenum in each type of plant against total and extractable molybdenum from each of the two depths in the soil. Graphical displays of the data points and regression lines were produced. Few significant correlations were discovered between content of molybdenum in various types of plants and molybdenum in the soil. Water-extractable molybdenum was much lower than total molybdenum.

Hand-drawn and computer-produced contour maps of total and extractable molybdenum concentrations in soil are presented for comparison.

BACKGROUND AND PURPOSES

Mining and milling of Mo presently takes place at two sites in central Colorado. It is difficult to assess the impact of these activities on the ecosystem because of the lack of adequate information on natural background levels in the regions prior to the beginning of mining and milling operations. As one approach to this problem, we have determined background concentrations of Mo in an undisturbed area of Mo mineralization on Mt. Aetna in south-central Colorado (Figure 1). This site lies about 20 miles west of Salida, Colorado at an elevation of 12,500 feet (Figure 1). It may be possible to use the background levels observed on Mt. Aetna as a basis of comparison for the other mountainous areas in Colorado which have already experienced mining and milling operation. Samples from the site on Mt. Aetna show high concentrations of Mo in undisturbed soils which overly the deposit.

We have also studied a number of plants which grow on the soils overlying the Mt. Aetna deposit in order to learn something about the transfer of Mo from bedrock through the soil and into the plants growing on the soil. The soils in this alpine region are acid in nature (pH 4.5 - 5.5) and the amount of Mo available to the plants is less than would be expected in more alkaline soils.[1]

METHODS

A sampling grid with an interval of 50 feet between grid lines was laid out over the exposed Mo mineralization in the alpine zone on Mt. Aetna. Samples of soils and plants were collected at the intersections of every other gridline, in other words, at 100-foot intervals. Eight different genera or families of plants were collected in adequate numbers for analysis. These plants were identified, dried at 70°C overnight, weighed, and then ashed at 450°C and analyzed by x-ray fluorescence methods. Splits of about 20% of the samples were checked by digestion and colorimetric analysis. The concentrations of Mo in

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these plants are expressed as parts per million (ppm) at 70°C dry weight.

Soil samples were taken from two different depths at most sample sites. The upper two inches, arbitrarily called the A-horizon, tend to be richer in organic materials than the soil samples from two to six inches in depth, which we called the B-horizon. Soil samples were sieved to (-)80 mesh (fine sand), fused with pyrosulfate, and analyzed by a modified colorimetric thiocyanate procedure.[2] The (-)80 mesh size was used because this is a standard size fraction generally used in geochemical prospecting. One of the secondary purposes of this study was to determine if the soils could be utilized in prospecting for Mo deposits in this type of environment. The results for these soils are expressed as parts per million of Mo on an air-dry basis. Most of the soil samples were split and one of the splits was sieved to (-)1.6 mm size. This coarser size was chosen because it more nearly approximates the soil fraction of interest in agriculture. This coarser-fraction was then extracted with hot water for 24 hours, using a soxhlet reflux apparatus (this is a glass apparatus in which boiling water produces steam, the steam is condensed and drips through the soil, and the water is then reboiled, i.e. continuous refluxion). These soxhlet soil extracts were digested with hydrogen peroxide, acidified, and analyzed by the colorimetric thiocyanate method. This method of extraction was utilized because of published information[3,4] which suggests that the Mo extracted by hot water may correlate with the concentration of Mo in plant plants on the soil.

A total of 1080 samples was used in the study, out of a larger number of samples analyzed. Each data point used represented the content of Mo in a particular sample of plant together with the total or soxhlet-extracted Mo from one of two depths in the soil. A few points had to be discarded due to analytical or recording errors.

RESULTS

1. Hand-drawn contour maps of the Mo content in the soils were produced for four specific cases. These were:

   a) total Mo in the upper two inches (A-horizon);
   b) total Mo in two to six inch depth (B-horizon);
   c) soxhlet-extractable Mo in the A-horizon; and
   d) soxhlet-extractable Mo in the B-horizon.

The contour maps in all four cases clearly delineate the center of the mineralized deposit and are useful for prospecting purposes (see Figures 2-5). A peak value of 580 ppm of total Mo was found in one of the A-horizon soil samples directly over the deposit (Figure 2a). The background levels in the area ranged from 5 to 10 ppm, which is higher than the usual worldwide average of 0.6 to 3.5 ppm.[5] The same general features are evident in all four maps whether or not we look at total or soxhlet-extractable Mo, or at the A or B-horizons. There is little, if any, difference in Mo concentration between the two depths. The soxhlet extraction procedure removes only a few tenths of a percent of the total Mo (compare Figures 2A and 3A, for example). This suggests a relatively low availability of Mo to plants growing on these acidic, alpine soils.

2. Using the data files of the Information Storage and Retrieval System of the Molybdenum Project, the computer was used to generate contour maps for comparison with the hand-drawn maps. The hand-drawn maps include some points which were not entered on the computerized data system because of a lack of a corresponding plant sample. All of the computer-drawn maps are therefore based on somewhat fewer points than the hand-drawn maps.

The computer program smoothed the data and extrapolated estimates of the concentrations of Mo at intermediate points and in regions of the sampling grid for which there were no real samples. This was done by means of a weighted averaging procedure. The formula used for the predicted concentration of Mo at each grid point is shown as equation 1 below:

$$g_{ij} = \sum_{k,\ell} w_{ij}(k,\ell) f_{k\ell} / \sum_{k,\ell} w_{ij}(k,\ell). \quad (1)$$

where

g_{ij} = smoothed estimated of Mo concentration at grid point i-j

$f_{k\ell}$ = observed Mo concentration at grid point k-ℓ

$w_{ij}(k,\ell) = 0$ if $f_{k\ell} \leq 0$ (no data at k-ℓ)

$w_{ij}(k,\ell) = \exp\{-.5[(i-k)^2 + (j-\ell)^2]\}$ if $f_{k\ell} > 0$.

The computer-generated maps show very good results when compared with hand-drawn maps and in every case all of the major features can be identified from either the conventional maps or from the computer-drawn maps (compare A and B on Figures 2-5). The computer-drawn maps were generated on a microfilm display and then printed photographically to match the scale of the hand-drawn maps.

The weighted averaging procedure used to generate the computer-displayed maps has been used to estimate air pollution densities over broad areas served by only a few actual sampling stations.[6] The computer-generated maps, utilizing an existing data file, were generated much more rapidly and at less expense than the hand-drawn maps. Revisions of the maps, such as including or excluding suspicious data points or changing the values of the contours, were readily accomplished in short order with the computer system.

Another aspect of the work was to study the relationship between the content of Mo in plants and content of Mo in the soils on which the plants grow. Again, because of the many data points involved, it was convenient to do these analyses using the computerized data file. For each of the eight types of plants sampled, the concentration of Mo was compared with the total and soxhlet-extractable Mo in the soil samples from both the A- and B-horizons for each grid point where both soil and plant samples were available. At some grid points in the field, no plants were available, in which case the soil values were omitted from consideration. The data points were plotted and straight lines were fitted to each set of points by the method of least squares, using a library computer program.

The results of the procedures of regression line-fitting and the analysis of variance tests of each regression line are given in Tables II through V. The abbreviations used for the plants are given in Table I. The relationship between Mo concentration in TRF (clover) with total and soxhlet-extractable Mo in both the A and B soil horizons is fairly good (Table II and Figures 6-9). The relationships are better for total Mo than for soxhlet-extractable Mo. This set of relationships could be marginally useful for purposes of geobotanical prospecting. The Trifolium (clover), although a legume, does not accumulate Mo to any great extent. This is in contrast to the behavior of legumes on more alkaline soils.[7] The pH of these alpine soils in our study is 4.5 - 5.5 and Mo appears to be relatively unavailable to these plants. In alkaline soils the concentrations of Mo seen here could yield high concentrations of Mo in forage which might be toxic to ruminants. This low availability may explain the fact that Kienholz[8] found no unusual Mo levels in pica and marmots collected in this area. There is some relationship between the Mo concentrations of the GRM (grass) samples and soil Mo values, but the relationships are not as strong for this plant as they are for the clover samples (Table II). Grass would not be a particularly useful plant for use for geochemical prospecting on the basis of these data. The content of Mo for most of the grass samples is 1 ppm or less, a level which would probably be nontoxic to grazing ruminants using this alpine environment.

The strongest relationship between plant and soil Mo is shown for CIR (Cirsium or thistle) (Table II and Figures 10 and 11). This correlation is consistently high for both total Mo and soxhlet-extractable Mo and for both the A and B soil horizons. Concentrations as high as 45 ppm, which is easily measurable, were observed in the CIR samples. Only this plant among the eight types sampled offers a really good possibility for useful geobotanical prospecting in this alpine environment. However, this plant is relatively rare in this ecological zone and therefore would not be particularly useful in prospecting.

TABLE I. Abbreviations, families, genera and common names of plants studied.*

Abbreviation	Family	Genus	Common name
GRM	Gramineae	none identified	Grass
TRF	Leguminosae	Trifolium	Clover
CAS	Scrophulariacae	Castilleja	Paintbrush
CAR	Cyperaceae	Carex	Sedge
ACH	Compositae	Achillea	Yarrow
BIS	Polygonaceae	Bistorta	Bistort
CIR	Compositae	Cirsium	Thistle
PEN	Rosaceae	Pentaphylloides	Cinquefoil

* identified by Wm. A. Weber, University of Colorado, see W. A. Weber, Rocky Mountain Flora (Colo. Assoc. Univ. Press, Boulder, 1972).

The five other types of plants sampled demonstrate no consistently good relationship between Mo concentration in the plants and Mo concentration in the soils (Table III). Our data may represent the actual lack of a good relationship or possibly reflect the smaller sample sizes collected for most of these five plant types. The two highest concentrations of Mo found in any of our samples were in the genus ACH (Achillea or yarrow). This is a surprising result because yarrow is not a legume. This finding may indicate that this plant has a specific physiological use for Mo. However, because several other samples of yarrow have extremely low Mo concentrations, it is possible that these two extremely high values represent surface contamination of the plant samples, either in the field or in the laboratory.

As shown in Tables II and III, the correlations between Mo in plants and Mo in soils were not improved by choosing either the A- or B-horizons, or by looking at either total Mo vs soxhlet-extractable Mo. In other words, the extra effort required for the soxhlet-

TABLE II. Regressions of plant Mo on soil Mo for three types of plants.* See Table I for meaning of plant abbreviations. Data for TRF are displayed graphically in Figures 6-9.

Variable 1	on	Variable 2		df	Slope	Intercept	F-ratio	p-value	r
TRF		Total	A	85	.0589	.034	32.4	.0001	.52
			B	91	.0243	.425	42.1	.0001	.56
		Soxhlet	A	82	3.469	.706	11.3	.0015	.35
			B	75	5.508	.786	3.9	.048	.22
GRM		Total	A	111	.0554	.651	12.4	.0009	.32
			B	124	.0192	1.048	7.4	.008	.24
		Soxhlet	A	106	5.020	.992	8.8	.004	.28
			B	102	8.854	1.222	4.0	.045	.20
CIR		Total	A	9	.053	.566	14.3	.0045	.78
			B	23	.062	.010	15.0	.001	.63
		Soxhlet	A	10	3.409	.513	14.7	.0035	.77
			B	21	13.635	.336	31.9	.0001	.78

* Variable 1 - dependent variable;
Variable 2 - independent variable;
df - degrees of freedom;
Slope - slope of fitted line;
Intercept - intercept of fitted line.

F-ratio - F-ratio test of whether of not true slope is different from zero;
p-value - significance level for the F-test. P-value of 0.05 or less indicates a true non-zero slope.
r - correlation coefficient. Range is from (-)1 (for perfect inverse) to (+1)(for perfect direct) linear relationship.

extraction procedure did not yield improved correlations between plant and soil values. The additional effort and expense of the soxhlet procedure in future studies could not be justified on the basis of our results. A specific soil test for Mo such as the resin-extractable procedure of Bhella and Dawson[9] and Jackson and others[10] may be more useful.

In looking at the concentrations of Mo in soil alone (Table IV and Figures 12 and 13) the soxhlet-extractable Mo correlates quite well with the total Mo. We therefore do not believe it necessary to make both of these determinations.

We also compared the concentration of Mo in samples of clover (TRF) and grass (GRM) taken from the same grid point (Table V and Figure 14). The correlation was extremely good and the relationship between concentration of Mo in clover and grass samples from the same grid point could be useful for predictive purposes.

CONCLUSION

Our study of the release of Mo from bedrock into soils and plants in the alpine environment of Colorado shows that high concentrations of this metal may occur in soils in undisturbed natural environments. The low pH of the soil restricts its movement, however, into plants. Even legumes do not concentrate the metal in this environment. Computer techniques can be used to great advantage in producing contour maps and displays of statistical correlations among soils and plants. A fairly good correlation is found between the concentration of Mo in Trifolium (clover), Gramincae (grass), and Cirsium (thistle) and the concentration in the underlying soil. No apparent improvement in correlation is achieved by choosing either total or soxhlet-extractable Mo in either the shallow (zero to two inch) or intermediate (two to six inch) depths of soil. The added effort and expense necessary to obtain soxhlet-extractions are not repaid by improved correlations between plant and soil Mo. Geobotanical prospecting would not be as useful in this environment as analysis of the soils. The low availability of Mo to the plants from the acid soils probably provides a safeguard against Mo toxicity in grazing ruminants.

TABLE III. Regressions of plant Mo on soil Mo for five types of plants.
See Table I for meaning of plant abbreviations.
See Table II for explanation of table headings.

Variable 1	on	Variable 2	df	Slope	Intercept	F-ratio	p-value	r
CAS		Total A	9	-.0450	2.564	0.2	.63	-.16
		B	9	.0072	1.618	0.005	.94	.02
		Soxhlet A	10	21.011	-.712	4.1	.068	.54
		B	8	-20.444	2.643	0.62	.54	-.26
CAR		Total A	2	.0070	.711	0.2	.69	.31
		B	7	.0135	.503	0.5	.51	.27
		Soxhlet A	5	7.423	.015	8.1	.035	.79
		B	4	9.215	.657	1.6	.27	.54
ACH		Total A	6	-2.002	28.070	1.0	.35	-.39
		B	5	1.336	-9.920	0.1	.80	.12
		Soxhlet A	7	16.470	1.925	0.4	.56	.23
		B	4	-293.786	16.310	5.4	.08	-.76
BIS		Total A	18	.0250	.224	14.7	.0015	.67
		B	23	.0172	.262	4.9	.035	.42
		Soxhlet A	16	1.130	.374	3.4	.08	.42
		B	15	-.2222	.573	0.02	.90	-.03
PEN		Total A	2	.0189	-.015	4.5	.17	.83
		B	2	.0060	.159	.2	.71	.28
		Soxhlet A	2	-1.657	.641	1.0	.42	-.58
		B	1	-2.391	.515	44.1	.10	-.99

TABLE IV. Regressions of soxhlet Mo on total Mo for soils.
See Table II for explanation of table headings.

Variable 1	on	Variable 2	df	Slope	Intercept	F-ratio	p-value	r
Soxhlet A		Total A	70	.00567	.0459	21.5	.0001	.48
Soxhlet B		Total B	78	.00285	-.00202	58.2	.0001	.65

TABLE V. Regression of TRF Mo on GRM Mo for plants from the same grid square.
See Table II for explanation of table headings.

Variable 1	on	Variable 2	df	Slope	Intercept	F-ratio	p-value	r
TRF		GRM	136	.582	.413	45.2	.0001	.50

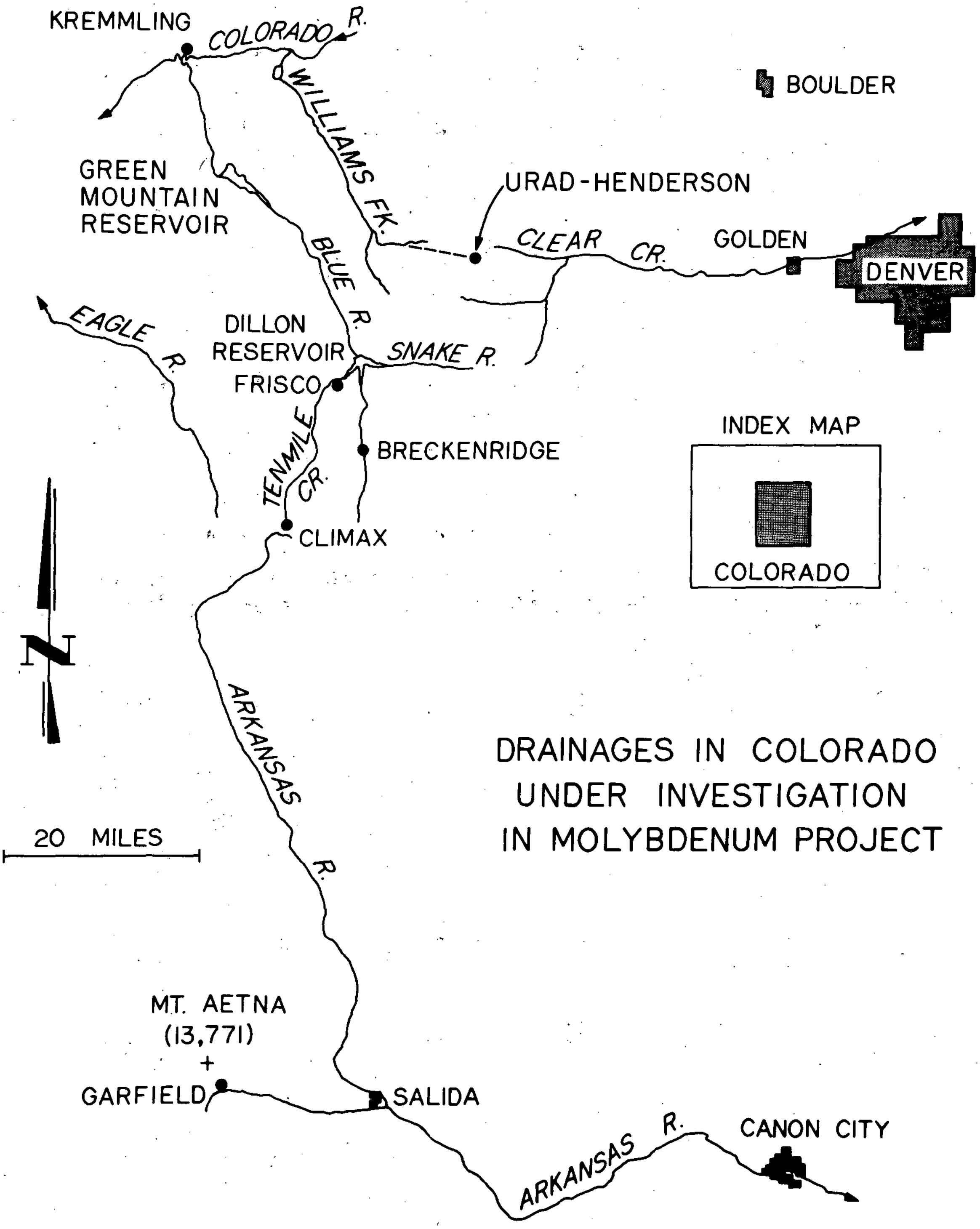
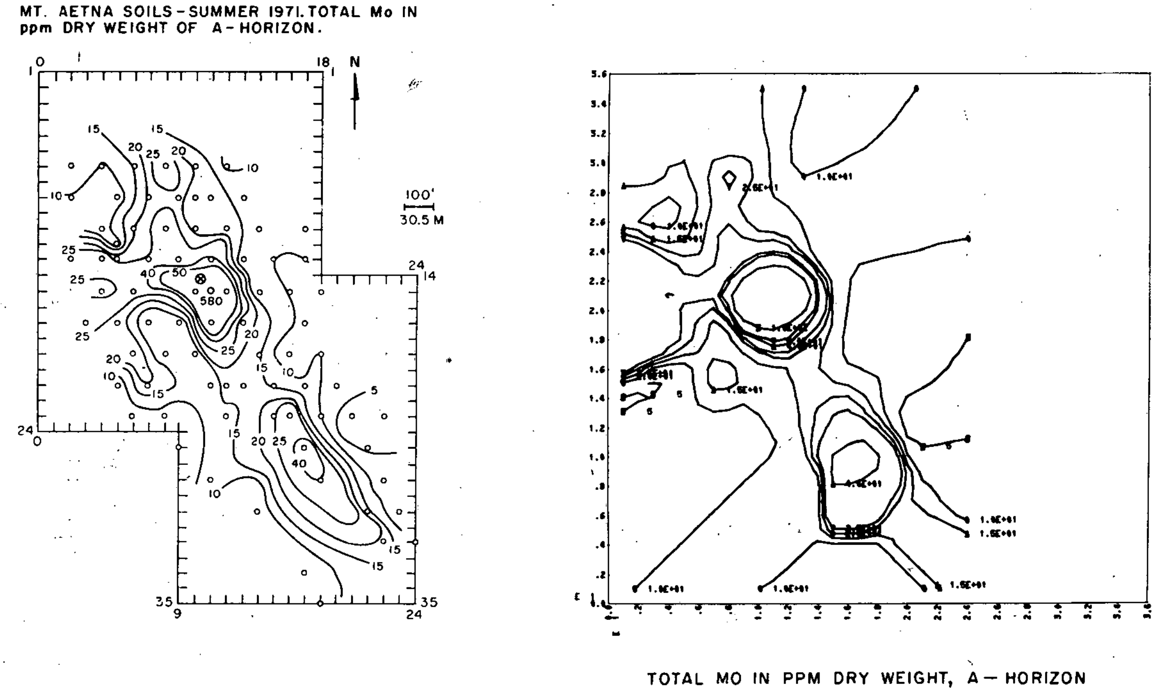


Figure 1. Drainages in Colorado under investigation.



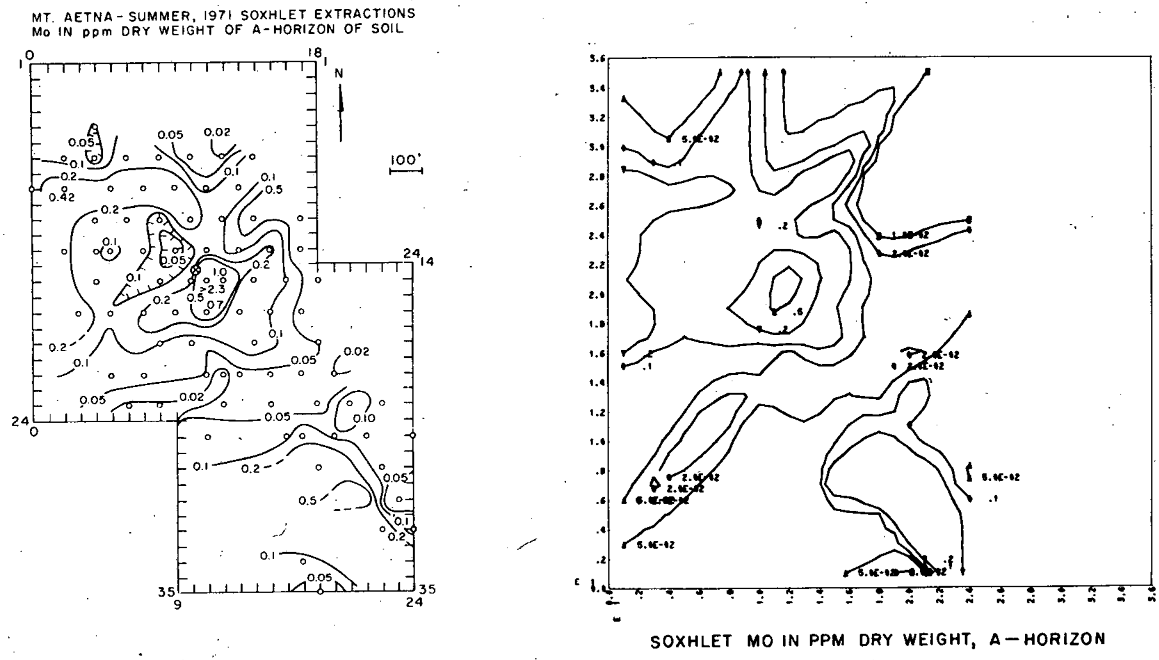
MT. AETNA SOILS-SUMMER 1971. TOTAL Mo IN ppm DRY WEIGHT OF A-HORIZON.

TOTAL MO IN PPM DRY WEIGHT, A — HORIZON

(A)

(B)

FIGURES 2A and 2B. HAND-DRAWN AND COMPUTER-DISPLAYED CONTOUR MAPS OF TOTAL MO IN 0-2" DEPTH OF SOIL ("A-HORIZON"). COMPUTER CONTOUR INTERVALS AT 10, 15, 20, 25, 40, 50 and 100 PPM.



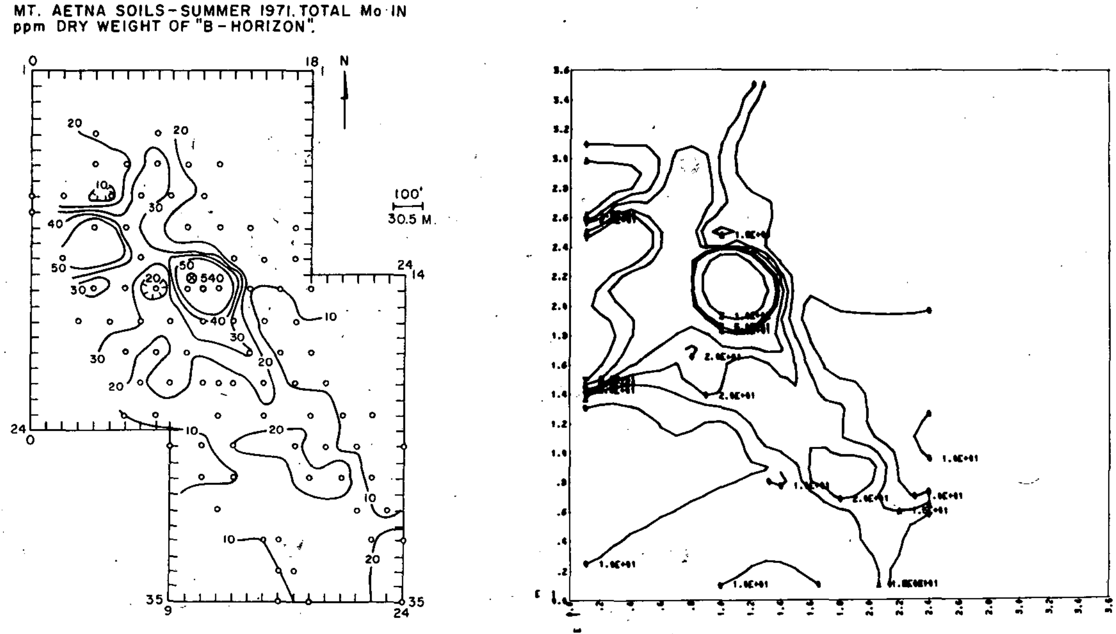
MT. AETNA - SUMMER, 1971 SOXHLET EXTRACTIONS Mo IN ppm DRY WEIGHT OF A-HORIZON OF SOIL

SOXHLET MO IN PPM DRY WEIGHT, A—HORIZON

(A)

(B)

FIGURES 3A and 3B. HAND-DRAWN AND COMPUTER-DISPLAYED CONTOUR MAPS OF SOXHLET-EXTRACTABLE MO IN 0-2" DEPTH OF SOIL ("A-HORIZON"). COMPUTER CONTOUR INTERVALS AT 0.02, 0.05, 0.1, 0.2 and 0.5 PPM.



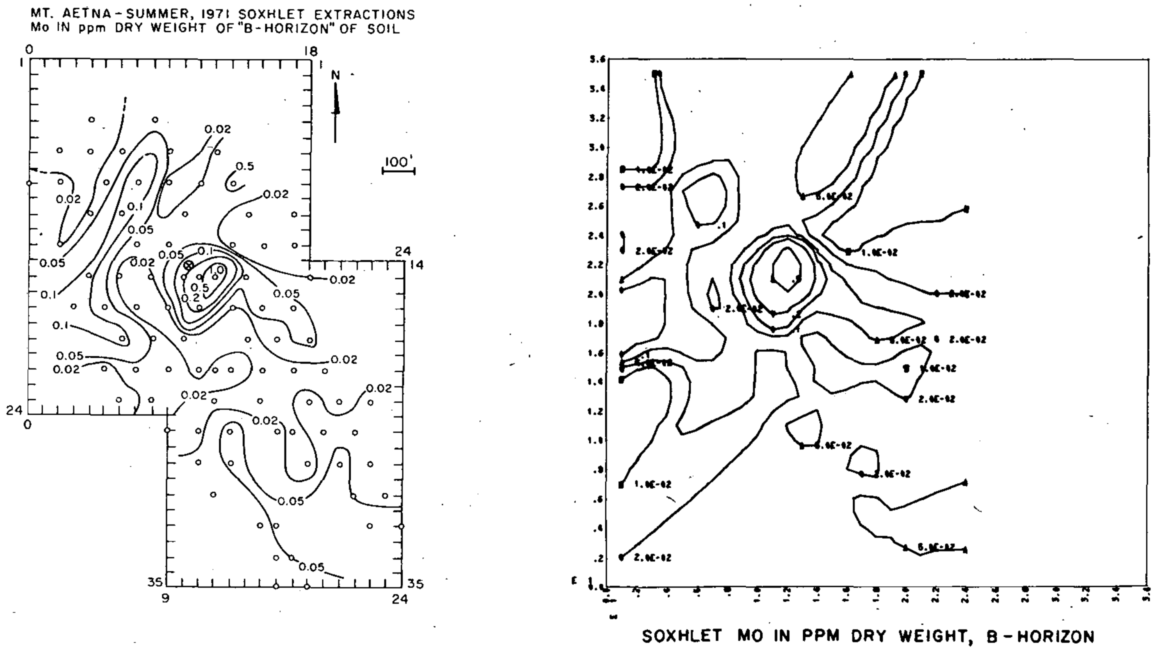
MT. AETNA SOILS-SUMMER 1971. TOTAL Mo IN ppm DRY WEIGHT OF "B-HORIZON".

TOTAL MO IN PPM DRY WEIGHT, B HORIZON

(A)

(B)

FIGURES 4A and 4B. HAND-DRAWN AND COMPUTER-DISPLAYED CONTOUR MAPS OF TOTAL MO IN 2"-6" DEPTH OF SOIL ("B-HORIZON"). COMPUTER CONTOUR INTERVALS AT 10, 15, 20, 25, 40, 50 and 100 PPM.



MT. AETNA-SUMMER, 1971 SOXHLET EXTRACTIONS Mo IN ppm DRY WEIGHT OF "B-HORIZON" OF SOIL

SOXHLET MO IN PPM DRY WEIGHT, B-HORIZON

(A)

(B)

FIGURES 5A AND 5B. HAND-DRAWN AND COMPUTER-DISPLAYED CONTOUR MAPS OF SOXHLET-EXTRACTABLE MO IN 2"-6" DEPTH OF SOIL ("B-HORIZON"). COMPUTER CONTOUR INTERVALS AT 0.01, 0.02, 0.05, 0.1, 0.2 and 0.5 PPM.

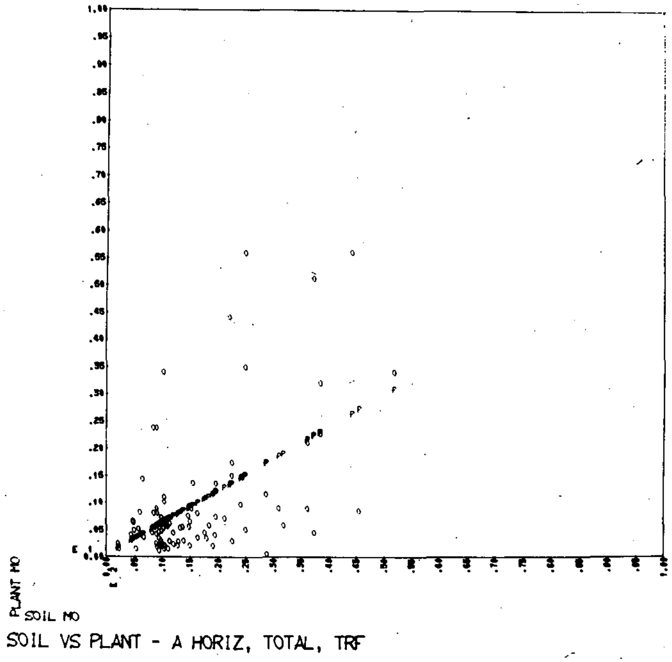


Figure 6. Linear regression plot of Mo in TRF versus total Mo in A-horizon of soil. Observed data points (O); predicted values (P).

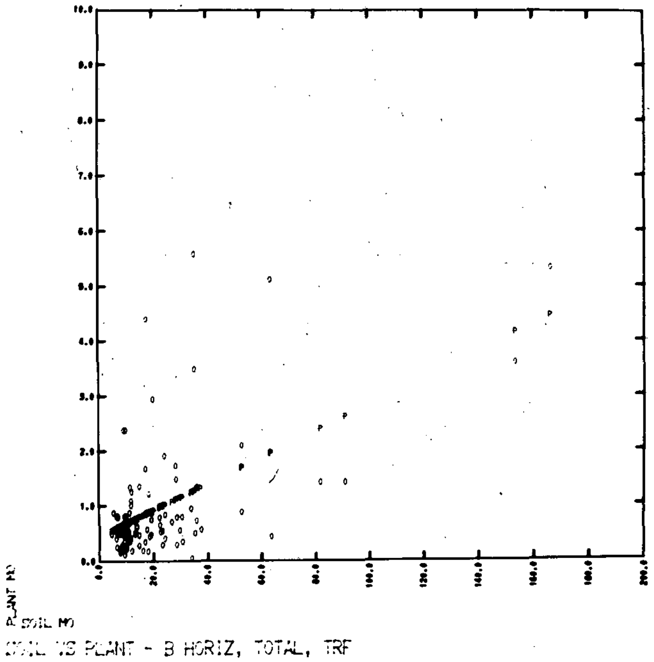


Figure 7. Linear regression plot of Mo in TRF versus total Mo in B-horizon of soil. Observed data points (O); predicted values (P).

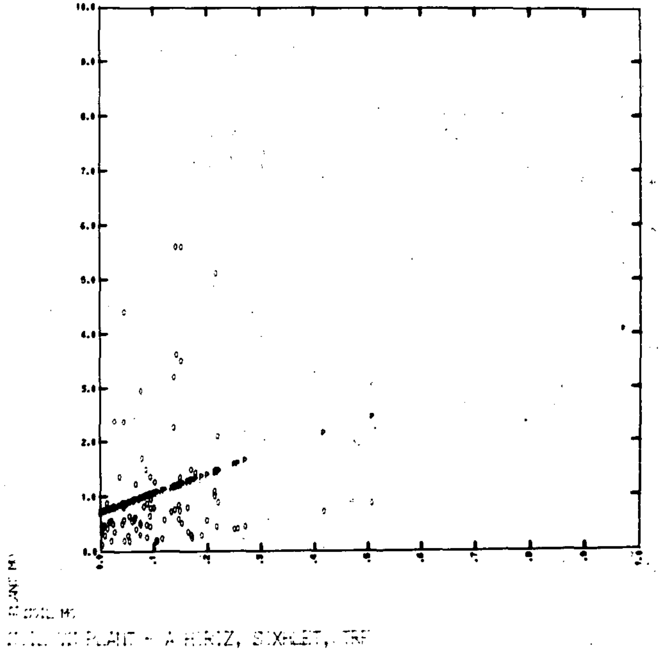


Figure 8. Linear regression plot of Mo in TRF versus soxhlet Mo in A-horizon of soil. Observed data points (O); predicted values (P).

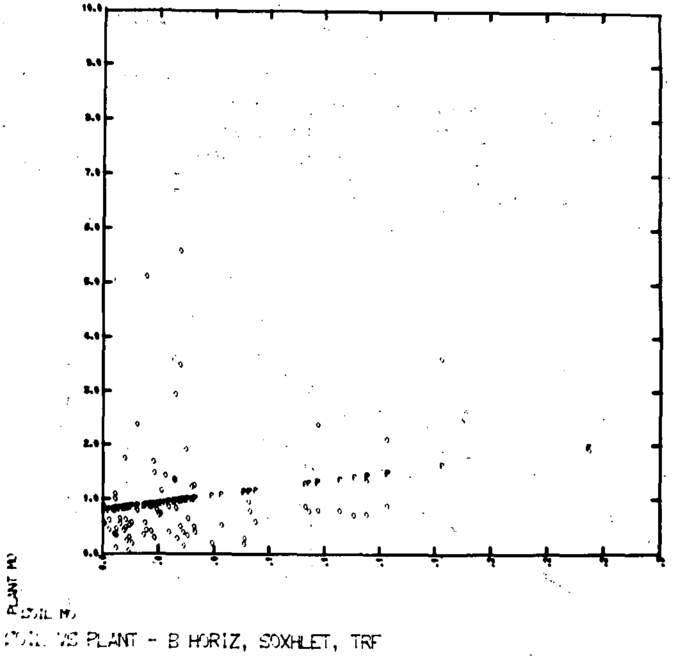


Figure 9. Linear regression plot of Mo in TRF versus soxhlet Mo in B-horizon of soil. Observed values (O); predicted values (P).

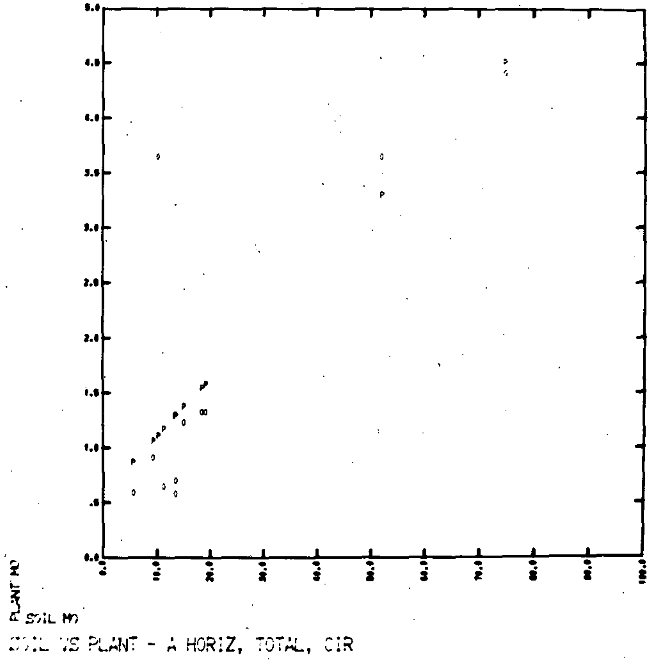


Figure 10. Linear regression plot of Mo in CIR versus total Mo in A-Horizon of soil. Observed values (0); predicted values (P).

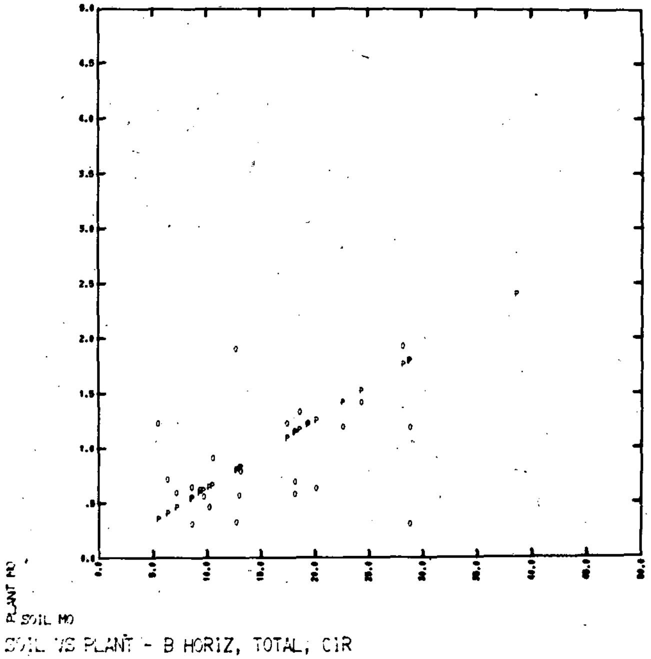


Figure 11. Linear regression plot of Mo in CIR versus total Mo in B-horizon of soil. Observed values (0); predicted values (P).

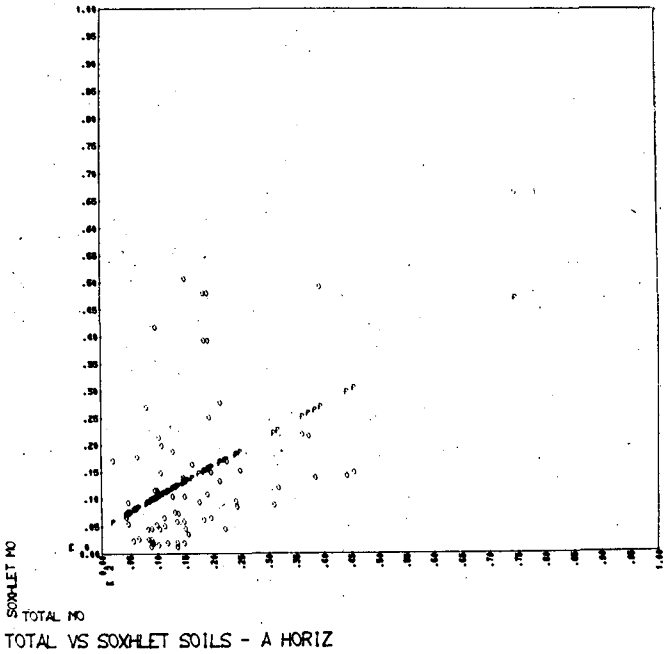


Figure 12. Linear regression plot of total Mo and soxhlet Mo in A-Horizon of soil. Observed values (O); predicted values (P).

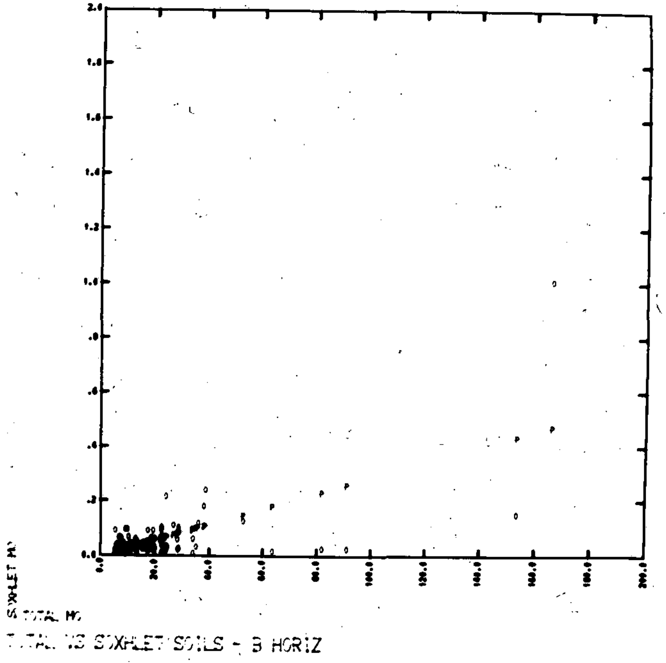


Figure 13. Linear regression plot of total Mo and soxhlet Mo in B-horizon of soil. Observed values (O); predicted values (P).

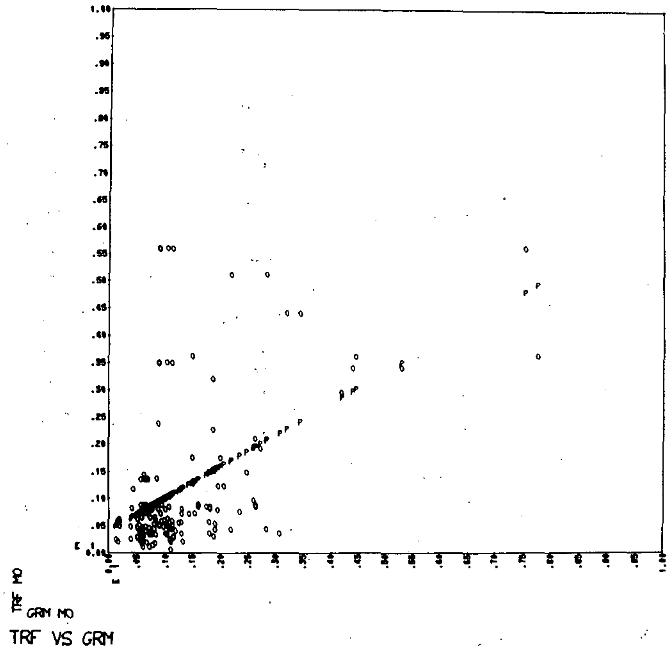


Figure 14. Linear regression plot of TRF Mo versus GRM Mo. Observed values (O); predicted values (P).

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TISSUE ACCUMULATION, MOLYBDENUM TRANSPORT, AND THE PHYSIOLOGICAL EFFECTS OF STRESS IN MOLYBDENUM-TREATED RATS*

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ABSTRACT

Dietary molybdenum at subclinical levels has been shown to reduce the efficiency of response to cold stress. The effects of short-term stress on oxygen consumption was then measured. Basal QO_2 ($m\ell\ O_2 \cdot cm^{-2} \cdot hr^{-1}$) was measured in an open-flow system by a para-magnetic O_2 analyzer. The QO_2 in rats given 10 parts per million molybdenum in food or water was higher by at least 5.0% than in rats given 0.5 parts per million ($p < 0.03$). Those given 100 parts per million molybdenum were higher by 18% ($p < 0.01$). The recording chamber was then dropped a distance of 1.5m and caught, three times; and the QO_2 then recorded at 15 second intervals for ten minutes. QO_2 dropped below basal for a short while in both experimentals (10 ppm Mo) and controls (0.5 ppm Mo) and then rose to a peak after which the rate declined. The initial lowering of the rate lasted less than one minute in the controls and for two minutes in experimentals. The actual peak was higher in the latter but the percentage increase was less than in controls. The rates for experimentals returned to baseline levels by nine minutes while control rates were still more than half the peak levels at that time.

Thus, QO_2 of the experimental rats, always at a higher rate, peaked later and proportionately less than control animals. They also returned to baseline levels much sooner showing a strong effect of a slight excess of molybdenum on both metabolism and on the stress response.

INTRODUCTION

Molybdenum has not been considered to produce clinical effects in humans and other non ruminant animals at levels anywhere near those that human individuals might take in chronically.[1,2] Our contention has been that stresses not unlike those to which humans might be subjected could elicit effects in laboratory rats at intake levels much below those required to produce clinical symptoms.[3] Earlier work has shown that Mo in the water at 10 ppm, less than an order above the usual intake, definitely affected the rats' ability to respond to severe cold stress.[4]

In the present, preliminary study we have measured metabolic rates because they are an indicator of the general stress response.[5] In addition, there is growing evidence that the Mo-containing enzyme, xanthine oxidase, is directly concerned with at least one aspect of electron transport[6] and that there may be interactions between Mo and Cu in the several enzymes of the respiratory chain that contain Cu.[7] Two aspects of our work will be reported here: the effect of small excesses of Mo on oxygen consumption in laboratory rats and the effects of short-term stress on QO_2 in the same animals.

MATERIALS AND METHODS

Adult, male, Sprague-Dawley rats of 450-550 gm were used for the experiments. They were of the first generation raised entirely on a pelletted diet containing the four possible combinations of Mo and Cu shown in Table I (0.5 ppm and 10 ppm of Mo and 1.5 and 10 ppm of Cu). The diet was adapted from Morris et al.[8] and prepared for us by General Biochemical Corp.[9] The low Cu was the minimum level obtainable with egg albumin and we felt that any lower would really make the rats sick with or without the added Mo. Growth of some representative animals on this diet is shown in Figure 1. It can be seen that this is quite high compared to similar animals on a standard laboratory diet, which average 231 ± 5.6 gm at 56 days, significantly less than the smallest group on the special diet.

Rats used in the following experiments were all mature, close to 500 gm, and within a few days of six months old. The differences in size were due to the diet and were unavoidable, and not considered to be important as the distinct differences among the four groups seen at eight weeks became blurred by six months. QO_2 ($m\ell\ O_2 \cdot cm^{-2} \cdot hr^{-1}$) was measured in an open system with the rat in an eight inch diameter chamber of "Plexiglass". Air was continuously drawn through the chamber at

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*Work supported by NSF (RANN) Grant GI-34814X.

TABLE I. Levels in diet.

Group	Mo	Cu	Mo	Cu
E	high	low	10	1.5
F	high	high	10	10
G	low	low	0.5	1.5
H	low	high	0.5	10

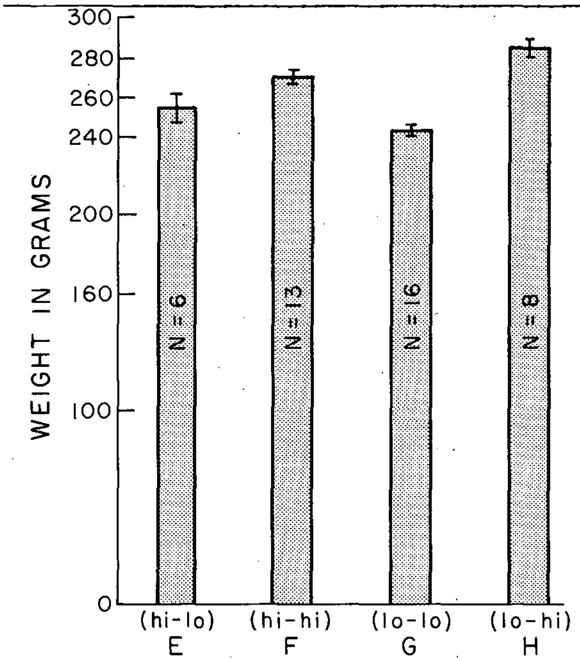

Figure 1. Weights of male rats at 56 days of age. These are the first generation totally on the defined diets. High designates 10 ppm for both Mo and Cu; low is 0.5 ppm Mo and 1.5 ppm Cu. Vertical lines indicate standard error of the mean. Comparing E-H, F-G, and G-H, $p<0.01$; while for E-F and F-H, $p<0.05$; and for E-G $p<0.10$.

1 ℓ/min. The stream was split and part was dried and led through a Beckman Paramagnetic O_2 analyzer. Rats were allowed to settle down for three hours without food in the experimental room before being placed in the chamber. In the latter they were provided with a small amount of their own bedding and left until they had gone to sleep. All tests were made between 1100 and 1300 hours and readings were taken after they were steady for four minutes. The chamber temperature was controlled at 26 ± 0.5°C. This was the only way to obtain consistent, repeatable basal levels and each rat showed a characteristic level that was quite repeatable. QO_2 was corrected to Standard Temperature and Pressure.

A short-term stress was applied to these animals in the chamber in which the QO_2 was measured. The chamber was hung on a rope and pulley system, hoisted up, dropped, and caught 1.5m below and with oxygen consumption monitored without interruption. This was done four times in one minute after which the QO_2 was recorded at 15 second intervals for the next ten minutes.

RESULTS

An unexpected result of the basal measurements was that the QO_2 of these rats was elevated by the higher levels of Mo (Table II). Rats getting 10 ppm Mo had significantly higher readings than those on 0.5 ppm. Thus, the E and F groups with high Mo were significantly different from the G and H groups with low Mo, with the exception of the two with low Cu (E and G) in which p was less than 0.07. In contrast, comparisons within the groups with either high (E-F) or low (G-H) Mo show no significant differences.

Rats on diets E and H (high-low and low-high) were given the "Drop Stress" and the QO_2 measured afterward. These two groups were chosen as providing the greatest contrast. Results presented in Figure 2 show that the QO_2 rose proportionately more above the awake level in H rats than in the E's. The QO_2 when the rat was awake before stress was used as the baseline because this was the level they would return to after recovery from the stress, not the basal (sleeping) level. The baseline for E's was higher than the H's but not significantly so.

It can be seen that the QO_2 drops in both groups right after the stress and that the E's (high-low) show a much greater and longer-lasting drop. The H's (low-high) not only did not drop as much below their baseline, but they took half as long to return to the baseline and begin increased oxygen consumption. Both groups peaked and then started back down, but those on high Mo rose proportionately less than the group on low Mo. They also returned to their baseline in less than ten minutes while those on low Mo sustained their increased metabolism for much longer, usually up to 20 minutes.

A typical record of single H and E rats is shown in Figure 3. Note that two start at different baselines and that the H rats rises higher and faster above its baseline than the E does. The E returns to its baseline well before the ten minutes were up while the H stayed up, in this case for 18 minutes. The E also continued its reduction in QO_2 and overshot, dropping well below the starting rate. These are typical responses for both groups except for an odd E rat, the QO_2 of which hardly went above the baseline. Our data have thus shown a definite effect of elevated Mo or reduced Cu on the pattern of QO changes after mild stress.

TABLE II. QO_2 (mℓ $O_2 \cdot cm^2 \cdot hr$) of male rats on four different combinations of Mo and Cu.

Mo	Cu	Diet	N	Weight (g)		Age (days)	QO_2		P	
High	Low	E	4	496	19.1	172	4.496	0.033	E - G:	<0.06
High	High	F	4	524	28.2	172	4.630	0.071	E - H:	<0.02
									E - F:	>0.10
Low	Low	G	4	511	8.5	169	4.010	0.231	F - G:	<0.02
									G - H:	>0.11
Low	High	H	4	493	26.5	168	4.230	0.064	F - H:	<0.01

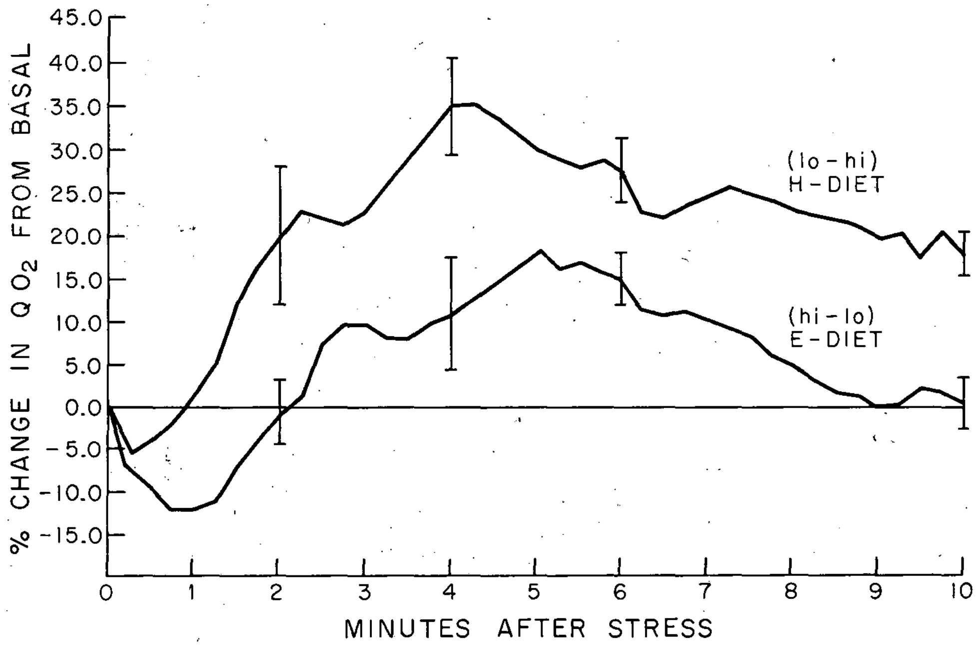

Figure 2. Percentage change in QO_2 from awake (inactive) levels on two regimes of Mo and Cu after "Drop Stress". Horizontal line is awake baseline for all animals. Vertical lines indicate Standard Error of the Mean. Readings taken at 15 second intervals.

DISCUSSION

The elevated basal QO_2 of rats on 10 ppm Mo is difficult to explain. It would seem logical that impairment of activity at the molecular level would reduce QO_2 rather than raise it. It is possible, however, that uncoupling of part of the electron transfer system in the mitochondria would necessitate increased oxygen consumption to provide normal amounts of ATP.[10] Another purely speculative possibility is that the Mo acts as a mild stressor itself and that the rats continually respond to this at a low level.

Even though Mo appears to be the major influence on these results, some influence of Mo on Cu-dependent reactions is probable.[1,6] It is worthy of note that the two groups of rats on low Cu were consistently lower than their counterparts receiving high Cu, though the differences were not statistically significant. If Mo were inhibiting a Cu-containing enzyme, the results might be expected to tend in this direction and not in the way of our significant results. Perhaps there are two reactions influenced by Mo and Cu.

The QO_2 would be expected to rise after a stress and, with this type of anticipatory response,[11] to then return to baseline levels. The rats on higher Mo did this for the most part, but they returned to the baseline much sooner than those on low Mo. This, coupled with the fact that the peak for the E's was not so high, relatively, as for the H's would suggest that their response to stress was not up to normal levels, that the higher Mo had

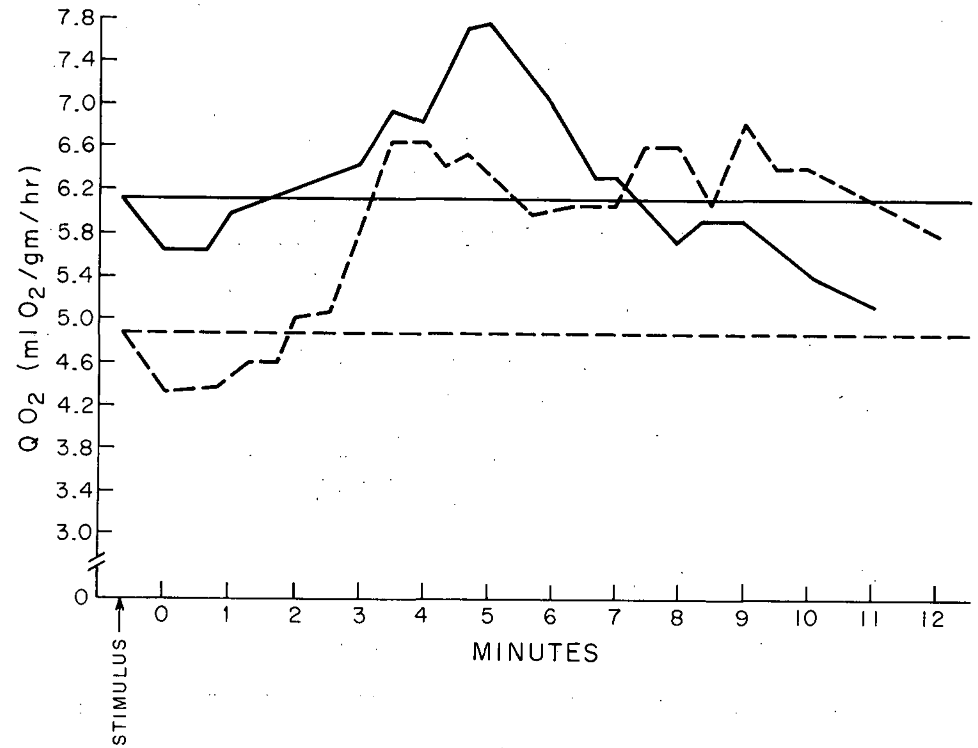

Figure 3. Curves of QO$_2$ after drop stress for two typical individual rats taken from the data of Figure 2. Horizontal line is the awake baseline just before stress was applied. Broken line for H rat, solid line for E rat.

impaired this response. Such results are in agreement with behavioral tests on the same animals in an "Open Field" arena,[12] which showed a lower "Anxiety Index" for the E rats.[13]

It is impossible to do more than speculate as to the reason for this impairment, but the effect on the anticipatory response would seem to implicate the catecholamines which are the principle agents of this response, as sympathetic outflow rises and epinephrine secretion increases. There is one Cu-containing enzyme (Dopamine-beta-hydroxylase) in the biosynthetic pathway for catecholamines[10] which might well be influenced by Mo. Rapid mobilization for "Flight or Fight" depends on the integrety of the sympathetic-adrenomedullary system[11] and it appears that this ability is reduced in these animals.

The elevated basal QO$_2$ does not in itself seem to be obviously serious for these animals if the first experiment is considered alone. It is only about 10% over those receiving 0.5 ppm, less than the rise with even mild activity. When this is considered with the impairment of the stress response however, in both short stress and long-term cold,[4] it is possible that elevation of oxygen consumption could be of real importance to the animal.

Elevated QO$_2$ of the same order as in these experiments have since been found in rats on 10 ppm Mo in drinking water and "Lab Chow" (1-3 ppm), compared to those on water and "Lab Chow" only.[13] Thus, a mature rat eating 15 g/day and drinking 15 mℓ of water per day would take in on the average either 30 or 180 μg/day, only a six-fold difference. In view of the way some food organisms concentrate Mo,[1] an intake like this may not be unusual for some individuals.

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MOLYBDENUM IN PLATELET METABOLISM

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ABSTRACT

When platelet-rich-plasma is incubated with U-C-14 adenine at 37°C under standard conditions, the ATP as a percentage of the platelet nucleotide pool decreased with time and a concomitant rise in the proportions of ADP and AMP occurred. The shift in nucleotide patterns of platelets from rats fed a normal purina chow diet compared to those given the purina chow diet plus equal concentrations of copper and molybdenum at the 10 parts per million level were indistinguisable from each other. In contrast to these results, rats who were fed supplements of 3 parts per million copper and 10 parts per million molybdenum showed a two to three fold greater decrease in ATP as well as the formation of appreciable amounts of IMP when compared to platelets from animals on the normal diet. These results will be discussed in relation to the roles of copper and molybdenum in cellular energy metaoblism and the importance of platelets in degenerative diseases.

MOLYBDENUM-COPPER STATUS OF FEEDS FOR BEEF AND DAIRY CATTLE IN COLORADO*

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ABSTRACT

Parts of the Denver milkshed lie in the drainage of streams that contain above average levels of molybdenum. Irrigation water at the farm was found to reflect these higher levels (up to 300 parts per billion). Milk samples were analyzed from tank trucks and from individual farms. No significant difference in molybdenum content of milk has been found between farms producing feed with irrigation water containing the higher molybdenum contents. Nearly all milk samples fall in the range of 25-75 parts per billion. Levels of molybdenum in feed were not closely related to levels in irrigation water, perhaps because of differences in soil types. Alfalfa hay ranged from two to five parts per million, corn silage from one to two parts per million (on a dry basis), and grain mixes contain 1.0 or less parts per million of molybdenum. The range for copper was 10-20 parts per million in hay and silage and five to eight parts per million in grain with no close relationship between levels of copper and molybdenum. The levels of molybdenum found in forage and milk were considered not to be a hazard to cattle. Cattle are sensitive to molybdenum by virtue of their ruminant type of digestion.

In some of the mountain valleys of Colorado, symptoms of frank or suspected molybdenum toxicity have been reported for the past 20 years. Elevated levels of molybdenum have been reported in forages from the Blue and Eagle River Valleys (up to 100 parts per million). Very low copper levels (less than five parts per million) have been found in forages from a few other mountain valleys of western Colorado, one of which has reported clinical sumptoms in cattle for many years. Molybdenum to copper ratios approach 1:0 in these regions.

INTRODUCTION

Ruminant animals, and particularly cattle, are much more susceptible to Mo toxicity than non ruminants. The reason is probably that the rumen bacteria under strong reducing conditions causes copper and molybdate ions to combine to form a cuprous molybdate which is absorbed but neither Mo nor Cu is available to animal tissues.[1] The result is a relative Cu deficiency. As a result Mo at concentrations as low as ten parts per million (ppm) can produce toxicity if Cu intake is low, whereas levels approaching 1000 ppm are necessary to produce toxic symptoms in rats, chickens, and pigs. The first symptom in cattle is a diarrhea which can become debilitating or even fatal. Reduced pigmentation of the hair and a stiff gait of the rear legs are other symptoms commonly seen.

The farming area around Brighton, Colorado includes a number of dairy farms producing milk for the Denver market. Most of these dairy farms produce alfalfa hay from fields irrigated with water from the South Platte River of Clear Creek which contain above average levels of Mo. Some farms are irrigated entirely by such water, some have water from two or more sources, and some dairy farms purchase all their hay from areas as far away as Wyoming and central Nebraska. Milk from these farms is collected every other day by large tank trucks. Milk is a good product for monitoring Mo because Mo is rather readily absorbed and excreted into milk as a function of the concentration in feed.

In the mountain valleys of Colorado clear symptoms or suspected cases of Mo toxicity have been reported for the past 20 years. Two areas are valleys below a large Mo mine. The other areas are not close to any mining activities. Finally, Mo has been reported as a constituent of fly ash from coal burning power plants and it seemed important to investigate forage that could be contaminated by this source of Mo.

METHODS

Irrigation water samples were taken on the farm during the time water was being applied to the land. Hay samples were collected with a forage sampler from stacks of baled alfalfa hay. Pastures are not used in this area for milking cows. Milk samples were collected from the farm tank following the last milking and after thorough mixing with the agitator on the tank. Silage samples were

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*Work supported by NSF (RANN) Grant GI-34814X.

collected from feeder wagons as the herd was fed. A representative sample of grain mixes was obtained from the farm storage system. Herd size varied from agout 50 to 300 milking cows.

Samples of forage from mountain meadows were obtained by cutting the entire vegetation enclosed by a ring which was randomly thrown to cover an area of the meadow. Unbaled hay was sampled by taking samples from hay stacks.

All forage samples were dried in a forced air oven and ground in a Wiley mill through a 100 mm screen. Analysis for Mo and Cu were made by x-ray fluorescence as described by Boyd, Rudolph, and Smythe.[2]

RESULTS

Feed-milk relationships. The irrigation water of the dairy farms studied contained 0-300 parts per billion (ppb) of Mo. Mo was not detectable in the water supply for cattle on any of these farms. The differences in concentration of Mo found in irrigation water was not reflected in hay samples. Hay samples as seen in Table I were low in Mo, averaging 3.5 ppm while corn silage and grain contained an average of only about one ppm of Mo. The ranges in concentration were relatively small. The absence of a relation between Mo in irrigation water and hay is probably due to the averaging effect of the large quantitites of hay involved; a small dairy of 50 cows consumes about 50 tons of hay per month. The average concentration of Cu in the feeds was above 10 ppm and rather variable particularly for the grain mixes which contained undetermined amounts of mineral supplement. The Cu:Mo ratio for hay was about 4:1 and at these low levels of Mo no toxicity would be expected. Furthermore, the other feeds fed to dairy cows have even higher Cu:Mo ratios as can be seen in Table I. Hay and other feed samples showed limited variability in milk samples as would be expected. The 140 samples represent both tank trucks and individual farm tanks, and in all cases the milk of many cows. In a study of four cows, milk obtained by hand milking contained 42.9, 35.4, 39.0, and 30.3 ppb compared to an average of 39.5 for a herd of 120 cows. The linear correlation between Mo in feed and in milk was -0.5 indicating no relation between the two for the sample in this study.

Mo and Cu in mountain valleys. The first published report implicating Mo toxicity in Colorado appeared in 1943 and was concerned with nutritional problems of cattle in the Kremmling area.[3] Mo toxicity was suspected in the Eagle River Valley but samples of forage collected in 1950 ranged from only 4.2 to 21 ppm of Mo and 1.8 to 7.5 ppm Cu.[4]

TABLE I. Mean concentration of Mo and Cu in milk and in feeds fed to dairy herds in the Denver milk shed. (Results in ppm)

Feed	Hay	Corn Silage	Grain Mix	Milk
# samples	35	13	19	140
Mo	3.54	1.26	1.19	44.6*
Std. Dev.	1.21	0.43	0.68	16.5*
Range	0.8-7.2	0.5-2.0	0.3-2.7	13-*134
Cu	13.5	13.5	10.3	
Std. Dev.	3.08	5.37	4.88	
Range	3.8-2.08	7.6-22.9	2.7-21.6	

*expressed in ppb.

In 1961 Dr. Robert Teagarden[5] diagnosed Mo toxicity on a ranch near Kremmling. Angus cows were grazing a meadow irrigated by the Blue River during the summer which had never been grazed before. It had not been the custom to pasture this meadow, traditionally it had been in hay production. These cows exhibited all the classic symptoms: lameness, diarrhea, and graying of the hair, and especilly ghosting about the eyes. The reduced pigmentation of the hair seemed much more apparent in the calves. This herd was removed from the meadow and soon recovered. It is perhaps important to note that these cattle had only been in the county and on these pastures for two or three months. Pasturing those meadows was no longer practiced on that ranch and no cases of Mo toxicity have been reported since in Middle Park.

A total of 20 hay samples collected from six ranches in the Blue River Valley in late August of 1961 were mostly low in Mo, one to six ppm with one sample at 44, one at 49, and one at 88 ppm.

A Cu deficiency in two flocks of lambs reared near La Jara was described in 1958 by Jensen.[6] Clinical signs and necropsy sections supported the diagnosis of enzootic ataxia.

Further north in the San Luis Valley, east of Saguache, is an area where problems have been reported in cattle for a long time. One ranch claims a history of lameness for the past 25 years. A total of 36 forage samples were obtained from this region in 1966, and the average analysis is included in Table II. Nearly all the samples were low in both Cu and Mo. A Cu deficiency seemed quite possible, for though Mo was not high enough to consider seriously, the Cu:Mo ratios are only 1:2.

TABLE II. Samples collected September 27, 1974 from Saguache area. (Results in ppm)

Sample No.	Cu	Mo
680	2.6	3.5
681	3.2	3.1
682	4.3	5.1
683	3.6	4.9
684	3.7	4.3
Mean	3.5	4.2
Mean 1966*	4.6	3.7

*Mean of 36 samples of forage collected in this area in 1966. Analytical method unknown.

In 1955 Angus cattle showing grey hair and lameness were reported in the Ridgeway area. Forage samples were collected and analyzed by Dr. Allaway of the U.S. Plant, Soil, and Nutrition Laboratory, Ithaca, New York.[7] Two samples averaged 4.4 ppm of Cu and 2.7 ppm of Mo.

Considering this background of reported cases it was decided to sample forage from these areas in the summer of 1973. In Table III are presented the Mo and Cu concentrations of forage samples from the Blue River Valley. The samples are arranged in order proceeding downstream. Two ranches show relatively high levels of Mo and higher levels in the spring. The forage from these meadows, however, is not grazed but is cut for hay and fed in the winter. One sample from the Eagle River Valley indicated no problem of excess Mo.

In Table IV are presented analysis of hay samples from the areas around Pagosa Springs and Ridgeway where Cu deficiency had been suspected. Samples were also collected from the La Jara area where Jensen[5] had diagnosed a Cu deficiency in sheep. It is apparent that Mo levels were all very low and Cu was probably adequate with rather high levels found in the Ridgeway samples.

Forage samples analysis from the Saguache area where Cu deficiency has been suspected are presented in Table II. The interesting fact about these data is the 1:1 ratio of Cu and Mo found in these samples which was almost exactly what was found in 1966. A relative Cu deficiency would be quite likely in animals consuming a sole diet of this forage.

Forage samples from areas nearer to Mo mines were also analyzed and data are presented in Table V. One sample obtained nearest the mine contained 24.3 ppm of Mo but otherwise the samples indicated low Mo and adequate Cu.

TABLE III. Forage sample analyses for Cu and Mo. (Results in ppm)

Ranches: Blue River	Date	Cu ppm	Mo ppm
EP	1972 hay	11.5	2.1
	1973 hay	3.8	2.0
BK	June 1972 hay	15.3	7.2
	June 1973 grass	19.2	10.3
	July 1973 grass	6.4	1.0
	Sept 1973 hay	2.7	8.8
GKL	June 1973 grass	20.1	42.8
	July 1973 grass	16.8	29.0
	Sept 1973 hay	4.6	31.6
GKL	1972 hay	13.5	20.2
	June 1973 grass	14.1	56.7
	June 1973 clover	18.0	100.2
	July 1973 grass	3.6	27.6
	Sept 1973 hay	3.4	41.8
Eagle River Valley	July 1973 hay	7.5	4.5

TABLE IV. Cu-Mo content of hay from areas of suspected toxicity. (Results in ppm)

Area	Cu	Mo
Pagosa Springs	5.2	0.4
	3.4	0.4
	5.4	1.9
	5.2	2.2
Ridgeway	12.8	3.2
	17.0	0.7
	15.8	1.0
	16.3	3.0
	12.4	1.5
La Jara	5.2	1.9
	6.2	0.6
	6.8	0.6

Coal from the Four Corners Power Plant was found to contain 1.5-2.0 ppm of Mo,[8] and some grazing and agricultural areas are found in the area of the plant. The samples presented in Table VI are arranged by distance down wind from the plant and indicate very low levels of Mo on the forage. An interesting observation is the very low Cu concentration in four of seven samples. Cu:Mo ratios of 1:1

were present in some forage and Cu deficiency might be expected in cattle and sheep in the area. No symptoms however, have been reported or have resulted from inquiries.

TABLE V. Forage Cu-Mo in areas near molybdenum mines. (Results in ppm)

Area	Cu	Mo
Upper Arkansas River Leadville Area	7.2	24.3
	3.2	0.4
	7.0	1.5
	3.6	1.7
Buena Vista	4.6	1.3
	3.7	2.8
South Park	7.5	1.9
	6.0	4.3

TABLE VI. Mo-Cu content of forages from area of Four Corners Power Plant. (Results in ppm)

Cu	Mo
8.5	2.9
4.0	0.6
3.1	1.9
1.7	0.6
11.6	1.4
2.6	0.4
1.6	1.2

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CADMIUM IN AN AQUATIC ECOSYSTEM: TRANSPORT AND DISTRIBUTION

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ABSTRACT

A unique opportunity for a study of cadmium and nickel in an aquatic system has occurred because of the contamination of a marsh and cove along the east side of the Hudson River in New York State. Discharges of these metals in waste waters from a nickel-cadmium battery plant have resulted in high concentrations of these metals in a large area of sediments in the cove.

The first studies of the system in 1971 showed that concentrations as high as 50,000 mg of cadmium/kg of dry sediment were found near the discharge point and that the contamination extended into the channels of an Audobon bird sanctuary in a marsh to the south of the cove. Subsequent dredging of the main deposit has increased the potential value of the data to be obtained.

Tidal flows resulting in depth changes of from 3-5 feet per tidal cycle have been shown to be a major factor in the redistribution of the contaminant metals in the sediment of the area. Both re-suspension of sediments and desorption-reabsorption are believed to be involved in the transport mechanism in the system. There is some evidence indicating a short term increase in sediment contamination in some parts of the cove following the first dredging operation. However, the overall evidence indicates that most of the sediments in the cove remain at approximately the same level of contamination as existed prior to the dredging.

INTRODUCTION

The location and geography of the Foundry Cove area are shown in Figure 1. The cove is about 50 miles north of the Battery in New York City along the east bank of the Hudson River, opposite the northern part of West Point. The battery manufacturer's plant, which is just north of the cove in the town of Cold Spring, has been in operation since 1953.

The process used in the manufacture of nickel-cadmium batteries requires the use of concentrated metal nitrate solutions and results in dilute waste solutions, and precipitates of the metals involved (5). Both cadmium and nickel are used in large quantities, and at one time a significant quantity of cobalt was used as an additive to the nickel.

No significant changes have been made in these process steps since 1953. Caustic solutions containing cadmium, nickel, and cobalt precipitates were customarily discharged (3), (5), through sewers to the local sewage system and the river, or directly to the cove. It is believed that occasional operator errors resulted in the discharge of concentrated solutions used in the process in addition to the slurries mentioned above.

The heavily contaminated outfall area near the discharge point and a portion of the channel leading to the cove were dredged in the summer and fall of 1972. Following additional evaluation of the contamination of the sediments by a consultant, a portion of the cove itself and the channel from the outfall area were dredged in the spring of 1973 to a contour line approximating the 900 mg Cd/kg sediment concentration profile.

The first steps in the present studies by New York University are aimed at the definition of the physical and chemical processes involved in the distribution and possible effects of the metallic contaminants in the ecosystem.

MATERIALS AND METHODS

Samples of water, bottom sediments (by an Emory spring loaded grab sampler), and plants were obtained on field sampling trips in 1971, 1972 and 1973. All samples were stored in plastic containers and both plants and water were stored frozen until prepared for analysis. Care was taken to obtain homogeneous subsamples of sediment prior to drying and wet ashing. All samples were wet ashed with nitric acid and brought to a final volume in 5% nitric acid.

Atomic absorption spectrophotometry (AAS) was used for metals analysis utilizing an Instrumentation Laboratories Model 453 dual-double beam AA spectrophotometer. Standards, samples containing standard additions, and procedural blanks were processed along with the samples with standards run every 15 to 20 samples during analysis.

RESULTS AND DISCUSSION

The 1972 data obtained for cadmium and nickel in water indicated that both dredging and tidal flows were involved in the transport of cadmium and possibly nickel, as expected (Table I). Dissolved cadmium concentrations on the ebb tide during dredging are 10 to 50 times higher than those observed before dredging for any tidal state. Maximum dissolved concentrations of a-out 50 μg/l were observed both near the dredge and in the cove waters near the end of the channel carrying the drainage from the dredged area to the cove.

TABLE I. Dissolved Cadmium and Nickel Concentrations, μg/l. (1972)

	Cove [(a)], ed	
Tidal Contition	Before Dredging	After Dredging
Ebb	<0.5	11.2-45.7
Low Slack	<0.1-0.65	1.0
Flood	0.1-1.0	2.4-4.2
High Slack	1.1 [(b)]	0.7-2.7
	Cove, Ni	
Ebb	<3-4.9	9.3-11.2
Low Slack	<3	<3
Flood	<3-9.5	<3-4.3
High Slack	<3	<3

(a) Samples taken near the end of the channel from the discharge area.
(b) Only one sample available.

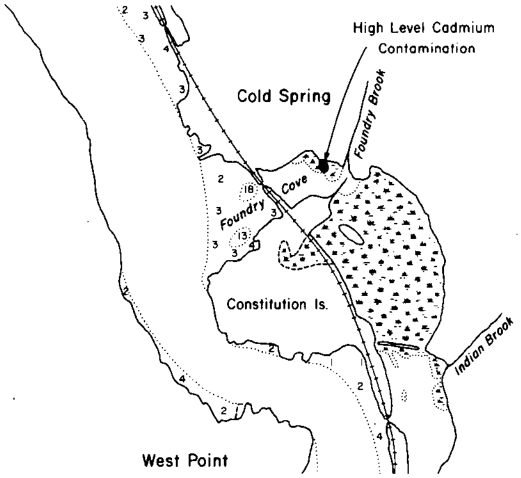

Figure 1. Location and geographical features of the Foundry Cove area.

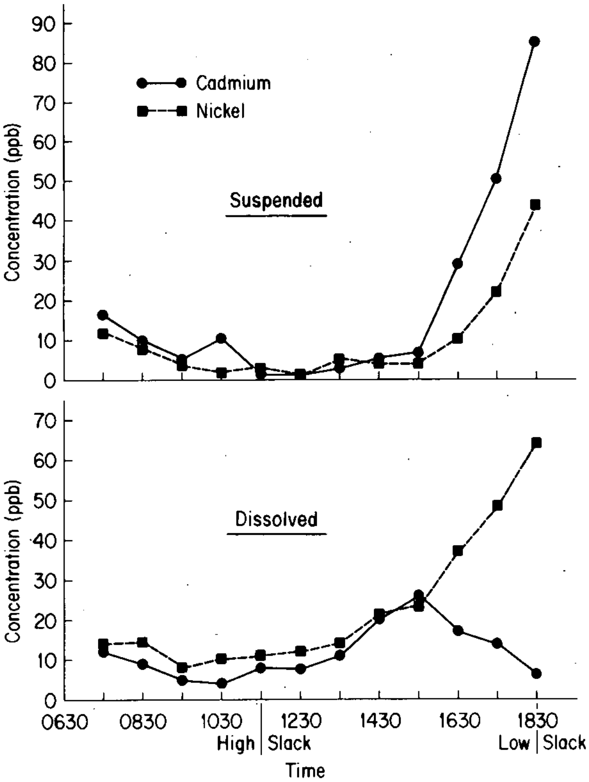

Figure 2. Cadmium and Nickel Concentrations vs. Tidal Condition.

The patterns observed in a tidal cycle sampling of 1973 confirm the effects of the tidal flow as seen in Figure 2. The water flow during the ebb tide obviously disturbs sediments of the contaminated regions resulting in increased concentrations of both cadmium and nickel in the cove waters at the end of the channel from the discharge area. The results from 1972 also showed this same pattern for cadmium and nickel.

Fourteen of a total of sixty-nine 1973 water samples contained over 10 μg/l dissolved cadmium, and all fourteen were taken within the dredged area. Only samples taken in or near the discharge area during dredging in 1972 gave values higher than these 1973 samples.

Cadmium concentrations in the bottom sediments of the discharge area and the channel to the cove were originally reported to exceed 2,500 mg/kg. The results from this study confirm the upper limit for this area in 1971 as shown in Table II. However, the post dredging values for November, 1972, and again in 1973 indicate higher metal concentrations. The values for samples taken toward the far side of the cove from the channel also indicate a possible increase in contamination over a relatively wide area. Data for mid-cove samples is similar although not given here. Calculations indicate that the 25 tons of cadmium originally estimated to be present in the cove (3) are still present but possibly more widespread.

TABLE II. Cadmium and Nickel in Bottom Sediments

	Cd, mg/kg dry basis	
	Channel Mouth	Western Cove
Pre-dredging	2,500-18,400	30-50
Post-Dredging I	<40,000(a)	--
Post-dredging II	3,000-50,000	40-970
	Ni, mg/kg dry basis	
Pre-dredging	800-8,500	7-100
Post-dredging I	30,000-40,000	--
Post-dredging II	2,000-11,000	60-540

(a) Confirmed in interlaboratory comparison (1).

The dredging was carried out by a roatry suction dredge pumping a slurry to an earthen dike holding pond. Water was carried from the holding pond, via an overflow pipe back to the discharge point in the cove. It would seem possible that this produced a recirculation rather than a removal of the metals. Suspended solids separated from water samples taken in 1972 near the dredge contained a maximum of 60,000 mg Cd/kg/dry sediment. This value is many times higher than any concentrations seen when the dredge was not operating. The findings of elevated and dissolved cadmium concentrations in the discharge area in 1973 may indicate a continued effect by drainage from the holding pond or a disequilibrium due to disturbance of the sediments.

CONCLUSIONS

The distribution patterns of both dissolved and insoluble metals in water with respect to time, tide, and dredging demonstrate that both dredging and tidal effects have been significant in transporting the metals. Sediment contamination is both extremely high and widespread. The dredging, perhaps because of the actual method used, does not appear to have had significant beneficial effects and may have accelerated the transport of the metals and spreading of the contaminated sediments.

Systematic examinations are continuing of the parameters affecting transport, chemical activity, bioavailability, and possible biological accumulation and effects in this system. The definition of these factors will permit more logical evaluation and correction of similar contaminated areas which may occur elsewhere.

ACKNOWLEDGEMENT

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CADMIUM IN AN AQUATIC ECOSYSTEM: EFFECTS ON PLANKTONIC ORGANISMS

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ABSTRACT

Cadmium, a toxic metal, has been shown to be an important contaminant at Foundry Cove, located near Cold Spring, New York on the Hudson River. Its distribution in water and sediments and effect on the microzooplankton in the area is being studied and evaluated. Microzooplankton may well be a critical link in the aquatic food web, involved in trophic levels utilizing nannoplankton such as bacteria, algae and protozoans, as food and in turn being consumed by larger organisms such as fish and their juveniles. The microzooplankton, may in turn reflect the number and possible composition of the nannoplankton populations since as grazers or croppers, they represent the next trophic level and have the advantage of being easily collected, observed and quantified. Preliminary toxicological studies are in progress on species found in the cove.

INTRODUCTION

This study was begun in 1971 to establish a systematic approach that could evaluate interactions between microzooplankton populations and the effects of metals discharged by Marathon Plant, predominantly cadmium. Until the completion of the 1973 sampling program there was virtually no information available to establish such relationships, particularly those pertaining to microzooplankton abundance and distribution, that also considered the season, tide and/or cadmium concentration.

The information representing available physical, chemical and biological parameters were selectively observed and quantified in 1973 between June and October. These observations indicate that clear cut effects of cadmium on the microzooplankton, including number and type could not be accurately determined. However, seasonal and tidal fluctuations were found.

The organisms selected for the toxicological studies were from those species found in the cove and obtainable in pure culture. Two of the three species include Chlamydomonas reinhardi and Euglena gracilis. Both of these organisms are unicellular green algae and are members of the primary trophic level. Euglena, however, is much larger (100u) than Chlamydomonas (23u). The third organism used in the exposure studies, was an undetermined ostracod specie. Ostracods are representative of the larger microzooplankton which are detritus feeders that are most often found scrambling on the sedimental surface. Toxicological tests with all of these organisms were done on nonexposed laboratory stocks of selected species found in the cove.

All organisms were exposed to varying concentrations of cadmium as soluble $CdCl_2$ for a period of seven days. Concentrations exceeding 1 ppm caused total mortality within 24 hours for Chlamydomonas reinhardi and the ostracods and those concentrations exceeding 10 ppm had the same effect for Euglena gracilis. The concentration that appears to cause major detrimental effects to survival and reproduction without total death are evident at 0.1 ppm with Chlamydomonas, at 10 ppm with Euglena, and at a concentration between .01 ppm and .1 ppm with the ostracods. All lower concentrations appear to have no appreciable effects.

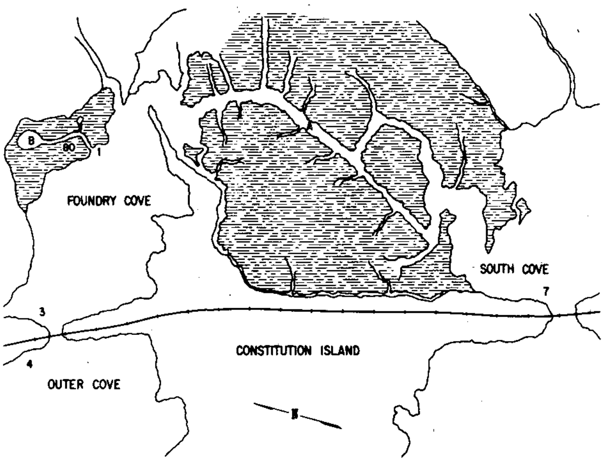
MATERIALS AND METHODS: FIELD INVESTIGATION

Sampling

During the first several weeks of the summer, the field studies primarily tested and evaluated various plankton collecting procedures. The procedure selected consists of concentrating 76 liters of water, using a #20-76 µ aperture net. Two replicates were made at each station, then placed in 1.5-liter wide mouthed jars in approximately 300 ml of water in a 10% formalin solution with Rose Bengal. When feasible, physical and chemical data of tidal condition, time, temperature, depth, D.O., pH, conductivity, salinity and alkalinity were taken.

Sampling Sites

Sampling was done at ten locations. six were within Foundry Cove, one in South Cove, one in the inter connecting canal, and two in the Hudson River (Figure 1, excludes Hudson River Stations).



The stations in Foundry Cove were selected to compare the populations, numbers and distribution at increasing distances from the Marathon manufacturing high cadmium outfall area, Stations B, 80 and 1. Stations in the Hudson River, the South Cove and the canal were also selected for population comparison studies in lower cadmium-level areas. Twelve-hour tidal cycles at one hour intervals were collected for diversity and/or abundance studies and for seasonal fluctuations. For detail of cadmium concentrations at various sites, see included paper by T. Kneip, G. Re´ and J. Hernandez.

Analysis - Counting Procedure

Three aliquots were counted in a Sedgewick-Rafter cell of each jar at 50 or 100X magnification. Samples from each jar were stored for taxonomic purposes.

MATERIALS AND METHODS: TOXICOLOGY

The effects of varying concentrations of cadmium have been observed on laboratory stocks of Chlamydomonas reinhardi*, Euglena gracilis*, and an ostracod specie*. At present three studies were made on C. reinhardi, one with E. Gracilis and three on the ostracods. A wheat-hay infusion medium was used in the ostracod studies, while Alga-gro* solutions were used for the Algal species.

For dosage series studies on the two algal species, serial dilutions were prepared from a stock solution of 1000 ppm cd^{++} (CdCl$_2$), which resulted in 10cc of 100 ppm, 10 ppm, 1 00m, 0.1 ppm and 0.0001 ppm. Three replicate series were set up with a control (no cd).

Counts of organisms were made initially at 0-hour, then at 24-hour, 48-hour, 96-hour and 7-day intervals. Three replicates were counted in a Sedgwick-Rafter cell. The cultures were maintained at 29°C under continuous Gro-lux illumination.

For ostracod studies, the test containers used were 4-ounce polypropylene cups,** filled with 45 ml of a cadmium solution (from 1000 ppm 50 0.00. ppm) and ten ostracods. Counts were made at the same intervals as the algal species. The cultures were maintained at room temperature (24°C ±).

RESULTS AND OBSERVATIONS:
FIELD INVESTIGATION

Eight microzooplankton collections were made including a tidal cycle. The population distribution of microorganisms indicates a noticeable decline in total numbers of organisms in September and October. Rotifers and copepods combined generally comprise between 75 and 99% of the total population i n the sample, which declined in October. Populations peak between late June and August, presumably due to the warmer temperatures. The data indicates great variability in the

*Obtained from Carolina Biological Supply Company, North Carolina

**Obtained from Falcon, Division of Becton, Dickinson and Company planktonic species in abundance and distribution.

A 12-hour tidal cycle was made at Station 1 on October 11, 1973, for any tidal effects on planton populations and incomplete tidal cycles were made on June 28, 1973, at Station 1 and on August 10, 1972, at Station 2 (Figures 2,3, & 4). They represent the rotifers and copepods comprising the major portion of the population. All three cycles show relatively the same trends, even though one group may be more abundant. The October 11, 1973, tidal cycle (Figure 2) reveals that at ebbing tide, there is a gradual increase in populations until low slack. This is also evident during both the June 28, 1973, cycle (Figure 3) and the August 10, 1972, cycle (Figure 4) and may be significant. The numbers of organisms collected in 1972 were slightly lower than those in 1973.

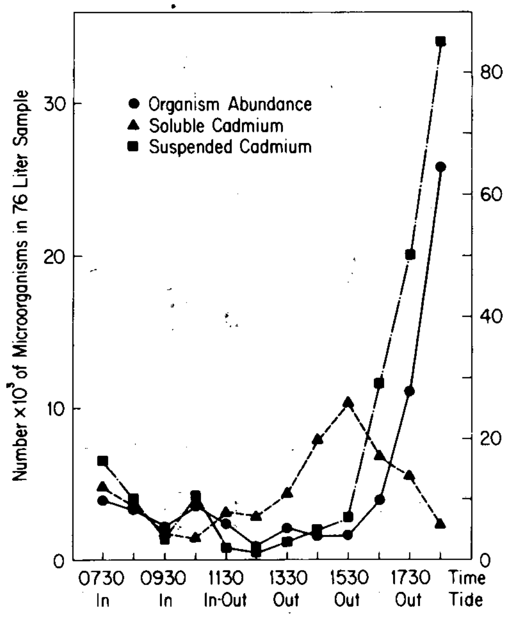


Figure 2. Tidal Cycle at Station 1, October 11, 1973

The genera of rotifers are not discussed separately but compiled as "rotifers" in the graphs; similarly for nauplius and adult copepod as "copepods". However in the original count, the genera and species were identified where possible and recorded. Organism dominance may be important should the population composition change in the future as a result of dredging and cadmium removal. The rotifers dominated from June until August. During September and October there is a shift to copepod larvae (nauplii) dominance.

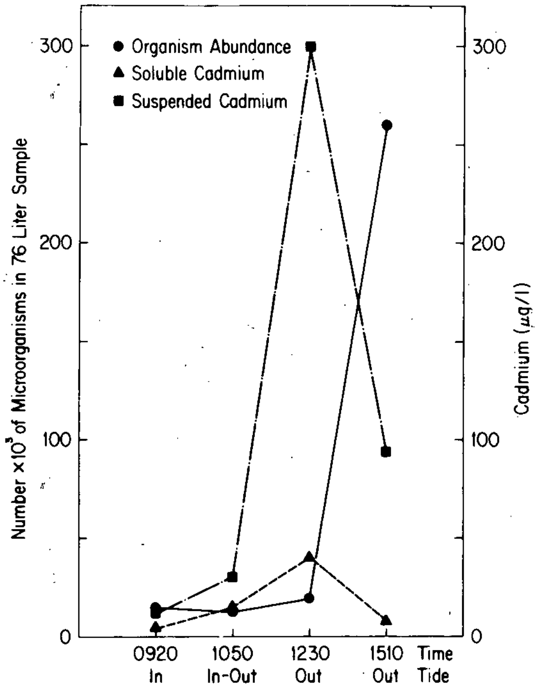


Figure 3. Partial Tidal Cycle at Station 1, June 28, 1973.

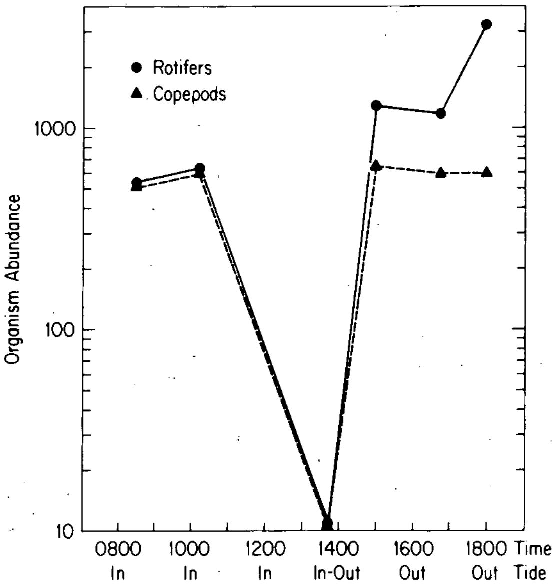


Figure 4. Tidal Cycle at Station 2, August 10, 1972.

Comparisons between organism abundance, soluble cadmium and suspended cadmium have been made for the two tidal cycles at Station 1, in 1973. The June 28 collection is graphically shown in Figure 5. Note that the soluble and suspended cadmium levels follow the same trend, with a peak at the beginning of ebb. The organism abundance increased with the ebb and continued to do so at a time when the cadmium levels began to fall.

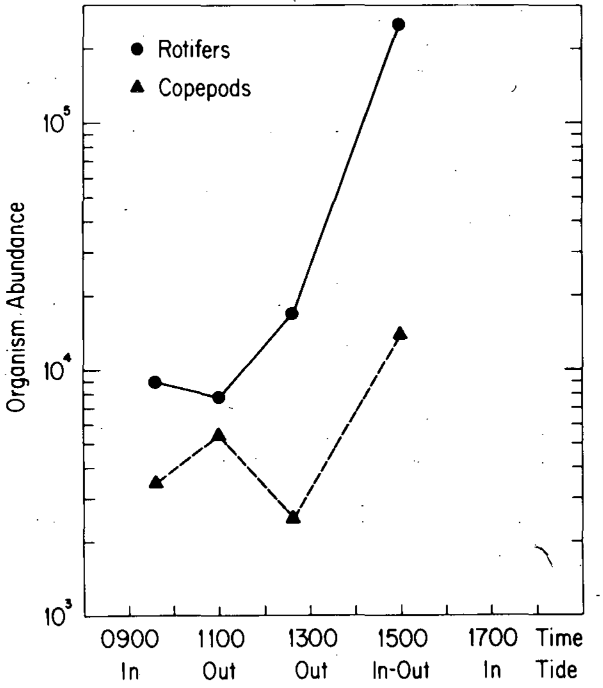


Figure 5. Variable Comparison at Station 1, June 28, 1973.

For a comparison at station 1 for October 11 see figure 6. It shows that the trend for suspended cadmium follows that of organism abundance; both increasing as the tide ebbs. The soluble cadmium levels on the contrary, decrease during the same period. It may be significant to note that from 1330 to 1530 hours the soluble cadmium level increases as organism abundance decreases. This trend reverses from 1530 to 1830 hours so that when the soluble cadmium level decreases, the organism abundance increases.

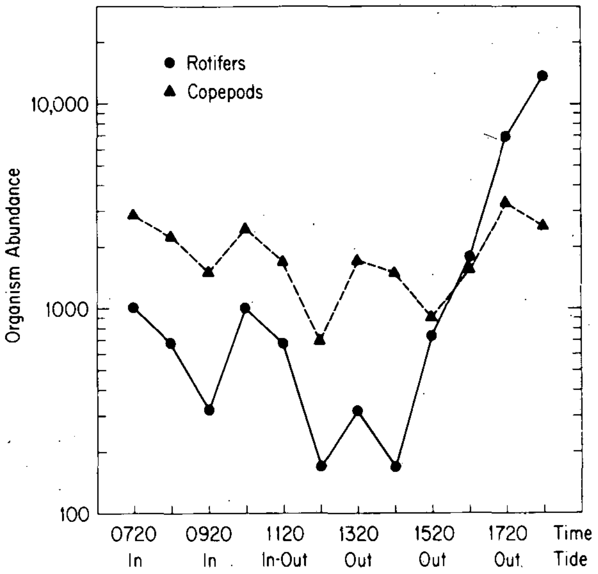


Figure 6. Variable Comparison at Station 1, October 11, 1973.

Tables I and II compare organism abundance, soluble cadmium and suspended cadmium at different stations during a collection day. The September 27 collection is shown in Table I. Note that the soluble and suspended cadmium levels follow the same trend. The highest values for cadmium were found at Station B and Station 80, near the outfall area. Included in Table I are available sedimental cadmium levels. These values can be seen to be extremely high at Station B and Station 80, and drop at Station 3. An apparent increase in organism abundance occurs with increasing distance from the outfall area.

TABLE I. Comparison of Organism Abundance, Soluble Cd and Suspended Cd

September 27, 1973

Station-Tide	Organism Abundance (per 76 liters)	Soluble Cadmium (μg/l)	Suspended Cadmium (μg/l)	(ppm) Sedimental Cadmium
B-in	4,000	7.2	20.9	12,800
80-in	3,200	7.2	17.2	12,700
1-in	3,400	1.9	3.2	--
3-out	17,500	3.2	5.0	419.0

The results of the October 25 collection are shown in Table II. As on September 27 (Table I), the soluble and suspended cadmium levels have a similar trend. Cadmium levels are lowest as distance increases from the outfall area, primarily Stations OC, HR (FC), HR (SC, and 7. However organism abundance seems to vary indiscriminantly from station to station. However at Station B where the soluble cadmium concentration reaches peak, the organism abundance is lowest.

TABLE II. Comparison of Organism Abundance, Soluble Cd and Suspended Cd

October 25, 1973

Station-Tide	Organism Abundance (per 76 liters)	Soluble Cadmium (μg/l)	Suspended Cadmium (μg/l)
1 - in	4300	7.7	18.1
3 - in	2300	5.0	8.5
OC - in	1800	3.4	< 1.9
HR(FC) - in	2500	3.4	< 1.9
HR(SC) - in	2800	4.0	< 1.9
7 - in	1800	<1.9	< 1.9
A - in -> out	2850	4.0	< 1.9
B - out	1100	8.4	5.0
80 - out	1700	5.0	7.5
1 - out	1400	<1.9	3.0
3 - out	2100	2.4	3.0

A comparison is made between organism abundance and bottom sediment cadmium levels from October 25 (Table III). Again cadmium levels decrease with increasing distance from the outfall, reaching the lowest level at Station HR (SC) and Section 7. The population abundance appears not to vary significantly with the sedimental cadmium concentrations, but note that at Station B where the cadmium concentrations peak at their highest levels, the organisms abundance declines to its lowest point.

TABLE III. Organism Abundance Versus Cadmium in Sediment

October 25, 1973

Station-Tide	Organism Abundance (per 76 liters)	Cadmium in Sediment (ppm)
1 - in	4300	8800
3 - in	2300	450
OC - in	1800	450
HR(SC) - in	2600	22
7 - in	1800	19
A - in -> out	3000	360
B - out	1100	14000
80 - out	1700	8900

Statistical Analysis

During 1973, two replicate samples were collected at each station and subsampled three times for organism counts. The mean and standard deviation were calculated for each replicate and an independant t-test was run to see whether the two replicates from each station were statistically similar. The critical t-value used was 2.78 for 4 degrees of freedom (3 subsamples - 1 = 2df for replicate #1 and 3 subsamples - 1 = 2df for replicate #2, ∴ 2df + 2df = 4df). The combined mean and standard deviation, with a 95% confidence interval of the two replicates were calculated and converted to $\log_{10}$ form. The means were averaged according to station. The 95% confidence interval was determined for each geometric mean.

Calculations show that there are no apparent differences in the populations between stations through the 1973 sampling period. The error bars about the means are large, which was expected since n (# of times samples were taken at a station) was usually small, ranging from 3 to 15.

RESULTS: TOXICOLOGY

The acute dose response to cadmium is shown in Figures 7-9. The values that were used for graphing the algal data are the average number of organisms from three counts per test tube observed in the microscopic field under 100X magnification. The values that were used for graphing the ostracod data represent percent mortality, which was based on exact numbers counted within each test container. The results obtained for the replicates were averaged together.

Two of the three tests on C. reinhardi appear to show similar results. Data of one study is shown in Figure 7. In both tests, total mortality occurred within 24 hours in concentrations exceeding 1 ppm. Death eventually occurs at 1 ppm. Apparent growth inhibition occurred at 0.1 ppm. As expected the lower concentrations showed decreasing effects.

Cadmium toxicity on Euglena gracilis is shown in Figure 8. Concentrations exceeding 10 ppm caused immediate death. Growth decrease was evident with the 10 ppm solution, with

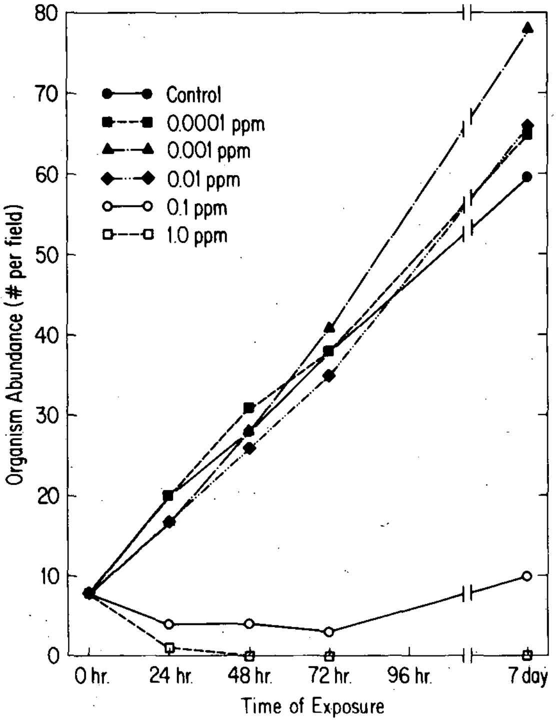


Figure 7. Toxicology: $CdCl_2$ on Chlamydomonas reinhardi

some recovery after 48 hours of exposure. No effects of concentrations lower than 10 ppm were found.

Similar results were obtained from the C. reinhardi and E. gracilis studies. One concentration distinctly impaired survival without killing all of the organisms. The results indicate that Euglena appeared to be more able to withstand higher cadmium concentrations than Chlamydomonas (approx 100X).

Cadmium toxicity on ostracods is shown in Figure 9 and is representative of two other tests done on these organisms. Those concentrations exceeding 1 ppm caused immediate death of all organisms. Death eventually occurs with organisms exposed to 1 ppm. Mortality is high with the 0.1 ppm solution in one study, while total mortality occurred after 96 hours in another study at this concentration. As expected, lesser effects were found at concentrations of 0.01 ppm and below.

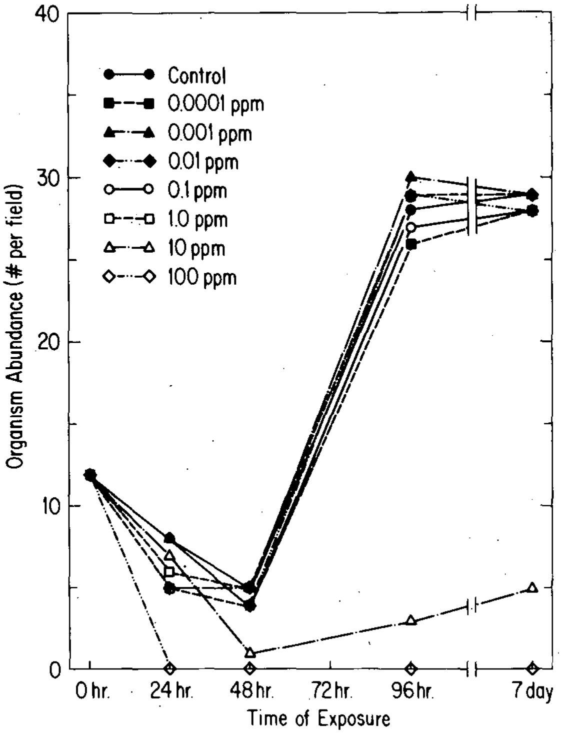


Figure 8. Toxicology: $CdCl_2$ on Euglena gracilis.

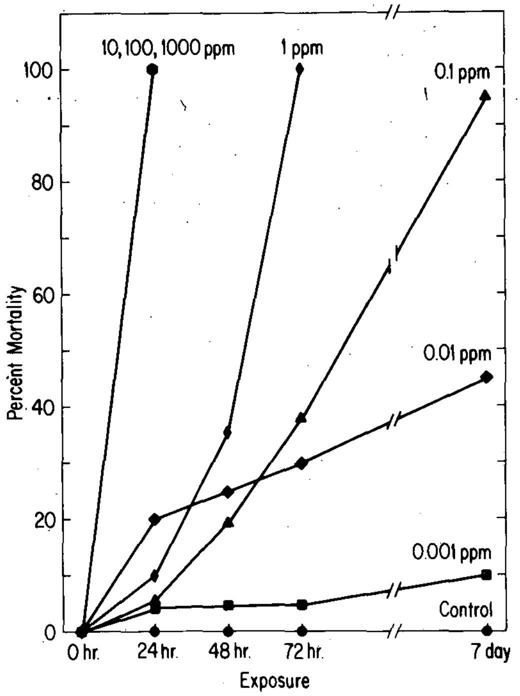


Figure 9. Mortality - $CdCl_2$ on Ostracoda - April 22-29, 1974.

DISCUSSION: FIELD INVESTIGATION

The samples collected in the field primarily consisted of rotifers and copepods. During most of the sampling period the abundance of rotifers exceeded that of the copepods. The maximum density of rotifer populations appears to be closely correlated with the relative amount of available substrate and exposed surfaces. Presumably this is associated with food, attachment protection and predation (Pennak, 1953).

Figures 2,3 and 4 all show a large increase in the number of organisms, primarily rotifers, as the tide ebbs. With water depth decrease it is probable that sediment stirring occurs, accounting for the presence of epibenthic rotifers and other organisms. This possibly explains the increase in populations at low tide.

Figures 5 and 6 show no consistent relationship between suspended or sedimental cadmium levels and organism abundance. Uncertainty exists as to a causal relationship between soluble cadmium and biotic population levels. During ebb tide, the soluble cadmium levels drop while the abundance of organisms increases, possibly due to sedimental stirring in shallow water and reduced soluble cadmium levels. Plankton also move with or are moved by the currents; therefore their residence time in any particular spot, including highly contaminated areas, may be relatively short and thus may not show immediate environmental effects. Statistically there seems little difference in populations between the different stations.

DISCUSSION: TOXICOLOGY

The results of the toxicity tests are shown on Figures 7 through 9. Note that the critical cadmium levels which noticeably impair the growth of the phytoflagellates were 0.1 ppm for Chlamydomonas and 10 ppm for Euglena, indicating a possible greater sensitivity of Chlamydomonas reinhardi to soluble cadmium. Soluble cadmium values from field samples, for Stations B, 80 and I show concentrations that range from 2.4 to 40.4 µg/l or 0.002 to 0.040 ppm, which are lower than the critical cadmium concentration for Chlamydomonas and Euglena. Therefore, the soluble cadmium levels, if available to biota in Foundry Cove, may not exist in large enough concentrations to elicit an acute harmful response in the resident or transient plankton populations of these species.

The reasons why Euglena may be more tolerant than Chlamydomonas is as yet undetermined. The organism is, however, larger and structured differently. A simple surface/volume variation might account for the difference in sensitivity. Further, the Euglena tests were done in a Tris buffer system. This is an organic compound from which the Euglena may extract nutrient materials.

At the present, the ostracods appear to be in the same range of sensitivity to cadmium as Chlamydomonas. The 0.1 ppm concentration is definitely detrimental to their survival, but their reaction to 0.01 ppm is questionable when the results of the 3 different tests are compared.

The above preliminary experiments indicate that growth and reproduction may represent a more sensitive measure of cadmium (or heavy metal) toxicity than the conventional LC_{50} or mortality studies.

CONCLUSIONS

In 1973 microbiota collections were made at Foundry Cove. The major groups were found to be rotifers and copepods. A tidal and seasonal effect was shown to occur, but an effect due to cadmium is questionable at this time. Two species of unicellular green algae and species of ostracod were used in preliminary toxicity studies and critical cadmium concentrations were observed.

Field collections of plankton were continued during 1974. The results obtained will assist in a continued evaluation of the possible interactions of environmental factors especially cadmium affecting this population.

ACKNOWLEDGEMENT

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EFFECTS OF SOIL PROPERTIES ON Pb UPTAKE BY CORN AND EFFECTS OF Pb AND Cd ON CORN ROOT ELONGATION*

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Abstract

The uptake of Pb into the shoots of six week-old corn plants was found to decrease with an increase in soil pH, cation exchange capacity (CEC), and available phosphorus. The Pb effects on growth of the corn plants were not as clearly related to these soil properties as was the uptake of Pb, although the greatest reduction of growth was seen in the low CEC and low pH soils. An experiment on corn root growth indicated that concentrations of Pb and Cd which by themselves would not inhibit root elongation did cause an inhibition when added together. A preliminary model of the Pb and Cd effects on root growth is presented.

Introduction

A previous study on Pb uptake and toxicity by Miller and Koeppe[1] demonstrated that corn plants will accumulate large amounts of Pb when it is supplied to them in sand culture. The same study demonstrated that as little as 24 μg Pb/g of sand caused a stunting of growth under phosphate deficient conditions. Several workers have indicated that although the Pb content of soil is raised substantially, the Pb accumulation of plant tops remains quite low.[2,3,4,5] However, other workers have found substantial accumulation due to soil contamination.[6,7,8] John[9] attempted to correlate Pb uptake of lettuce and oats to soil factors and found that soil pH was an important parameter in predicting plant Pb, although no relationship with organic matter was observed. Rolfe[8] demonstrated that soil phosphate levels affected Pb uptake by tree seedlings and suggested that further research should be done on soil factors affecting lead mobility.

Cadmium uptake and toxicity to plants is also well documented.[10,11,12,13,14] It appears from these studies that Cd is more toxic than Pb and probably more mobile in the soil and plant. However, as with Pb the soil conditions affecting its uptake by plants need to be further described.

The following report describes a study presently underway to define the importance of soil cation exchange capacity (CEC), pH, and available phosphorus (Bray P_1 test) on Pb uptake by corn plants and its toxicity, as these properties have been related to Pb binding by soils.[15] In addition, preliminary results concerning the interaction of Pb and Cd on corn root growth are included.

Methods

A series of Illinois Soils (Table 1) were selected to provide a range in three characteristics (P level, CEC, and pH) believed to be important in the plant uptake of Pb.

TABLE 1. Characteristics of Experimental Soils

Soil		Textural Class	CEC	Bray P_1	pH
1	Cisne	si. l.	6.8	82	4.5
3	Cisne	si. l.	8.5	107	6.1
4	Cisne	si. l.	6.7	33	7.0
4L	Cisne	si. l.	6.7	33	7.9*
5	Cisne	si. l.	7.9	64	6.0
6	Cisne	si. l.	7.7	9	5.5
8	Sidell	si. l.	15.9	76	6.5
9	Drummer	si.c.l.	30.3	44	6.1
10	Bloomfield	l. s.	2.3	125	5.7
11	Cisne	si. l.	8.0	32	6.4

*Soil 4 with 1% $CaCO_3$

Finely divided $PbCl_2$ was added to the soils at rates of 0, 250, 500, 1000, and 2000 μg Pb/g soil. The soils were fertilized with the equivalent of 150 lbs/A of N and 100 lbs/A of K. Phosphorus fertilizer was not added as the effect of available P was one factor to be tested. After adding fertilizer and Pb to the soils they were throughly mixed in a

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mechanical mixer and 500 g of each soil was placed into 4" x 4" pots. There were three replications of each Pb and soil combination. Soils were watered to field capacity and allowed to dry 4 times to allow the Pb to react with the soil.

Pots were then planted with corn and thinned to two plants per pot following emergence. Six weeks after emergence the shoot portion was harvested for Pb analysis. The corn plants were dry ashed at 490°C for 4 hours after allowing 4 hours for the muffle furnace to heat from ambient to 490°C. The ash was taken up in 3N HCl that had been diluted from constant boiling HCl. Lead was determined by atomic adsorption.

In the root elongation studies corn was grown in flats containing Bloomfield loamy sand with $PbCl_2$ and $CdCl_2$ at the indicated concentrations. The metals were added as solutions and allowed to react with the soil for a week before planting. The soil had 2.1 % organic matter, a CEC of 2.3 m. eq./100g, a Bray P_1 test of 56, and a pH of 5.7. It had a binding capacity as measured by adsorption isotherms and leaching experiments of 9.7 μmole Pb and 5.2 μmole Cd per g dry weight of soil. Fifty corn seeds were planted per flat and watered daily with distilled water. On the third, fourth, and fifth day 10 seeds were removed from each flat and the length of the radicle determined.

RESULTS & DISCUSSION

I. Lead

TABLE 2. Accumulation of Pb in Shoots of Corn Grown on Soils Amended with $PbCl_2$. Effects of Soil CEC, pH, and Bray P_1 Extractable P

	Added Pb (μg/g dry weight of soil)				
Soil #	0	250	500	1000	2000
CEC Series					
9	5*	14	13	27	17
8	5	9	10	23	36
5	3	12	26	80	120
10	4	99	220	422	4083
pH Series					
4L	4	13	23	61	43
4	2	19	37	61	101
5	3	12	26	80	120
1	3	66	58	170	249
Bray P_1 Series					
3	3	7	19	31	41
5	3	12	26	80	120
11	9	10	42	47	97
6	3	17	30	81	233

*μg Pb/g dry weight of tissue; average of 3 replicates

The effects of the three soil variables (CEC, pH, and available P) on the Pb content of six-week-old corn plants are illustrated in Table 2. The Pb content of the plants generally decreased as CEC, pH, and Bray P_1 test values of the soil increased. Hassett 15 related these soil properties to the measured Pb sorption capacities of the soils used in these experiments and expressed the results in the following regression equation.

$$Pb_s = -34.3 + 0.0774\ P_1 + 5.358\ pH + 5.337\ CEC \qquad (1)$$

where Pb_s is the predicted sorption capacity in μmoles Pb/g soil, pH is soil acidity, CEC is cation exchange capacity in m. eq./100 g of soil, and P_1 is extractable P in pp2m. The Pb_s of the soils used in this experiment were calculated from the soil pH, CEC, and Bray P_1 values from Table 1. From this the ratio of total added Pb to predicted sorption of lead (Pb_t/Pb_s) was obtained and is plotted versus Pb_p (total plant lead) in Figure 1. This relationship illustrates that the approximate amounts of Pb uptake by six-week-old corn plants from $PbCl_2$ amended soils can be predicted based upon knowledge of the pertinent soils properties. Lead which has been in the soil over a period of time may behave differently in this respect and further investigation is in progress pertaining to this question.

The plot of fresh weight of six-week-old corn plants vs. Pb added to the soil (Figure 2) clearly demonstrated that the effects of Pb are dependent on the soil type. For example, growth was greatly reduced in soils 10 and 1 with increasing Pb levels while in soils 8 and 9 little difference, if any, was noted with increasing Pb. Since CEC, available P, and soil pH are soil variables modifying available Pb, the following was an attempt to express Pb effects as a function of these variables.

To quantify the effects of Pb on fresh

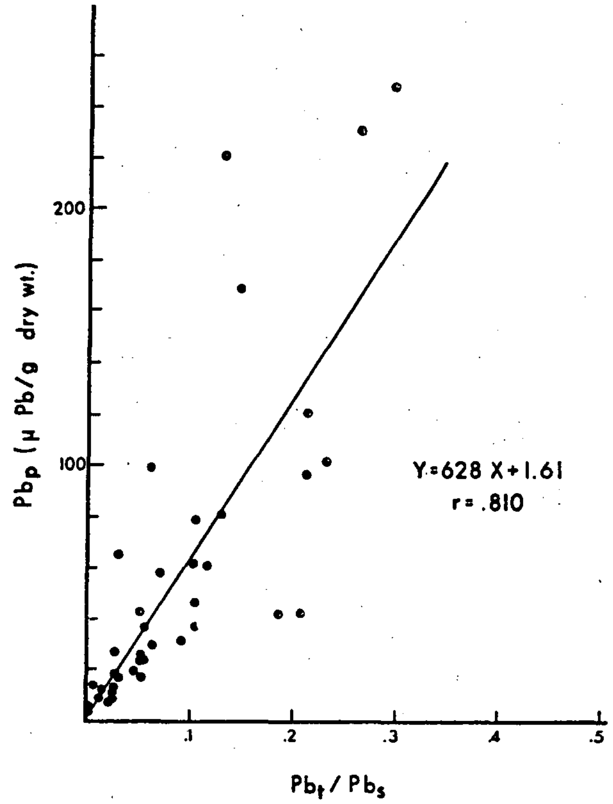

Figure 1. Lead in corn shoots (Pb_p) vs. the ratio of total added Pb to the predicted sorption of Pb(Pb_t/Pb_s)

weight, fresh weight was regressed against linear, square, and cubic terms for Pb for each of the 10 soils. The resulting coefficients are in Table 3. Coefficients followed by an asterisk are significant at the 5% level.

To determine if the coefficients in Table 3 could be expressed as a function of the 3 soil variables, the coefficients were regressed against linear, 2 factor and 3 factor interactions for CEC, available P, and pH. A search of the 7 combinations of the variables demonstrated that only the 3 factor interaction was significant (α = .05). In each case about 40% of the variation can be attributed to the 3 factor interaction. The model for lead effects in the 10 soils is:

$$Y_i = b_{oi} + CEC*P*pH(-0.032\ Pb + 0.077\ Pb^2 - 0.00055\ Pb^3) \qquad (2)$$

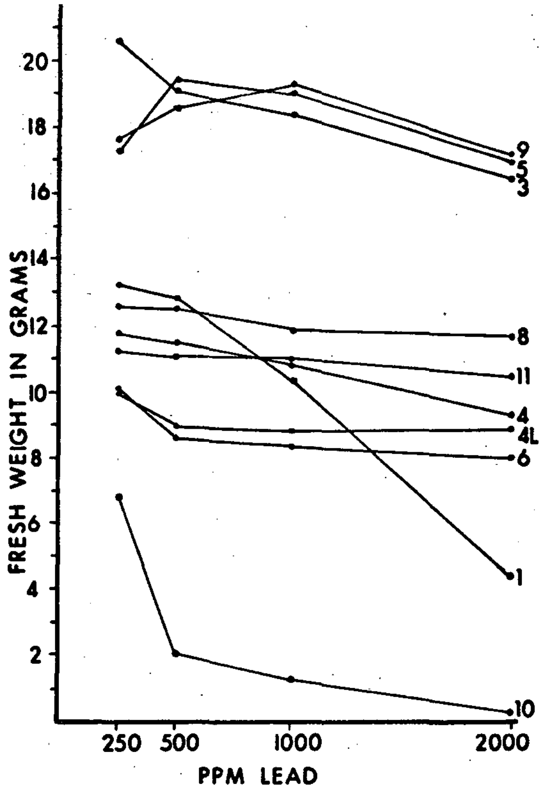

Figure 2. The effects of Pb on the fresh weights of six-week-old corn shoots.

TABLE 3. Regression Coefficients for the Response of Fresh Weight of 6 Week-Old Corn to Pb

	Regression Coefficients		
Soil	Pb	Pb^2	Pb^3
1	.72*	-.45	-.03
3	-3.43*	.75	-.05
4	-5.60*	.06	-.005
4L	-3.11*	.74*	-.05
5	5.60*	-.02*	.10*
6	-.52	.08	-.006
8	.42	-.21	.02
9	1.30	-.20	.005
10	-11.1*	2.62*	-.18
11	-.63	.11	-.008

*Significant at α = .05

where Y_i is the fresh weight of six-week-old corn in soil i, and b_{oi} is an intercept for soil i.

At this stage the model is empirical. Further work is necessary on the factors that govern Pb mobility and activity.

II. Lead-Cadmium Interaction on Corn Root Elongation

The possibility of a Pb-Cd interaction on corn growth was tested by measuring root elongation in the presence of Pb, Cd, and combinations of concentrations of the two metals. The effects of Pb and Cd separately and in combination for five-day-old corn roots are shown in Figure 3.

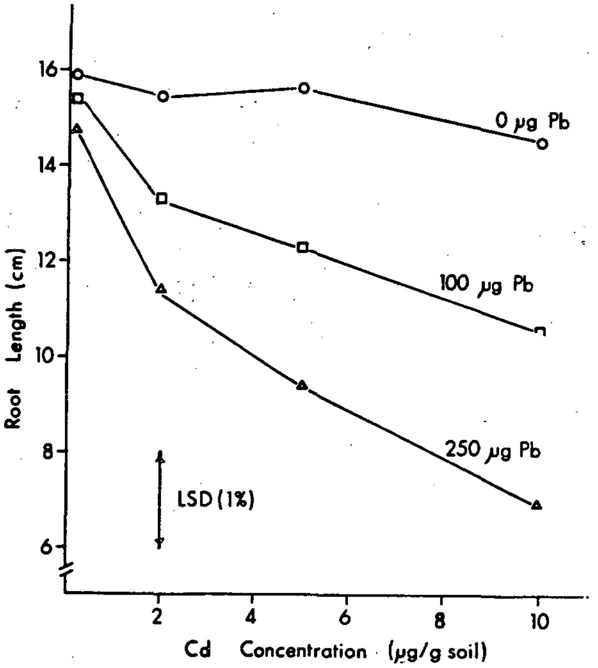

Figure 3. Effects of Cd and Pb in soil (µg/g soil) on the elongation of corn roots at 5 days.

In the concentration ranges shown Pb or Cd separately did not significantly affect root elongation, however in combination a negative interaction was apparent.

The reasons for this effect are not apparent from this work, but a number of possible explanations exist. For example, it might be that the metals are affecting separate biochemical pathways or physiological processes. The inhibition of one or the other separately might not lead to immediate reduction of radicle elongation, but the inhibition of both would. This was suggested for fluoride and copper interactions on the respiration rate of Chlorella vulgaris[16]. Also, it may be that the Pb imposed enough osmotic stress on the corn to make the roots more susceptible to Cd, althought the majority of the Pb should have been adsorbed to soil surfaces and/or precipitated with phosphate under these conditions. Another possibility is that one metal in some manner caused increased uptake of the other by the radicles. This possibility is not easily tested since root surface sorption of the metals tends to mask true accumulation even when the roots are thoroughly washed.

Regardless of the explanation for the interaction, it is apparent that in studies of heavy metal toxicity related to environmental effects, it is important that the studies be extended to take into account possible interactions such as have been observed here.

To develop a model incorporating the effects of Pb and Cd on root growth, we made the initial assumption that the growth of corn roots to five days is exponential or

$$\frac{dW}{dt} = rW \tag{3}$$

where $\frac{dW}{dt}$ is the time rate of change, W is the length at time t and r is the growth constant. The integral of this function is: $\ln W = \ln W_o + rt$. To estimate the values of $\ln W_o$ and r, lnW was regressed against time (3 days) for each of the 16 combinations of Pb and Cd. These values are listed in Table 4. To express r as a function of Cd and Pb the values for r from Table 4 were regressed against Cd, Cd^2, Pb, Pb^2, and Cd*Pb.

The result of the analysis suggest that r can be expressed as a function of Cd^2, Pb^2, and Cd*Pb in the following way:

$$r = .73 - 0.003\ Cd^2 - 0.0000018\ Pb^2 - 0.00011\ Cd{*}Pb \tag{4}$$

with a variance of 0.0056 and a correlation coefficient of 0.96.

If the assumptions of exponential growth are valid, then $\ln W_o$ can be estimated as the

TABLE 4. Estimated Initial Length and Growth Rates of Corn Roots for Treatment Combinations of Cd and Pb

Treatment Combination (μg/g)		Initial Length ($\ln W_o$)	Growth Rate r
Cd	Pb		
0	0	-1.0	.77
0	100	-1.4	.84
0	250	-1.4	.82
0	500	-.9	.56
2	0	-1.2	.81
2	100	.1.1	.76
2	250	-1.0	.69
2	500	-.9	.55
5	0	-1.2	.79
5	100	-2.2	.96
5	250	-1.5	.76
5	500	-.8	.27
10	0	-1.4	.82
10	100	-.7	.63
10	250	-1.2	.63
10	500	-.04	.04

mean of the estimated values from the 16 regressions. For this data set the value is -1.13.

The final growth model is

$$W = 0.323 \exp^{rt} \qquad (5)$$

where W is root length in cm, and r is growth rate as defined in equation 4 and t is time.

This model was developed to investigate the effects of Cd and Pb on early root growth when the assumption of exponential growth should be valid. Additional work is needed to determine how Cd and Pb affect the parameter values of such a function, or how different soils modify the effect of Cd and Pb.

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LIFE, LIBERTY AND THE PURSUIT OF LEAD: THE IMPACT OF LEAD MINING AND MILLING ACTIVITIES ON AQUATIC ORGANISMS

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Abstract

A study of the various environmental factors and current industrial practices which may affect stream conditions in Missouri's New Lead Belt has led to the conclusion that the most serious threats to aquatic life and those most likely to cause serious community alteration are: 1) the release or escape of finely divided particulate material (gangue) with varying amounts of residual heavy metal ores, and 2) the release of toxic milling reagents into receiving streams as the result of inadequate treatment of tails. The presence of increased amounts of silt are sufficient in some cases to account for elimination of benthic conditions appropriate for normal community development and perpetuation. The results of preliminary toxicological studies utilizing several common organic milling reagents and a number of stream organisms are presented. There is little analytical data available relative to actual concentrations of residual milling reagents in tails or effluents, but simple calculations based on known additions, amounts of ore treated, and volumes of water involved suggest that extreme care should be exercised to provide adequate treatment or recycling to avoid adverse effects in the receiving streams. Significant differences in toxicity of functionally-related compounds should be explored to select the least toxic reagents where possible to diminish the potential hazards to aquatic organisms. Aquatic vegetation and leaf litter material have been shown to bind large quantities of heavy metals, especially lead, in the vicinity of industrial activities. Available evidence suggests that the lead is bound to the anionic sites on the surface of aquatic plants or in leaf litter by a process of ion exchange. Ion exchange capacities of mixed live algal cultures, utilizing lead acetate in solution applied to a packed column of algae have been determined, and average approximately 65 meq/100 grams dry weight. Similar cation exchange capacities for leaf litter collected in the vicinity of a smelter approximate 180 meq/100 grams dry weight.

Bound lead in field or laboratory specimens was removed by washing with ethylenediaminetetraacetate (EDTA) in concentrations as low as 0.01 M at pH 7.5. The results of analyses of various consumer organisms have indicated no biomagnification of lead in the grazing food chains involving aquatic vegetation heavily laden with lead in or near industrial tailings systems. The elevated total body concentrations of lead in fish, tadpoles, crayfish, and aquatic arthropods captured in or near such tailings operations largely reflect the complexed metals associated with the gastrointestinal contents, with some additional lead bound or chelated to the mucous membranes of gills or mucous covering body surfaces. The increased level of stream productivity in some tailings systems known to have high heavy metal content in sediments and bound to aquatic vegetation suggest that the presence of heavy metals along cannot account for serious stream alteration or absence of typical consumer organisms in other problem industrial sites.

It is unlikely under the attendant set of physical and chemical conditions in Ozark streams that lead toxicity is or will become a problem to aquatic life forms. There is a greater probability, though difficult to predict exactly, that some normal stream organisms or communities may be adversely affected by the observed levels of zinc, copper and manganese. Furthermore, the observed concentrations of zinc and copper in some receiving streams approach the established toxic limits.

Introduction

The development and impact of the world's largest lead and zinc producing region within the Ozark Mountains of southeastern Missouri have been the focal points of cooperative effort and watchful scrutiny since industrial operations began in 1968. Industrial representatives and teams of investigators from a number of state and federal agencies have shared in the collection of pertinent data, analytical procedures, and in the institution of corrective measures to alleviate real or potential problems. It is a source of satisfaction to all concerned that after six years of full-scale operation, and despite being the largest lead producing region of the world, the New Lead Belt remains one of the most beautiful parts of the nation.

The utilization of abundant mineral resources obviously can and should be compatible with the development of other natural resources and preservation of the environmental qualities important to all of us. This goal of compatability, however, is not automatic. It commands constant vigilance by industry -- continual self examination to establish procedures optimized not only for economic profit, but also optimized with regard to environmental effects. It is the intent of the present paper to provide observations and data which may be useful to industry and interested regulatory agencies as they attempt to achieve and maintain those optimized conditions.

Mines and Environment

The operations of the mines in the New Lead Belt present few problems to the environment. The excess mine water generally stimulates photosynthetic productivity at the surface in the settling ponds and receiving streams, but increased productivity is not necessarily objectionable. The most significant threats to surface ecology presented by the mines are in the forms of: a) petroleum wastes and spills incurred during operation of underground equipment, and b) fine particles of ore carried to the surface by the pumps. These problems are effectively controlled by proper maintenance policies underground and simple settling ponds for removal of particles. Aquatic vegetation within the settling pond and decant ditches assist in this procedure.

The "Tails" of the Mill

The mill with attendant reagents, products and wastes, on the other hand is undoubtedly the larger environmental concern. A brief review of milling procedures is perhaps in order as we attempt to identify potential ecological hazards. The ore is blasted loose and crushed underground to a size that is convenient for conveyance to the surface. At the surface, the ore is crushed again so that as it enters the mill the particles are less than an inch in diameter. A number of milling reagents; frothers, activators, promoters, depressants, etc. (See Table 1) are added along with water and the ore is crushed again in rod mills or ball mills to produce a very fine slurry. The ore mixture is then subjected to a series of flotation cells where injected air creates a froth which carries certain minerals to the surface while leaving other minerals and rock gangue in the bulk suspension. By successive flotation procedures the lead, zinc, and in some cases copper sulfides are separated and concentrated. The finely ground rock particles and unrecovered minerals are taken as a slurry to the tailings ponds, while the concentrated mineral salts are taken to the thickeners. In the thickener vat, specific depressants are added to permit the settling of the mineral particles and decantation of the liquids. The liquid wastes are sometimes recycled, or alternatively, taken to the tailings pond.

There is considerable variation from one company or operation to another in a) the quantities of ore treated, b) the type and amount of milling reagents employed, c) whether copper concentrate is produced, d) the manner in which the tails, thickener overflows and excess mine water are handled, and e) the number and placement of settling ponds, tailings ponds, and other treatment devices prior to the release of industrial effluents. Some mills attempt to recycle the mill waters, others do not. Total recycle is extremely difficult, if not impossible to achieve, and the eventual possibility of legislating and enforcing "zero discharge" of effluents poses some difficult practical problems. Current practice in the construction of tailings dams involves the use of cyclone separators designed to separate the coarse particles from the tailings slurry and deposit them in the body of the dam. Fine particles and liquid wastes are released on the upward side of the dam, but considerable leaching cannot be avoided. The occasional accidental release of the liquid wastes off the front face of the dam should and could easily be minimized or eliminated. The toxicity of residual milling reagents in the tails or leachates as just described is a factor which can cause considerable environmental concern. The release of such residual milling reagents, and the release of considerable particulate material including unrecovered heavy metal salts constitute the environmental threats posed by the mill.

Problem: Silt and Heavy Metals in Industrial Effluents

The release of finely ground rock particles and some vagrant mineral particles from the settling ponds and tailings ponds is worst during periods of heavy storms, but accumulates in the benthos to a greater extent under less turbulent conditions. The magnitude of silt accumulation varies from one situation to another, and may be complemented by additional precipitation or co-precipitation of dissolved minerals as industrial effluents mix with natural surface waters. No attempt has been made to estimate the extent of such contribution to silting in New Lead Belt streams, but should perhaps merit some attention. The accumulation of silt has, on occasion, achieved such density as to seriously alter normal stream communities. The turbulence of winter stream flows usually achieves at least annual resuspension and redistribution of stream sediments. Studies have been made by Jennett and his colleagues to assess the heavy metals content and distribution patterns in the sediments of receiving streams, and reservoirs, as well as in the tailings treatment system itself.(1)

The ability and tendency for local producer organisms, living or dead, to trap and concentrate vagrant Heavy metals have been observed in both terrestrial and aquatic environments(2-5). In the aquatic environments under study in the New Lead Belt, quantities of lead associated with aquatic vegetation have exceeded 74,000 ppm (dry weight basis) at the point of mine water discharge, and more than 8,000 ppm at the discharge of some tailings ponds. Roadside vegetation along heavily traveled highways and especially along ore or concentrate haulage routes have also shown high lead content. Bolter has reported that in the heavily forested area around the smelters and concentrate storage piles and haulage routes, heavy metal pollutants are concentrated mainly in the leaf litter. Very little of the heavy metals are found in the underlying soil.(2) In both aquatic and terrestrial situations, the degree of heavy metal contamination of vegetation decreases with distance from the source, and little is known about the eventual fate of such heavy metals over relatively long periods.

The consistency of association of heavy metals with living, dead, or decomposing plant material emerges in all these studies, with few obvious variations which can be traced to differences in source or the initial chemical nature of the heavy metals. The exact nature of the association of lead with plant materials, possible exchange and eventual disposition are as yet unanswered questions. These questions and others related to potential food chain concentration have posed challenging problems in the effort to establish rates and routes of dissemination of potentially toxic substances in the surrounding environment. Further serious questions arise related to possible physiological effects of elevated levels of lead, zinc, copper, and manganese in or on the various trophic levels of aquatic and terrestrial communities affected by the lead industry.

The heavy metals are most commonly introduced to stream biota as sulfides, or less likely as the sulfates, carbonates, or phosphates -- all of which are quite insoluble in the hard and slightly alkaline stream waters. The presence of abundant anionic sites known to be present in cell walls and surrounding matrix provide ample opportunity for ion exchange. The electron microscopic studies reported by Malone, et al(6), suggest that when hydroponically-grown corn roots are treated with dissolved or chelated lead, insoluble lead particles appear in isolated membrane-lined vessicles within the root cells. Few vessicles containing lead were found in stems or leaves. More recent autoradiographic studies by Rule, et al(7), on the other hand, indicate that some of the lead applied as lead nitrate to leaves of radishes and lettuce may enter the vascular tissue of the plant and be transported to other plant structures. The lead which remains associated with aquatic vegetation in the receiving streams of the New Lead Belt is believed to be bound primarily to the surface. Extensive washing of the plant material in distilled, tap, or stream water fails to remove the bound lead. Washing with ethylenediaminetetraacetate (EDTA) at pH 7 to 7.5 in concentrations as low as 0.01 M effectively removes most of the associated lead without cell rupture(8). The results of laboratory studies in which filamentous algae or leaf litter were used to pack columns which then served to determine cation exchange capacities are shown in Figures 1 through 4. The ability of either live or dead plant matter to bind soluble lead salts is obvious, even in the presence of abundant monovalent cations which do not interfere with the selective binding of the lead ions. Once the lead was bound to the column of plant matter, washing with water or sodium acetate solution was relatively ineffective in removing the heavy metal. However, EDTA at concentrations as low as 0.01 M was found to effect its rapid removal. Cation exchange capacities based on these column studies were calculated to approach 65 meq/100 g for the filamentous algae (dry weight basis) and 180 meq/100 g of dried forest litter material. From these data, it is apparent that those concentrations of lead reported in forest litter by Bolter and found in aquatic vegetation do not often approximate the total cation exchange capacity of the vegetation involved. Control columns using glass wool with overlaying lead sulfide (concentrate) indicated vast differences in the leaching rates of chelated lead from insoluble particulate material (PbS) and the removal of lead bound to the surface of plant material by washing with EDTA.

Two Mills in Comparison

The amount and variety of consumer organisms vary remarkably from one situation to another. In some operations, the seasonal algal blooms reach problem proportions, and this usually occurs in the absence of normal consumer populations. The increased productivity encouraged by industrial effluents has occasionally created unsightly conditions for several miles downstream as unusual and dense algal communities bloom and lead to undesirable patterns of succession. On the other hand, increased productivity in some operations has only served to maintain encouraging conditions for increased numbers of game fish. It is doubtful that vagrant heavy metals are responsible for the remarkable differences in community development in various streams, since comparable amounts of lead, zinc and copper have been found in virtually all receiving streams, or at some point within the treatment system where normal consumer organisms and typical desirable communities are established.

Figure 5 is a schematic borrowed from Dr. Jennett(1) to show the arrangement of tailings ponds and the meander system of one of the New Lead Belt mills. This particular mill produces lead and zinc concentrates. Principal milling reagents employed are shown in Table 1 under Mill A. Since the completion of the meander system and final settling pond in the summer of 1972, this operation has been rather successful in eliminating nuisance algal blooms in the receiving stream below, and has markedly improved the retention of particulate material and heavy metals within the system. Abundant aquatic vegetation within the meander system and final settling pond effectively trap and bind most of the vagrant mineral particles released from the first pond, and the overall retention time in the system permits effective degradation or dilution of milling reagents. Aquatic vegetation collected at the head of the meander system normally displays lead content of several thousand ppm, and these values drop to a few hundred ppm within the final settling pond.

Normal consumer organisms abound in the lagoons and meanders, including aquatic insects, snails, tadpoles, crayfish, bluegills, bass, carp, and catfish. Total body analyses for heavy metals in the larger consumer organisms reflect the high content of metals in consumed vegetation and that trapped in the mucous coverings of insect larvae which comprise the diet of the higher trophic levels. Considerable quantities of lead and zinc in the gills, mucous membranes, and bone were also noted. See Tables 2 - 6. The edible portions of those animals likely to be consumed by humans are relatively free of detectable heavy metal contamination. Washing of the intestinal contents removes most of the lead from the hollow organs, (see Table 5), but extensive washing of gills and outer body surfaces repeatedly in water or 0.1 M EDTA at pH 7.5 failed to remove the heavy metals. The marked difference in retention of lead by plant and animal tissues after EDTA washing is of considerable interest. As shown by the tabulated data, heavy metal contents of the intestine and gills vary from one season to another, and in the intestine, the data probably also reflect seasonal and species differences in diet. There has been no evidence of significant food chain concentration of heavy metals in higher trophic levels of aquatic communities.

The schematic for a second representative mine and mill tailings system is shown in Figure 6. This operation produces lead, zinc and copper concentrates and is considerably more confined in geographical space available for tailings treatment. The principal milling reagents employed are also included in Table 1 as Mill B. For the past two years, because of restricted space and in the effort to improve conditions in the receiving stream, this company has attempted to separate mine and mill wastes and recycle the latter. Because of a number of unique problems in design, total recycle of mill wastes has not been achieved, and considerable quantities of mill wastes and residual organic reagents have been observed in the final effluent. Company representatives are currently involved with other researchers to evaluate the possible contribution of these non-intentional effluents to stream community alteration. Considerable improvements in stream conditions have been observed since those initial modifications took effect, but further improvement is desirable.

Growth of aquatic vegetation in the short interconnecting channels below the final (mill) tailings pond has been limited to seasonal blooms of blue-green algae, diatomaceous mats and a few pond weeds within the stilling lagoons. The development of aquatic vegetation in the receiving stream has usually been retarded in the early spring months as compared with other streams, or upstream from the point of mixing with industrial effluent. Normal community development is replaced by a dense diatomaceous mat community which develops during the summer months, especially under low flow conditions. Relatively high manganese content in the industrial effluent has been cited as one possible contributing factor along with residual milling reagents to the unusually dense diatom populations and exclusion of the usual normal flora. Dominant aquatic consumers include a few minnows, small bluegills and small-mouth bass. The other consumer organisms common to most Ozark streams; snails, crayfish, tadpoles, and various aquatic insects, are extremely rare or absent. Though the actual numbers of existing consumer organisms are small, contamination of body tissues with heavy metals is practically negligible, as shown in Tables 7 and 8. Heavy metal recovery within the tailings system is good, however, the diatomaceous mat which develops during summer shows considerable silt accumulation.

The possibility that residual milling reagents in the industrial effluents contribute to the sparcity of consumer organisms is presently under study.

Toxicity of Milling Reagents

The toxicity of the various reagents utilized in the mill when released into the aquatic environment is not yet fully understood nor appreciated. Persistent indentifiable smells and appearance of froth in the final industrial effluents of some operations provide the biologist some pretty good clues as to possible reasons for serious changes in aquatic communities downstream. There are, unfortunately, very few data available on the toxicology of milling reagents relative to aquatic organisms, and even less is known about actual concentrations of residual reagents in industrial effluents. A summary of 96-hour median toxic limits (TL_m) determined by Hawley(9), (Ontario Ministry of the Environment), the U. S. Department of Interior Fish Pesticides Laboratory, and the University of Missouri is shown in Table 9. The data indicate the range of concentrations in which 50 percent mortality of test organisms occurred. More precise determinations were impractical and probably meaningless, since considerable variation may be observed from one batch of organisms to another depending on age, nutritional state, season, sex, water hardness, etc. The data are additionally plagued with the obvious shortcomings of short-term static toxicity studies. They offer little or no information regarding toxicity under conditions of continuous flow, long term effects, nor embryological or teratogenic effects. Despite the deficiencies in methodology, however, the results allow some approximate comparison of relative toxicity of the tested reagents.

Many of the test reagents have absorption maxima in the ultraviolet range, but the extinction coefficients are often too small to permit detection in the very low concentrations known to be toxic to aquatic organisms (10). The lack of adequate analytical techniques is a serious frustrating factor in the determinations of concentrations of milling reagents at various points in the mill circuit or in the tailings ponds and final effluents. Some of the reagents remain bound to the mineral particles and thus never enter the tails. Others do not bind to ore particles, and remain unaltered in the final tails. In those mills having a copper circuit, the addition of SO_2 to separate the lead and copper minerals also effects the release of considerable quantities of xanthate collectors, and these may be detected in the thickener overflows under certain conditions. Degradation rates vary considerably(11) and may be affected by pH, temperature, or redox.

Addison, *et al*(12) have provided some early data related to effluents in New Brunswick operations dealing with sulfide ores. These researchers identified xanthate residuals of 0.2 to 1.2 ppm, dithiophosphate residuals in the range of 0.3 to 2.7 ppm and isopropyl ethylthionocarbamate residuals of 1.8 ppm in mill effluents. A limited number of analyses performed on effluents of one mill in the New Lead Belt have shown xanthate concentrations of 0.3 ppm in thickener overflows, but undetectable levels (less than 0.1 ppm) in final effluent. Long chain alcohols have been estimated in final effluent to exceed 200 ppm on one occasion, and on other occasions were undetectable (less than 10 ppm).

More detailed data should be sought relative to final effluent concentrations of these toxic substances, and greater care should be exercised in elimination of those circumstances which would permit toxic concentrations of milling reagents to enter receiving streams. In those situations where problems exist and mill effluents are suspect, every precaution should be taken to insure adequate treatment of tails and effective isolation of those mill effluents known to contain toxic levels of reagents. Where possible, reagents should be selected on the basis of favorable degradability properties or their reduced toxicity.

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TABLE 1. Principal Milling Reagents Employed By New Lead Belt Mills

	Mill A No Copper Circuit	Mill B With Copper Circuit
Frother	Methyl Isobutyl Carbinol Propylene Glycol-methyl Ethers	C_6-C_9 Aliphatic Alcohols
Promoters	Sodium-diethyl-dithiophosphate Sodium-isopropyl-ethylthionocarbamate	Sodium-isopropyl-ethylthiono-carbamate
Collectors	Sodium Ethyl Xanthate	Sodium Isopropyl Xanthate
Zinc Depressant	$ZnSO_4$ + Cyanide	$ZnSO_4$ + Cyanide
Zinc Activator	$CuSO_4$	$CuSO_4$
Iron Depression and pH Control	Lime	Caustic Soda
Lead Depression and Copper Flotation	--	SO_2 + Starch

TABLE 2. Mill A: Heavy Metals in Tadpoles From Meanders

	PPM		
	Pb	Zn	Cu
I. 100 Yards Down Meanders			
Eviscerated Body	213	256	20
Intestine & Contents	4419	2926	234
II. At Cave Hollow Jct.			
Liver & Heart	22	67	91
Eviscerated Body	93	240	15
Intestine & Contents	7329	4696	260
Total Body	4139	2808	169

TABLE 3. Mill A: Heavy Metals in Bluegills From Meanders

	PPM		
	Pb	Zn	Cu
Muscle	1	45	11
Bone	104	152	21
Skin & Scales	132	229	21
Intestine & Contents	390	381	53
Gills	161	109	19
Total Body	84	157	24

TABLE 4: Mill A: Heavy Metals in Bass From Meanders

	PPM		
	Pb	Zn	Cu
Muscle	<1	30	13
Bone	142	89	22
Skin & Scales	194	176	27
Intestine & Contents	259	279	159
Gills	160	105	24
Total Body	7	117	28

TABLE 5. Mill A: Heavy Metals in Bluegills Final Tailings Pond (Spring)

	PPM		
	Pb	Zn	Cu
Muscle, Bone, Skin & Scales	20	82	7
Intestine & Contents	626	437	37
Washed Intestine	9	77	13
Liver	<1	83	12
Ovaries	<1	98	8
Gills	52	93	7
Total Body	50	100	10

TABLE 6. Mill A: Heavy Metals in Bluegills Final Tailings Pond (Summer)

	PPM		
	Pb	Zn	Cu
Muscle	<1	42	20
Bone	15	77	14
Skin & Scales	22	121	20
Intestine & Contents	30	61	16
Gills	38	82	16
Total Body	32	98	13

TABLE 7. Mill B: Stilling Pool: Heavy Metals in Bluegills

	PPM		
	Pb	Zn	Cu
Muscle & Bone	17	91	2
Gills	28	90	2
Intestine & Contents	22	151	10

TABLE 8. Mill B: Final Effluent: Heavy Metals in Bluegills

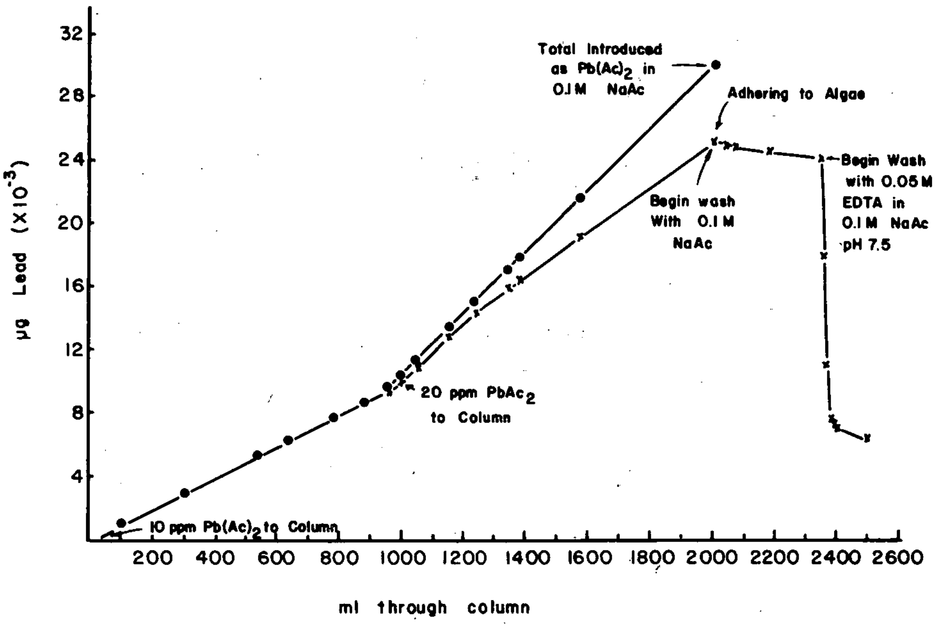
	PPM		
	Pb	Zn	Cu
Muscle & Bone	<1	90	3
Gills	<1	80	1
Intestine & Contents	<1	81	6
Total Body	6	165	3

TABLE 9. Toxicity of various milling reagents, 96 hour TL_m.

Reagent	Fathead Minnow	Emerald Shiner	Water Flea	Bluegill	Catfish	Snails	Tadpoles	Crayfish	Golden Shiners	Algal Photosynthesis
Methyl Isobutyl-carbinol	100-1000	-	-	-	-	-	-	600-1000	-	-
Propylene Glycol-methyl ethers	> 1000	-	-	> 1000	-	100-500	-	> 100		-
Long Chain Aliphatic alcohols	100-1000	-	-	50-100	100-500	100-1000	10-100	10-100	< 23	100-200
Potassium or Sodium Amyl Xanthate	1.8-18	10-100	.1-1.0	100-200	-	1.0-10	-	100-200	-	100-200
Sodium Isopropyl Xanthate	.18-1.8	.01-.1	.1-1.0	.01-.1	> 10	10-100	10-100	1-10	-	10-100
Sodium Ethyl Xanthate	.18-1.8	.01-.1	.1-1.0	10-100	-	100-1000	-	100-500	-	100-200
Isopropyl Ethyl Thionocarbamate	10-100	-	-	10-50	10-100	10-100	-	100-200	-	100-200
Sodium Diethyl-dithiophosphate	-	-	.1-1.0	660-1000	-	> 1000	-	-	-	-
Minerec B (Dixanthogen)	-	-	-	1.0-10	-	100-200	-	-	-	-
Aero-130 Thiocarbanalide	-	-	-	> 1000	-	100-1000	-	-	-	-

Data on Fathead Minnows, Emerald Shiners, and Water Fleas from Hawley (Ministry of Environment, Ontario); on Catfish from U.S. Department of Interior Fish Pesticide Lab (Columbia, Missouri)

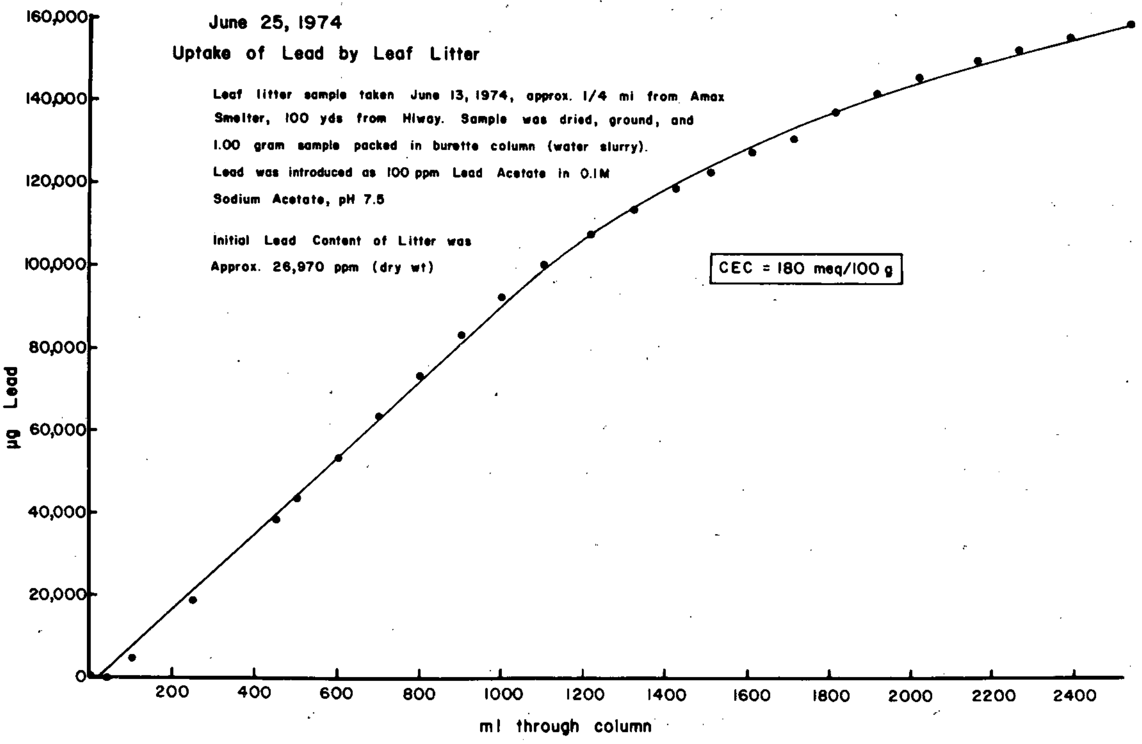
FIGURE 1



Cation Exchange Using Algae (40 g wet weight Spirogyra) Column

Pretreated with 400 ml 0.1 M NaAc

FIGURE 2


June 25, 1974

Uptake of Lead by Leaf Litter

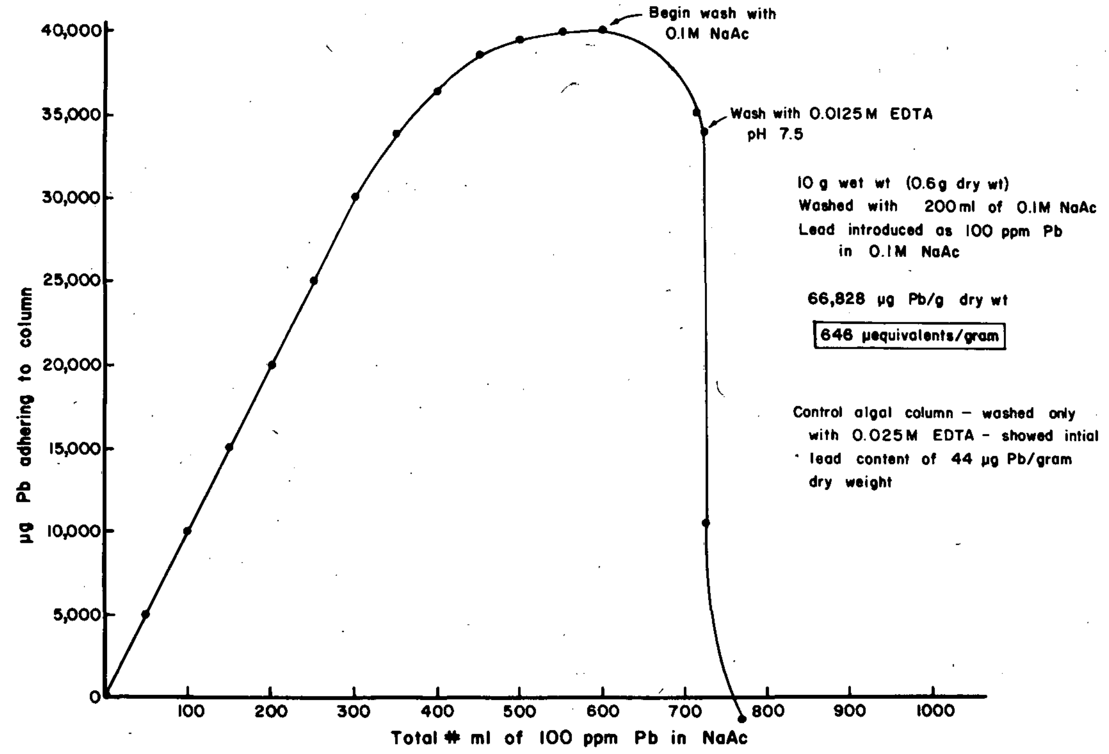
Leaf litter sample taken June 13, 1974, approx. 1/4 mi from Amax Smelter, 100 yds from Hiway. Sample was dried, ground, and 1.00 gram sample packed in burette column (water slurry). Lead was introduced as 100 ppm Lead Acetate in 0.1M Sodium Acetate, pH 7.5

Initial Lead Content of Litter was Approx. 26,970 ppm (dry wt)

CEC = 180 meq/100 g

FIGURE 3

Mixed Culture - Rhizoclonium and Spirogyra - Frisco Pond



10 g wet wt (0.6g dry wt)
Washed with 200 ml of 0.1M NaAc
Lead introduced as 100 ppm Pb
in 0.1M NaAc

66,828 µg Pb/g dry wt

646 µequivalents/gram

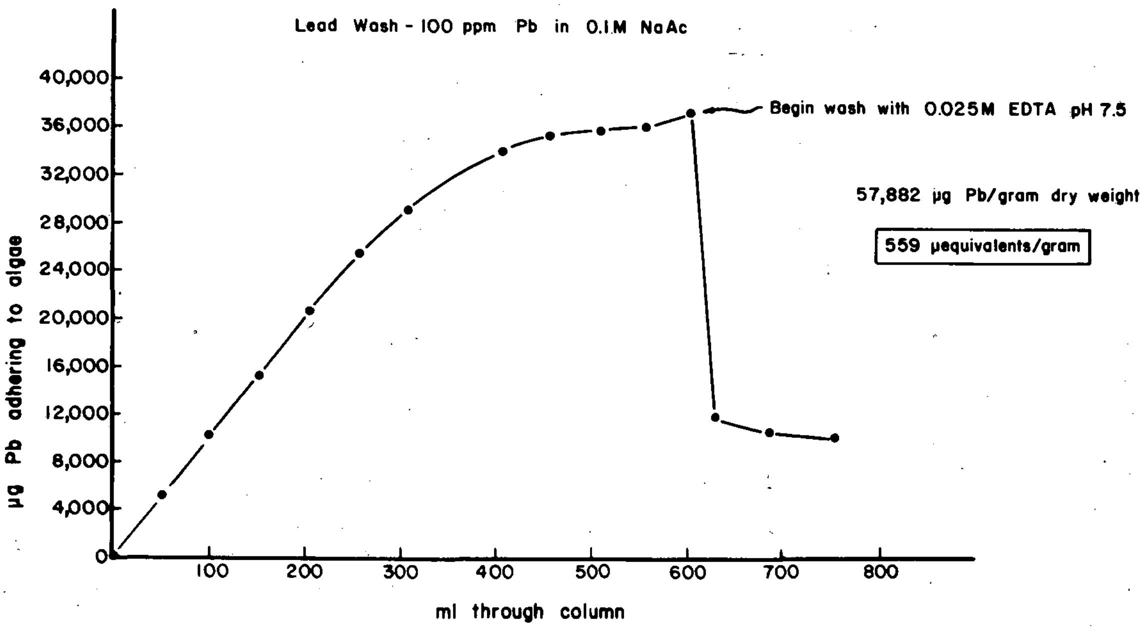
Control algal column – washed only with 0.025M EDTA – showed intial lead content of 44 µg Pb/gram dry weight

FIGURE 4

5 Grams (wet weight) Autoclaved Algae
Rhizoclonium and Spirogyra from Frisco Pond

Washed in 0.1M NaAc

Lead Wash - 100 ppm Pb in 0.1M NaAc



57,882 µg Pb/gram dry weight

559 µequivalents/gram

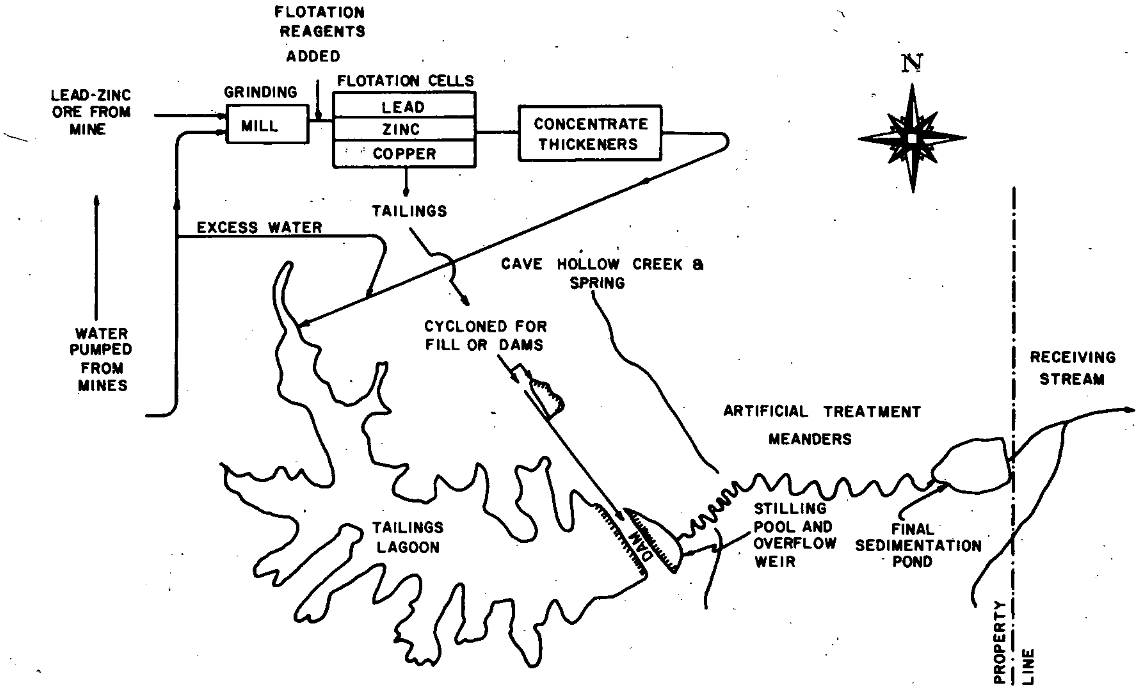


FIGURE 5. Schematic of Tailings System, Mill A.

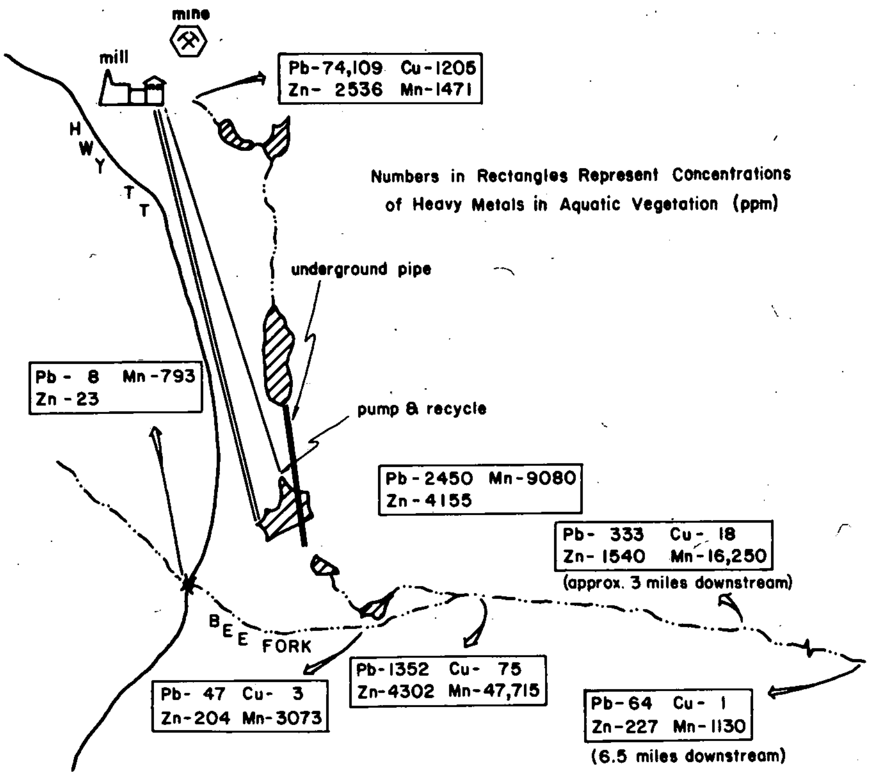


FIGURE 6. Schematic of Tailings System, Mill B.

HUMAN UPTAKE OF DIETARY AND ATMOSPHERIC LEAD: STABLE ISOTOPE AND BALANCE STUDY*

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Abstract

Four healthy adult male volunteers have been maintained in a hospital metabolic unit for periods up to six months with controlled diets and environments in order to assess lead absorption, excretion, and physiological pools under typical urban conditions. The subjects ate constant diets selected to be low in lead content supplemented with stable isotopes of lead, which serve as a non-radioactive tracer distinct from other (atmospheric and internal) sources of lead. The concentration and isotopic composition of lead in the diet, feces, urine, blood, hair, nails, sweat, bile, gastric and pancreatic secretions, and bone were measured by mass spectrometric isotope dilution analysis.

It was found that the alimentary absorption rates of both the tracer lead nitrate and food lead varied among the individuals (6 to 14%). Absorption rates as high as 50% were seen when lead nitrate or sulfide were administered while fasting.

The kinetics of lead within the body could be adequately described by a three compartment model. Balance considerations and the incomplete labelling of blood by a dietary source indicate a respired input of about 17 micrograms per day, about 1/3 of the total daily input. This was verified by placing one subject in a room with filtered air and observing the decrease in his blood lead.

Additional results indicate erythrocyte uptake of lead to be independent of their age. Facial hair was seen to reflect previous blood lead levels.

Introduction

Despite the great concern over lead poisoning there is a lack of data concerning normal human lead metabolism during typical urban conditions. In this study the absorption, excretion, and physiological pools of lead were studied with the use of stable isotope tracers, administered under conditions of controlled dietary and atmospheric exposure. Such a technique has the advantage of allowing kinetic studies without abnormally high lead intake and without the introduction of radioactivity. Another significant benefit of this approach is that the tracer lead under consideration may be decoupled from lead contamination originating in the laboratory because of their markedly different isotopic compositions. Thus the tracer lead data are independent of any blank or yield corrections.

The general methodology involves maintaining a healthy adult male volunteer in a hospital metabolic unit for periods of up to six months with controlled diets consisting of foods selected to be low in lead content. This is supplemented at each meal with a stable isotope tracer, usually ^{204}Pb as nitrate, to provide a total lead intake approximating the pre-study level while providing an input of lead distinct from other (atmospheric or internal) sources of lead.

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*Work supported by the National Science Foundation Research Applied to National Needs (RANN)

The concentration and isotopic composition of lead in the diet, feces, urine, blood, hair, nails, sweat, bile, gastric and pancreatic sections, and bone were measured by mass spectrometric isotope dilution analysis. Simultaneous metabolic balance studies were carried out for calcium, phosphorus, nitrogen, and magnesium.

Results obtained from the first subject were reported at last year's meeting and subsequent publications (1, 2,3) included preliminary results from a second subject. Today I would like to present a compilation of the results to date from four subjects stressing these areas of interest:

1) Gastrointestinal absorption of lead, especially as it varies with mode of administration among individuals.

2) Compartmental and balance analyses of lead physiology, stressing an assessment of respired input.

3) Red blood cell uptake of lead from plasma.

4) Delayed appearance of tracer lead in facial hair.

Gastrointestinal Absorption of Lead

During the long term studies ^{204}Pb as nitrate was substituted for approximately $\frac{1}{2}$ of the lead in the subjects' pre-study diet. This soluble lead was administered in the midst of each meal of the constant low-lead diet. The absorption rate of the ^{204}Pb was assessed from the difference between dose and fecal output, which was pooled into 10 day periods. It should be noted that at the outset no tracer lead is yet present in the bile or other digestive secretion, so all of the fecal tracer is simply unabsorbed lead. There is no absorption and subsequent re-secretion of tracer lead until several tens of days later, when it is seen in the sampled secretions and as an apparent decrease in absorption rate. In contrast to this situation, determining the absorption rates for food lead is complicated by the sizable (10-15 μg/day) and rather poorly measured quantity of unlabelled lead in feces which is contained in digestive secretions. Also food lead is isotopically indistinguishable from laboratory contamination lead. For these reasons absorption rates are more precisely known for isotope tracers.

In addition to these long term studies, several shorter investigations were undertaken. Several stable isotopes, each in a different chemical form, were fed simultaneously to three subjects, both with and without food, about 75 μg each of ^{204}Pb, ^{206}Pb, and ^{207}Pb. Feces were collected for up to 20 days to measure absorption. Blood and urine were also analyzed to see whether the lead not in the feces was actually absorbed, not simply lodged in the gut or inadvertently uncollected. Table 1 displays a summary of absorption rates as percentages for the several subjects for each chemical form, taken with food and while fasting. Absorption is measured in two ways. The first column shows percentages derived from fecal data, and the second column shows absorption rates based on comparing the appearance in the blood of the listed form of lead with the appearance of the isotope as nitrate. That the two columns are in general agreement shows that fecal collections were complete and that the response seen in the blood is proportional to the amount absorbed from the diet.

Several trends are apparent in the data. Food lead and nitrate lead eaten with food are absorbed at about the same rate for each subject, 6 to 14%, depending on the individual, a wide variation but within the range found by Hursch and Suomela working with radio-isotopes[4]. Lead cysteine, when eaten with food, has a similar absorption rate. It appears as if food lead and the soluble tracer lead are, at least partially, isotopically equilibrated and then handled in the gut in about the same way.

A striking result is that the absorption of lead salts ingested while fasting is markedly higher, up to 50%.

The presence of food inhibits lead absorption by up to 8-fold. Perhaps substances within food compete with lead for absorption sites or perhaps unabsorbable portions of food bind the lead. For lead sulfide, there appears to be considerable variation among the subjects. It should be noted that subject B may have been hyperacidic and secreted stomach acid even on an empty stomach. He had a history of intermittent gastritis. So, perhaps in this subject the otherwise insoluble lead sulfide was dissolved in hydrochloric acid and then absorbed.

Table 1.

GASTRO-INTESTINAL ABSORPTION

SUBJECT	MODE	ABSORPTION % DIET-FECES	 BLOOD RESPONSE
A	Food Lead	11	
B	Food Lead	7	
D	Food Lead	~12	
A	Nitrate with Food	8.5	
B	Nitrate with Food	6	
C	Nitrate with Food	14	
D	Nitrate with One Dose	11	
D	Nitrate with Every Meal	13	
B	Cysteine with Food	6.	6
B	Fasting Nitrate	40	35
B	Fasting Nitrate	28	25
C	Fasting Nitrate	36	41
D	Fasting Nitrate	43	35
B	Fasting Cysteine	30	22
B	Fasting Sulfide	52	45
B	Fasting Sulfide	45	41
C	Fasting Sulfide	14	14
D	Fasting Sulfide	15	10.5

This data shows that gastrointestinal absorption of lead salts is not a simple function of lead intake, but varies among subjects and depends on chemical form. There is also a strong tendency for increased absorption when lead is eaten without food.

Lead Balance and Respired Input

The experimental design, which involves periodic analysis of the constant dietary input and complete collection of all body outputs, allows determination of a lead balance. The results for the two completed long term studies are shown in table 2. Diets were measured every tenth day and feces and urine were pooled into ten day collection periods. The tabulated numbers are for total lead, common lead plus the added isotope tracer. Most of the lead output is in urine but "others", hair, nails, and desquamated skin, were also measured.

Table 2.

Lead Balance Data (μg/day)

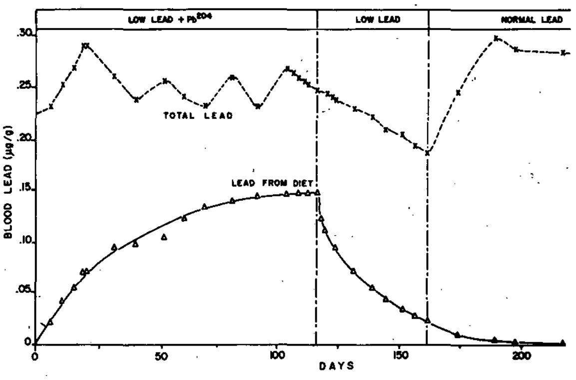
Subject	Days	Input Diet	 Diet-Feces	Output urine	 others	Balance
A	116	362	26	38	4	-16±4(SD)
B	124	366	12	27	4	-19±3(SD)

Both subjects were apparently and consistently in negative lead balance. That is they put out more lead than was provided in the diet. However, during this balance period, over 100 days, their calcium and phosphorous balances were positive, and their blood lead levels did not fall. We therefore believe that the subjects were in neutral lead balance and the excess output represents the size of a respired input. Three independent lines of reasoning support this conclusion.

(1) An airborne input of this magnitude is consistent with the observed concentrations of air-lead, about two micrograms per cubic meter, using generally accepted values for ventilation and particle retention rates. Both subjects smoked eight cigarettes per day of a brand having only one microgram of lead per cigarette, resulting in only about one microgram of lead per day being absorbed from this source[5]. The other 17 or so micrograms represent absorption of lead from ambient urban air.

(2) The second reason to believe that the subjects were receiving this much lead from the air each day is that the isotopic composition of their blood leads never became identical with their dietary input alone. Figure 1 shows the blood lead concentration for different species of lead for subject A. This upper curve shows the total amount of lead in blood and

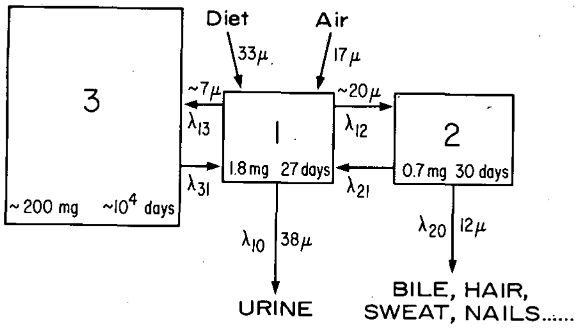
Figure 1.



this lower curve shows how much of it has the isotopic composition of the labelled dietary source. The difference represents unlabelled lead, either lead in the subject's body from before the study began or lead from an unlabelled source. It is noteworthy that the blood lead did not become entirely labelled with dietary lead even though duration of study with Pb^{204} exceeded several mean-lives of the blood compartment. This suggests input into the blood from other non-labelled sources of lead, the skeleton and/or the atmosphere. Since the blood was at most about one-half labelled with dietary lead, a strict upper limit of about one-half can be set on the fraction of daily lead intake which was derived from an unlabelled source.

The question then is how much of this unlabelled lead is from the atmosphere and how much is from a source within the body. This was approached by considering the blood to exchange lead with two body pools, as shown in figure 2, also based on subject A. The second pool has a mean life comparable to blood. Its existence is suggested by the slow labelling of secretions. Another larger one with a much longer residence time is perhaps in hard tissue. Tracer data makes it possible to measure the exchange rate of blood with each of these hypothetical pools. By using this model, one can project the growth curve for labelled blood lead to a time when a steady state is achieved in labile body pools. For the first subject, 60% of the blood would come to resemble an unlabelled source, either internal or external. Analysis of the flux of lead out of blood indicates about nine micrograms per day of lead enters the skeleton or other long term pools from the blood. Since medical examination revealed no evidence of bone loss and since calcium and phosphorous balances were not negative, it may be inferred that the skeletal mass was in a steady state. If blood and skeletal lead were also in a steady state, it can be concluded that these deeper pools yield approximately the same amount of unlabelled lead back to the blood, nine micrograms per day for subject A and 5 for subject B. Thus, the remaining amount of the total unlabelled assimilated lead was derived from the atmosphere, 17±5 micrograms per day for subject A and 16+6 micrograms per day for subject B.

Figure 2.

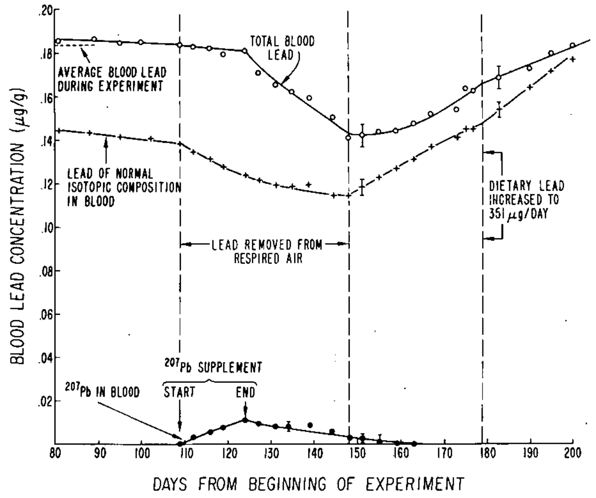


(3) The third independent reason to believe a daily respired input of about 17 micrograms per day is the response of subject B to a lowering of the air lead content and observing changes in blood lead. This was accomplished by having the subject stay 23 hours each day for 40 days in a room with two air purifiers, each consisting of a blower pulling room air through a fiberglass pre-filter, a HEPA fiber filter, and a bed of activated charcoal, recirculating the air

in the room every 3 minutes. The room entrance was provided with a double door air lock. Both particulate, aerosol lead salts as well as organic vapor lead levels were measured and averaged 0.07 and 0.05 micrograms per cubic meter, respectively. After this period the subject was moved to another room across the hall with open windows, resulting in a higher lead exposure.

During the first 15 days in the clean air room lead-207 nitrate was added to the diet so that the subject's total daily lead intake from all sources would not change, labelled dietary lead being substituted for unlabelled airborne lead on a nearly atom-for-atom basis. This was done so that the total blood lead would not fall, so that even if there were some homeostatic mechanism the body would not, for example, mobilize skeletal lead which would be isotopically indistinguishable from air lead. Then both the 204 and 207 supplements were withdrawn and the subject continued to breath "lead-free" air for 25 more days. Figure 3 shows the results of this procedure.

Figure 3.



It can be seen that the normal, unlabelled blood lead fell as a result of breathing "lead-free" air. The rate of change of blood lead can be equated to the change in daily intake by a proportionality factor related to the size of the subject's lead pool. This proportionality factor was obtained from tracer data where a measured amount of tracer is absorbed and a change is seen in the blood concentration of the tracer.

From this change in slope in unlabelled blood lead, it appears that as he began breathing less lead, his daily intake dropped by 14.6 μg per day and when he left for the open-air room it rose by 18.3. This filtered air technique will soon be applied to another subject.

It should be remembered that this balance discussion is based on measurements of lead of largely normal isotopic composition, and, although small yield and blank corrections (about 5%) have been made, there is inherently less certainty about these results than about any conclusions based on tracer measurements alone.

In summary, the apparent negative lead balance, the incomplete labelling of the blood lead with a dietary tracer, and the response to breathing filtered air all suggest a daily intake of about 17 micrograms per day of lead from the ambient urban atmosphere.

Red Blood Cell Uptake of Lead

An auxiliary study was conducted to observe in vivo the erythrocyte uptake of lead from blood plasma. It has been known from in vitro studies, some with radioisotopes, that 90-95% of the lead added to whole blood will reside with the red blood cells and that the equilibrium distribution is reached within several hours[6,7]. This affinity of lead for red cells was verified in one of the hospitalized subjects by sampling plasma and red cells 6 hours after oral ingestion of ^{204}Pb nitrate on three separate occasions, as shown in table 3. This data shows that in each case only about 10% of the blood lead is in the plasma.

It was also possible to separate red cells by age by centrifugation, making use of the increase of density with age[8]. Such a separation was attempted on three occasions with subject B. The results are shown on table 4. During the first attempt (day 1) no means were employed to verify age separation, but on days 148 and 174 a reticulocyte count was performed on each red cell fraction to see if any age differential settling had ocurred. On day 148 only an incomplete separation had occurred. A third attempt was made (day 174) in which the heparinized blood was allowed to stand for 20 minutes before centrifuging. This resulted in a more clear-cut age separation, demonstrating that there is no markedly preferential uptake of lead by red cells by age. Lead does not enter a red cell only while it develops in the marrow, as is the case for iron[9]. Rather it appears that circulating red cells are able to absorb and desorb lead throughout their lives.

Table 3.

Lead in Whole Blood, Red Cells and Plasma

Day	Whole Blood	Red Cells		Plasma	
	(μg/g)	(μg/g)	Fraction	(μg/g)	Fraction
1	.171	.36	88%	.038	12%
112	.179	.38	88%	.040	12%
148	.137	.29	89%	.037	11%

Table 4.

Age Dependence of Red Blood Cell Lead Content

Day	Top(younger)Layer		Bottom(older)Layer	
	Pb^{204}(μg)	Reticulocyte count(%)	Pb^{204}(μg/g)	Reticulocyte count(%)
1	.00049		.00043	-
148	.045	1.3±.2	.044	1±.2
174	.047	1.3±.3	.047	.3±.1

To pursue this in more detail a third investigation involved separating red cell content from cell debris to localize the lead. *In vitro* studies with radioactive lead have demonstrated that 90% of the lead in red cells is bound to the cell contents[10], specifically to hemoglobin. This was was verified *in vivo* by lysing red cells with distilled water, vigorous centrifugation and washing of the debris, and drying. The dried stroma and the cell contents were each analyzed for isotopic lead content; the results are shown in table 5. It appears that most of the lead is in the cell contents. This result is in close agreement with the *in vitro* studies of Stover[10] and Barltrop[11]. It is also apparent that the concentration of lead in the debris is five times as great as that of the cell contents, although most of the lead is in the contents, which makes up 98% of the cell. This observation is interesting in light of the red cell's biochemical alterations associated with lead poisoning: Red cells become more mechanically fragile, their life-span is shortened non-randomly, the sodium and potassium ATPase activity of the membrane is decreased, glucose consumption increases, and osmotic resistance increases[12,13]. All of these observations are associated with membrane phenomena.

Table 5.

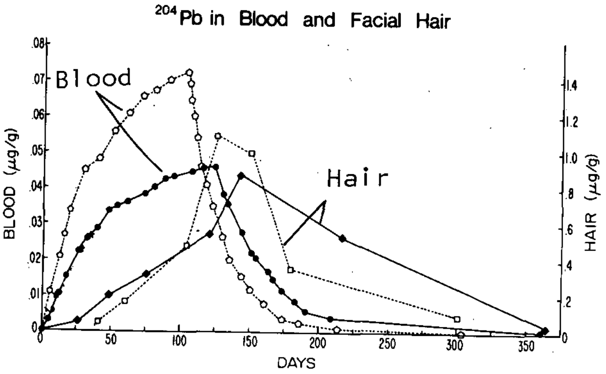
Lead in Red Blood Cell Components

	Whole RBC	Debris	Cell Contents
Fraction of mass	100%	2%	98%
Lead Concentration (μg/g)			
Pb^{204}	0.076	0.145	0.069
Total Lead	0.330	1.60	0.307
Fraction of Lead			
Pb^{204}	100%	4%	96%
Total Lead	100%	10%	90%

Tracer Lead in Hair

I would now like to discuss another of our findings: the delayed appearance of tracer lead in facial hair. As part of the long term metabolic studies, all shed body hairs were collected by vacuuming clothing, bedding, and shower drain screens. Scalp hair was marked at the outset and cut later to estimate the mass of hair production. Periodically facial hair was also collected with an electric razor, and its lead isotope content was measured. The data for two subjects is shown on Figure 4.

Figure 4.



This is a plot of the ^{204}Pb concentration in blood, displayed on the left hand axis, and in facial hair, referring to a less sensitive scale on the opposite side. The horizontal axis is time in days from the start of the ^{204}Pb diet. The data for subject A is open symbols; for B, filled symbols. The tracer content of the blood rose quickly and fell abruptly when the ^{204}Pb was discontinued. The maximum concentration of tracer lead in hair appears about 30 days after the maximum labelling of the blood. However, hair takes only a few days to grow through the skin. Furthermore, the hair pattern does not look like a simple displacement or time delay of the blood picture. Rather, the hair data shows a more gradual appearance and disappearance of the tracer. A similar pattern was presented last year by Drs. Berg and Giovanelli discussing mercury in lengths of scalp hair[14]. Their detailed analysis of portions of several hairs suggested to them that their broadened pattern seen in bunches of hair is the result of difference in rates of growth or relative displacement during sampling of adjacent hairs. However, for facial hair where adjacent hairs grow at nearly identical rates and where the samples represent simultaneously produced hair another explanation is required. The hair might also be considered the output from another physiological lead pool, fed by the blood. Before the hair is completely labelled, this pool, in addition to the blood must become totally labelled. This pool has the effect of accumulating lead from the blood and producing hair reflecting a weighted average of blood lead levels over its recent history. There may also be a time delay before hair leaving this pool is sampled. Tentative modeling of this pool suggests a mass of 10 or 50 grams and a mean residence time of 20 to 100 days. This pool is perhaps located in the bulbs of the hair follicles. This effective time delay of about 30 days is similar to the delay seen in the labelling of hair with radio-sulfur administered as cysteine or methionine[15]. These amino acids and lead are probably both incorporated together into hair keratins. These results suggest that elevated lead levels in hair may reflect blood lead levels about a month earlier and that hair lead values be interpreted in light of the physiological processes which produce it.

These experiments demonstrate that stable isotopes are a useful tool in studying the kinetics of human lead physiology. We have applied them to healthy adult male volunteers and hope to soon expand our experience by examining infants and lead poisoned workers.

Acknowledgement

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LETHAL AND TERATOGENIC EFFECTS OF METALLIC POLLUTANTS ON VERTEBRATE EMBRYOS*

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Abstract

In order to determine the sensitivity of embryogenesis to metallic trace contaminants, fish and avian embryos were treated continuously until hatching with sodium arsenite and chloride salts of cadmium, lead, mercury and methyl mercury. Compared to survival in control populations, all heavy metals produced significant degrees of lethality and/or gross anatomical anomalies at 10 ppb or less. Treatment with methyl mercury at 10 ppb produced 66%, 12% and 2% mortality rates in populations of rainbow trout, channel catfish and goldfish embryos, respectively. In addition, 20% of the surviving trout embryos bore gross morphological deformities. Lethality or severe developmental impairment occurred in 53% and 33% of trout embryos treated with 5 ppb and 2 ppb methyl mercury. Rainbow trout and chick embryos suffered 10-22% lethality when exposed to 1 ppb of either inorganic or methyl mercury. Lead and cadmium at 1 ppb produced 26-34% lethality in chick embryos. Arsenic was found to be highly toxic to chick embryos, producing 35% mortality at a concentration of 1 ppb. However, arsenic-induced lethality was significantly lower in the trout embryo, with a TL_{50} value of approximately 0.5-0.75 ppm. It appears that eggs and/or embryos of homeothermal species are much more susceptible to arsenic than those of poikilotherms. Survival values reported above were based upon all embryos which lived to complete the hatching process, including those bearing gross teratologies. The latter often comprised 1/3 or more of surviving populations.

Based on a comparison of survival values approaching threshold (90-95% hatchability), embryos of the trout and catfish, in respective order, were approximately 50 and 10 times more sensitive to mercury than goldfish embryos. This differential sensitivity to mercury correlates with differences in both egg size and hatching time of these species, indicating that fish with larger eggs and/or longer periods of embryological development are more susceptible targets of mercurial poisoning.

Concerning the toxic effects of cadmium, lead and mercury, the embryonic stage appears to constitute the critical "sensitive link" in the vertebrate life cycle. Reproductive potential of vertebrate populations may be severely restricted, through the production of embryonic mortality and teratogenesis, by trace levels of metallic pollutants which are sublethal to adult animals. Environmental standards based on tolerances of adult forms likely do not provide adequate protection for sensitive developmental stages.

Results of this investigation further indicate that vertebrate embryos are particularly suited for use as sensitive bioassay and bioindicator organisms with which to 1) determine reliable protective limits for environmental trace contaminants, and 2) monitor the quality of environmental resources.

Introduction

During the past few decades, investigators have worked largely with adult organisms in assessing the effects of environmental trace contaminants upon animal communities. As a consequence, comparatively little information exists concerning the toxicity of trace contaminants to embryonic, larval or immature stages of most animal species (1). In an initial study of vertebrates, Birge and Just (2) found mercury and certain other metals to be substantially more toxic to embryonic stages than to adults. Should developmental processes prove to represent the most sensitive target site(s) of metallic poisoning, then it follows that many natural animal populations could be reduced or extinguished through a loss of reproductive potential (e.g., embryonic mortality, teratogeny) effected by concentrations of trace metals considered safe or sublethal for adult organisms.

Operating upon the premise that environmental standards for metallic pollutants should be established at levels which will insure "safe limits" for the most "susceptible stage(s)" in the life history of organisms, we have undertaken a series of investigations on the biological effects of trace metals on development and reproduction in piscine, amphibian and avian species.

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The principal objectives are to 1) determine the toxicity of selected metals to different embryonic stages, 2) analyze for possible antagonistic, additive or synergistic effects of combinations of metals upon developmental processes, and 3) ascertain the extent to which metals may accumulate in vertebrate eggs prior to ovulation and the degree to which such preaccumulated egg metals diminish fecundity and embryonic survival. The present paper, which deals in part with the first of these objectives, concerns the sensitivity of chick and fish embryos to arsenic, cadmium, mercury and lead.

Procedures

Toxicity experiments were performed on embryos of the domestic fowl (Gallus domesticus, White Plymouth Rock strain), rainbow trout (Salmo gairdneri), channel catfish (Ictalurus punctatus), goldfish (Carassius auratus) and the largemouth bass (Micropterus salmoides). Populations of chick and fish embryos were treated with a number of heavy metals, including chloride salts of cadmium, lead, mercury and methyl mercury. In addition, chick and trout embryos were treated with sodium arsenite, and sodium selenate was administered to chick embryos. Treatment was continuous through hatching, giving exposure periods of 3, 4, 6, 21 and 24 days for goldfish, bass, catfish, chick and trout embryos, respectively. Metals were administered to chick embryos by a new method of yolk sac injection recently described by Birge and Just (2). Fish embryos were exposed to metals in aqueous culture by procedures previously stated (2). Concentrations reported for metallic test solutions were based only on actual metal content.

In computing survival frequencies, each datum point was determined on a minimum of 250 observations for fish embryos and 100 observations for chick embryos. All survival values reported were based on frequencies of hatchability for populations of experimental embryos/hatchability in corresponding control populations.

Results and Conclusions

Our toxicity studies on the chick embryo are summarized in Table I. Selenium, arsenic and cadmium produced quite similar responses, giving survival rates (hatchability) at 1 ppb of 64-66%, and an approximate TL$_{50}$ value of 0.01 ppm. These extremely embryopathic metals also produced substantial percentages of gross embryological anomalies among survivors (e.g., hydrocephaly, and other brain deficiencies; absent eyes; various skeletal defects), with frequencies ranging from 11% and 29% for selenium and arsenic at 0.5 ppm to 33% for cadmium at 1.0 ppm (Table I).

Lead, mercury and methyl mercury also were highly toxic to chick embryos, giving survival rates of 74-78% when used at 1 ppb (Table I). Survivors treated with these metals again displayed high frequencies of anomalies. Teratogenic development for all metals diminished with reduced concentrations, resulting in low frequencies of occurrence at 0.01 ppm. Minor anomalies,

TABLE I. Toxicity of metals to chick embryos.

Concentration^3 (ppm)	Percent Survival^{1,2}					
	Se^{+6}	As^{+++}	Cd^{++}	Pb^{++}	CH$_3$Hg$^+$	Hg^{++}
0.001	64	65	66	74	78	78
0.010	43	54(2)	55	73(1)	71	73
0.050	38(7)	47(6)	48	74(7)	65(4)	64
0.100	30(9)	43(17)	41(6)	63(10)	54(7)	61(2)
0.500	24(11)	18(29)	25(15)	57(16)	45(11)	56(3)
1.000	0	0	8(33)	52(14)	26(15)	51(8)
5.000	0	0	0	23(24)	23(22)	37(12)
10.000	0	0	0	0	10(25)	8(33)
50.000	0	0	0	0	0	0

[1] Each percentage represents frequency of survival for 100 experimental embryos/100 controls.

[2] Percentages of surviving embryos which bear gross teratologies are given parenthetically.

[3] Metals were administered by yolk sac injection in amounts calculated to dilute egg yolk to specified concentrations.

TABLE II. Survival of trout, catfish, goldfish and bass embryos treated continuously with methyl mercury.

Concentration (ppm)	Percent Survival[1,2] Trout(24)	 Catfish(6)	 Goldfish(3)	 Bass(4)
0.001	90(3)	100	100	98
0.002	76(9)	-	-	-
0.005	57(10)	94	97	94
0.007	46(17)	-	-	-
0.010	34(20)	88	98	84
0.025	29(35)	66	-	-
0.050	0	33	95	79
0.075	-	-	68	73
0.100	0	24	50	64
0.250	-	-	26	54
0.500	0	4	11	21
1.000	0	0	0	1
5.000	0	0	0	0
10.000	0	0	0	0

[1] Each percentage based on frequency of survival for 250 experimental embryos/250 controls, and percentages of surviving trout embryos which bear gross teratologies are given parenthetically.

[2] Hatching time (exposure period) is given in parentheses after each species.

TABLE III. Correlation of percent survival with exposure time for goldfish and trout embryos treated with methyl mercury.[1]

CH_3Hg^+ in ppm	Exposure Time in Developmental Days[2] Goldfish 1	 2	 3	 Trout 3	 6	 9	 12	 15	 18	 21	 24	 27
0.001	100	100	100	95	92	91	91	90	90	90	90	90
0.005	100	100	99	91	82	74	69	63	60	58	57	57
0.010	100	100	97	75	66	54	48	42	39	34	33	33
0.050	100	97	94	59	43	12	6	0	0	0	0	0
0.100	70	61	47	13	0	0	0	0	0	0	0	0
0.500	40	6	2	0	0	0	0	0	0	0	0	0
1.000	28	3	0	0	0	0	0	0	0	0	0	0

[1] Data from Birge & Just, 1974.

[2] Hatching occurred on day 3 in the goldfish and on day 24 in the trout. Data given on day 27 for the trout represent percent survival at 3 days posthatching.

as well as physiological and behavioral impairments, were not tabulated in this study.

Embryos of four species of fish, including trout, catfish, goldfish and bass, were treated continuously with methyl mercury (Table II). Trout embryos proved to be the most sensitive of this group, with frequencies of hatchability of 90%, 76%, 57% and 34% at concentrations of 1, 2, 5, and 10 ppb, respectively. Gross anomalies affected 35%, 20%, 9% and 3% of surviving trout alevins exposed to concentrations of 25, 10, 2 and 1 ppb methyl mercury. It should be emphasized that minor morphological defects, physiological impairments and behavioral deviations were not included in these figures. Though such factors remain to be fully investigated, initial observations suggest that appreciable numbers of trout alevins which survive treatment with mercury at 1-2 ppb

TABLE IV. Toxicity of metals to trout embryos (*Salmo gairdneri*).

	Percent Survival[1]			
Concentration (ppm)	CH_3Hg^+	Hg^{++}	Cd^{++}	As^{+++}
0.001	90 (3)	90 (2)	98 (2)	-
0.002	75 (9)	72 (8)	-	-
0.005	57 (10)	59 (12)	97 (7)	-
0.007	46 (17)	46 (19)	-	-
0.010	34 (20)	34 (22)	97 (6)	100
0.025	29 (35)	24 (43)	96 (7)	100 (2)
0.050	0	0	91 (9)	99 (1)
0.075	0	0	82 (6)	98
0.100	0	0	58 (11)	96 (5)
0.250	-	-	-	83 (11)
0.500	0	0	32 (28)	67 (8)
0.750	-	-	-	47 (18)
1.000	0	0	5	30 (27)
5.000	0	0	0	1

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[1] Percentages of anomalous survivors given in parentheses.

show such afflictions. Quite obviously, such impairments may seriously affect maturation, longevity, fecundity, etc.

Though less sensitive than developmental stages of the trout, embryos of the catfish, goldfish and bass suffered significant levels of lethality when treated with methyl mercury at 5 ppb, and survival was markedly reduced at higher concentrations (Table II). At levels which approach threshold (90-95% hatchability), embryos of the trout and catfish are approximately 50 and 10 times more sensitive than developmental stages of the goldfish. The variation in sensitivity to mercury among these species correlates with differences in egg size and hatching (exposure) time, indicating that species with larger eggs and/or longer periods of development are more susceptible to mercurial poisoning. Increased exposure time would be expected to affect survival. However, egg size also may be an important factor, since larger eggs imbibe greater quantities of water subsequent to fertilization. This post-fertilization period of water imbibition well may represent the time during development when egg permeability is most altered and when developing systems are exposed to greater quantities of trace metals.

In the bass and goldfish, where developmental time and egg size are generally similar, embryonic survival values are in relatively close agreement (Table II). Though not reported in this study, embryos of the catfish, goldfish and bass which survived treatment with mercury displayed frequencies of gross teratologies approaching those given for trout embryos.

As previously noted by Birge and Just (2), inorganic mercury was found to produce degrees of lethality and anomalous development comparable to those given for methyl mercury.

Mercurial toxicity generally was found to vary progressively with developmental time for each species, as shown for the goldfish and trout in Table III. However, somewhat higher rates of lethality normally were observed to occur in the first one or two days following initiation of treatment. This is evident in data reported for trout embryos, where 25% and 41% lethality occurred during the first 3 days of treatment at concentrations of 0.01 and 0.05 ppm (Table III). Following continuous exposure to mercury during development, those animals which lived through hatching showed high postembryonic survival. This is illustrated in Table III where trout alevins, which hatched following 24 days of embryonic exposure, experienced little or no lethality during 3 days of postembryonic treatment with methyl mercury. This is in contrast to the toxic effects of zinc and copper on embryos of certain other species of fish, in which late developmental stages and early fry have been reported to be more sensitive than early embryos (3 - 6). In comparing embryopathic effects of such metals to mercury, it should be noted that zinc and copper are essential metals which are required at trace levels for normal embryonic development. Unpublished data developed in our laboratory indicate that nonessential metals, such as mercury, generally are more toxic to embryos than are the essential metals. Also, zinc and copper likely affect target sites in tissue systems which mature and begin to function moderately late in development (e.g., gill development and respiratory mechanics).

Trout embryos also were treated with cadmium and arsenic. Exposure to cadmium resulted in survival values of 98%, 91% and 58% at concentrations of 0.001, 0.05 and 0.1 ppm (Table IV). Arsenic was less toxic, with 96% and 47% hatching frequencies at 0.1 and 0.75 ppm, respectively (Table IV). Concerning trout embryos which survived cadmium treatment, gross anomalies affected 28%, 9% and 7% of populations treated at 0.5, 0.05, and 0.005 ppm. Frequencies of gross anomalies among arsenic-treated populations were 27%, 11% and 2% at concentrations of 1.0, 0.25 and 0.025 ppm.

Judging from the results with chick and trout embryos, it seems evident that the developmental stages of homeotherms are substantially more sensitive to arsenic than are those of poikilothermal species. This may be due in part to the higher rate of oxidative metabolism in the former, as arsenic oxides are known to uncouple oxidative phosphorylation (7).

It is obvious from the above data that chick embryos are extremely sensitive to a wide variety of trace metals. Assessing the effects of metallic toxicants to avian reproduction depends largely upon 1) levels of contamination in avian food sources, and 2) the rates at which metals consumed by laying females are incorporated into eggs during oogenesis. This is based on the assumption that "preaccumulated" egg metals constitute the principal source of exposure of environmental contaminants to avian embryos. Mercury is known to accumulate rapidly in eggs of the domestic fowl (8,9). Should this prove to be the case for other avian species, as well as for other metals, then metallic trace contaminants could prove most hazardous to avian populations.

Fish embryos are subject to two principal avenues of exposure to environmental metals, including the effects of 1) metals dispersed in natural waters (primary exposure), and 2) preaccumulated egg metals (secondary exposure). Should fish eggs concentrate metals in excess of background levels during oogenesis, which appears likely (10), then secondary exposure may prove especially hazardous.

Considering the high sensitivity of piscine embryos to toxic metals, and the alternative avenues by which developmental stages may suffer exposure, embryogenesis may well constitute the critical "sensitive link" relative to the effects of certain metallic pollutants on natural fish populations.

It seems evident that concentrations of trace metals which are not harmful or fatal to adult vertebrates may prove lethal or teratogenic to embryonic forms. Thus, it appears essential that protective environmental standards for toxic metals be established at levels which will safeguard embryonic development and reproductive potential in more sensitive species.

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SOIL-PLANT-WATER EFFECTS ON UPTAKE AND MOVEMENT OF CONTAMINANTS*

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Abstract

Soil-plant water relations are important in determining both the amount of solutes draining out of the root zone and the uptake and movement of materials within the vegetation. Computer simulation models of these processes have been coupled into a Unified Transport Model for contaminant movement in terrestrial ecosystems. Model applications to oak-hickory vegetation at a mesic site (Walker Branch Watershed, Tennessee) and a more xeric site (Crooked Creek Watershed, Missouri) suggest that solutes could be transported into the groundwater during most of the year at Walker Branch and during the February-May period at Crooked Creek. The period of high evapotranspiration water loss (June-Sept.) greatly reduces the amount of water and solutes draining from the root zone.

Introduction

Soil-plant water relations can be viewed as an interface between two contrasting scales of contaminant movement. Fluxes of materials on the watershed scale on one hand depend on the hydrologic properties of large land masses and may involve material transport between different ecosystems from ridge top to valley, for example. The second scale of contaminant movement occurs within the vegetation and the associated food webs. Material transport both within an ecosystem and within a watershed depends on the soil-plant water relations. Solar energy intercepted by vegetation is utilized in two important ecosystem processes; the photosynthetic fixation of carbon dioxide and the evapotranspiration loss of water from the soil and vegetation. Computer simulation models of these processes[2,4] have been coupled into the Unified Transport Model[1] and applications of the model to two experimental watersheds have been undertaken. An outline of this modeling development and the applications, together with some of the concomitant field research are given below. Aspects of the role of soil-plant water relations on uptake and movement of contaminants are considered.

Methods and Results

The Walker Branch Watershed (WBW) in eastern Tennessee[6] and the Crooked Creek Watershed (CCW) in southeastern Missouri are the two experimental watersheds in which contaminant movement is being studied. These two watersheds have similarities and contrasting features that can be used in a comparative analysis of material transport. The annual precipitation at WBW is about 30% higher than at CCW; however, the potential evapotranspiration at the two sites is about the same (Table 1). The difference between precipitation and potential ET represents an amount of water that may be draining through the root zone into the ground water system. This difference is two times higher at WBW than at CCW and solute movement may be expected to be considerably higher at WBW. The frost free

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period represents the approximate growing season of vegetation. The forests of WBW have a longer growing season than those at CCW and thus have a greater leaf exposure to airborne contaminants and possibly a greater period for root uptake of contaminants from soil. The soils(6,3) and vegetation at the two watersheds show similarities as outlined in Table 1. The oak-hickory deciduous forests have associations with more mesic species (e.g., tulip poplar) at WBW, whereas at CCW, associations include more xeric species (e.g., post oak). The watersheds contrast in the deposition of contaminants. There are three coal burning plants in the vicinity of WBW that introduce trace amounts of contaminants to the watershed(1). The CCW, however, has high levels of contaminants (Pb, Zn, Cu, Cd, SO_2) resulting from the lead mining and smelting operations(10) located on the ridge boundary of the watershed.

Table 1. Some characteristics of Walker Branch and Crooked Creek Watersheds.

		Walker Branch Watershed East Tennessee	Crooked Creek Watershed SE Missouri
Average Precipitation ($cm \cdot yr^{-1}$)		139	107
Potential ET ($cm \cdot yr^{-1}$)		81	78
Frost Free Period (days)		220	177
Soil	Order	Ultisol	Ultisol
	Subgroup	Typic Paleudult	Humic Haplaquept
	Type	Fullerton and Bodine cherty silt loam	Clarksville and Wilderness cherty silt loam
	Characteristics	Infertile, very permeable, well drained, low soil water storage (4.2 to 7.2%), strongly acid	Infertile, moderately rapid permeability, well drained, low soil water storage (4–18%), strongly acid
Vegetation		Chestnut oak (Quercus prinus L.)	Black oak (Q. velutina Lam.)
		Short leaf pine (Pinus echinata L.)	White oak
		Hickory (Carya spp.)	Post oak (Q. stellata Wangenh.)
		White oak (Q. alba L.)	Hickory
		Tulip poplar (Liriodendron tulipifera L.)	Short leaf pine

Field observations at both watersheds show that most of the root biomass occurs in the upper 30 cm of soil, however, some roots can be detected below 180 cm. Plant species composition, biomass per unit area and tissue concentration of contaminants are being determined(9) and these data will provide a monitor of contaminant movement and effects on vegetation. Soil hydraulic properties have been estimated by laboratory methods for WBW(6) and are being determined at CCW by Mr. J. C. Doll and Dr. C. L. Scrivner, University of Missouri, Columbia, using the instantaneous profile method(7) in the field. These laboratory and field studies give the relationships of soil water content to both suction and hydraulic conductivity for each of the characteristic horizons in the soil profile.

Meteorological data being measured in the vicinity of each watershed include solar radiation, maximum and minimum air temperature, average daily dew point temperature, average daily wind speed and hourly precipitation. The various plant, soil and meteorological data are used as input values in the application of the Unified Transport Model to the watersheds. The model is a tool that links field data into functional relationships for ecosystem processes using the common language of mathematics. Comparison of field observation with model forecast can provide insights into the important pathways of contaminant movement in deciduous forest ecosystems.

An overview of the contaminant uptake and movement in a forest and the modeling methods used to describe this system is given in Figure 1. The coupling of the atmosphere-soil-plant water relations model with the plant growth and uptake model provides two pathways for contaminant movement within vegetation. Liquid water movement from roots to leaves and sugar translocation from leaves to roots provide carrier pathways for movement of contaminants. Further modeling developments will link litter decomposition and food web models to the soil-plant process models. A soil chemistry model under development(1) will provide soil solution concentrations of solutes that can be taken up with the transpiration stream. Empirically determined osmotic efficiency coefficients for root uptake of contaminants are required in the model.

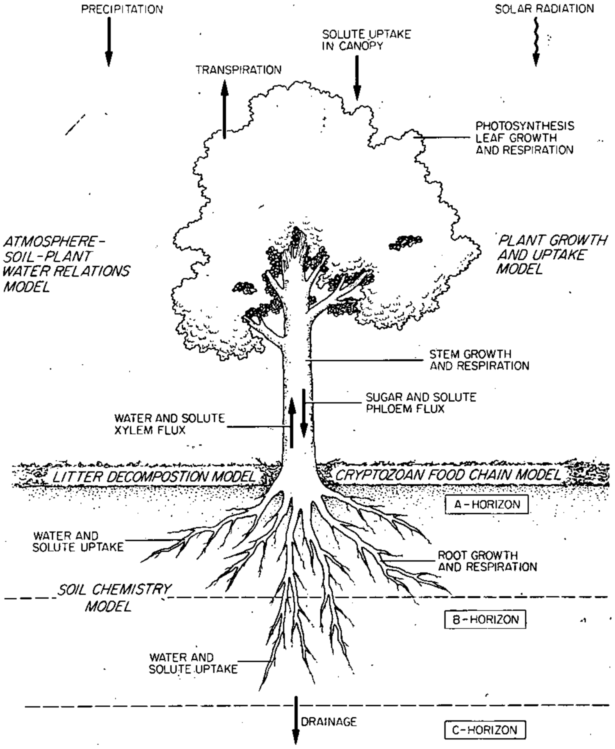

Figure 1. Solute transport processes in the soil-plant-litter-atmosphere system.

The input data requirements and the structural equations of the atmosphere-soil-plant water relations model are given in Figure 2. The four equations and four unknowns are solved hourly to describe the water fluxes in the system and the water status of the soil and vegetation. More detailed descriptions of the model are given in the documentation(4).

Location	Properties	Structural Equations
Atmosphere	Environmental conditions (daily) Solar radiation Precipitation Dew point temperature Max. and min. air temperature Average wind speed	Vapor flux from surface $F_v = f(R_x)$ (1) Calculation uses combined energy balance-aerodynamic method
Boundary Layer	Resistance to vapor and heat flow	
Evaporating Surface	Resistance to vapor flow (R_x) Surface water potential (PSI)	Surface characteristic $R_x = f(PSI)$ (2)
Plant and Soil System	Plant and root resistances Root distribution in upper two soil layers Soil water characteristic for each soil layer Hydraulic conductivity vs water content for each soil layer Soil layer thicknesses	Liquid flux to surface $F_w = f(PSI)$ (3) Calculation uses electrical network equations
Whole System	Steady state	Vapor flux = Liquid flux $F_v = F_w$ (4)

Figure 2. Input properties, data requirements and structural equations of the atmosphere-soil-plant water relations model.

The boundary layer resistance, stomatal resistance and leaf water potential values are transferred to the plant growth model as indicated in Figure 3. The production, allocation and consumption of sugar materials by vegetation is represented by functions based on the studies of Penman and Schofield(5) and Thornley(8). The simulated root and leaf biomass values are transferred back to the water relations model.

PHOTOSYNTHESIS Penman and Schofield (1951)

$$\text{Sugar Production} = A \cdot \frac{(CO_2^{\,air} - CO_2^{\,chl})}{r_a^* + r_s^* + r_i}$$

*Values from atmosphere-soil-plant water relations model.

ALLOCATION Thornley (1972)

$$\text{Sugar Transport} = \frac{(\text{Sugar}^{\text{leaf}} - \text{Sugar}^{\text{stem or root}})}{\text{pathway resistance}}$$

CONSUMPTION

Sugar Consumption by respiration + growth (nonsugar materials)

Respiration = f(temperature,* amount of tissue)

Growth = f(temperature,* water potential,* sugar supply, empirical growth pattern)

Figure 3. Component functions of the plant growth and uptake model. Note, ra, rs and ri are boundary layer, stomatal and internal resistances to CO_2 movement from the atmosphere to chloroplasts (chl). A is a coefficient that converts CO_2 into an equivalent amount of sugar.

These coupled models are based on simplified soil physical and plant physiological processes and are not purely empirical models. The interaction of environmental conditions on the system of coupled processes may give insights into contaminant movement that may not have otherwise become apparent. In other words the model outputs may not be necessarily obvious from the values of the model inputs.

Hydrologic simulation results for WBW during 1969-70 and of CCW for 1971-72 are summarized into three time periods each with about the same precipitation input for a particular watershed (Table 2). The drainage and streamflow results suggest that there would be very little or no contaminant movement into and from the ground water during the October-January and June-September periods for the Crooked Creek area. All time periods at WBW and the February-May period at CCW could have solutes transported into the ground water and stream from the root zone soil mass. The period of high evapotranspiration water loss (June-Sept.) greatly reduces the quantity of water draining from the root zone.

Table 2. Hydrologic inputs and simulated outputs for Walker Branch Watershed (WBW) and Crooked Creek Watershed (CCW). ET is evapotranspiration. Drainage represents the water moving across the five foot soil depth into the ground water. Data are in cm per unit area.

	Oct-Jan	Feb-May	June-Sept	Annual
WBW (1969-70)				
Precipitation	41.5	41.3	42.0	124.8
ET	9.0	21.8	35.3	66.1
Drainage	31.4	26.7	5.8	63.9
Streamflow	25.0	26.2	13.5	64.7
CCW (1971-72)				
Precipitation	26.6	32.2	32.7	91.5
ET	5.2	20.9	44.2	70.3
Drainage	0.0	19.6	0.0	19.6
Streamflow	0.6	18.8	1.0	20.4

These simulation results are given as examples. The quantitative reliability of the forecasts will become apparent with model applications to data for several other years. These two deciduous forest watershed research studies and the model applications will provide greater understanding of the transport and residence times of contaminant materials in forested areas.

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Accumulation of Lead and Other Heavy Metals by Vegetation in the Vicinity of Lead Smelters and Mines and Mills in Southeastern Missouri*

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Abstract

The accumulation of lead and other heavy metals in or on vegetation near lead smelters and mines and mills in southeastern Missouri was studied during the period 1971-1974.

An area 12 x 25 miles in the New Lead Belt encompassing four (4) mines and mills and one (1) smelter and an area 14 x 14 miles outside the New Lead Belt with a smelter at the center were sampled.

Post oak (Quercus stellata) and shortleaf pine (Pinus echinata) foliage collected within 0.5 mile of the AMAX smelter accumulated maximum levels of Pb of 8,125 ppm and 11,750 ppm, respectively. Elevated levels of Pb in white oak (Quercus alba) and blueberry (Vaccinium pallidum) leaves were detected at distances greater than 7 miles from the smelters and at distances of four (4) miles from mines and mills.

Similar patterns of elevated levels of Cd, Cu and Zn were found; however, anomalous levels of Zn at certain sampling sites could not be correlated with their proximity to the mines and mills or smelters or other possible industrial sources.

Introduction

Plants due to their rapid phytotoxic responses have been shown to be excellent indicators of certain types of contamination of the environment. However, the presence of contaminants such as heavy metals may not be readily detected by visual observations of plants but an analysis of their foliage, roots or other tissue may serve as an excellent indicator of their geochemical environment.

Plants require sixteen elements, thirteen of which are normally obtained from the soil; however, an analysis of plant tissues may show the presence of several-fold this number.

The accumulation of lead in or on vegetation near mines and mills and smelters has created problems in many countries (Djuric, et al. (1), Schmitt, et al. (2), and Goodman and Roberts (3)). The problem that has caused the first and usually the greatest concern has been the death of horses which have been pastured in the near vicinity of smelters, although in some cases there have been alleged effects on human health.

Experimental Methods

To determine the level of accumulation of lead and other toxic heavy metals in the vicinity of mines and mills and smelters leaf samples of white oak (Quercus alba), post oak (Quercus stellata), shortleaf pine (Pinus echinata) and dryland blueberry (Vaccinium pallidum) were collected in the summers and falls of 1971, 1972, and 1973 and in the spring and summers of 1974.

Intensive sampling of post oak and pine was carried out in the vicinity of the AMAX Smelter. Also, a systematic sampling of white oak and blueberry foliage was made over an area approximately 12 x 25 miles encompassing most of the Viburnum Trend or New Lead Belt. The area encompasses four (4) operating mines and mills, one mine and mill (Brush Creek) under development and the AMAX Smelter. Most of the study area is situated in the Clark National Forest and is heavily wooded, however, the small towns of Bixby, Boss, Reynolds, and Vibrunum and other individual dwellings are in the area. The sample sites for white oak and blueberry leaves were the same, however it was not possible in all cases to collect both plant species at each site. In addition to Pb, samples were analyzed for Cu, Cd, Mn and Zn.

In the springs and summers of 1973 and 1974 white oak leaves were collected at 203 sites in the vicinity of the ASARCO Lead Smelter at Glover, Missouri. The ASARCO Smelter is outside the New Lead Belt approximately 25 miles southeast of the AMAX Smelter, however, lead ore (PbS) from the New Lead Belt is transported to this smelter for smelting. Initially, it was intended that sampling would be limited to an area 7 miles in all directions from the smelter. Later samples were taken at distances greater than 7 miles be-

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*Not presented at the Conference.

cause analyses of leaf litter indicated lead accumulation beyond the 7 mile distance.

All samples were analyzed by atomic absorption spectrophotometry without washing so the results represent internal as well as surface accumulation.

Results

Unusually high levels of lead in or on leaves of post oak and shortleaf pine in the near vicinity (0.5 miles or less) of the AMAX Smelter were detected. As indicated in Table 1, maximum values were 8,125 and 11,750 ppm for post oak and pine, respectively. The area encompassed in this study was limited but elevated levels of lead were detected at distances greater than 2 miles.

The lead contents of white oak and blueberry foliage in and on samples collected during the period 1971-1973 from the 12 x 25 mile study area are indicated in Figures 1 and 2 and Tables 2 and 3.

In the north half of the study area, the AMAX Smelter is perhaps the primary source of contamination, however, the influence of the mines and mills is evident in Figures 1 and 2 and undoubtedly some lead contamination results from ore haulage by truck and railroad to the AMAX Smelter and to smelters outside the study area.

Although it is not possible from these data to establish with a high degree of accuracy the background levels of Pb in white oak leaves, it appears that it would be less than 20 ppm. Figure 2 and Table 2 support this thesis. At distances of 6 to 7 miles Pb values had a range of 29.0 to 101.0 and a mean of 53.7 ppm. Blueberry leaves collected at a distance of 100 yards from highways outside the study area and along where there had been no Pb ore haulage contained a mean of 10.7 ppm lead and a maximum level of 18 ppm (4).

In the south half of the study area, the Fletcher Mine and Mill complex is perhaps the primary source of Pb contamination; however, leaded motor fuel and truck transportation of Pb ore are contributing factors. As indicated by a comparison of Figures 1 and 2 and by a comparison of Table 2 and 3, accumulation of Pb in and on vegetation in the vicinity of a mine and mill is not nearly as great as around a smelter. The distances to which anomalous levels of Pb occur are also less than in the vicinity of a smelter.

The amount of lead accumulated by white oak leaves tended to be only slightly higher than that accumulated by blueberry leaves. Perhaps this slight difference could be explained by the fact that the blueberry is an understory plant and may be subject to less aerial deposit.

Figures 3 and 4 indicate sampling sites and levels of cadmium in white oak leaves and blueberry leaves, respectively. Cadmium levels ranged from 4.9 ppm for white oak and 4.12 for blueberry at a distance 1 1/2 miles from the AMAX Smelter to less than 0.5 ppm at distances of 5 miles or greater from the smelter. There is excellent correlation between Pb and Cd content of vegetation as indicated by a comparison of Figures 1 and 2 with Figures 3 and 4. When the level of Pb is 20 ppm or less the level of Cd is usually less than 0.5 ppm.

Elevated levels of zinc were present in or on vegetation in the vicinity of smelters, mines and mills (Figures 5 and 6). Levels in white oak leaves in the north one-half of the study area ranged from a high of 90.5 ppm adjacent to the Buick Mine and Mill to a low of 11.2 ppm 6 miles southwest of the smelter and 5 miles west-southwest of Buick Mine and Mill. The second highest level was 55.0 ppm 1 1/2 miles northwest of the smelter.

In the south one-half of the study area levels of zinc in white oak leaves ranged from a high of 43.5 ppm 5 miles northeast of the Fletcher Mine and Mill to a low of 7.9 ppm 4 1/2 miles northwest of the mine and mill. Although the levels near the mine and mill appear somewhat elevated, the highest levels cannot be correlated with their proximity to the mine and mill or any other industrial source of zinc. The white oak trees in these cases may be reflecting their natural geochemical environment.

Blueberry leaves reflected the Zn contamination as a result of the mining activity with highs of 87.0 ppm adjacent to the Buick Mine and Mill, 50.3 ppm 1 1/2 miles northwest of AMAX Smelter and 44.5 ppm adjacent to the Fletcher Mine and Mill. The lowest level was 9.9 ppm at the sampling site 5 miles west of Fletcher Mine and Mill.

Copper levels in white oak and blueberry leaves were somewhat elevated near smelters and mines and mills (Figures 7 and 8); however, there does not appear to be a serious Cu contamination problem at present in the New Lead Belt. A maximum level of 14.9 ppm was found in white oak leaves 1 1/2 miles northwest of the AMAX Smelter. Although a low value of 1.7 ppm was found at one site the mean level at a distance of more than 7 miles from the smelter was 4.7 ppm and at a distance of 5 to 6 miles from Fletcher Mine and Mill it was 5.1 ppm.

Unwashed white oak leaves collected in June 1973 in the vicinity of the ASARCO Smelter ranged from 340 ppm Pb at a distance of 1 1/2 miles from the smelter to 5.6 ppm at 7 miles in a southeastern direction from the smelter. Levels of Cd in these samples ranged from 2.4 ppm to 0.25 ppm with only a few of the 203 samples greater than 1.0 ppm.

Conclusions

Vegetation in the near vicinity of smelters and to a lesser extent in the vicinity of mines and mills accumulate levels of Pb that are many fold that of background levels. All samples were analyzed without washing, consequently, the ratios between internal and external lead are not known.

From these data, it is concluded that elevated levels of Pb occur at distances greater than 7 miles from the AMAX Smelter which has a stack height of 200 ft. Also, results of the study in the vicinity of the ASARCO Smelter (stack height 612 feet) indicate elevated levels of Pb at 7 mile distances or greater from this smelter. Although the ASARCO stack is 3 x height of the AMAX stack the area of elevated levels of Pb is not appreciably greater.

Elevated levels of Pb appear to occur in vegetation at least 4 miles and possibly at greater distances from mines and mills, however, the level of accumulation is markedly less in the vicinity of mines and mills than in the vicinity of smelters.

Examination of the data for cadmium, copper and zinc indicates a similar pattern of anomalous levels for these elements as for Pb.

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Table 1 Concentration of lead in leaves of post oak (Quercus stellata) and needles of shortleaf pine (Pinus echinata) in vicinity of lead smelter operations.

	Micrograms per Gram - Dry Weight			
	Post Oak		Shortleaf Pine	
Distance from smelter (mi.)	Range of Values	Mean	Range of Values	Mean
0 - 0.5	230-8125	3776.70	420-11750	3546.36
0.5 - 1.0	71-3800	771.40	101-1475	497.37
1.0 - 1.5	50-1580	250.00	52-1050	273.56
1.5 - 2.0	45-640	192.80	62-412	142.85
More than 2.0	18-1360	168.97	22-661	123.29

Table 2 Concentration of lead in leaves of white oak (Quercus alba) and leaves of blueberry (Vaccinium pallidum) in vicinity of lead smelter operations.

	Micrograms per Gram - Dry Weight					
	White Oak			Blueberry		
Distance from smelter (mi.)	Range of Values	Mean	n	Range of Values	Mean	n
1 - 2	75.8-1221.0	574.3	3	141.0-874.0	495.3	3
2 - 3	122.0- 557.0	299.0	7	93.0-338.0	203.9	10
3 - 4	39.8- 155.0	80.2	4	21.0-146.0	76.1	5
4 - 5	28.2- 276.0	93.0	10	34.2-181.0	68.6	11
5 - 6	23.5- 228.0	75.6	12	24.0-155.0	64.3	10
6 - 7	26.0- 121.0	54.5	9	29.0-101.0	41.6	11

Table 3 Concentration of lead in leaves of white oak (Quercus alba) and leaves of blueberry (Vaccinium pallidum) in vicinity of Fletcher Mine and Mill.

	Micrograms per Gram Dry Weight					
	White Oak			Blueberry		
Distance from road (mi.)	Range of Values	Mean	n	Range of Values	Mean	n
0 - 1	39.0	39.0	1	39.0 - 132.0	85.5	2
1 - 2	16.5 - 70.0	35.9	6	16.5 - 40.0	25.8	5
2 - 3	20.0 - 26.5	22.6	6	16.5 - 27.5	20.6	5
3 - 4	10.8 - 57.7	20.7	10	11.5 - 42.5	20.6	12
4 - 5	12.5 -124.0	29.5	15	5.8 - 73.9	27.1	17
5 - 6	12.5 - 36.5	22.6	11	5.9 - 24.0	17.7	11

LEAD IN WHITE OAK LEAVES

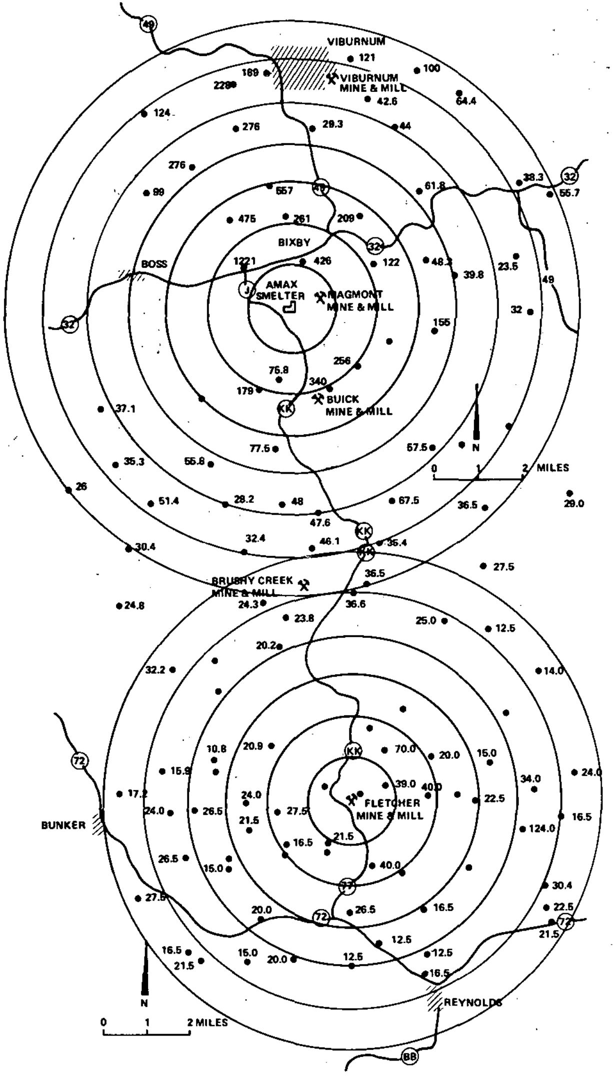

FIGURE 1

LEAD IN BLUEBERRY LEAVES

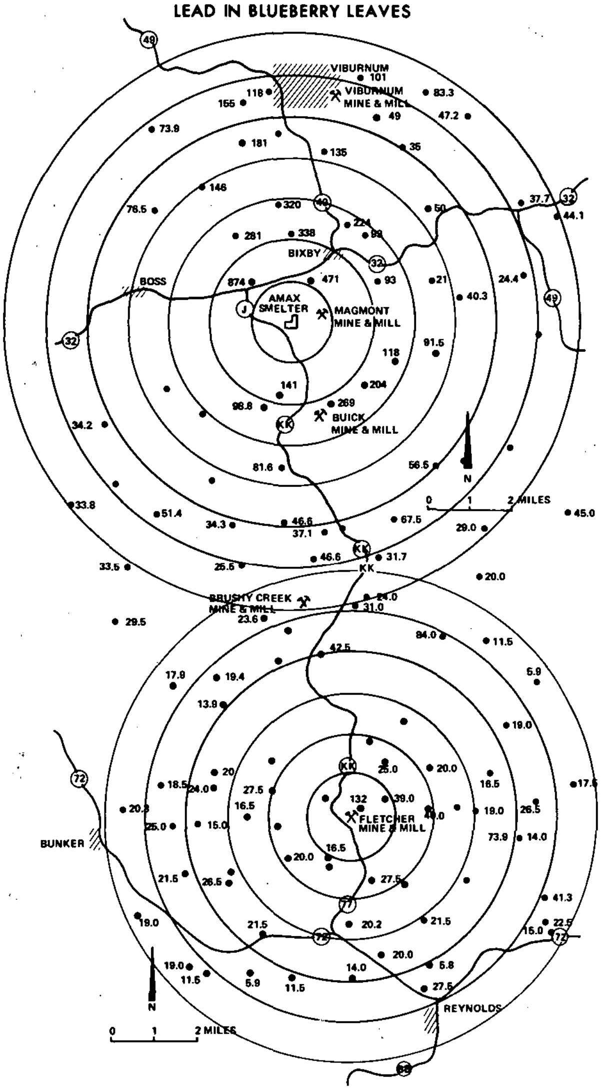

FIGURE 2

CADMIUM IN WHITE OAK LEAVES

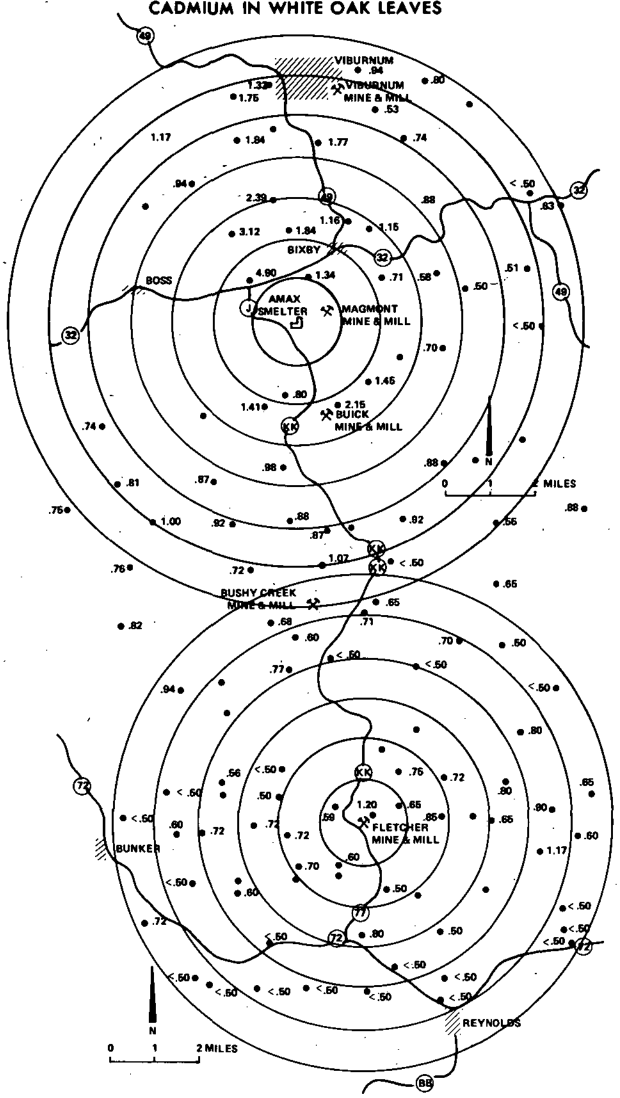

FIGURE 3

CADMIUM IN BLUEBERRY LEAVES

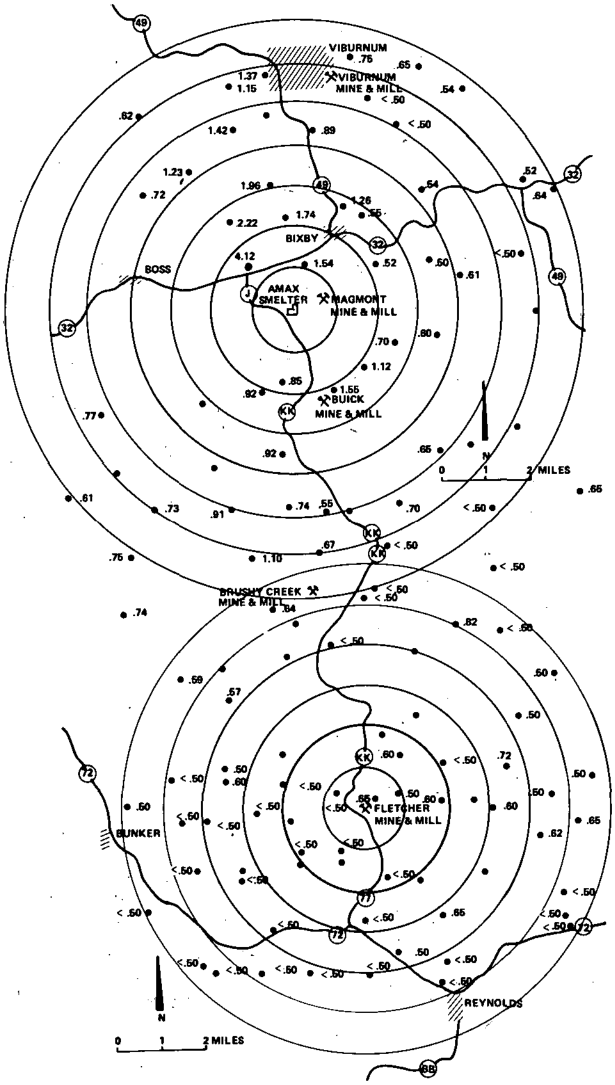

FIGURE 4

ZINC IN WHITE OAK LEAVES

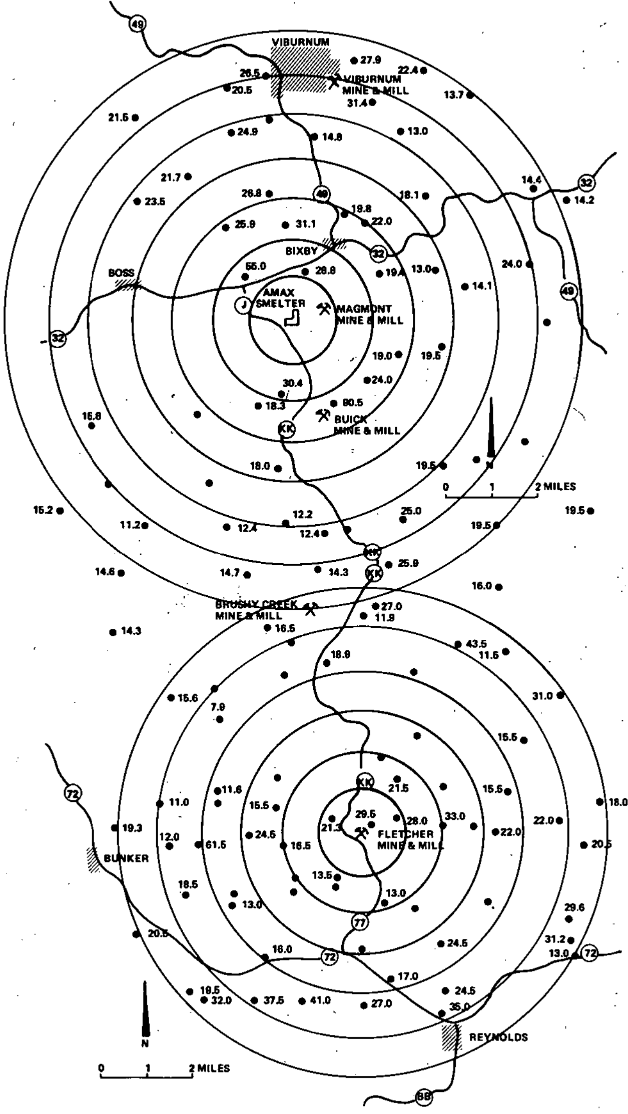

FIGURE 5

ZINC IN BLUEBERRY LEAVES

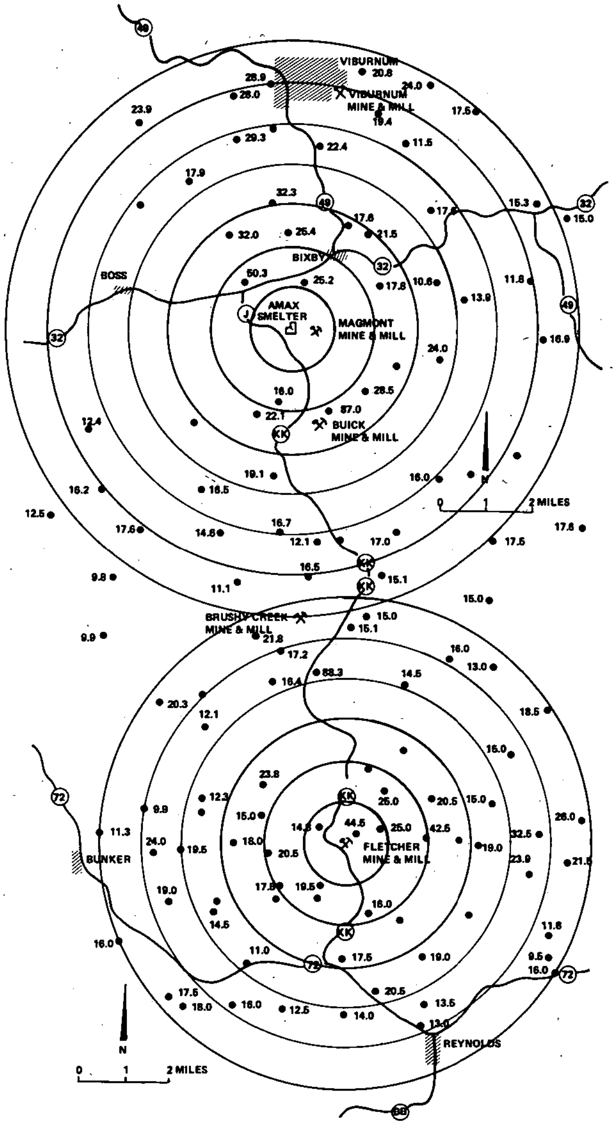

FIGURE 6

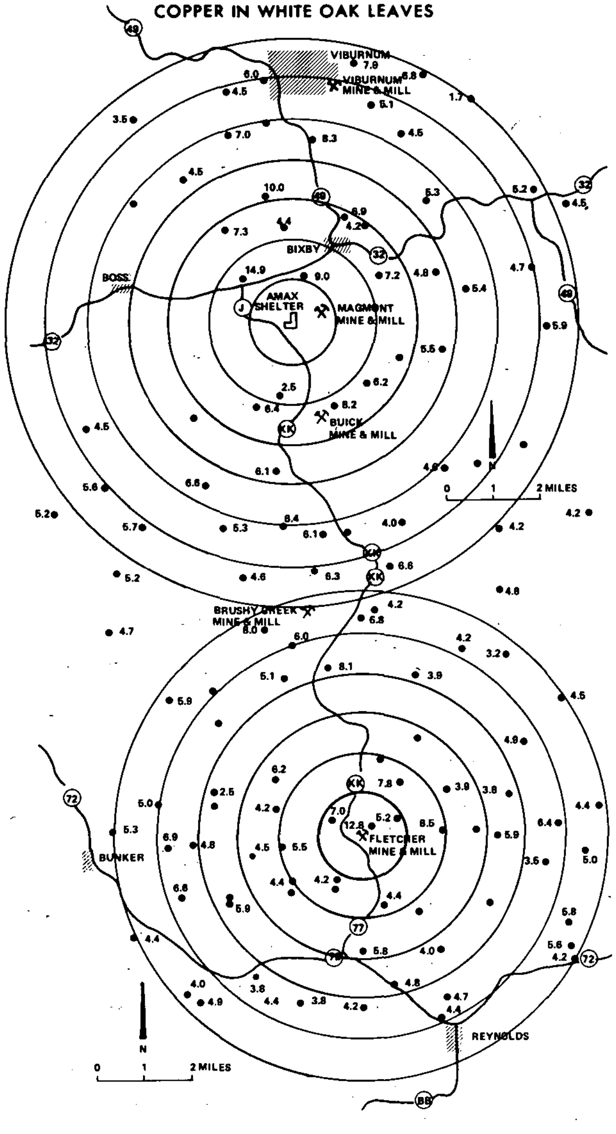
COPPER IN WHITE OAK LEAVES

FIGURE 7

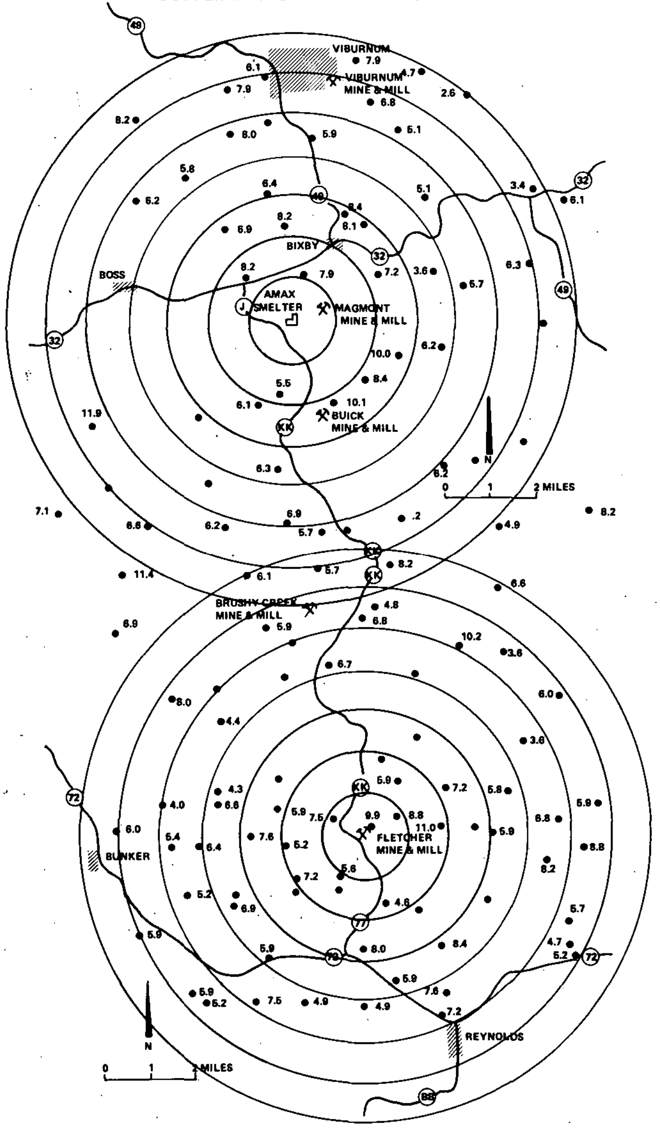
COPPER IN BLUEBERRY LEAVES

FIGURE 8

THE USE OF ^{210}Pb AND ^{109}Cd ISOTOPES IN A PRELIMINARY STUDY OF THEIR UPTAKE AND TRANSLOCATION BY PLANTS*

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Abstract

Leaf lettuce and white icicle radish were grown under greenhouse culture for a period of three and one-half weeks. Appropriate solutions of $Pb(NO_3)_2$ or $CdCl_2$ were applied to foliage via a micropipette. These solutions also contained radioisotopes of Pb or Cd. The plants were grown for an additional three and one-half weeks, harvested and analyzed. Results of autoradiography and scintillation analyses of the radioisotopes showed foliar absorption and subsequent translocation of both metals. In the lettuce the greatest translocation was to the youngest leaves of the plant and in the radish to the storage root, in both cases the edible portion of these plants. Thus, it seems that foliar absorption of heavy metals may well be an important source of contamination of radish and leaf lettuce.

Introduction

Plants absorb toxic heavy metals from soils as well as the mineral elements essential to their growth. Additionally, toxic metals can be absorbed by the foliage in aerosol form and can accumulate in particulate form on the foliage from aerial fallout. Since plants are directly or indirectly the source of sustenance for all animals, the importance of these phenomena in the food chain cannot be over-emphasized.

It has been reported by Brewer (1) and Keaton (2) that heavy metals, and particularly lead, are not accumulated to any great extent from the soil by plants. Most studies which are limited in number, indicate that lead is unavailable to the plant or is "fixed" in the roots and only small amounts are translocated to the above-ground parts of the plant.

The extent to which Pb in aerosol form and Pb that accumulates on plant leaves in particulate form are absorbed is unknown. A few studies have indicated that it is all or largely external. The problem of distinguishing between external and internal Pb or other metals becomes very difficult. Particulate Pb becomes embedded in the surface cuticle and is extremely difficult to remove by washing.

Undoubtedly some Pb enters the leaves and can be translocated to other plant parts. In alkaline or near alkaline soils Fe, Mn, Cu and Zn can be unavailable and foliar applications have long been used to supply these essential mineral elements. To better understand the possible environmental effects of the dispersal of toxic heavy metals in the New Lead Belt of Missouri, it was deemed desirable to conduct certain experiments in the greenhouse and laboratory under controlled conditions.

Materials and Methods

Foliar absorption and translocation of Pb and Cd were studied on white icicle radish and leaf lettuce under greenhouse culture. Solutions of soluble salts of Pb ($Pb(NO_3)_2$) and Cd ($CdCl_2$) were applied to the plant foliage via a micropipette. Radioisotopes of each metal (^{210}Pb and ^{109}Cd) were included with the stable salts to facilitate investigations and sensitivity. Plants were grown in pots for three and one-half weeks, treated with the appropriate metal (Pb or Cd), grown to maturity seven weeks, harvested, and analyzed. Care was taken to insure that none of the treatment solution reached the soil in which the plants were being grown. In one set the soil surface was protected by tissue paper over styrofoam and in a second set the soil surface was protected by a plastic sheet through which the young plants had grown with appropriate sealing around the stem at the base of the leaves. In both sets, analyses of the surface soil of all pots after plant harvest showed no evidence of ^{210}Pb or ^{109}Cd.

Application of 50 ppm Pb to the foliage did not appear to cause burning of the tissue but about three weeks after treatment, a dark coloration was visible on the leaf surface of the treated areas indicating the possible formation of insoluble compounds of Pb. Application of 10 ppm Cd caused burning of the foliage

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*Not presented at the Conference.

in many instances, pointing out the much greater toxicity of Cd over Pb.

During harvesting, the plants were separated into various portions and dried at 60°C before analysis. Some plants from each treatment were pressed and dried for the purpose of making autoradiographs.

The autoradiographs were made using two groups of exposure times of plant material to film. Leaves to which the treatments were applied required exposure of the plant material to the x-ray film for one or two days. All other parts of the plants required exposure times of up to or over 30 days.

Results

Figure 1 shows an autoradiograph of ^{210}Pb -treated leaves of a lettuce plant. The leaves were the youngest on the plant at the time.

Exposure time of the leaf to x-ray film was two days. Most movement of Pb was toward the leaf margins but movement to the base of the leaf can be seen especially in the leaf at the right. Most probably the treatment on the leaf to the left spread over the surface causing the large darkened areas. Later treatments included barriers on leaf surfaces to prevent surface spread of the treatment from occurring.

Figure 2 shows an autoradiograph of six (6) radish leaves to which Cd(Cd^{109}) was applied. The three very intense images on each leaf is the area which was treated. Note that as before the largest movement was toward the leaf tip but the pattern of redeposition of the Cd is much different. The Cd appears to be precipitated in spherical bodies, most along the transport tissue area but more in the interveinal area than the Pb in the lettuce and more than Pb in radish leaves. Cystoliths of amorphous $CaCo_3$ have been found in plant leaves and appear to be a Ca storage mechanisms. Iron has been found as crystalline inclusions in plastids of willow cambium and stored as a Fe-protein complex in the stroma of chloroplasts. Bodies of Al (probably alumino-silicates) have also been found. The same type of Cd deposition has also been found in lettuce foliage.

An autoradiograph of a radish plant to which Pb (Pb^{210}) was applied is shown in Figure 3. The younger of the two non-treated leaves contains the most Pb^{210}. The storage root was sliced longitudinally into five pieces. Note the highest concentration in the three inner slices is around the edge of the pieces, the location of the phloem tissue.

Figure 4 shows an autoradiograph of a radish plant after Cd(Cd^{109}) treatment. The storage root was sliced as described above. Note here, however, the nearly even distribution of Cd^{109} throughout the storage root of the radish.

Other autoradiograms of lettuce plants show transport to other leaves but the highest amount other than the treated leaf was the lettuce stem, near the treated leaf.

The following data are from a preliminary experiment on foliar absorption and thus parts of plants which were analyzed varied from set to set. Subsequent experiments with more uniform design, treatment, and harvest are now being analyzed. The data given are for an average of five replications with four plants in each replication. A fifth plant from each pot (replication) was processed for autoradiography. Plants were treated with 180µl of 100ppm Pb or Cd per plant (three leaves per plant) at 3.5 weeks after emergence and harvested at seven weeks after emergence. The following abbreviations are used in the tables below:

APA - Foliage (leaves) above the leaves which were treated (youngest leaves of plant).
LOA - Leaves which were treated, excluding the area of application.
BPA - Leaves below those which were treated.

Table 1 presents data from the Pb^{210} analysis of leaf lettuce after treatment of the youngest leaves of the plant. From the high values of some of the replications of the treated leaves (LOA), there is some possibility of surface movement of the treatment solution outside the small area of application. The area of treatment removed was as small as possible but large enough to remove the residue of the original treatment unless some of the solution had moved along the leaf's surface.

Numerous other analyses and autoradiographs show such contamination to be minimal and no contamination of other plant parts or soil. Note that in Table 1 the percent translocated and the concentration (cpm/g) was highest in the youngest leaves and the next highest concentration was in the roots, excluding the leaf of application.

Data from Pb^{210} analysis of leaf lettuce after Pb(Pb^{210}) treatment of the oldest leaves of the plant are given in Table 2. The percent translocated and the concentration was greatest in the leaves.

Table 3 presents results of Pb^{210} analysis after Pb(Pb^{210}) treatment of radish leaves. The highest total amount, percent translocated, and final concentration (cpm/g) is for the storage roots, the edible portion of this plant. Although the percent translocated was low, the total amount applied was also low. In cases of high foliar contamination the a-

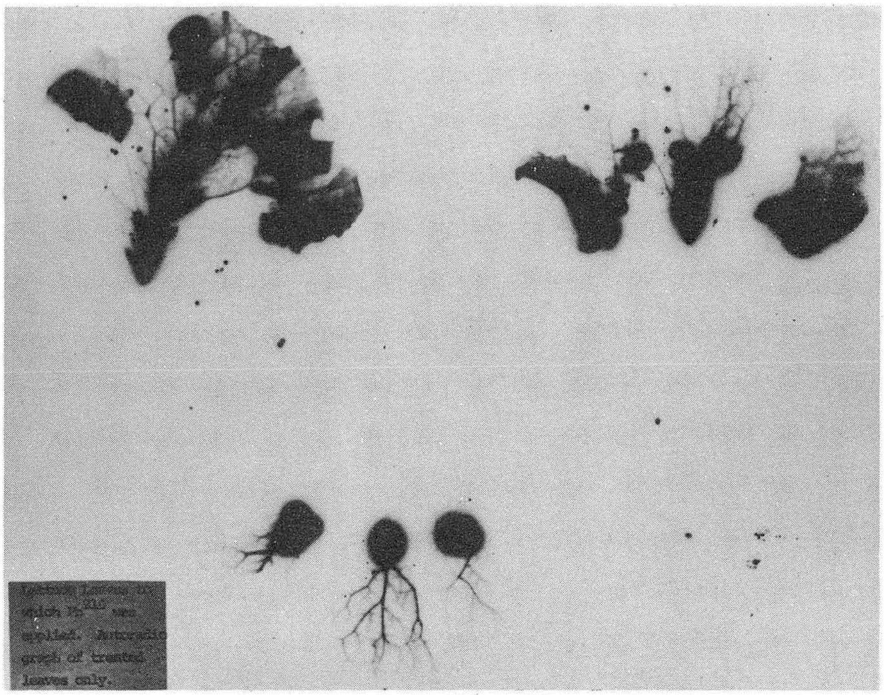

Figure 1. Autoradiograph of three lettuce leaves after treatment with Pb^{210}.

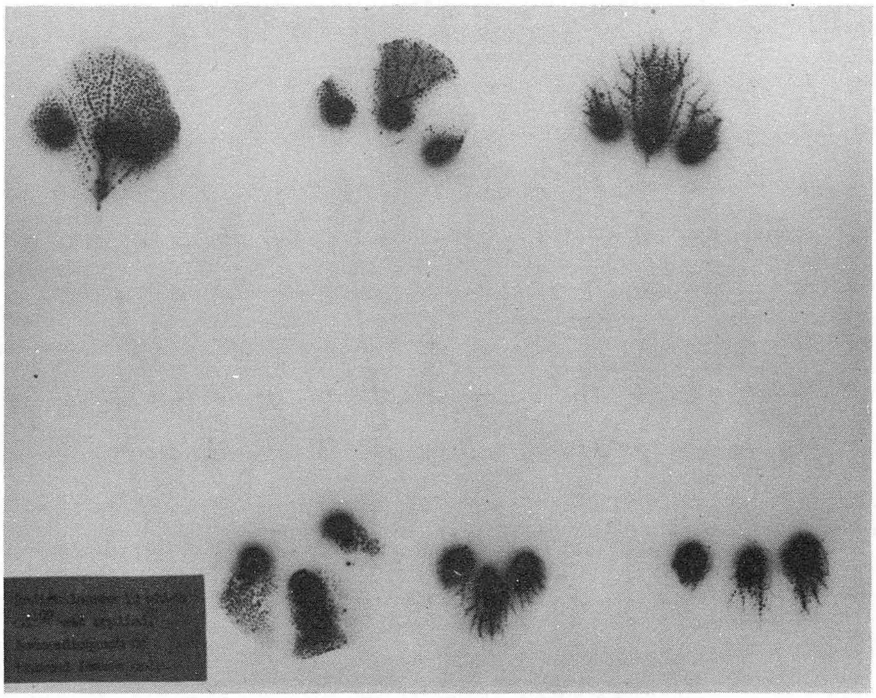

Figure 2. Autoradiograph of six radish leaves after treatment with Cd^{109}.

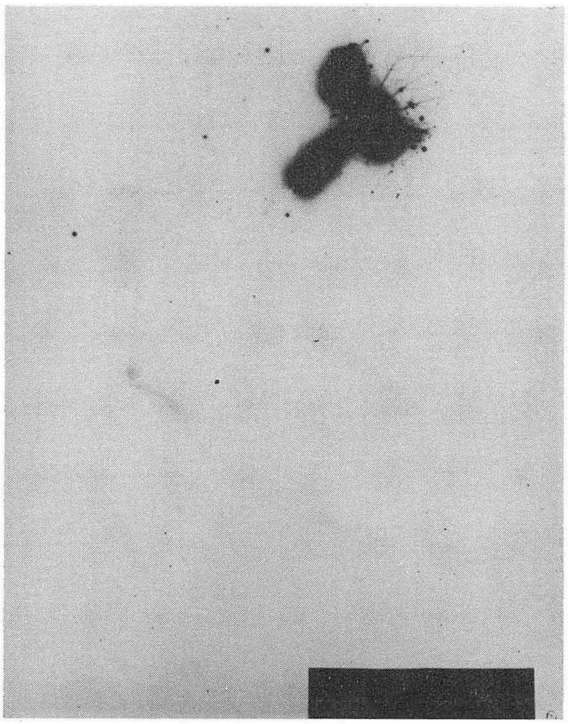

Figure 3. Autoradiograph of a radish plant after treatment with Pb^{210}.

Figure 4. Autoradiograph of a radish plant after treatment with Cd^{109}.

Table 1. Data from Pb^{210} analysis of $Pb(Pb^{210})$ treatment of youngest lettuce leaves.

Plant Portion	Yield, g	cpm/portion	% Trans-location	cpm/g
APA	1.41	172,213	0.59	122,136
LOA	0.94	2,575,251*	8.80*	2,739,628
BPA	0.41	6,378	0.02	15,556
Stems	2.12	21,226	0.07	10,012
Roots	0.75	2,624	0.01	34,988

* Possibility of surface contamination.

Table 2. Data from Pb^{210} analysis of $Pb(Pb^{210})$ treatment of oldest lettuce leaves.

Plant Portion	Yield,g	cpm/portion	% Trans-location	cpm/g
Leaves*	2.62	59,968	0.20	22,885
Stems	2.19	31,520	0.11	14,393
Roots	0.75	5,199	0.018	6,932

* Treated leaves removed.

Table 3. Data from Pb^{210} analysis of $Pb(Pb^{210})$ treatment of radish leaves.

Plant Portion	Yield,g	cpm/portion	% Trans-located	cpm/g
Leaves*	1.74	10,658	0.042	6125
Storage Roots	2.71	21,020	0.083	7756
Fiberous Roots	0.42	1,380	0.0054	3285

* Treated leaves removed.

Table 4. Data from Cd^{109} analysis of $Cd(Cd^{109})$ treatment of radish leaves.

Plant Portion	Yield	cpm/portion	% Trans-located	cpm/g
APA	0.57	4,214	0.29	7,635
LOA	1.04	57,800	4.03	55,138
BPA	0.55	1,858	0.13	3,401
Storage Roots	2.72	20,843	1.43	7,671
Fiberous Roots	0.51	773	0.054	1,541

mount translocated could well become very significant.

Data from Cd^{109} analysis after $Cd(Cd^{109})$ treatment of radish leaves are presented in Table 4. As was the case with Pb^{210}, the percent translocated (other than the LOA in this case) was highest to the storage roots. The storage roots and young leaves (APA) had the same final concentration.

Scintillation analysis and autoradiography of Pb^{210} and Cd^{109} after foliar treatment of leaf lettuce and radish with $Pb(NO_3)_2(Pb^{210})$ and $CdCl_2(Cd^{109})$ have shown that foliar absorption and subsequent translocation did occur. This phenomena can be an important source of contamination especially where foliar accumulation is large. Rabinowitz (3) has reported foliar absorption and translocation of Pb halide aerosols by oats and lettuce grown near the San Diego Freeway.

Many factors, as yet unelucidated, undoubtedly affect the root uptake and translocation of Pb, Cd and other heavy metals from the soil, and nutrient solutions as well as foliar absorption and translocation of atmospheric and aerially deposited particulate forms of Pb and other heavy metals.

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1. R. F. Brewer, Lead, In: Diagnostic Criteria for Plants and Soils, Homer D. Chapman, Ed., University of California (1966).

2. C. Keaton, Soil Science, 43:401-411 (1937).

3. M. Rabinowitz, Chemosphere, 4:175-180 (1972).

NITRATE LEACHED INTO THE UNSATURATED ZONE FROM IRRIGATED SOILS IN COASTAL SOUTHERN CALIFORNIA

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Abstract

Where the saturated zone (water table) is sufficiently deep that tile drains are not needed to keep the root zone well aerated (free from saturation), drainage water moves by unsaturated flow through an unsaturated zone between the root zone and the ground water or zone of saturation. The unsaturated zone is extremely variable in depth and in texture and type of geological material. This "free drainage" condition exists in most of the croplands of California. Water movement through the unsaturated zone into the water table is considered to have a very small horizontal component, if any, so that flow is downward until the water reaches the saturated zone. Thus the drainage water does not appear at any point where it can be easily sampled. When the drainage water reaches the saturated zone it is subject to horizontal movement and to dilution so that there is no certainty that samples taken at the top of the saturated zone represent the drainage water that came from the overlying cultivated land. Thus, sampling and analysis of the unsaturated zone has been used as a method of appraisal of losses of nitrate by leaching. The rate of flow of water through the unsaturated zone is dependent on the volume of drainage water and the volumetric water content of the materials through which the water flows. Flow rates, estimated from about 100 study sites, ranged from 10 to 50 years for a 100-foot depth. This means that a deep unsaturated zone represents a time buffer, i.e., the time between changes in surface management and the reflection of the change in quality of water at the top of the saturated zone. A recent study showed that the nitrate concentration in the water of the unsaturated zone in 65 sites in the coastal Counties of Southern California averaged 56 ppm nitrogen. In inland valleys of Central California the average of 41 sites was 37 ppm nitrogen. The range of concentrations in both areas was from less than 10 to more than 100 ppm nitrogen. In Orange County the nitrate concentration under citrus culture averaged 42 ppm nitrogen with a range of from 24 to 100 ppm in the drainage water, whereas, under mixed field and vegetable cropping systems the average was 27 ppm nitrogen with a range of from 6 to 46 ppm. Estimates of amounts of nitrogen leached averaged 140 pounds per acre per year from citrus and 90 pounds per acre per year from the mixed field and vegetable cropping systems. The range in the data was 80 to 260 and 20 to 200 pounds per acre per year for citrus and mixed cropping, respectively. One characteristic of the data obtained from sample of the unsaturated zone is a large variability both horizontally and vertically that is probably related to horizontal variability in water infiltration and transmissivity rates in the soil profile. Thus, the limitation of this sampling technique for monitoring the drainage water in the "free drainage" situation is the large number of samples needed to obtain a representative sample for a given area or field.

THE PROBLEM OF ELEVATED MOLYBDENUM LEVELS IN IRRIGATION WATERS

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Abstract

Many of the waters that drain mining areas in Colorado contain elevated levels of molybdenum, and some of these are used for irrigation. Incidences of molybdenosis have been found in some areas. The present study was undertaken to investigate the problems of using high-molybdenum irrigation waters of agricultural soils. The magnitude of molybdenum accumulation in soils is illustrated by the following example: Application of 30 inches of irrigation water containing 150 ppb of molybdenum deposits per acre, which, if distributed in the upper 6 inches of the soil, would raise the normal molybdenum level of a soil from 1 to 1.5 ppm, an increase of 50 percent. In 20 years sufficient molybdenum would be added to raise the content of the upper 5 feet of soil by 100 percent. How might this much added molybdenum affect cattle and sheep grazing of pastures irrigated with such waters? A greenhouse study was conducted with two acid and two calcareous soils to which 0, 2, and 4 ppm of molybdenum was added. Addition of 4 ppm of molybdenum increased the molybdenum content of alfalfa from 0.5 to 7 ppm of the acid soils and from 8 to 40 ppm on the calcareous soils. Thus, the molybdenum level of forages in the calcareous soils was well above the 10 ppm considered safe in order to avoid molybdenosis in cattle. These findings show there is concern that elevated levels of molybdenum in irrigation waters for calcareous soils may eventually result in molybdenosis problems. Investigations are underway to study the fixation mechanism of molybdenum in soils, the movement of molybdenum-enriched water through soils, and the development of a soil test to assess plant-available molybdenum. The difficulty of establishing water-quality standards for molybdenum are discussed.

ENVIRONMENTAL BIOMETHYLATION OF TRACE ELEMENTS

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Abstract

Evidence is growing that certain trace metals can be mobilized out of natural environmental sinks by the mechanism of biomethylation, alone or in combination with other naturally occurring physical and chemical processes. Moreover, some of these transformations result in mobilization across air water interferes and all result in a change in the degree of toxicity of the element in question. At least six trace elements either have been found in the methylated forms in the environment, or have been shown in laboratory studies to possess such a susceptibility. These elements are mercury, arsenic, selenium, antimony, tin, and iron. Of these, mercury and arsenic have received the greatest attention with good and substantial evidence for environmental biomethylation. Laboratory culture work and preliminary environmental analysis has indicated the presence of biomethylated forms. Laboratory work indicates that both aerobic and anaerobic biomethylation can occur. Evidence for trace element biomethylation will be reviewed on an element-by-element basis.

V. GENERAL INTEREST PAPERS

BENEFITS AND PERILS OF FIELD PROGRAM

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Abstract

The benefits and problems associated with a major National Science Foundation - RANN interdisciplinary field research program on lead and other trace metals in the "New Lead Belt" of Southeast Missouri are presented so that other investigators, agencies, and industries considering or involved in similar research might utilize these experiences in their programs. Factors that must be considered prior to the establishment of a successful coordinated laboratory-field program include the initial selection of a representative study area to meet the objectives of the proposed research. Preliminary determinations on the type of tests needed, chemicals and equipment required, space and time allocated, and administrative procedures are discussed. Initial on-site reconnaissance and selection of sampling stations must consider accessibility, utility requirements and special needs.

Logistical considerations used in estimating project expenses and time are discussed, illustrated by examples of situations encountered such as statistical estimates of samples required, projections of number of sites needed, man hours necessary to travel to sampling locations, problems with seasonal variations, and special analytical requirements. Design of the projected schedule of performance has been found to be a major consideration for project management.

Program implementation is discussed with reference to the pleasures and problems associated with the construction-operation of sampling equipment, protective design and environmental blending of equipment, training and supervision of field personnel, and the collection, recording, priority and validation of samples. Effective communications have proven to be of major importance to the operation of an effective field program requiring coordination between all participants.

Information utilization and experiences gained through the cooperative efforts developed between industries and agencies are stressed. Methods for presenting applied research knowledge to appropriate user groups and decision makers are presented for future considerations and implementation in similar programs.

Introduction

A majority of the research programs sponsored by the National Science Foundation's - RANN (Research Applied to National Needs) Program are concerned with practical field work. The conception, development and initiation of effective field work may be very rewarding or a total diaster dependent upon how the investigator or research group approaches the problems of stalking and bagging the *Samplus elusivens* A well-organized field research program usually involves a large number of researchers, faculty, technicians, graduate and undergraduate students and therefore assumes all the trappings, clamor, logistics and problems usually associated in one's mind with a full-fledged safari into the remote jungles of some lost continent. However, many of the answers needed for the NSF-RANN projects are to be found in the field and brought back to the laboratory where they may be analyzed, evaluated and hopefully applied to solve some of the real world problems faced by our nation at the present time.

Experiences gained from the benfits and perils associated with a major NSF-RANN interdisciplinary field research program concerned with lead and other trace metals from industrialization in the "New Lead Belt" of Southeast Missouri may therefore be helpful to other investigators, agencies, or industries considering or involved in similar environmental research programs. Experience has been called the best teachers (if you live through it) so one should go forth armed with the shield of planning, the sharp sword of scientific approach, the armor of knowledge, and a desire to compete with "Mother Nature" in her environment which seldom conforms to the idealized situations as visualized from textbooks, films, television, scientific journals or comic books. By being prepared and flexible to change, the field program can benefit all while achieving program objectives. Be aware that you will face problems (such as we had with the proverbial 200-year flood in the Missouri study area -- not once but twice during 1973-74), but turn them to your advantage where possible. With this concept in mind, certain factors should be considered for the planning and development of an effective field study.

Selection of Study Site

The primary consideration for a coordinated laboratory-field program must be the initial selection of a representative study area suitable or specified by the objectives of the proposed research. The investigator or project director and his team must go through a serious planning session that defines and limits the actual field area to be studied or monitored. These discussions should include the following rationale:

A. Determination of size and location of area. This may initially be proposed and outlined on maps and aerial photographs where possible.
B. Conduct an on site reconnaissance and update and modify maps where necessary. The U. S. Geological Survey 7.5 minute series maps at a scale of 1:24,000 are excellent for determining contours, land features, and other important information.
C. Select the initial sampling sites with regard to accessibility, utility requirements (electricity, water, gas) and special needs of your project.

Sampling sites should be accurately marked on maps and photographs made which can be used to insure duplication in sampling from the same site by different investigators. Usually at this stage of planning many investigators will learn the value of map reading, especially after stumbling off a cliff or into a stream. The field checking of maps is also most important since new roads may have been constructed, old roads closed or portions of the selected area altered since the map was printed. Also, be alert to any possible problem source which might contaminate your selected sampling location. For example, our project had initially selected one sampling site only to find that a causeway approximately 200 meters upstream was continually used for washing automobiles and draining crankcase oil. Needless to say, this would have caused some stress on the people carrying out precision analysis for trace metals in the analytical laboratory. All of these factors must be considered in the selection of an appropriate, economical and accessible study site.

Selection of Laboratory and Field Tests

Many investigators initially propose to do the full spectrum analysis of the periodic chart without regard to equipment, chemicals needed, personnel and time necessary to conduct the proposed test program. Again, a scientific approach must be made to determine what actually may be done as against what one would initially like to do. The speedometer on most cars registars up to 120 or 140 miles per hour (doubtless to keep the dashboard in harmonic balance), but that is not a realistic speed (for most anyway). The same concept usually holds true for scientific equipment used in the laboratory and the field. One approach to this problem that has been successful during the development of the lead study project at the University of Missouri has been to:

A. Determine exactly what equipment is currently available and in working order.
B. Run initial proposed analysis to determine how much time, what kind of reagents and what specific glassware is required. (With ships, this is a shake-down cruise, and in many labs will become the breakdown cruise).
C. Order replacement parts, chemicals, glassware, special items and new equipment needed immediately since a delay time is usually experienced connected with administrative procedures, transportation and assembly

problems that have become even more acute due to the present energy problem.

D. Spend whatever time necessary with your purchasing or supply group to insure that everyone understands proper administrative procedures and may acquire supplies in the most efficient and economical way possible.

Logistical Considerations

Logistics in military terminology has to do with moving, supplying and quartering of troops which is a fair assessment of what also occurs in most field sampling campaigns. Fortunately, or unfortunately dependent upon your viewpoint, most research programs are not run by a project general with the authority to declare martial law or shoot deserters from his research and monitoring group. However, some of the logistical problems that must be overcome to conduct scientific field programs would stagger the imagination of most military commanders.

A project director, coordinator or leader by any other assorted names (most of which are unprintable) must be designated to bear the responsibility of reporting directly to the funding agency, coordinating and working with the team involved and trying to use the wisdom of Soloman (which is difficult dependent upon your temple). Considerations which must be calculated, tried, revised and updated should include the following:

A. Estimate number and type of samples needed for each sampling site. Initial suggestions and revisions should be made by team members qualified in that area.

B. Plan man (people) hours necessary for travel to and from the field, placement and maintenance of equipment and use of special vehicles.

C. Remember seasonal variations in the studied area and take into account the loss of time and fewer samples due to weather conditions. For example, during the rainy season in Missouri, it is important to keep on paved or gravel roads, otherwise one spends many long hours in the spring trying to determine which mud hole the pickup might be sunk in.

D. Special analytical requirements which necessitate sample collection, preparation and analysis in a specified time period must be considered and blended into the total program where possible (1). Train personnel to take several types of samples so that maximum utilization can be made for each persons travel and field time.

E. Design a performance schedule but realize that it will require constant modifications to rapidly adjust to unforeseen circumstances. Settle upon a standardized method for reporting which is acceptable both to the research group and references with measurements and data reporting efforts by agencies or industries working with the same problems.

Program Implementation

Once the program has been planned, the field operation is implemented, and while often difficult, confusing, or time consuming, it is always exciting and definitely not routine. Evaluations by trained people in the field actually taking the sample are one of the most critical parts of the program. All the testing and analytical precision may be without value if they lack the on-site evaluation of the field worker to judge what conditions prevailed at the moment of sampling and its relationship to the total program.

The field program also brings a fresh sense of relief to the desk bound warriors who can return from the field work refreshed, in touch with reality and to allow their sunburned, wind-chapped, chigger swollen, tick-bitten, weather worn countenance to be the envy of their not so fortunate colleagues. The non-field people must also suffer through lengthy tales of of heroic adventure and fantastic actions necessary to collect and bring back alive the specimens needed for the project.

Areas which must be considered during the active field program include:

A. The construction, modification and operation of equipment in the field.

B. The protection and environmental design of equipment so that it will not be damaged, removed or noticeable.

C. The training and supervision of field personnel to gain maximum utilization for their efforts and time spent.

D. The proper collection, preparation, transportation and testing of samples. This requires that a standard method of recording and reporting be employed so that the information is understood by all investigators. It is also important to establish a priority to determine which samples are collected and analyzed in what order to best achieve the objectives of the project.

E. The validation of samples is important since many investigators, industries or agencies may initiate control or correction action based on analytical data. It is, therefore, important that some type of validation be maintained in analytical laboratories by means of sample splitting, spiked samples, reference samples and sampling sharing and comparison with other qualified analytical laboratories.

F. Communications between-within-without, written, telephone and person-to-person remain as one of the most important aspects of any field or laboratory program. Most problems arise through the lack of communications. A good sense of humor helps or "laugh and the world laughs with you, cry and you cry alone" and stain your best tie.

Always attempt to learn and observe the local ground rules applicable to your study area since most projects depend upon the cooperation of the local population if their equipment and field personnel are to function properly. This requires that you keep the local population informed on what you are doing and seek their acceptance and assistance. Remember, General Custer thought he had the best field program available.

Information Utilization

The National Science Foundation RANN Program was initially charged with the development of national goals and priorities by the National Academy of Engineering in their report entitled Priorities for Research Applicable to National Needs (2). Therefore, the test or success of any NSF-RANN Project must be the ultimate application and development of such research findings by appropriate user groups. This information exchange and utilization may be accomplished through the following methods:

A. The development of progress reports, technical and general publications which are used by appropriate user groups and the concerned public, as well as the scientific community (3).

B. The identification of specific user groups in appropriate sectors to receive research findings in a usable form for their decision making process.

C. The utilization, where possible, of research findings from field programs, by agencies, industries and other interested groups that have the capabilities to implement such technology.

It has also been shown that universities can play an important role in the development of cooperative programs between industries and government (4). Well planned and executed scientific field and laboratory research by unbiased groups are more easily accepted and utilized by user groups that are often cast in an antagonistic role. The NSF-RANN lead study carried out in Southeast Missouri has been successful in solving many of the problems encountered with field programs and the applications of this work has been beneficial to both government and industries concerned with the development of mineral resources and the protection of the environment.

Many investigators continue to think of the familar quotes "shoulder to the wheel, ear to the ground and nose to the grindstone" approach but it becomes increasingly difficult to do applied research in that position. Research utilization must continue to be the main thrust of good field programs and investigators should continue to develop findings that will have practical applications for effective technology transfer.

Field programs do pose interesting and sometimes difficult problems but most of these can be overcome by careful planning and evaluation. Such work in the real world offers personal and professional benefits through the development of findings that may have excellent potential toward solving national problems. It is hopeful that some of the experiences gained and presented may be useful for future considerations and implementation in field research programs.

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SOME COMMENTS ON THE MANAGEMENT OF PROBLEM-ORIENTED INTERDISCIPLINARY RESEARCH*

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ABSTRACT

Problem-oriented interdisciplinary research presents several unusual challenges and problems to the university and the directors of such programs. These problems include: (1) the relationship of members of the project to their departments, especially with regard to the reward structure, (2) the difficulties of persuading people of different disciplines to listen to each other, (3) the competition of these programs with more traditional programs for university resources, and (4) the unaccustomed interest of external user groups such as government, industry, and the press in the research.

The role of the manager. Ideally, organizations are created in order to accomplish some set of objectives. Given a set of objectives it is possible to bring into being a more or less structured set of activities which must be performed to accomplish the desired ends. In general these activities will have to be directed, coordinated, and integrated in order to accomplish the objectives. In most cases the continued support of the activities will depend on an effective communication of the progress to the organizational entity which provides the support.

The role of management in this scheme is simply to make sure that all this gets done. This role can, and often does, encompass the following functions:

1. The conceptualization of the program and the communication of the concept to external support groups.
2. The organization of activities necessary for obtaining the objectives.
3. The direction, coordination, and integration of the activities.
4. The communication of results to external user groups.

In general, the skills needed by the person in this role are:

1. Administrative Competence -- the ability to think and act in terms of the total system.
2. Human Relations Competence -- the understanding of factors involving human behavior and the use of this understanding in day-to-day interactions.
3. Technical Competence -- the ability to use pertinent technical knowledge to direct, integrate, and plan technical activities.
4. Program Representation Competence -- the ability to communicate the mission and accomplishments of the organization to external individuals or groups.

These functions and skills are required of any manager in any organization. The exact mix required, however, varies widely from one organization to the next and within an organization from one time to another. Clearly, the closer to the bench one is the greater the importance of technical skills, whereas these skills are not an important part of the mix needed for a university president.

Where does the manager of a problem-oriented, interdisciplinary program of the type represented at this meeting fit into this picture? What are the special demands and pressures of this job and where are the pitfalls? Before giving you some of my own thoughts on this matter,[1] I want to warn you that I will speaking almost entirely in terms of a project in the university setting. There will be, I suspect, some problems that are shared by government and industrial laboratories.

Organizational problems. I submit that the planning, direction, and coordination of an interdisciplinary, problem-oriented effort is a far more complex task than is the case of more traditional research. That should come as no surprise to those of us here, but many of our discipline-oriented colleagues need convincing. Once one begins to cross departmental lines and to involve faculty and students in the shadowy area between disciplines and at the same time to focus on a practical end, the difficulties multiply very rapidly indeed.

I won't go into the more technical aspects of planning because Bobby Wixson gave a far better presentation of these than I can. Rather I would like to touch on some of the basic problems encountered in this function. To a certain extent these problems also have technical, human relations, and program representational aspects as well.

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In many ways the organizational problems involved in this type of work are similar to those in a government or industrial laboratory.[2] The fitting together of people and tasks in an appropriate way to reach an objective is shared by all organizations. However, many new problems arise because:

1. The presence of many disciplines creates communication coordination problems.
2. The location in the university substrate with its departmental structure gives rise to centrifugal forces which tend to tear the enterprise apart.

In order to work with someone from another discipline each person must learn at least some of the other's vocabulary. This is a time consuming, often frustrating process. But professionals find it difficult to take the time to listen effectively to someone whose language or methods are different. This natural tendency requires someone to help it get done. The managerial role here is to monitor this process and to act as an interpreter. The effective integration of efforts requires a constant realization of the system as a whole.

One of the most difficult problems I've encountered is that of getting physical and social scientists to listen to each other. I must say I am largely at a loss with this one. I do think that there is some hope for our students whose prejudices in this direction are hopefully, somewhat less firmly established.

The natural opposing forces, generated by our traditional disciplinarian training are reinforced by the power structure of our institutions. Most universities, at least large ones, are characterized by a pancake structure with authority and power spread out among trustees, administrators, faculty, and students in a very confusing way. In fact, we might better characterize the power structure as a blueberry pancake because set within the diffuse pancake structure are small power centers such as departments, schools, and colleges. Basically organized around disciplines or collections of related disciplines, these city-states are sources of considerable power and they guard their boundaries quite vigorously.

The division into discipline-oriented departments carries with it a number of important consequences. Among these are:

1. The faculty member is evaluated and rewarded at this level.
2. The physical location of faculty and students may be determined by this division.
3. The department is the sole judge of what constitutes acceptable work by students.

The result of this is that unless there is an intervening power, the project members are at the mercy of their departments in terms of rewards, physical location, and freedom to define some areas of their work. In turn the project manager can find his ability to organize the group into an effective whole severely affected by the uncoordinated actions of several different departments.

In some institutions the division of overhead can be a source of considerable problems. In our institution the amount of overhead returned to the departments is so small that it isn't worth fighting over.

There are, of course, many different institutional arrangements for interdisciplinary research ranging from no special arrangement, as is our case, to formal institutional structures. At an earlier time I believed that the loss of flexibility that often occurs with formal institutes was not worth the gain. I now am convinced that ad hoc arrangements are inherently unstable. The people engaged in these efforts need a home other than or in addition to their department.

There are four reasons for my strong conviction concerning a need for an institutional home for this work. The first is rather general, the remaining three more specific:

1. The forces operating in a strictly departmental structure are almost always in a negative direction.
2. With rare exceptions, the reward system at a departmental level will at best be neutral -- more often negative.
3. The commitment of resources by the university puts the program in direct competition with the departments.
4. The possibility of controversy arising from problem-oriented research carries a risk for the entire university.

I believe that the importance of this type of work to society, science, and education is too great to leave to the mercy of departments which will largely see this work as a threat. There are risks to creating institutes, and these risks should be recognized, but universities must decide whether to fish or cut bait.

Technical problems. Although the project manager may often have a research effort of his own, the basic technical skill that is needed is the ability to plan, coordinate, integrate, and communicate the efforts of the various members of the project. This requires a spectrum of effort and knowledge which is fairly flat over the spread of disciplines involved rather than peaked as would be the case with the other members of the group. But the intensity must be high enough to be above the noise level.

Thus the project manager must be careful to read widely and follow closely the efforts of the various members of the group. Even the most prodigious efforts may not be sufficient to allow the director to be fully aware of possible gaps or trouble spots, and the site visit team can, if well chosen, bring to the director important insights into the program. The site visit team may be particularly helpful with the technical evaluation of the performance of the group. I have found the site visits, while an ordeal, to be immensely valuable in correcting my evaluation of the technical work. Needless to say, a well-done site visit can be immensely valuable at budget-cutting time.

The technical skills demanded of the manager are thus not those of an individual researcher. This person must paint with a broad brush and act in a coordinating, interpreting, facilitating, and integrating manner. But the director must have a capability for scientific criticism that enables him to see serious flaws and appreciate the value of the work of individuals with far greater technical competence in a particular area than he. Moreover, when gaps are noticed, or when the work of an individual seems to veer away from the objectives of the program the director must not only have sufficient technical skills to be aware of the situation but also to communicate effectively enough on a technical level to solve these problems.

Human relations problems. Since I discussed a number of aspects of this area last year, I will concentrate mostly on those problems which are present because we are in a university. As we all know a university is a rather odd subculture with a value system which is rather different from the rest of society. We must expect that behavior of individuals in this setting to be determined in part by the commonly shared values of the university community. Since many of the well-established values of the university community run counter to the mode that we are working in, we can expect members of such projects to have mixed feelings at times concerning the values of their work -- even if their colleagues and friends are supportive. Perhaps those involved in management have a particular problem because administrators or managers are generally held in low esteem by the university community.

The individuals involved in these projects are thus subject to strong cultural forces which oppose interdisciplinary problem-oriented activities. These forces arise from values and goals which seem to be in conflict with the purposes of the research effort.

Thus, one of the most important functions of the manager is to try to integrate the goals of the individuals with the goals of the project. It is important to design the program to provide intellectual stimulation and growth. This means that there must be sufficient flexibility to allow for changes of direction which maintain intellectual excitement while still meeting the objectives of the program.

Another way to help with this problem is to build a cohesive group which shares values that are more in line with the goals of the project than the values of the university community. The members then obtain reinforcement from this smaller group which helps the process of developing compatibility between individual and organizational goals.

While I believe that many of the values in the university community are in great need of revision, I do not advocate a wholesale change of these values. Rather there should be a tension that exists between the more traditional value of knowledge for its own sake and knowledge for society's sake. This tension will help us keep a proper perspective. Clearly, there are many societal problems which the university cannot deal with very effectively. Those problems requiring immediate and massive responses don't easily lend themselves to the university atmosphere.

Institutional representation. At various times in the life of a program, but particularly toward the end when user interactions often increase, the representation of the organization to external groups and individuals is a crucial activity. This activity is not easily separable from the organizational function because the ability to see the effort as a whole, in a systematic way, is necessary in order to present it to the outside. The preparation of research plans, management plans, and the like benefits both of these areas for these efforts demand a cogent presentation which helps the manager view the effort as a whole and aids in his representation of the project to external groups. I believe that these efforts, if used wisely by those who evaluate the program, are very worthwhile. We all know that possible danger that is connected with a too literal interpretation of these very coarse descriptions and I will spell out one of these dangers shortly.

But, whether used wisely or poorly, it seems clear that management plans and other plans are here to stay. In fact, they've been with us so long that I find it hard to imagine life without them. Indeed, maybe we were never without them -- we just didn't realize that they were around. Perhaps, in some dusty files somewhere, we might someday find the management plans submitted by Attila the Hun or Napoleon, or George Washington. In fact, I'm sure that this activity dates back to what I refer to as the "original management plan." We can only guess at its shape -- and only the most virtuous of the N.S.F. program managers will ever know its true form. A crude guess would indicate that the initial plan was for an exploratory and planning effort. An attempt to reconstruct this plan is shown in Figure 1, clearly many details have been omitted.

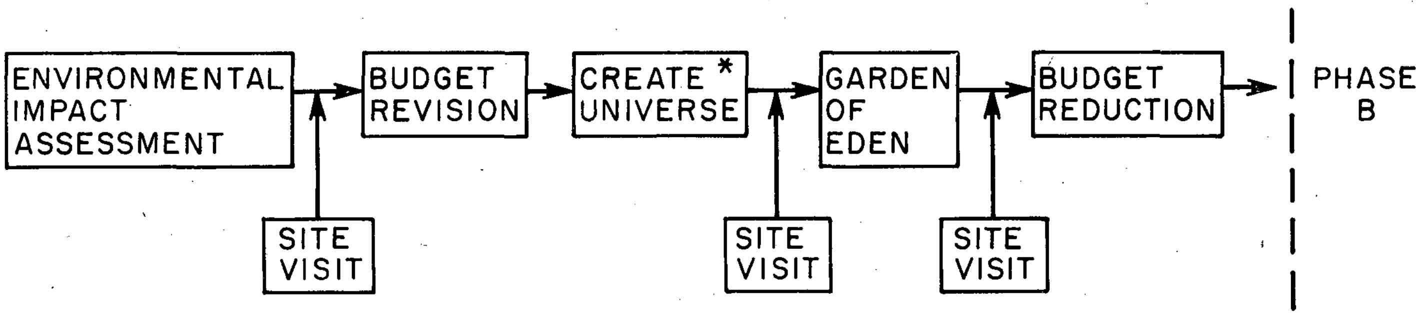
As useful as these plans are, they really are only a beginning. The effort of

MANAGEMENT PLAN

"A PILOT STUDY IN CREATION" EXPLORATORY AND PLANNING PHASE

PROJECT DIRECTOR - GOD   PROGRAM MANAGER - ARCHANGEL ROB

PHASE A



* FOR DETAILS OF CREATION - SEE APPENDIX A

APPROVED BY C.O.M.B. (CELESTIAL OFFICE OF MANAGEMENT AND BUDGET)

Figure 1

communicating the mission and results involves a great deal of interaction on an individual level. The manager must try to be aware of all possible groups that might have a stake in the effort and try to establish and maintain communication with them on a person-to-person basis. The writing and distribution of reports is useful -- but reports can be misinterpreted or not read. The real difficulties and risks of this type of work are principally in the user interaction effort.

Let me warn you of one type of problem which is very difficult indeed. I call this the "But you said you could walk on water" syndrome. This problem arises when the program is externally given, either innocently or malevolently, a function it cannot fulfill, such as coming up with the "complete" solution to a given problem. Then when you fail to perform this impossible feat you are taken to task for not producing.

This problem can arise in many ways. Sometimes it may be generated internally because we almost always are optimistic about what we can achieve. I believe we should be optimistic, but it is well to be aware of this danger. Another way this problem can occur is through a user group consciously or unconsciously trying to put you between them and an adversary. Some of the people we deal with are under great pressure from various quarters. This leads to a very human tendency to set up groups such as ours as "the experts with all the answers." This is a very precarious position indeed. I don't have too many good answers for this problem -- it requires diligence, good communication, and fast footwork.

Having had our small experience with the news media this year, I have some thoughts to pass on that may be useful. Perhaps the foremost one is that it is very useful to generate periodic news releases. This may help to avoid the situation of bursting on the scene as a great surprise. These releases are not a matter of P.R., but rather should be used to try to communicate an accurate view of the mission and its results. They should be prepared with great care and it helps to circulate them widely among one's colleagues for their comments. It is a painful, time-consming process, and at best, only the local newspaper will print all of it. Other papers will abridge it, usually to one's dislike (we all have a pride of authorship), but in the long run it can save a lot of grief. If the media interest becomes intense, contacting the university news service may be helpful. Unfortunately, this is a very weak spot at some institutions.

I have found the interaction with user groups to be one of the most satisfying activities of the role. It has given me the opportunity to interact with a wide range of individuals outside the university whom I would not have met otherwise. The appreciation I have gained for the dedication, capability, and concern of many people in government, industry, and citizens' groups has given me a sense of renewed optimism.

CONCLUSION

I have tried here to present a rough picture of some of the functions of a manager of a problem-oriented interdisciplinary research project and the types of skills -- organizational, technical, human relations, and program representational -- needed to perform these functions. I have suggested that in many ways the departmental structure of the university gives rise to counter-productive or centrifugal forces which tend to tear such programs apart. I believe that new institutional arrangements are necessary if this work is to flourish. Many institutions have recognized this and are creating various organizational forms which can help to balance the centrifugal forces. From what I can see there is no general agreement concerning the optimal arrangement.

It seems clear that we have entered a new era. Unlike the era of the late fifties and early sixties when there was an almost blind faith in the ability of basic science to produce a better world, the public and its representatives are demanding that universities apply their resources more directly to societal problems. We have been fortunate to be a part of this early development. I believe that we have seen that this new era presents new challenges and opportunities to the universities. Those institutions that fail to respond may find themselves becoming monasteries. There are many risks involved in making institutional commitments to this type of work, but I feel we have no choice -- it is an obligation.

The universities stand to gain much by joining with society in solving important social problems. We can produce students with a greater understanding of the contributions they can make. We can strengthen our capabilities in both basic and applied research. And, with hard work and broadmindedness we can rebuild the constituencies we lost by becoming isolated from much of society.

The rather unusual functions which are involved in directing projects of this type has generated a need for individuals with more management capabilities than are usually required to direct research efforts in universities. This creates a responsibility on the funding agencies and universities to develop a more sophisticated management capability than we usually encounter in universities.

I would suspect that many of us who have been in the role of project director have found our goals and values to have been changed significantly by the role. I know that some of us have gone through periods of great uncertainty concerning our futures. The management role is seductive and there are many personal conflicts with the images we had of ourselves previously. Many of us will probably find our futures to be considerably different from the comfortable faculty images we had in mind earlier.

I suspect that many of us, whether involved in managing these programs or not, will be agents of change in the universities. Perhaps the most significant effect of the RANN program will be that it created a subversive group of faculty and students who helped change the role of the university and in the process helped society and the university.

ACKNOWLEDGMENTS

Every person in a managerial role knows the importance of an administrative assistant in carrying out the many important tasks that leave the manager free for planning and coordination. The ability of this person to grow with the job and to relate to others effectively and with sensitivity are two key qualities of this role. Everyone who has been associated or had contact with our project is aware of the important contribution Kathy Petersen has made in this role. I know that my own effectiveness and enjoyment of this experience would have been greatly diminished without her capable assistance.

I know that all of us who have been involved in the Trace Contaminants Program, and especially the project directors, share a deep sens of gratitude for the wise guidance we have received from Bob Rabin, Dick Carrigan, and Ron Goor. These people have shown a sensitivity that has made the project director's job infinitely easier. I know that I have found their site visits, although stressful, to be times of great growth. I am constantly amazed by the fact that after I receive the budget revision letter (always downward) from Bob that I feel I have just read a work of art.

If I have said anything here worth communicating it is because I have had the opportunity over the past twenty months to interact with an eminent organizational psychologist, Dr. Floyd Mann, Director of the Environmental Council, University of Colorado.

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[2] See, for example, R. M. Hower and C. D. Orth III, Managers and Scientists (Harvard College, Boston, 1963).

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