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Authors

Blatchley, E.R.
Daughton, C.G.
Thomas, J.F.

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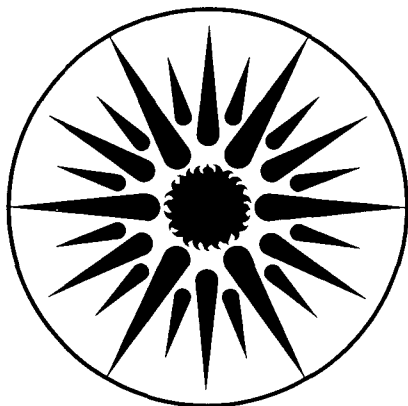
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E.R. Blatchley III, C.G. Daughton,
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April 1986

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E.R. Blatchley III,¹ C.G. Daughton,² and J.F. Thomas¹

¹Applied Science Division
Lawrence Berkeley Laboratory
University of California, Berkeley, California 94720

²Sanitary Engineering and Environmental Health Research Laboratory
University of California (Berkeley), Richmond, California 94804

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ABSTRACT

The elevated temperature of an oil-shale codisposal process will enhance the atmospheric emission of volatile components. Important among the organic compounds are the nitrogen heterocycles and aromatic primary amines, which are characterized by malodor and low odor thresholds and by resistance to biotreatment. Atmospheric lifetimes are determined by various transport (e.g., dispersion, washout) and transformation phenomena. Photochemical alteration will be the major transformation process. Those compounds that degrade quickly may increase the atmospheric NO_x concentration, giving the potential for photochemical smog formation. Those with longer lifetimes may present health and aesthetic problems. The broad spectrum of compound types and isomers present in process-water headspace samples may result in a range of atmospheric lifetimes.

The work reported here is the first investigation of vapor-phase atmospheric photoreactions leading to degradation of organonitrogen compounds emitted from process waters. Only direct photochemical reactions were studied. Headspace samples (65°C) were generated in an inert atmosphere (N₂ gas) and exposed to atmospheric radiation in Tedlar gas-sampling bags. Headspace composition was monitored by capillary gas chromatography with flame thermionic or flame ionization detection. Time-course headspace analyses compared exposed and unexposed samples, and individual compounds were monitored to determine the degree of individual photochemical losses. Under these conditions, the alkylpyridines did not photodegrade, in contrast to other nitrogen heterocycles (e.g., pyrrole) and aromatic primary amines. This is significant because alkylpyridines comprise the largest portion of organonitrogen compounds emitted from process waters. It is anticipated that indirect photoreactions (e.g., radical-mediated) will be more extensive and important; this will be the subject of another investigation.

INTRODUCTION

Oil shale developers anticipate the use of minimal upgrading of retort process wastewaters prior to disposal or reuse (Frankel and Drabkin 1985). Some disposal and reuse schemes will probably involve temporary storage of these waters in open-air ponds. For some above-ground retorts, process waters will be used to quench hot, retorted shale; steam and codistilled organic compounds would presumably be condensed, but fugitive evaporative emissions are possible. Codisposal of the retort waters and condensates together with retorted shale would take place at elevated temperatures (>65 °C) (Fox et al. 1984). During these various stages of pond storage, quenching, and codisposal, the major transport process that will determine the immediate, short-term environmental disposition of organic solutes will be volatilization. The major chemical transformation processes that will determine the short-term fate of these volatilized compounds would be vapor-phase, sunlight-mediated reactions.

Volatile Emissions during Codisposal

Volatile emissions from codisposal could be substantial (Hawthorne, Sievers, and Barkley 1985) and are a function of diffusion rates through the codisposal pile as well as sorption to the retorted shale surface (Persoff, Hunter, and Daughton 1984). In a laboratory simulation of codisposal over a temperature range of 80-450°C, the major classes of organic compounds emitted were N-heterocycles (NHCs), ketones, phenols, nitriles, and aromatic primary amines (Fig. 1) (Hawthorne 1984). Organonitrogen compounds (ONCs) compose a major portion of these organic emissions. These compounds are of particular interest for the following reasons (Daughton 1986): (1) they crosscut the spectrum of compounds produced by most synfuel conversion processes (e.g., oil shale, tar sands, coal conversion), (2) unlike most of the non-nitrogenous emissions, they do not occur commonly in nature, nor are they emitted to the environment in

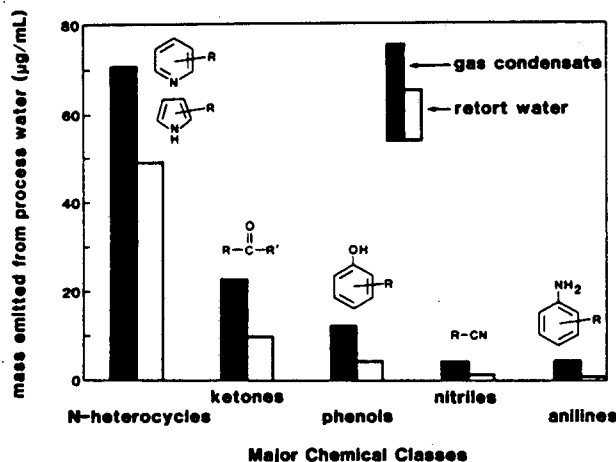


Figure 1. Predicted mass emissions from a codisposal operation (80°C) as a function of major chemical class; data from Laramie 150-Ton retort (run 20) gas condensate and retort water (Hawthorne 1984).

substantial amounts from anthropogenic activities (esp. petroleum processing), (3) since they are particularly refractory to removal by conventional biotreatment (Healy, Jr., Langlois, and Daughton 1985) and cannot be completely removed by steam stripping, they are likely to show high persistence and undergo uncontrolled emissions, (4) phototransformation presents the possibility of formation of atmospheric NO_x , a known precursor to photochemical smog, (5) most of these compounds are not currently regulated, mainly because they would be unique to the emerging synfuels industry, and little is currently known about their environmental fates, and (6) they have low odor thresholds and most are malodorous (they are the primary cause of the characteristic odor of retort water). With regard to the last point, nuisance odor could be a major problem, especially since many areas of the U.S. (e.g., Colorado) have provisions for regulation of air emissions based on smell.

The EPA is supporting research to determine the potential effects of oil shale activities on the atmosphere. Although much of this work concerns new and innovative control technologies for gaseous emissions from oil shale retorting, SO_x and NO_x emissions have been the major concern (Bates 1985). The federal government regulates air emissions through the Clean Air Act, which sets limits for only six atmospheric pollutants: particulates, Pb, O_3 , NO_2 , SO_2 , and CO. The individual state governments are responsible for establishing regulations for pollutants not covered by the Act.

The subject of this report is gas-phase phototransformation of the malodorous, low-molecular-weight alkylated NHCs (e.g., pyridines and pyrroles) and aromatic primary amines (e.g., anilines). It should be emphasized that although these compounds reside in the polar-basic fraction of retort waters and shale oils (where most of the toxicity, especially mutagenicity, resides), they are of little toxicological significance in comparison with the highly mutagenic primary amine derivatives of the fused-ring aromatics and their thia and aza heterocyclic analogs (see references in Daughton 1986). These polycyclic aminated derivatives are not sufficiently volatile to exist in the gas phase; they are probably associated with the particulate phase and are therefore of interest only with respect to surface-phase phototransformation.

Phototransformation

A compound can undergo (direct) phototransformation only if it is capable of absorbing available radiation. Absorption of radiation yields an electronically excited state. The excess energy can be released in several ways (Cowan and Drisko 1976): (1) emission of light at wavelength(s) with energy less than or equal to that of the absorbed radiation (fluorescence or phosphorescence, depending on the excited state), (2) transformation to another, lower energy, electronic state via bimolecular collision (vibrational relaxation), or (3) scission of a covalent bond (with bond energy less than or equal to the absorbed energy) to form structurally altered reaction products. The latter is referred to as direct photoreaction. Phototransformations can take place in the solid, liquid, and gas phases, but the mechanisms often differ. In the solid and liquid (condensed) phases, vibrational relaxation is more important than in the gas phase because the higher molecular density promotes rapid intermolecular transmission of absorbed light energy. The photoreaction rate therefore depends on the composition of the condensed phase. If photosensitizers (compounds that transfer absorbed light energy to other molecules through bimolecular collision) are present, organic compounds that cannot absorb light of sufficient energy to react can be electronically excited and subsequently degrade (Ross and Crosby 1985). For these reasons, results from photochemical studies of condensed phases are not generally applicable to the gas phase. The possible importance of condensed-phase (i.e., liquid phase) photochemistry at oil shale processing sites has been noted (Sakaji et al. 1982).

In the gas phase, collisional frequencies are low relative to those in condensed phases because of lower molecular density. This low frequency, coupled with a low concentration of reactants, means that for bimolecular collisions, only those having a high probability of subsequent reaction will show significant reaction rates. For some reactive species

(e.g., atomic oxygen), nearly 100% of the collisions with organic species will result in reaction (Johnston 1985).

Light exhibits properties of both waves and particles. The energy associated with the smallest unit of light energy (photon or quantum) is a function of its wavelength (λ) (Turro 1978) and is commonly expressed in einsteins, E, the energy of one mole of photons of wavelength λ , (Fig. 2):

$$E = Nh\nu, \nu = c/\lambda, \text{ where}$$

- N = Avogadro's number,
- h = Planck's constant,
- ν = frequency, and
- c = speed of light (Castellan 1983).

For bond scission to occur, a photon with energy at least as great as the bond energy must be absorbed. The minimum energy required for electronic excitation of organic molecules is 30-40 kcal/mol, and the maximum (which is commonly used in laboratory photochemical work) is approximately 140 kcal/mol. This corresponds to light with wavelengths falling in the visible and ultraviolet ranges. Artificial sources of light (e.g., mercury arc lamps) are used to investigate higher-energy organic photoreactions.

The spectrum of solar energy is a function of altitude, latitude, time of day, time of year, and atmospheric conditions. The first four factors determine the path length, or mass of air, through which light must travel. As path length increases, available energy decreases, due to atmospheric attenuation (by absorption and reflection). The atmospheric composition, especially the concentrations of H₂O, CO₂, O₃, and particulates, is always changing. Each of these components attenuates light in different areas of the sunlight spectrum. Therefore, as their concentrations

change, so will the spectrum of incident sunlight. A "typical" noon summer sunlight spectrum at Chicago, Illinois (elev. 200 m) is shown in Figure 2. The tropospheric (below the stratosphere) sunlight spectrum is generally cut off below 295 nm. This lower limit is primarily determined by stratospheric absorption of the shorter wavelengths by O₃. An important factor in analyzing rate data determined at sea level is that photochemical reaction rates may increase with altitude. An experimental investigation of the photodegradation rates of three compounds revealed that one of the three photodegraded faster with increasing altitude (Miller, Mendoza, and Gohre 1985); the affect of lower temperature at the higher elevation was not accounted for and may have been a factor in preventing an increase in the photodegradation rates of the other two compounds. Altitude could play an important role in photochemical reactions at oil shale development sites in the western U.S., where most facilities are planned for semiarid areas above 2000 meters elevation.

Atmospheric Photochemistry

Several models have been proposed to predict the ultimate fate of pollutants emitted to the atmosphere (MacCracken et al. 1978; Carmichael, Peters, and Kitada 1986). These models are based on the diffusion equation with appropriate source, transport, and reaction terms included. For oil shale facilities, source terms should describe all possible volatile emissions (e.g., codisposal, pond storage, fugitive emissions). Transport terms should describe mass transfer between physical states (e.g., aerosol formation). Reaction terms need to include important photochemical and bimolecular reactions. Many of the bimolecular reactions involve radicals or other excited species, which are themselves photoreaction products. These are called indirect photoreactions. Naturally occurring reactants include the free radicals HO[•], HO₂[•], and NO₃[•], as well as the excited species of various oxygenated gases, ozone (O₃), NO_x (primarily NO and NO₂), atomic oxygen (O[¹D] and O[³P]), and molecular oxygen (O₂[¹Δ_g]). It is important to note that these indirect photoreactions do not require concurrent light energy and can therefore take place at night. For some organic compounds, nighttime reactions with radicals can be the dominant reaction mechanism (Atkinson et al. 1985). For many organic compounds, reaction with HO[•] represents the primary gas-phase sink (Atkinson et al. 1979). Stable photoreaction products often have lower vapor pressures or higher water solubilities than the parent molecule. They therefore tend to aerosol formation (Yokouchi and Ambe 1985) and are more amenable to atmospheric washout.

The term "smog" was first used to describe the combination of smoke and fog that plagued London in the early 1900's. Smog is now used to describe any smoky or

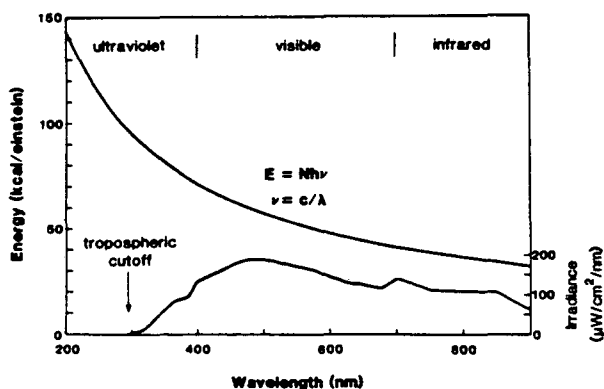


Figure 2. Upper Curve: Light energy as a function of wavelength (left axis). Lower Curve: Solar spectral irradiance for noon summer sunlight at Chicago, Illinois (Atlas 1974).

hazy pollution of the atmosphere. It is usually qualified as "London" (classical) or "Los Angeles" (photochemical) (Wayne 1985). Photochemical smog is a characteristic common to large metropolitan areas. Its formation requires hydrocarbons (HCs), NO_x , and sunlight. Through a series of photochemical reactions, NO_x interacts with O_2 and sunlight to oxidize available HCs. These oxidized forms, including aldehydes, ketones, and peroxyacynitrates (PAN), along with the ozone formed in the same process, cause eye irritation, plant damage, and visibility reduction. Biogenic HC emissions (esp. terpenes) result in the formation of "natural" photochemical smog via these same reactions (Yokouchi and Ambe 1985; Isidorov, Zenkevich, and Ioffe 1985).

A large body of literature exists describing these atmospheric processes. Compounds characteristic of photochemical smog have been studied extensively in single-compound experiments and in complex mixtures. Kinetic and mechanistic data are available for a large number of the reactions known to be important to photochemical smog (Atkinson et al. 1979; Leone and Seinfeld 1985; Atkinson and Lloyd 1984). Terpene emissions have also been studied in terms of emission rates and atmospheric fate. For the most part, however, NHCs and aromatic amines have not been investigated, largely because they are not an air pollution problem of current anthropogenic activities.

To determine the fate of these compounds in the atmosphere, the dominant reaction mechanism(s) leading to chemical alteration must be determined. These reaction mechanisms must be investigated stepwise with experiments designed to: (1) determine the importance of direct photochemical reactions (i.e., delineate reactions in an inert atmosphere, e.g., N_2 gas), (2) determine the importance of interactions with O_2 (delineate reactions in air or O_2), (3) show the effects of O_3 (e.g., impact on visibility), and (4) establish the relative importance of reactions with other reactive species.

Only photochemical reactions of oil shale process water ONCs in an inert atmosphere (direct photoreaction) will be discussed here. This is only a first step toward an understanding of the photochemistry relevant to oil shale processing. With a thorough understanding, atmospheric lifetimes could be predicted and management practices designed (e.g., nighttime versus daytime shale codisposal) to minimize associated hazards (e.g., production of toxic or nuisance photochemical products). Alternatively, advantage could be made of reactions that serve to degrade compounds that may otherwise be hazardous. It is noteworthy that the native air quality in the western U.S. oil shale region is high. Any anthropogenic introduction of pollutants to the atmosphere could be significant. Compounds with

sufficiently long lifetimes could be used as tracers or indicators of pollution resulting from oil shale operations since their ambient, baseline concentrations are essentially zero.

Properties of Organonitrogen Compounds

Aromatic amines and NHCs comprise the compounds investigated in this study. The NHCs are characterized by low odor thresholds and malodor; they are primarily responsible for the smell associated with retort waters (Daughton 1986). Odor thresholds for several process water headspace components are illustrated in Figure 3 (Verschueren 1983). Note that the thresholds of the NHCs and aromatic amines listed are bounded by those of three familiar compounds with strong odors: ammonia, ethanethiol (the odorant in natural gas), and hydrogen sulfide.

The concentration of each compound in the retort water headspace is a function of its aqueous concentration and Henry's constant. The aqueous concentration is a function of solubility, which is partially determined by the structure of the compound (both nuclear and electronic). The electronic structure will also determine the relative reactivity of each compound.

Heterocycles can be classified according to their aromatic electron density relative to benzene (Newkome and Paudler 1982). Compounds are termed π -excessive if their aromatic (π) electron density is greater than that of benzene. Since these compounds are relatively electron-rich, they more readily undergo electrophilic substitutions and oxidation (relative to benzene). Pyrrole and substituted pyrroles are the π -excessive compounds among those studied here; they have six π electrons distributed over five atoms, exceeding

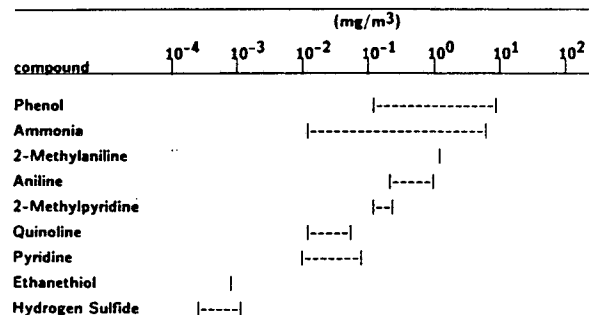


Figure 3. Recognition threshold odor concentrations for oil shale process water headspace components. Values shown are 50% and 100% recognition threshold values (i.e., half or all of an odor panel defined the odor as being representative of odorant at concentration shown) (Verschueren 1983).

the π electron density of benzene. Their reactivity is probably one of the reasons for their relative scarcity in retort waters and headspaces, especially in old samples (Daughton 1986).

Nitrogen is more electronegative than carbon, and therefore decreases the π electron density of six-membered NHCs relative to benzene. These compounds are referred to as π -deficient. Their low electron density makes them less likely to undergo electrophilic attack or oxidation than more electron-rich compounds. Pyridine and alkyl-pyridines comprise the π -deficient compounds studied here.

The relative ability of a compound to oxidize or undergo electrophilic substitution is important in determining its atmospheric lifetime because these two reaction types are primarily responsible for degradation of organic compounds in the troposphere. Reaction with HO^\cdot determines the atmospheric lifetimes of many organic compounds. Since radicals are electrophilic, they react faster with electron-rich compounds.

The atmospheric chemistry of NHCs and aromatic amines is largely unknown because these compounds are not natural products and they currently are not significant emissions of other industries. Photochemical data have been reported for a few individual compounds. Comparison of the reaction rates of pyrrole with NO_3^\cdot , OH^\cdot , and O_3 suggests that the gas-phase lifetime of pyrrole in the atmosphere might be determined by the NO_3^\cdot reaction rate (Atkinson et al. 1985). Aqueous pyridine photochemistry has been investigated using ultraviolet light ($\lambda=256$ nm), and the primary reaction product was an aminopentanal (Jousot-Dubien and Houdard 1967). This work cannot be applied to the atmospheric chemistry of pyridine, however, because it is aqueous phase and the wavelength is not relevant to the tropospheric sunlight spectrum. Some work has been done concerning the homogeneous, gas-phase atmospheric reactions of several ONCs. Bimolecular reactions of pyridine and aniline with HO^\cdot , O_3 , and HNO_3 were investigated and found to yield atmospheric lifetimes of 23 days and 1.2 hours, respectively, in a "moderately polluted atmosphere" (Atkinson 1986).

METHODS, MATERIALS, AND EXPERIMENTAL DESIGN

Photoreactors

Gas-sampling bags made from Tedlar (E. I. DuPont de Nemours & Co., Wilmington, DE) were used as photoreactors to contain headspace samples during sunlight irradiation. Tedlar is a polyvinylfluoride film that is relatively inert and chemically similar to Teflon. Bags were made by folding a 25-cm X 60-cm piece of Tedlar film in half (25-cm fold) and sealing the three unconnected sides with a rotary-band heat sealer (Ralph Chaffee Co., Burlingame, CA). The heat sealer

was set at 290°C with a band speed to yield equal heating and cooling times of approximately 5 s. The resulting bags had a capacity of approximately 2 L. Each bag was equipped with a black polypropylene purge-fill valve and a Teflon septum-valve for sample withdrawal using a gas-tight syringe.

Tedlar has properties well suited for headspace containment during photoreaction studies. Tedlar transmits tropospheric radiant energy well (see Fig. 4). This is especially important in the near ultraviolet range since these wavelengths represent the most energetic portion of the sunlight spectrum (see Fig. 2). The permeability of Tedlar to most gases is low relative to other gas-sampling bag materials (see Table I). Low permeability minimizes the permeation losses of headspace components and the contamination of the headspace by atmospheric components. High moisture vapor transmission and low moisture absorption capacities allow for the selective escape of water prior to irradiation. This is important for preventing interaction of headspace components with water vapor and for preventing compounds from being scrubbed from the gas phase by liquid water, thereby minimizing condensed-phase reactions. The physical and chemical inertness of Tedlar (Du Pont 1984) makes it capable of withstanding extended immersions in many types of solvents and makes it resistant to aging in air; the bags can therefore be easily cleaned and reused. Finally, since Tedlar can be heat sealed, bags can be custom-designed.

Generation of Headspace Samples

Process waters were obtained from two above-ground retorting processes (Paraho and TOSCO), as well as an MIS

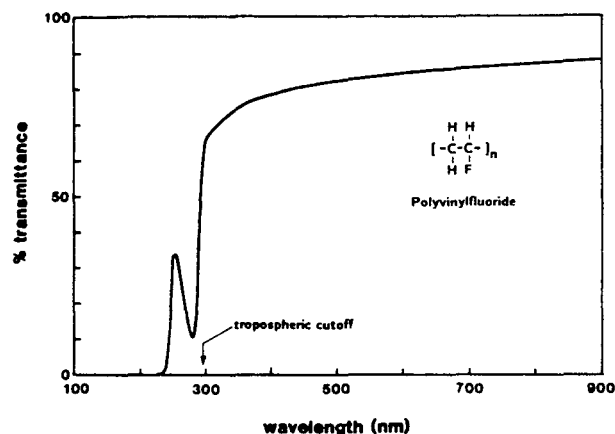


Figure 4. Transmittance of Tedlar (200SG40TR) film (polyvinylfluoride) as a function of wavelength (from Hoefling 1985).

Table I. Gas Permeabilities¹ of Gas-Sampling Bag Materials

gas	bag materials		
	Teflon ²	Halar ²	Tedlar ³
O ₂	750	25	3.2
N ₂	320	10	0.25
CO ₂	1670	110	11.1
He	4500	1100	150

¹expressed in cc/(100 in²)(24 hrs)(atm)(mil); ²Alltech 1984; ³Du Pont 1984.

process (Oxy-6 gas condensate) (see Langlois et al. 1984). Process-water headspace samples were generated in an inert atmosphere, created by using N₂ to displace water from an inverted 5-gal glass carboy submerged in a water bath; the neck was stoppered before removing the carboy from the bath. A 400-mL sample of basified process water (pH 11) was then added to the carboy through a pinch-clamp valve in the stopper. The carboy was then placed in an environmental chamber (model TTB-4-C-1-T, Conrad Inc., Holland, MI) and allowed to equilibrate at 65°C for one hour. Samples were displaced from the carboy by filling an internal bladder (also made of Tedlar) with tap water; the displacement water was preheated to 65°C inside the chamber to prevent condensation of headspace components on the bladder exterior. The displaced headspace passed through a drying tube containing granular anhydrous Na₂SO₄ (AR grade) before filling the 2-L evacuated Tedlar gas-sampling bags. Although some water vapor passed through the drying tube, Tedlar acts as a drying membrane, and the headspace samples became dry after overnight storage in a dark, dry room.

To facilitate headspace analysis, the concentrations of ONCs in the headspace were maximized. To increase the volatility of these components, retort waters were basified with anhydrous NaOH pellets, and the retort water and its headspace were heated in the environmental chamber. Basification was necessary because aromatic amines and NHCs are weak bases in aqueous solution; increasing the solution pH increases the concentration of deprotonated (volatile) forms and therefore the headspace concentrations as well. Heating increases the vapor pressures of the compounds; 65°C was chosen as a conservative representation of what is to be expected in codisposal operations.

Headspace Irradiation

The photoreactors were numbered in their order of filling. Six bags were filled with headspace samples for each process water. From these, three controls and three samples

were randomly selected by use of a table of random digits. Controls were wrapped in aluminum foil to prevent irradiation while allowing exposure to a similar temperature regime as the irradiated samples. Samples and controls were placed on the roof of Building 112 at the University of California's Richmond Field Station (sea level), and were constrained with bird netting, which kept the bags in place without inhibiting irradiation.

Headspace Analysis

Time-course headspace analyses by capillary gas chromatography, with flame thermionic or flame ionization detection, used a Shimadzu GC-9A gas chromatograph with a 30-m fused-silica, KOH-deactivated, Carbowax 20M column (J & W Scientific, Rancho Cordova, CA), which was programmed from 30°C-220°C at 4°C/min. Chromatographic data were compiled using a Shimadzu C-R3A computing integrator.

Samples and controls were removed from the roof daily in late afternoon to ensure that all bags received maximum solar exposure and that all bags received the same exposure between analyses. Following analysis of all six headspaces, the bags were placed back on the roof for the next day of exposure. Bags were always analyzed in numerical order.

RESULTS AND DISCUSSION

Results from sunlight-exposed samples and unexposed controls were compared for each of three process waters to determine the extent of the direct photoreactions at sea level. Losses of individual compounds from the sample and control bags as a result of sorption and leakage were approximately the same for most of the NHCs. These non-reactive losses were not large enough to prevent detection of photochemical losses. Losses that could be ascribed to phototransformations were evident for only 3 of the 60 major ONCs: pyrrole, aniline (aminobenzene), and *o*-toluidine (2-methylaminobenzene). Reactive components were identified using retention index matching (Hunter et al. 1985). No significant photochemical losses were evident for alkyipyridines (the principal headspace components; Hunter et al. 1985).

A comparison of losses for pyrrole and pyridine is given in Figure 5. All losses were assumed to be first order. The total pyridine loss rates were approximately equal in the irradiated sample and control, suggesting that exposure to radiation did not cause pyridine losses. Total loss rates for pyrrole were much faster in the irradiated samples than in the controls, suggesting that irradiation increased the loss rate. Note also that the loss rate for pyrrole was always higher than that of pyridine, a reflection of the inherent instability of pyrrole relative to pyridine.

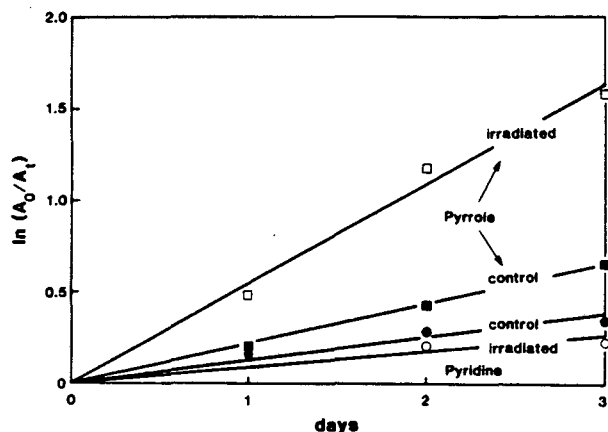


Figure 5. Losses of reactive and non-reactive components from an oil shale process water (Paraho, bbl 36) headspace as a function of time. Best fit line through data as plotted has a slope directly proportional to 1st order rate constant (k).

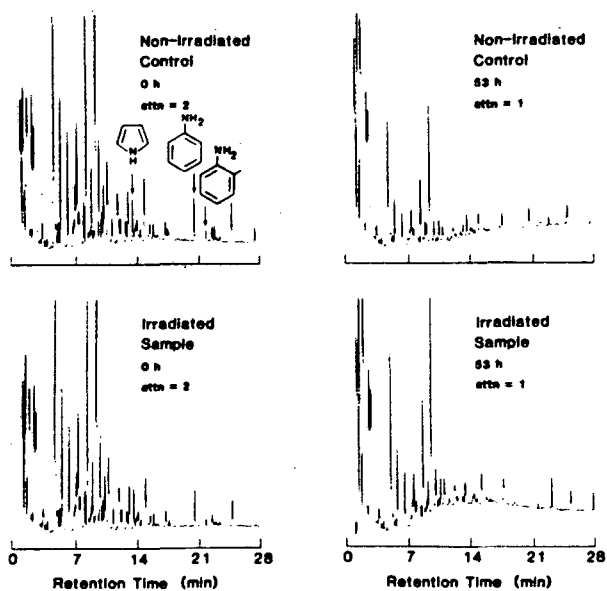


Figure 6. Time-course headspace chromatograms. Note similarity between initial chromatograms (0 hours), as well as between the time-course chromatograms (53 hours); attn = relative electrometer attenuation.

These results suggest that direct photodegradation of alkylpyridines will not be important and that the atmospheric lifetimes of these compounds will instead be determined by their rates of reaction with atmospheric species such as HO^\cdot . Even the lifetimes of those compounds that do undergo direct photodegradation may be determined by these indirect photoreactions if the kinetics are sufficient to dominate those of direct photodegradation.

In these experiments, it is possible that other compounds were photodegraded, but they were not among the major nitrogenous compounds. In particular, it is possible that some or all of the alkylpyrroles, as well as the other two toluidine isomers photodegraded, but their initial concentrations were too low. No attempt was made to identify reaction products, but since no new component peaks appeared in the chromatograms during the course of irradiation, any products were either present at low concentrations, did not contain nitrogen, or were not volatile.

Direct photodegradation is probably not an important atmospheric sink for most organonitrogen species present in retort water headspaces. The three compounds that did photodegrade represent a small fraction of the total ONCs present in the headspaces (see Fig. 6). Most of the larger peaks (alkylpyridines) were unaffected by sunlight exposure. The reactive components have high odor thresholds relative to those of the alkylpyridines. Therefore, gas-phase direct photoreactions are probably unimportant in altering the odor associated with oil shale process waters.

These experiments were performed in an inert atmosphere. Emissions under field conditions will be exposed to a more reactive environment. The next step, therefore, in investigating the atmospheric chemistry of these volatile compounds, is to include oxygen in the reaction mixture. Photodegradation experiments done in air with pyridine, 2,4,6-trimethylpyridine, and quinoline suggest that oxygen may be important in the degradation of these compounds (Blatchley III 1985). Losses of quinoline and 2,4,6-trimethylpyridine were noticeably larger in an air atmosphere when headspace samples were exposed to sunlight than without irradiation; photodegradation of pyridine was not detectable.

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