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Harte, J.

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June 1982

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J. Harte

Energy and Resources Program
and Energy and Environment Division
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720
USA

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J. Harte

Energy and Resources Program
and Energy and Environment Division
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720
USA

ABSTRACT

Recent progress in acid precipitation research is summarized, and major experimental uncertainties are identified. Research tools that are available and those that are needed are described.

KEY WORDS

Acid precipitation; ecosystems; air pollution sources; international relations.

INTRODUCTION

Evidence has now accumulated to show that acid precipitation is occurring not only in Scandinavia and the northeastern U.S., but at various other sites throughout the world (1-7). Three important questions are raised by this development:

- (1) What are the sources of this widespread acid precipitation and how can they be controlled?
- (2) What will be the ecological and human consequences of acid precipitation at these new sites?

- (3) What is the potential for new incidents of international dispute arising over transboundary movement of atmospheric acid-forming pollutants?

I describe here the methods that have been developed to answer these questions and summarize the major facts and uncertainties. A complete review of the acid precipitation problem is not intended. Most of the past research on acid precipitation has been concerned with Scandinavia and the northeastern U.S. whereas the focus here is mainly on acid precipitation in other regions of the world. Even the latter topic is too broad to review here, and only selected highlights will be discussed. A useful and quite complete review of the acid precipitation is contained in a recent U.S. National Academy of Sciences report (8).

SOURCES

It is widely believed that in the absence of environmental pollution, the pH of precipitation would be 5.6 or greater, with greater values observed in areas where natural alkaline dust is present in the atmosphere. The value 5.6 is derived by assuming equilibrium between carbonic acid in precipitation and atmospheric carbon dioxide. Prior to the late 1970's, all reported incidents of acid precipitation, (with pH below 5.6) could be plausibly accounted for by industrial, electric generating, home heating, and automotive activity; areas with acid precipitation were downwind from sites of major fossil fuel combustion. Coal and fuel oil, rather than gasoline, were particularly implicated as the major sources because of the high ratio of sulfuric to nitric acid in precipitation. During the past decade or two, the nitric acid component has been increasing faster than the sulfuric acid component (9),

suggesting that sulfur emission control is having an effect.

More recent discoveries of acid precipitation fall into two categories: those for which a number of possible sources are identified but the most important source or sources are not singled out, and those for which no candidate sources have been discerned. A good example of the former is on the western slope of the Colorado Rockies, where precipitation pH has been observed to average well below the hypothesized background level of 5.6 for the past several years (7), with storm events with pH = 3.6 observed. Among the possible sources of acidity in this region are coal-fired power plants in the western U.S., metal smelters located in Utah, Nevada, and Arizona, and mobile sources in California. It is also possible that in high mountain regions like the Colorado Rockies, precipitation storms carry down to the surface pollutants from the high troposphere and these pollutants originate from very distant sources; thus world-wide sources might be responsible.

A number of methods have been developed in recent years to determine the predominant source in such a situation. The relative nitric and sulfuric acid concentrations provide some insight. Mobile sources emit virtually no sulfur, and thus if the acid precipitation is comprised largely of sulfuric acid, then non-mobile sources are implicated. In regions of Europe and the midwestern U.S., where coal is believed to be major contributor to acid precipitation, the nitric-to-sulfuric acid ratio (on an equivalents basis) is roughly 1:2.5. However, coal combustion can produce either largely sulfuric or largely nitric acid and the precise circumstances under which one or the other predominates are not well understood. In one city in China, where coal

is virtually the only fuel burned, and a rain storm with a pH of 2.25 was observed, the nitric-to-sulfuric acid ratio (on an equivalents basis) was measured to be about 15:1 (6). The type of coal, the combustion conditions, and the distance from the source to place of precipitation (10) can all exert an influence on this ratio; other factors are probably important as well and without further research the use of nitrate/sulfate ratios is only of limited value in source determination.

Other chemical signals in coal that can be used to help locate sources are trace metal concentrations and weak or Bronstad acids (including ammonium and organic acids). Because the metal content of petroleum and coal differ from each other considerably, trace metals are a particularly interesting signal. The vanadium-to-manganese ratio in precipitation has been proposed (11) as a useful indicator of the relative importance of petroleum-to-coal sources. However, here too, there are ambiguities. For example, not all metals travel the same distance in the atmosphere. Moreover, storms bearing acid precursors from one region may pick up trace metals from other sources in a second region and drop the moisture on a third region.

A method of source determination that holds considerable promise but is still in need of refinement and testing, is the brute force approach of storm tracking -- correlating precipitation event chemistry with meteorological information about the movement of air parcels accompanying the individual storms. No single method is likely to yield completely convincing information about acid sources, however. The use of all the above mentioned methods should be explored further; only when a number of approaches point toward a common source will we have confi-

dence in the answer.

Acid precipitation has also been observed in areas where the problem is not one of "which of the many sources is responsible," but rather "what could possibly be causing acidity in such a remote location". For example, the observation of acid precipitation in Hawaii (4,5) has prompted some to declare that the oceans are a source of acid precursors to the atmosphere and the background acidity of "pure" precipitation is below 5.6. My belief is that it is probably true that background precipitation pH can be somewhat below 5.6 in regions of the world where alkaline materials are not present in the atmosphere. In remote oceanic sites this is particularly likely. In remote mountainous sites, however, where low pH events have been recorded and precipitation averages at least a full pH unit below 5.6 (2,7), the sources are very likely anthropogenic. In the Tibetan Plateau of China, where acid precipitation has been observed in remote urban areas (and to a much lesser degree in the surrounding mountains), there can be no doubt that fossil fuel combustion is the cause (6).

Control of the anthropogenic sources of acid precipitation is a major problem today. Sulfur emission control technologies are established; making the decision to use them is complicated by the difficulty of deciding whether the cost is worth it. Because SO_2 may not always be the limiting factor in sulfate and sulfuric acid formation (12), sulfur emission reduction does not necessarily reduce sulfuric acid formation proportionately (13). Small particle emission control is required in some circumstances and that is a more expensive undertaking.

Control of emissions of oxides of nitrogen is more difficult than control of sulfur oxides. Several promising technologies are under study now, however, for application to large centralized burners such as coal-fired electric power plants. In the developing areas of the world, coal is likely to play a large role in energy supply (14). An expected pattern of development is a large number of small-scale coal combustion sites, and it is under such conditions that high nitric acid concentrations are likely to be an acute local problem (6). Research on small coal stove combustion efficiency and NO_x emission control would be especially important in this regard.

ECOLOGICAL AND HUMAN CONSEQUENCES

To predict ecological effects of toxic substances, ecotoxicologists have relied traditionally upon a combination of field studies and laboratory single-species bioassays (15). In recent years the use of ecosystem microcosms has been proposed to augment the traditional tools (16). Microcosms are segments of natural ecosystems of a size convenient for laboratory study. The advantage of toxicology studies in microcosms over laboratory single-species bioassays is that microcosms possess many of the complex features of natural systems that cannot be investigated by studying a single organism in a contrived environment. Among these complex features, the microbe-detritus-nutrient interactions are particularly suited to microcosm investigation and are both critical to ecosystem function and sensitive to a number of toxic substances. The advantage of microcosm investigations over field investigations is that the former are generally easier and less expensive to carry out; moreover microcosms allow replicability and control of experimental

conditions.

Although the use of microcosms for study of toxicological effects is in its infancy, several completed studies have provided new and predictive information about chemical and biotic changes in aquatic ecosystems (17,18). In an investigation by K. Tonnessen, a graduate student in the Energy and Resources Program at U.C. Berkeley, effects of acidification on lakes of the California Sierra Nevada were studied. Impacts of a pH reduction on phytoplankton and zooplankton populations, and on alkalinity and trace metal concentrations were quantified. In addition, she has demonstrated how microcosms can be used to obtain useful information about the time frame over which real lakes will lose their buffering capacity and acidify. We expect the microcosm approach to be used increasingly in the future to obtain quantitative and predictive information about ecological impacts of a wide variety of toxic substances.

The human consequences of acid precipitation can be divided conveniently into five categories, ordered here by decreasing ease of assigning monetary cost but not necessarily by decreasing magnitude of impact.

- (1) Direct damage to materials. Acid precipitation can erode buildings and statuary, damage painted surfaces, and corrode synthetic products.
- (2) Damage to natural resources of direct commercial or recreational value. Fish populations have been reduced severely in lakes of southern Scandinavia and the Adirondack Mountains of New York State, USA (8). Commercial and recreational losses result. Clear

and irrefutable evidence for damage to forest and agricultural crop productivity from acid precipitation is lacking, but studies suggest the likelihood that continuing acidic precipitation may cause short-term enhanced growth (under certain nutrient-limited circumstances) and long-term decline in productivity. More research is needed to resolve the large uncertainties in this area.

- (3) Effects on human health. The concentration of certain hazardous trace metals is increased in acidified waters by a process of accelerated mobilization of these metals from soils and lake and river sediments. The effect is exacerbated when acidified water flows through metal water pipes carrying drinking supplies. While the phenomenon of metal mobilization by acidified surface waters has been amply documented (8,19), further research is needed to identify the circumstances under which human impacts would be likely to occur. Other direct effects of acid precipitation on human health, particularly on respiratory function, are most likely to arise in urban areas where acid rain, mists, and fogs occur with $\text{pH} \leq 3$ on occasion (6,20).

- (4) Damage to human services derived from healthy ecosystems. These are the most difficult to investigate and quantify, but their impact could also be the most profound. Healthy ecosystems sustain a number of life-supporting processes vital to human well-being. These include the cycling of nutrients, the purification of air and water by natural biological processes, the modulation of local weather and global climate, the maintenance of a genetic "library," the maintenance of a protective ozone layer in the stratosphere (by

the denitrification process), and many others (21,22). An example that is particularly pertinent to the acid precipitation problem is the role of nitrogen-fixing organisms in supplying nitrogen in useful form to certain ecosystems and agricultural crops. In alpine ecosystems and in the tundra, nitrogen fixing lichens are so vital to the functioning of the plant and animal communities that they are called "keystone" species - if they are damaged the entire ecological edifice can tumble. In the Alaskan tundra, for example, the nitrogen supply to off-shore fisheries is supplied largely from terrestrial nitrogen-fixing lichen populations. Because the rate of nitrogen fixation slows under acidic conditions (23), acidic precipitation in the tundra could exert a profound effect on offshore fishing. Thus, there is an indirect ecological link between the lichen and an important commercial activity; study of direct effects of acids on the fish and shellfish would not have revealed this threat. A similarly profound effect could occur in high-mountain ecosystems, such as watersheds in the high Colorado Rockies, where lichens probably are a keystone species and acid precipitation is presently falling (2,7).

The search for keystone species that are sensitive to acid precipitation or other anthropogenic toxicants has just begun. Considerable research is needed to discover linkages such as the one just described. A combination of field research and laboratory studies with microcosms will be needed to do justice to the complexity of the problem. Because of the strong linkages between ecosystem services and human well-being, it is most critical that this subject

be further investigated.

- (5) Effects on International Relations. Because of its unique character, this topic is taken up in the follow section.

INTERNATIONAL CONSEQUENCES

International tensions resulting from transboundary movement of acid forming air pollutants are likely to arise between two nations (call them A and B) when the following conditions are met:

- (1) Nation A burns large amounts of fossil fuel, particularly high sulfur coal and petroleum with little or no pollution control in the fuel pretreatment stage or in the combustion process. From past experience, a rough order-of-magnitude estimate for "large amounts of fossil fuel" is 10^8 tonnes coal (or equivalent)/year.
- (2) The movement of air masses, particularly those accompanying precipitation events, is from nation A to nation B.
- (3) Within nation B there are regions where the waters and soils are low in alkalinity (i.e., they are regions with "soft water") and organisms are present that are sensitive to acid conditions, such as fish of the salmonidae family, certain amphibians, many nitrogen fixing organisms, and certain taxa of the plankton.

Between the U.S. and Canada, and between a number of countries in northern Europe and Scandinavia these conditions are met and international tensions have resulted. Within the Asia-Pacific region, where the use of coal is expected to increase in the future, the potential exists for the outbreak of similar tensions. Fisheries, which play an important role in the economies of many nations, are particularly

vulnerable to acidification. Research to identify possible regions of the world where the problem could arise, coupled with an effort to develop appropriate pollution control strategies where needed, could reduce significantly the possibility of future international disputes over the causes and adverse effects of transboundary acid-forming air pollutants. Complementary efforts should be made to identify existing laws and institutions that may help resolve tensions and to promote the exchange of technical information.

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REFERENCES

- (1) H.M. Liljestrand and J.J. Morgan, Environ Sci. Technol. 12, 1271 (1978).
- (2) W.M. Lewis and M.C. Grant, Ecology 60, 1093 (1979).
- (3) J.G. McColl, "A Survey of Acid Precipitation in Northern California", final report to the California Air Resources Board for contract A7-149-30, Sacramento, CA (1980).

- (4) J.M. Miller and A. Yoshinaga, Geophys. Res. Letters 8(7), 779 (1981).
- (5) R.A. Kerr, Science 212, 1014 (1981).
- (6) J. Harte, "An Investigation of Acid Precipitation in Quighai Province, China", Atmos. Environ., in press (1982).
- (7) J. Harte, G. Lockett, and R. Schneider, "Acid Precipitation and Surface-Water Vulnerability on the Western Slope of the High Colorado Rockies", submitted to Environ. Sci. Technol. Energy and Environment Division, Lawrence Berkeley Laboratory, Berkeley, CA 94720 (1982).
- (8) National Academy of Sciences, National Research Council, "Atmosphere-Biosphere Interactions: Toward a Better Understanding of the Ecological Consequences of Fossil Fuel Combustion." A report prepared by the Committee on the Atmosphere and the Biosphere, National Academy Press, 2101 Constitution Avenue, NW, Washington, DC 20418.
- (9) J.M. Galloway and G.E. Likens, Atmos. Environ. 15, 1081 (1981).
- (10) H. Rodhe, P. Crutzen, and A. Vanderpol, Tellus 33, 132 (1981).
- (11) K.A. Rahn, Atmos. Environ. 15, 1457 (1981).
- (12) T. Novakov, S. Chang, and A. Harker, Science 186, 259 (1974).
- (13) R.E. Meyers and E.N. Ziegler, "Environ. Sci. Technol." 12, 302 (1978).
- (14) D. James and T.A. Siddiqi, "The Increased Use of Coal in the Asia-Pacific Region: Achieving Energy and Environmental Goals." Working

paper, Environment and Policy Institute, East-West Center, Honolulu, Hawaii.

- (15) National Academy of Sciences, National Research Council, "Testing for Effects of Chemicals on Ecosystems", A report by the Committee to Review Methods for Ecotoxicology, National Academy Press, 2101 Constitution Avenue, NW, Washington, DC 20418 (1981).
- (16) J.P. Giesy, ed., Microcosms in Ecological Research, Selected papers from a Symposium held at Augusta, Georgia, November 8-10, 1978, National Technical Information Service, U.S. Department of Commerce, Springfield, VA 22161 (1980).
- (17) H.P. Kollig and T.L. Hall, Water, Air, Soil Pollut. 17, 225 (1982).
- (18) K. Tonnessen, "Aquatic Ecosystem Acidification in the Sierra Nevada, CA: Potential for Chemical and Biological Changes," in Acid Rain Symposium Ann Arbor Science Publishers, Inc. in press (1982).
- (19) C.S. Cronan and C.L. Schofield, Science 204, 304 (1979).
- (20) D.R. Lawson and J.G. Wendt, "Acid Deposition in California," California Air Resources Board, P.O. Box 2815, Sacramento, CA 95812.
- (21) J. Harte and A. Jassby, Ann. Rev. Energy 3, 101 (1978).
- (22) R. Budnitz and J.P. Holdren, Ann. Revs. Energy 1, 553 (1976).
- (23) National Academy of Sciences, National Research Council, "Energy and the Fate of Ecosystems", A report by the Risk-Impact Panel of the Committee on Nuclear and Alternative Energy Systems, J. Harte,

ed., National Academy Press, 2101 Constitution Ave., NW, Washington, DC 20418, 285-286 (1980).

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