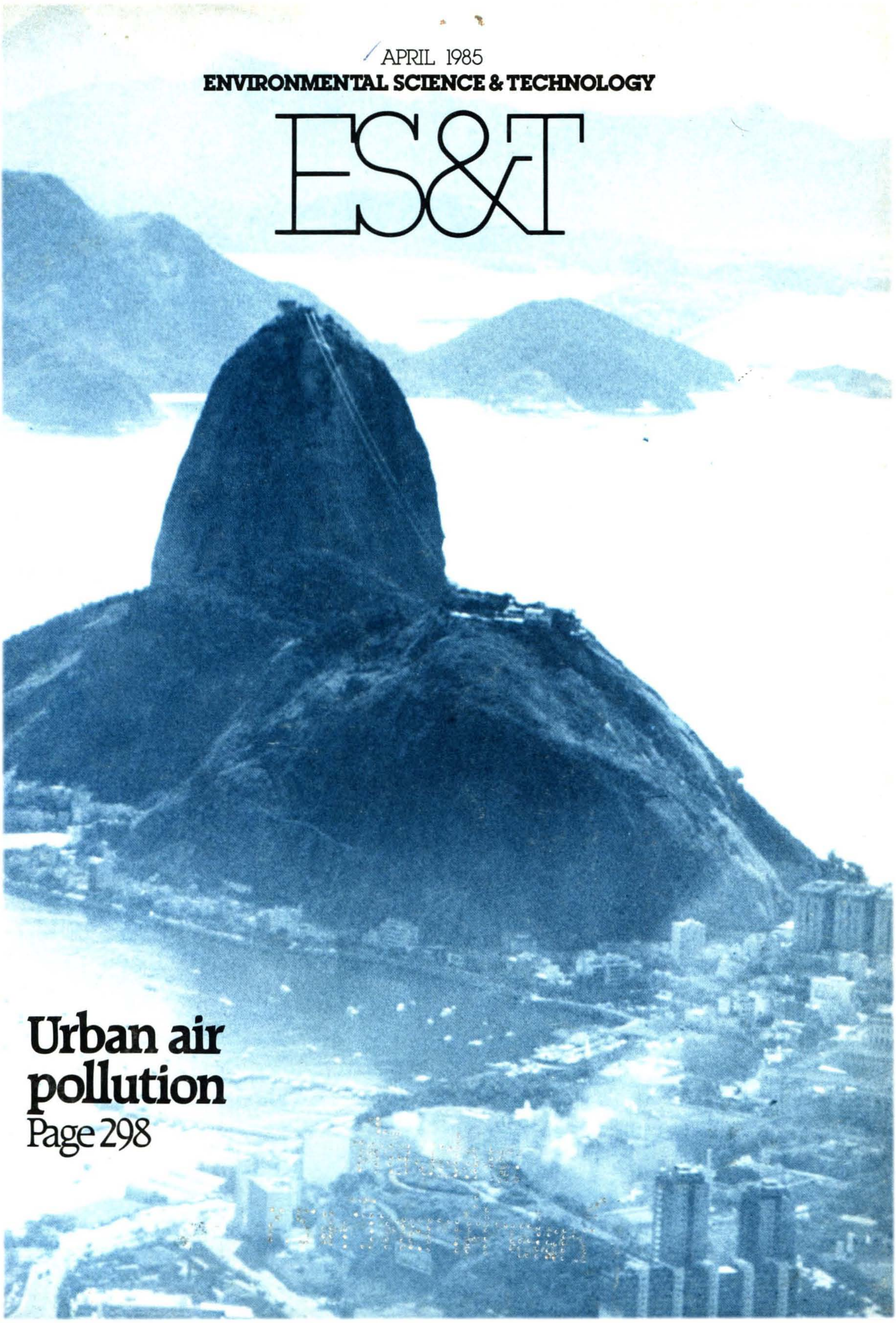
APRIL 1985

ENVIRONMENTAL SCIENCE & TECHNOLOGY

ES&T



Urban air pollution

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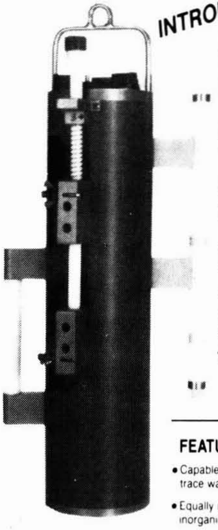

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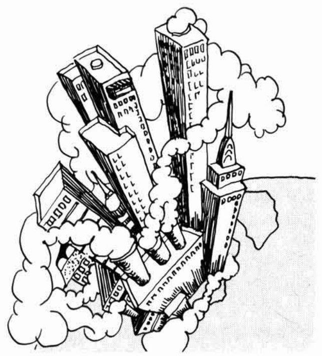

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ES&T

GUEST EDITORIAL

A note of hope for resolving environmental conflict

There is nothing extraordinary in the controversial nature of environmental issues. Environmental disputes are in the headlines every day. What is new is the demonstration that many of these issues can be resolved by the parties involved with the assistance of a mediator. Since 1974, mediators have been involved in at least 165 environmental controversies—some large, some small. The diversity of the issues resolved is remarkable, and overall the success rate is high, with agreement in 78% of the cases documented.

Results in many cases have been dramatic: In one instance, 31 diverse interests in Colorado agreed to principles that will guide major water projects over the next several decades. Representatives of pesticide manufacturers, church groups holding stock in pesticide companies, and environmental groups agreed to methods that would reduce the misuse of pesticides in developing countries.

Mediation and other consensus-building processes show considerable promise for resolving environmental disputes. But those affected by environmental controversies care about more than just reaching an agreement. They want agreements that satisfy their interests and their sense of the public interest. They also care about the process—whether it is fair and efficient. And, to the degree that they have a continuing relationship, they care about their ability to solve future problems with one another.

Mediation offers an opportunity to achieve these goals, but the path may not be easy. Conflict often makes people uncomfortable. This may explain current enthusiasm for the word nonadversarial in characterizing mediation. But it is acknowledging and learning how to deal with differences—not avoiding them—that are the real value of mediation. The success of the process suggests that parties, although remaining adversaries, can be challenged to invent more creative solutions to problems as they attempt to persuade each other to agree.

For mediation to succeed, attention must be given to the assumptions on which the process is based—in particular, how the issues are defined and how well all parties are represented. In this country, the concept of mediation has been shaped largely by the resolution of labor-management disputes. Environmental disputes differ from labor disputes, however, in at least two significant ways.

First, labor-management negotiations are set by law, and certain issues, such as the right of workers to organize and to strike, are not negotiable. Because mediation of environmental disputes has proceeded on a case-by-case basis, similar assumptions about what is negotiable may be unclear or still in dispute. Unless all parties look carefully at the assumptions, the way issues are defined may not be in their best interests.

Second, choices made by those involved in resolving environmental disputes are likely to have important consequences affecting the interests of many hard-to-represent parties. In labor-management disputes, the rules of the game and who gets to play are clear. In resolving environmental disputes, it may be much more difficult to identify the participants. The choice of participants can significantly affect the outcome of mediation. What satisfies one set of parties may not protect the interests of others who do not take part directly. Thus, before taking part in mediation, the parties must ask whether the process involves all those affected and whether it allows for public review and comment.

Efforts are now under way to incorporate mediation more systematically into public decision making through court-linked programs, mediation services offered by public agencies, and new state or federal laws and administrative procedures. If these new opportunities are to work in the best interests of all concerned, as much attention must be paid to the assumptions governing negotiations as to the settlement of individual cases.

Gail Bingham

***Gail Bingham** is a senior associate at the Conservation Foundation, a nonprofit environmental research group in Washington, D.C. She is the author of the forthcoming book, "Resolving Environmental Disputes: A Decade of Experience," which will be published by the foundation this spring.*

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ES&T LETTERS

Correction

The photo caption naming conference rapporteurs ("Photochemistry of natural waters," *ES&T*, December 1985, p. 371A) did not identify Jürg Hoigné. He appeared on the extreme right-hand side of the picture.

Advertising

Dear Sir: It is certainly disappointing to hear that *ES&T* has fallen on hard financial times ("Something you should know," *ES&T*, October 1984, p. 297A). But it may be more appropriate to take a harder look at your own house, rather than blame the Reagan administration for *ES&T*'s problems. It is disturbing that your readers are being told that the lack of advertising dollars will result in a decrease in "front end" articles and an increase in research articles. Frankly, those of us who regularly read *ES&T* would like to see the reverse happen. Your front section articles help the environmental profession more than your research articles, which are narrow in scope.

I am not saying that research is not necessary. I am saying that *ES&T* is, and should continue to be, a forum in which current topics and issues are presented in an easy-to-read manner. Let's face it—environmental coordinators who are in the trenches are more concerned with persuading their management to spend money on pollution control than they are concerned with research. Your front section articles have helped these coordinators convince their management because they are hard-hitting, readable, and easily understood. Remember that plant managers sign authorizations to spend money on pollution control, environmental coordinators do not.

Rather than blame the Reagan administration for your loss in advertising income, I would suggest you find an advertising agency that can fulfill the needs of your advertisers. Between 1973 and 1982, the petroleum industry alone spent more than $28 billion on pollution control. More than $4.8 billion was spent in 1982, two years after Reagan took office and during the time that Anne Gorsuch Burford was administrator of EPA. Also, generally there hasn't really been a flood of breakthroughs in pollution control technology in the past five years. Why? The marketplace hasn't forced a burning desire for new technology. It just so happens the "old" installed technology works.

I would strongly encourage *ES&T* to consider increasing the number of its excellent front end articles, which make our jobs easier to perform.

James E. Leemann
Conoco Inc.
Houston, Tex. 77252

The editors reply:

Our opinions obviously differ from those of Mr. Leemann regarding any slackening of compliance pressure. The opinion expressed in the editorial is not only our own, but we are sure there are certain companies, evidently Mr. Leemann's included, that continue to exert their conscience regarding environmental issues. Thank goodness for that.

We do agree strongly with the assessment of the value of *ES&T*'s front section. Actually, under the changes made, the Currents section and all of the feature articles remain. Contraction of the front end was necessary because it is the more expensive part of the journal to publish. We are faced with a Society mandate to bring our budget into balance. Further, the marketing strategies of Centcom, the advertising arm of ACS publications, are not under our control.

We are trying hard to maintain the front end, but out of financial necessity must decrease staff costs associated with that section. Therefore we will have fewer staff-written articles. We will still have room, however, for the excellent and interesting articles to which Mr. Leemann refers as making his job "easier to perform."

Dear Sir: I read, with dismay, your October 1984 editorial. You have asked for comments so I am offering mine for your consideration.

I am an environmental geologist who deals frequently with waste disposal, water pollution, and land degradation problems. I have found your journal extremely useful, primarily for the feature articles and the other material in the front section. Most of the research articles are incomprehensible to me, dealing as they do with highly technical and narrow subjects. In the nine years I have been subscribing to *ES&T,* I don't think I have read five of them.

I find your allotment of more space to research articles and less space to front end material very disturbing. *ES&T* has been my only source of general information and general review articles on current research and procedures in my broad areas of interest as they relate to chemistry. Articles on waste disposal, acid precipitation, groundwater pollution, and the Regulatory Focus column have been especially useful. In other words, I subscribe to *ES&T* for the magazine section, not for the journal section. I am afraid that the elimination or reduction of the pages devoted to such material will probably lead me to allow my subscription to lapse. (I am not an ACS member.) I will watch with interest to see what happens.

R. Laurence Davis
Associate Professor of Geology
Alfred University
Alfred, N.Y. 14802

Dear Sir: I am not unhappy to see a larger space devoted to current research and less to the front end. My reasons are simple: Much of the material in the front end, with the exception of the regulatory issues, can be found in several other places, but the research section is nearly unique. *ES&T* is, for many of us who are authors and readers, the best place to publish our material and to learn what our colleagues are doing. For nonatmospheric chemistry, I cannot think of another journal of equal reputation and standards. I wish there were more. Any change that provides more research space and shortens publication time is a positive one.

Theodore Mill
Physical Sciences Division
SRI International
Menlo Park, Calif. 94025

Dear Sir: I, too, can be counted as one of your readers who reads the front end, as you call it. Specifically, the editorials, letters, and Currents departments and the Regulatory Focus columns are always informative in a way other periodicals are not. As an environmental engineer, I seldom find useful information in the research section.

Our scientific library pays the institutional subscription rate. A subscription is also paid for by our environmental affairs division. I am not concerned about the price, because I read the circulated copy.

You produce a great magazine and I felt I should inform you of what I find important, as suggested in your editorial. Otherwise, I would simply be accepting any changes without having made any input.

Dennis L. Gehlhausen
Environmental Affairs Division
Eli Lilly and Company
Indianapolis, Ind. 46285

November editorial

Dear Sir: I want to commend you for the creative and thought-provoking editorial, "It's only halftime" (*ES&T,* November 1984, p. 323A). It is a sad commentary that B. M. Beal, your "regulated" reader (Letters, January 1985, p. 4) is not satisfied with the administration's reversal of environmental and health protections. Rather, he will apparently not be content until all such "absurd" vestiges of concern for environmental health are obliterated.

To assume that the president's attitudes on the environment are shared by the majority flies in the face of the many polls taken, as well as the recent congressional elections. Perhaps those in the regulated community should make the effort to stand up and peer beyond the trenches.

Earon S. Davis
Environmental Consultant
Evanston, Ill. 60202

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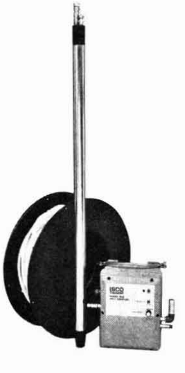

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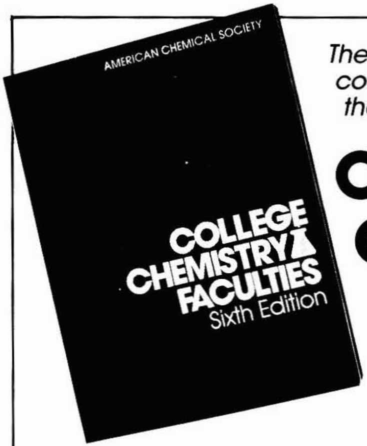

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ES&T CURRENTS

FEDERAL

EPA's fiscal year 1986 operating budget will be $1.367 billion, which is $40.4 million more than that for fiscal year 1985, if President Reagan has his way with Congress. Under the terms of the administration's budget, Superfund will rise by 45% to $900 million and no Superfund money will come from general revenues. Rather, taxes on chemical ingredients could be increased, and a waste generation tax could be imposed. Also, Resource Conservation and Recovery Act funding will rise by $54 million to $247 million; water pollution control funding will fall from $248 million to $239 million. Funding for air pollution control will be $236.1 million, a $300,000 increase from fiscal year 1985. Pesticides and toxic substances control funding may rise 2% and 13%, respectively, from the current $67.6 million for pesticides and $82.9 million for toxic substances. The research and development outlay will increase by $19.4 million to $324.8 million, with a significant increase for the study of acid rain.

The Council on Environmental Quality (CEQ) may be granted a reprieve from the budget axe (*ES&T,* February 1985, p. 103). The administration is asking Congress for $705,000 for fiscal year 1986, which is the same as the 1985 appropriation. However, this figure could be cut in half for fiscal year 1987. Also, the administration's proposal calls for the Office of Environmental Quality, which oversees an environmental management fund, to give CEQ $1.06 million. This sum goes to CEQ outside the channel of congressional appropriations. The 13 staff positions at CEQ, the same number provided for in the fiscal year 1985 budget, will be maintained.

Rules for Superfund site cleanup could be waived under certain circumstances. Under the Superfund National Contingency Plan, EPA proposes that federal cleanup standards be waived if a site's location makes it technologically impossible to meet them. Waivers also could be granted if cleanup is done to stabilize conditions at a site, if achieving standards could cause unacceptable effects on human health or the environment, if the cost is excessive in view of other demands on the fund, or if there are certain "overriding public interest concerns" that call for selecting a noncomplying remedy. EPA also proposes ways to make cleanups easier and decrease the amount of time and money spent on studying solutions to routine site management problems.

Dingell: Sees five-year renewal

Rep. John Dingell (D-Mich.) expects that Superfund will be extended for five years. The law is due to expire Sept. 30. Calling the one-year extension that some have proposed "not for real," Dingell said a five-year extension, "with a proper and equitable tax, would be politically saleable." The $900 million for Superfund would come from special taxes imposed on the chemical manufacturing, petroleum, and petrochemical industries, rather than from general revenues. "I recognize that the chemical industry cannot be an infinite source of Superfund dollars," Dingell told a Chemical Manufacturers Association forum. He would prefer Superfund money to come from a broader industrial tax base.

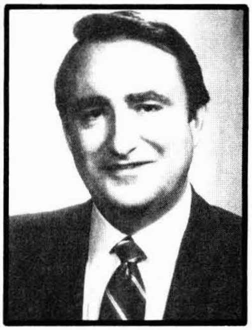
EPA has proposed rules for incinerating liquid hazardous wastes at sea. These rules incorporate performance standards for land-based incinerators and call for 99.99% destruction of liquid hazardous wastes. If the wastes consist of polychlorinated biphenyls, dibenzodioxins, or dibenzofurans, destruction efficiencies of 99.9999% must be demonstrated. Moreover, the proposal sets forth standards to limit acid-forming emissions and requires incinerator emissions to be below marine water quality criteria. Under the rule, permits would be classified for research, operating, and emergency applications.

EPA might not strictly enforce a provision of the Resource Conservation and Recovery Act that requires hazardous waste landfill operators to comply with all groundwater monitoring and financial responsibility requirements by Nov. 8, 1985. Section 3005(e) of the act requires operators to certify that they meet these requirements or close their landfills on that date. EPA fears that a strict interpretation of this "hammer provision" would cause the abrupt closing of up to 70% of existing land disposal facilities. The agency also foresees increases in illegal dumping if a large number of facilities close. The agency would prefer that facilities come into compliance and pay enforcement penalties in the meantime. Vigorous congressional and public opposition to this move is expected.

The concentration of blood lead that is considered poisonous has been lowered by the Centers for Disease Control (CDC, Atlanta, Ga.). CDC has determined that a blood lead level of 35 μg/deciliter (dL) constitutes lead poisoning. The previous level, established by CDC in 1978, was 50 μg/dL. CDC recommends that all children be screened for lead poisoning. The agency reasons that since the original 50-μg/dL level was established, investigators have reported adverse effects from lower levels of lead exposure. CDC also defined an excessive lead burden as 25 μg/dL, as compared with the 1978 definition of 30 μg/dL in whole blood. Lead poisoning is reported to cause disorders of the brain and nervous system.

STATES

States can now receive Superfund money to supervise cleanups conducted by responsible parties under state enforcement actions. A memorandum from Gene Lucero, director of EPA's Office of Waste Programs Enforcement, ends a controversy between several state environmental agencies and EPA. The funds made available through Lucero's decision will allow states to hire staff to oversee site cleanup as EPA presently does at those sites where cleanup is being carried out under a state action. This money replaces the state tax revenues that have been used to cover the costs of such actions. States will need EPA regional office permission to use the Superfund money.



Kremer: *Increase DEC's budget*

The New York Department of Environmental Conservation (DEC) is not fulfilling its mission, says Arthur Kremer, chairman of the New York State Assembly Ways and Means Committee. He notes that the DEC does not have a budget large enough to allow it to meet increasing responsibilities and that its staffing levels have not kept pace with those of other state agencies. Kremer says hazardous waste disposal laws are not being strictly enforced and air and water quality standards are not being met. He also notes that federal funding cuts further undermine DEC's effectiveness. He calls for a "multiyear commitment to restore DEC to a level where it can adequately accomplish its mandate."

Producers of toxic wastes in Missouri will be liable for the costs of removing dioxin contamination even if a third party is responsible for having the wastes dumped at a given site. Judge Edward Filippine of the U.S. District Court for the Eastern District of Missouri decided that under Superfund the definition of a release of waste includes the disposal of waste by a third party at a site other than the one designated by the producer of the waste. The decision stemmed from a suit brought by the state of Missouri against five companies and three persons to recover costs for cleaning up a site near Imperial, Mo. The judge also rejected one firm's argument that it was not responsible for cleaning up hazardous wastes disposed of by a corporate predecessor.

Biological controls for water weeds are being tested in Texas. At Lake Conroe, about 45 miles northeast of Houston, grass carp have been used to prey on water hyacinths and hydrilla, the fast-growing weed species that were choking the lake. According to researchers from Texas A&M University, the lake is much clearer than it was during 1981 and 1982 when the grass carp were stocked. But scientists still have several questions. For instance, will the eradication of all water weeds be detrimental to the lake? Also, if all lake vegetation is removed, will that damage the lake's ecology? What other organisms besides the voracious grass carp can be used for weed controls? Experts from the university and the Texas Agricultural Experiment Station are still seeking answers.

AWARDS

The German Marshall Fund of the United States (Washington, D.C.) has awarded fellowships to four European environmentalists who will study policy innovation in the U.S. This is the first time that the fund has made an award for Europeans to come to the U.S. The fund also committed $113,000 over the next two years to fellowships for U.S. environmental experts who will study environmental management practices in European countries. Since the program began in 1979, 25 U.S. environmental professionals have spent two months each in Europe examining advanced environmental management practices there. Fellows are chosen from government and private organizations. Last month, the fund announced its program for the sixth year of fellowships.

SCIENCE

Alkaline groundwater pumped into acidified trout streams might restore them more effectively and less expensively than other restoration methods. Scientists from Pennsylvania State University drilled several 100-gal/min wells into the bedrock along a stream near Ligonier, Pa., and studied the effects of pumping the well water onto fish kept in cages in the acidic stream water. With water from no wells or one well, all the caged fish died within four days. With water from two or three wells, about 50% of the fish survived for the 30-day test period. The pH of the untreated stream water was 4.8, but it rose to 5.6 or 6.6 when water from two or three wells was introduced.

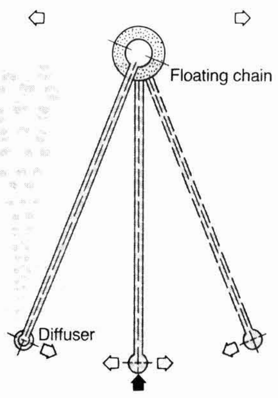
Lichens are living monitors of pollution, according to Larry St. Clair of Brigham Young University (Provo, Utah). The plants, composed of algal and fungal cells that live in symbiosis, obtain most of their nutrients from the atmosphere. This makes them unusually sensitive to such pollutants as sulfur and nitrogen oxides, heavy metals, and other products of fossil fuel combustion. Depending on the level of exposure, the pollutants can cause color changes, slowed growth, or mortality in the plants. Exposed lichens apparently develop weakened cell membranes and lose needed electrolytes. Thus, damage caused by exposure can also be measured by examining differences in electrical conductivity between healthy and exposed plants.

TECHNOLOGY

Specially adapted bacteria can be used to treat wastewater even in cold weather. Each drop of 10 °C can decrease microbial growth rates by as much as 50%, according to ChemLink (Newtown Square, Pa.), a subsidiary of Atlantic Richfield Company. Because microbes often handle biological oxygen demand, total suspended solids, and shock loadings poorly in cold weather, they can fail to remove contaminants. ChemLink is marketing a mutant bacteria strain that can work under low-temperature conditions. This approach will be less costly than heating conventional microorganisms.

Prevention of hazardous laboratory waste at the source is the subject of a new publication of the American Chemical Society's Office of Federal Regulatory Programs. "Less Is Better" is intended for persons who are responsible for managing hazardous waste generated in laboratories. The book argues that prevention is the commonsense approach to hazardous waste management because it is more cost-effective than cleanup and there is less risk of harm to personnel. The book was produced by the ACS Task Force on the Resource Conservation and Recovery Act.

Floating aeration chain



Source: Parkson Corporation

Wastewater aeration systems can be built at lower cost when they have earthen basins. Previous problems with earthen basins were solved by floating aerator chains, according to Parkson Corporation (Fort Lauderdale, Fla.). The flexible chains move back and forth across the aeration basin, allowing high oxygen transfer efficiencies through uniform and intense distribution of air. The aeration system is in use in Europe at treatment plants that range from 100,000 gal/d to 10 million gal/d in treatment capacity. The system was developed by von Nordenskjöld Verfahrenstechnik GmbH (West Germany) and is being marketed in the U.S. by Parkson.

The first large-scale, nonradioactive test of a process to immobilize buried wastes and contaminated soil in glass blocks has been conducted by Battelle (Richland, Wash.). Known as in situ vitrification, the process fixes hazardous wastes by melting contaminated soil and rock in place. Current passed between electrodes inserted in the soil causes the melting. The fused product resembles a natural volcanic glass and is twice as strong as reinforced concrete. The cost of electricity for this process is estimated at \$3–\$6/ft^3 of product material. Battelle is carrying out the project under the sponsorship of the Department of Energy.

Fluidized-bed combustion (FBC) of coal is "the most significant innovation for sulfur dioxide control in combustion in over a century." In making this assessment, the Electric Power Research Institute (EPRI, Palo Alto, Calif.) explains that FBC results in sulfur abatement because coal—even high-sulfur coal—can be burned together with limestone in a suspended mass atop a cushion of air. The limestone absorbs the sulfur oxide and some of the nitrogen oxide emissions. This technique can reduce the need for costly sulfur scrubbers. EPRI is helping to fund FBC demonstrations at up to 160 MW of power in plants in Colorado, Kentucky, and Minnesota.

A kit for removing polychlorinated biphenyls (PCBs) from transformers is being offered by Retro Serv (Rancho Cordova, Calif.). The DeChlor Kit reduces PCB concentrations in transformer oil to less than 500 ppm, the concentration that allows transformer operators an exemption from stiff EPA regulations for PCB transformers that will take effect Oct. 1. According to the company, installation requires one hour plus 8–24 hours of down time to drain PCB fluid. Moreover, the kit can be used to reduce PCB levels in transformer fluid to below 50 ppm in 39 days or less, say company representatives. PCB levels under 50 ppm could make a transformer eligible for nonregulated status. The kit contains all the equipment necessary for PCB reduction operations, and the company provides services for removal and disposal of the old PCB oils.

BUSINESS

Several U.S. multinational corporations and the U.S. Agency for International Development have set up a program to help developing countries respond to or prevent industrial accidents. Among the 25 companies involved are Combustion Engineering, Dow Chemical, 3M, and Tenneco. They will work on improving or creating new safety systems at the factory level to handle or prevent accidents and safeguard populations living around plant sites. The program, known as the International Environment and Development Service, will be administered by the World Environment Center (New York, N.Y.).

Kidder, Peabody & Company (New York, N.Y.) has developed a Superfund data base that identifies companies associated with about 550 hazardous waste sites on the National Priority List. It even shows the number of times a company—and, in many cases, its subsidiaries—is mentioned on the list of sites. One purpose of the data base and its associated report is to determine whether any companies have Superfund liabilities not already revealed. Another is to document a list of potentially responsible parties among publicly held companies. The report also gives a case study of how a group of firms settled a \$14-million site cleanup liability with the Department of Justice. For more information about the data base—said to be the only one of its kind—contact Marion S. Brown at 212-510-3770.

Anderson: *New air laws needed*

Warren Anderson, chairman of Union Carbide (Danbury, Conn.), has called for new legislation to control hazardous air pollutants. Discussing possible Clean Air Act amendments, particularly those for Section 112, Anderson suggested requiring new sources, as well as existing ones, to obtain emission permits. He also advocated well-defined scientific criteria for establishing whether an air pollutant is hazardous. Anderson recommended that pollutants not meeting hazard criteria be governed under other applicable sections of the Clean Air Act and that standard setting take into account the extent to which health risks from sources may be reduced as a result of projected reductions in emissions.

EPA has announced that it will indemnify Clean Sites Incorporated against legal liability arising from efforts to promote and carry out cleanups of hazardous waste sites. Indemnity will be limited to \$5 million per site. This guarantee covers third-party injuries that result from the process of cleaning up a hazardous waste site. Any claims that arise will be paid from the trust fund established under Superfund.

ES&T FEATURES

Urban air pollution worldwide

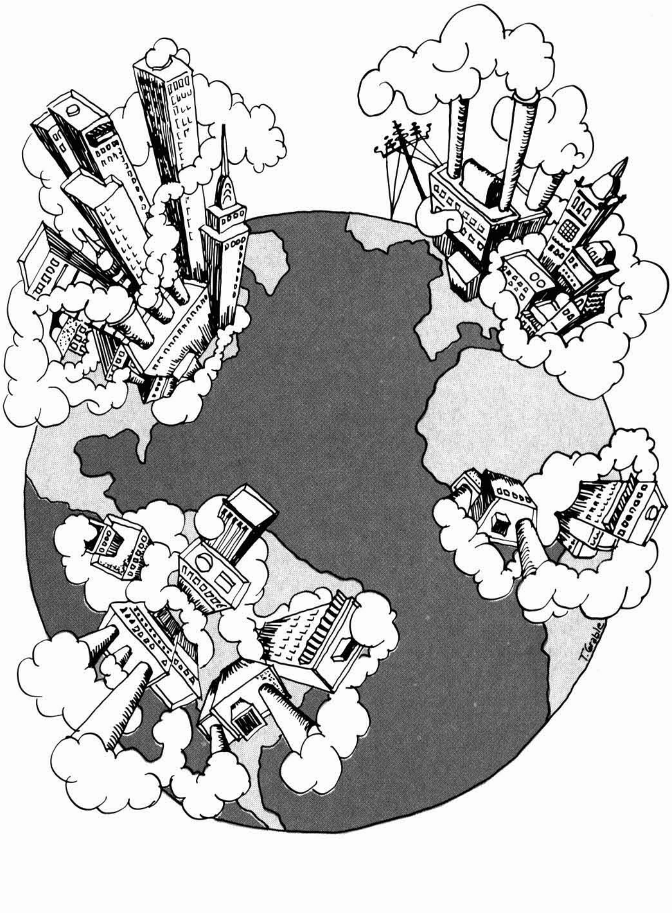
Results of the GEMS air monitoring project

Burton G. Bennett
Monitoring and Assessment
Research Centre
Chelsea College
University of London
London SW10 0QX, U.K.

Jan G. Kretzschmar
Study Centre for Nuclear Energy
Mol, Belgium

Gerald G. Akland
Environmental Protection Agency
Research Triangle Park, N.C. 27711

Henk W. de Koning
World Health Organization
Geneva, Switzerland



A global program of air quality monitoring was established by the World Health Organization (WHO) in 1973. Its objectives are to assist countries in operational air pollution monitoring, to improve the practical use of data in relation to the protection of human health, and to promote the exchange of information.

During the initial phase of the project, 14 countries participated, supplying data on sulfur dioxide (SO_2) and suspended particulate matter (SPM) from selected sites of their national networks. In each country information was routinely collected from three sites of primarily industrial, commercial, and residential character of a major urban area.

In 1976, the air monitoring project became a part of the Global Environment Monitoring System (GEMS). Financial support provided since then by the United Nations Environment Programme (UNEP) has been used to extend the network into developing countries and to continue efforts to improve monitoring methods and procedures. In 1976, the World Meteorological Organization became a cooperating agency in the project and has assisted in preparing guidelines and in organizing training workshops to demonstrate measurement techniques and to consider network design and data analysis.

The results of pollutant measurements at the monitoring sites in the network are published in biennial data reports (*1–4*). Reports have been published that give details of monitoring methods (*5*), air monitoring program design (*6*), methods of analyzing and

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interpreting air monitoring data (*7*), and estimating human exposure to air pollutants (*8*). The first interpretive report of data collected in the network from 1973 to 1980 has been prepared and is being published (*9*). This paper is a summary of the report; in it we present additional analyses of the data accumulated from the networks.

GEMS network

At present, some 50 countries are participating in the GEMS air monitoring project in which data are obtained at approximately 175 sites in 75 cities. Measurements have so far been limited to SO_2 and SPM as indicators of industrial pollution in urban areas. This network encompasses a wide range of urban conditions, such as population distribution, industrial development, local topography, and climatology. The air monitoring project is expected to provide a global view of air quality conditions in urban areas.

The geographical coverage of the GEMS network is fairly representative of the world regions. The highly industrialized countries of the Northern Hemisphere are well represented. Most sites in the developing countries became operational after 1976, and fewer data are available from these locations. A map of the monitoring sites and a discussion of the early development of the project have been published (*10*).

The air quality measurements are made at two or three designated sites in every city. These are usually representative sites from national air monitoring networks. Sites have been classified as city center or suburban and further characterized as commercial, industrial, or residential.

Daily average measurements of SO_2 and particulate concentrations in air are made by a number of different but well-accepted methods (*5*). Determinations of SO_2 in the network are made by the acidimetric titration or hydrogen peroxide method (at 36% of the sites), the colorimetric pararosaniline or West–Gaeke method (27%), the amperometric or coulometric method (21%), and the conductimetric method (12%). At a few sites (4%), flame photometry or pulsed fluorescence detection is used. There are two methods primarily used for determination of SPM concentrations: gravimetric measurement using the high-volume sampler (at 46% of the sites) and the smoke shade method (43%). The remainder of the sites use the membrane sampler (4%) or fully automated, continuously measuring nephelometry or beta absorption (7%).

Because many of the sites are included in national networks, quality control procedures should normally be part of the earlier phase of data collection. The reliability of the various methods for SO_2 detection has been checked in independent studies. An intercomparison exercise for participants in the GEMS network using the reference West–Gaeke method has been completed (*4*). The results from 16 laboratories showed most analyses of standard samples grouped within ±25% of the reference mean, with four laboratories having somewhat larger deviations. Such intercomparisons are of great value in maintaining high standards for independent sampling and analysis in large networks.

Awareness of the field sampling difficulties under the varying local conditions is required. For example, with the colorimetric method for SO_2, higher temperatures may affect the absorption of SO_2 and the stability of the solution prior to analysis. In using the conductimetric method for SO_2, precautions are necessary to eliminate or account for other substances in air which could affect the readings.

Comparisons of the two main meth-

SO_2 measurement methods

Acidimetric titration method—Air is bubbled through 0.5% hydrogen peroxide solution adjusted to pH 4.5. Any SO_2 present forms sulfuric acid, which is titrated against standard alkali.

Colorimetric pararosaniline method—Air is bubbled through a dilute aqueous dipotassium tetrachloromercurate solution. SO_2 is continuously absorbed to form the nonvolatile dichlorosulfitomercurate ion, which then reacts with formaldehyde and bleached pararosaniline to form red purple pararosaniline methyl sulfonic acid. The reaction is specific for SO_2 and sulfite salts. The color intensity of the dye, which is proportional to the concentration of SO_2, is measured at a wavelength of 560 nm.

Amperometric (coulometric) method—Air is passed through a cell containing a neutral buffered iodide or bromide electrolyte with which the SO_2 reacts. The change in electrical current necessary to maintain a constant concentration of free I_2 or Br_2 is a quantitative measure of the SO_2 input.

Conductimetric method—An air sample of about 2 m^3/d is collected and returned to the laboratory for an analysis based on the oxidation of SO_2 to sulfuric acid by aqueous hydrogen peroxide and the subsequent measurement of the increased electrical conductivity of the solution.

Flame photometry—Emissions from sulfur compounds introduced into a hydrogen-rich flame are measured with a photomultiplier tube in a flame photometric detector. The method can be used to measure total sulfur, which is generally equivalent to the SO_2 concentration in the vicinity of the station, or in specialized applications in conjunction with gas chromatography to measure concentrations of various sulfur compounds.

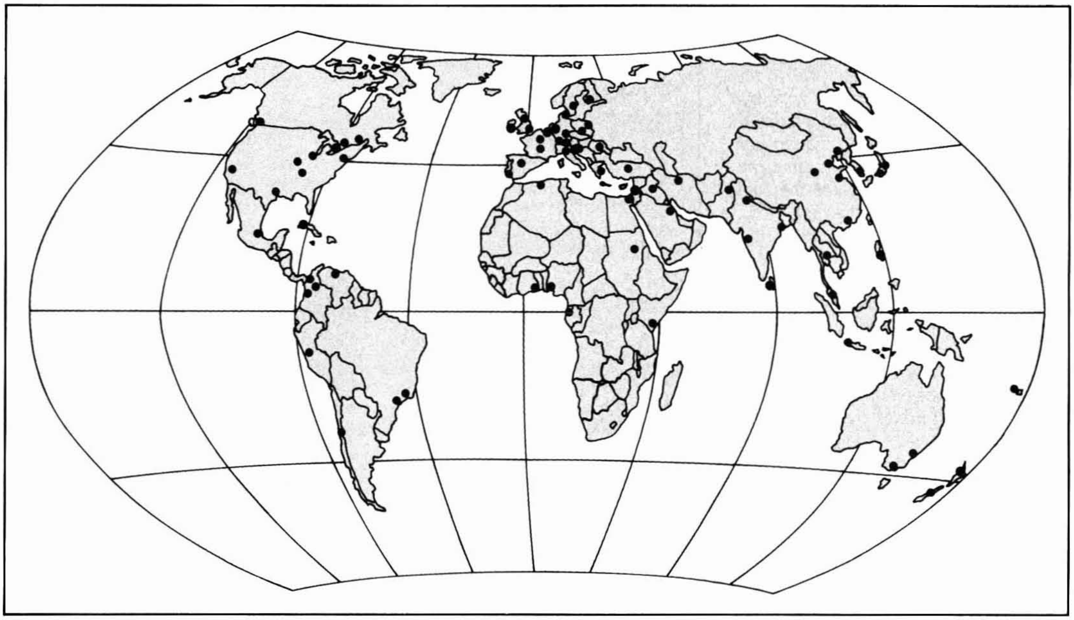
Pulsed fluorescence—A pulsed lamp is used as an excitation source for SO_2, which has a fluorescence band centered near 340 nm. The fluorescence is measured with a photomultiplier and is directly related to the concentration of SO_2 in the air.

SPM measurement methods

High-volume sampler—Air is drawn through a glass or synthetic organic fiber filter by a motor and blower. The filter surface is arranged horizontally, facing upward, and is protected by a roof and shelter enclosure that keeps out rain and snow and generally prevents the collection of particles larger than about 100 μm. The air flow rates range from 1.1 m^3/min to 1.7 m^3/min. The concentration of SPM is determined by dividing the net weight of the particulate by the total air volume sampled.

Smoke–shade method—Air is drawn through a filter paper, forming a stain, the density of which is measured with a photoelectric reflectometer. Each day, particles of ≤ 10-μm diameter are collected in about 2 m^3 of air. The density of the stain depends partly on the mass of the smoke particles and partly on the nature of the smoke. A calibration curve relating the stain density to the weight of deposited smoke particles has been established for standard urban smoke. The concentration of smoke is expressed in terms of the standard smoke equivalent.

Nephelometry—Measurement is made of light loss caused by scattering when a light beam is passed through a given volume of particle-laden air. Under some conditions (e.g., when the air is sufficiently dry) the result can be related to the mass concentration of suspended particles.



Air pollution has been monitored routinely at these sites since 1976.

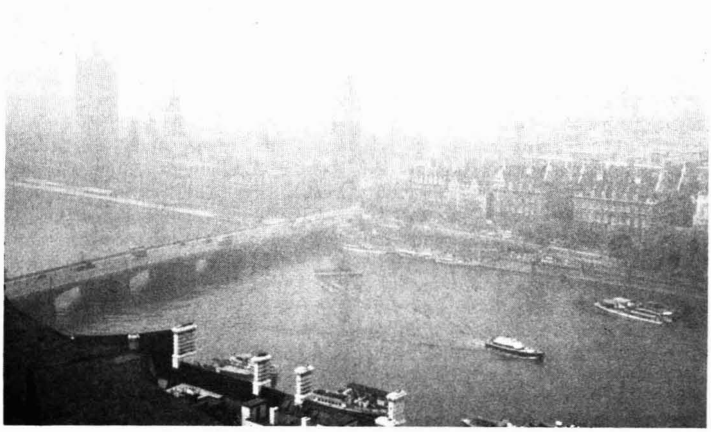
ods for SPM determinations in parallel operation at various sites show that high-volume and smoke measurement results differ by a factor of around two or three (*9*). The methods depend on the physical characteristics of the particles; the high-volume determinations are based on mass measurement and the smoke method depends on the reflectivity from the filter stain. The specific relationship between the two methods depends on local conditions at specific sites. In the analyses of these data, separate distinction is made of the high-volume particulate measurements and the smoke determinations.

Data analysis

The operation of the GEMS air monitoring network has resulted in the acquisition of substantial amounts of data. In more recent years, 25,000 to 30,000 daily measurements for each pollutant have been added each year to the data file. It has been convenient to summarize annual measurements at each site in a cumulative frequency table. The minimum and maximum daily averages are recorded along with the arithmetic and geometric means and the standard deviations of the annual results (*1–4*).

Graphical illustration of the data is useful, and for this purpose the lognormal representation appears to be satisfactory. Approximately straight line plots are formed on log-probability graph paper, especially in the range from the median to the 98th percentile values. In the majority of data sets, the lowest values are close to or even be-

The tourist's view of Big Ben and the Houses of Parliament . . .



. . . is obliterated on a smoggy day

low the detection limit, so their accuracy is questionable. At the upper range of the distribution, the representativeness and accuracy of maximum values are often hard to evaluate. Errors in sampling, analysis, or reporting are frequently involved. In some cases local and exceptional phenomena also may explain certain outliers.

During the period 1973–80, 1451 sets of yearly statistics were formed from the network results, each set consisting of SO_2 or SPM concentration values at a specific site for a specific year. There are 736 sets of yearly SO_2 values and 715 sets of yearly SPM values. Not all of these results are complete for entire years. Only if the daily values are relatively uniformly distributed throughout the year can representative annual values be presumed. Based on a careful examination of each yearly set of daily values, 74% of the SO_2 sets and 79% of the SPM sets were judged to be representative (*9*).

A tabulation of all the representative yearly SO_2 averages obtained in the network up to 1980 is given in Table 1, which shows the number of annual average values from all sites and the median and the range of annual averages. Because of the changing composition of the network, it is difficult to compare values from one year with the next. Over the entire eight-year period there are 541 annual average values of SO_2 concentration at all sites of the network with a median value of 45 $\mu g\ m^{-3}$ and a range of 3–242 $\mu g\ m^{-3}$.

Figure 1 shows the distribution of SO_2 measurements for 1973 to 1980. The distribution is peaked in the lower range with long tailing out to the upper range, approximately lognormal in the same way as the daily values at individual sites. Four values from two center city sites in Milan are $>200\ \mu g\ m^{-3}$. At the other extreme, with annual means $\leq 5\ \mu g\ m^{-3}$, although not always consistently reported year to year, are some sites in Melbourne, Kuala Lumpur, Lima, Toulouse, Hong Kong, and Houston. Most of the sites (90%) are within the range of 11–135 $\mu g\ m^{-3}$. The central range for 50% of the values is 27–72 $\mu g\ m^{-3}$.

The results of SPM measurements in the GEMS network are given in Tables 2 and 3. For the gravimetric determinations of SPM by high-volume sampling, including the miscellaneous methods of SPM determination (nephelometry, membrane filtration, and beta absorption), there are 334 annual average values at all sites of the network from 1973 to 1980, with a median concentration of 89 $\mu g\ m^{-3}$ and a range of 24–547 $\mu g\ m^{-3}$ (Table 2). The distribution of these measurements is somewhat similar to that for SO_2 (Figure 1). A large number of values in the upper end of the distribution were recorded in Calcutta, Delhi, and Tehran. At the lower end of the distribution, several annual means of $<40\ \mu g\ m^{-3}$ were reported at Melbourne and Copenhagen. The range for 90% of the SPM values of this distribution is 49–413 $\mu g\ m^{-3}$ and for the central 50% of the data, 67–142 $\mu g\ m^{-3}$.

For the smoke determinations of particulate matter levels (Table 3), there are 228 annual average values with a median of 36 $\mu g\ m^{-3}$ and a range of 4–307 $\mu g\ m^{-3}$ for the entire period. The distribution of these measurements again shows a lognormal pattern. In only two cities, Tehran and Madrid, were annual average values $>200\ \mu g\ m^{-3}$ reported. Most smoke values are in the lower range ($<130\ \mu g\ m^{-3}$). The range for 90% of the smoke values is 6–196 $\mu g\ m^{-3}$; the central 50% of the data is within 22–66 $\mu g\ m^{-3}$.

Separate analyses of the SO_2 and SPM data have been made as a function of type of site. For example, either city

TABLE 1

Results of SO_2 measurements in the GEMS network

			Annual average concentrations	
Year	Cities	Sites	Median ($\mu g\ m^{-3}$)	Range ($\mu g\ m^{-3}$)
1973	12	31	73	20–195
1974	10	28	71	14–178
1975	17	45	63	15–149
1976	40	78	46	3–149
1977	36	81	48	3–215
1978	40	94	40	4–240
1979	40	101	41	3–153
1980	35	83	40	7–242
1973–80		541[a]	45	3–242

[a] Site-years of data (the total number of representative yearly data sets)

TABLE 2

Results of SPM measurements in the GEMS network[a]

			Annual average concentrations	
Year	Cities	Sites	Median ($\mu g\ m^{-3}$)	Range ($\mu g\ m^{-3}$)
1973	6	15	127	64–365
1974	6	16	126	48–519
1975	10	27	86	28–547
1976	23	45	84	26–380
1977	25	53	90	24–419
1978	28	64	93	30–450
1979	24	59	89	32–498
1980	24	55	84	30–535
1973–80		334[b]	89	24–547

[a] Includes high-volume gravimetric sampling, nephelometry, membrane filter sampling, and beta absorption methods

[b] Site-years of data

TABLE 3

Results of smoke measurements in the GEMS network

			Annual average concentrations	
Year	Cities	Sites	Median ($\mu g\ m^{-3}$)	Range ($\mu g\ m^{-3}$)
1973	4	9	38	26–304
1974	3	8	29	23–307
1975	6	15	44	22–236
1976	16	29	33	4–233
1977	17	43	30	4–206
1978	18	42	32	4–234
1979	17	46	35	4–214
1980	13	36	44	5–222
1973–80		228[a]	36	4–307

[a] Site-years of data

center or suburban; and industrial, commercial, or residential (*9*). These distributions are not greatly different from the aggregate distributions for the sites discussed above. In general, there are usually slightly lower values reported at suburban and residential sites than at city center, commercial, and industrial sites.

Intercity comparisons

Comparisons of pollution levels between cities require that truly representative conditions be presented. For this, data must be collected over a long term and with substantial completeness of measurements at several sites within each city. Data have been accumulated regularly for a limited number of sites of the network. This allows the comparisons shown in Figures 2–4.

For cities with complete or nearly complete records of pollutant levels, the data have been averaged over the period 1976–80. A composite average of the different sites in each city has been obtained as follows: The value for the residential site is averaged with the value for the commercial or industrial site, or with the mean of the commercial and industrial sites where both are available.

The comparison of SO_2 levels in cities with relatively complete reporting during 1976–80 is shown in Figure 2. A relatively wide range in annual averages for individual sites occurs in some cities, notably Hong Kong. Composite averages range from 17 $\mu g\ m^{-3}$ in Auckland to 207 $\mu g\ m^{-3}$ in Milan.

The intercity comparison of SPM measurements for 1976–80 is shown in Figure 3. The ranges between individual sites in each city are tighter than for SO_2. The composite averages extend in a fairly regular fashion from 59 $\mu g\ m^{-3}$ in Tokyo to 142 $\mu g\ m^{-3}$ in Zagreb. Unusually high average concentrations, $>300\ \mu g\ m^{-3}$, are obtained for Tehran and Calcutta. These are not due entirely to industrial pollution; naturally high dust levels can also contribute to the figures. Explanation of specific results requires more information on the pollutant sources and the local environmental conditions.

The comparison of smoke measurements in cities with relatively complete reporting during 1976–80 is shown in Figure 4. Data from seven cities are available, with the composite averages ranging from 5 $\mu g\ m^{-3}$ in Auckland to 164 $\mu g\ m^{-3}$ in Tehran. The median value for this group is 32 $\mu g\ m^{-3}$ in London.

Correlations

Correlation analyses have been undertaken to determine the relationships

FIGURE 1

Distribution of annual average levels of SO_2 at all sites of the GEMS network during 1973–80

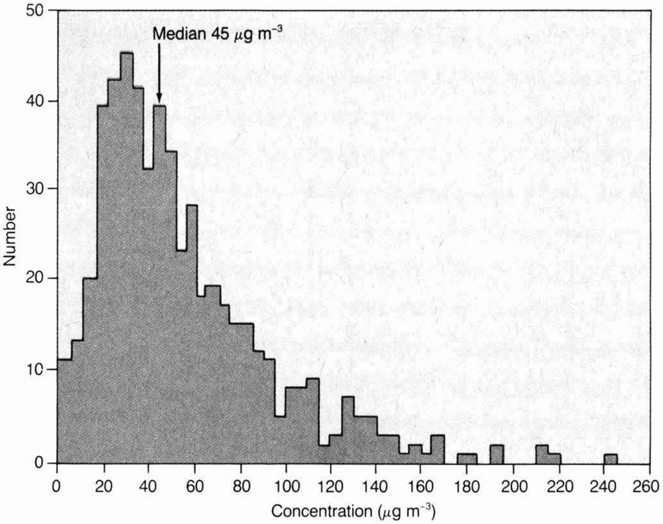
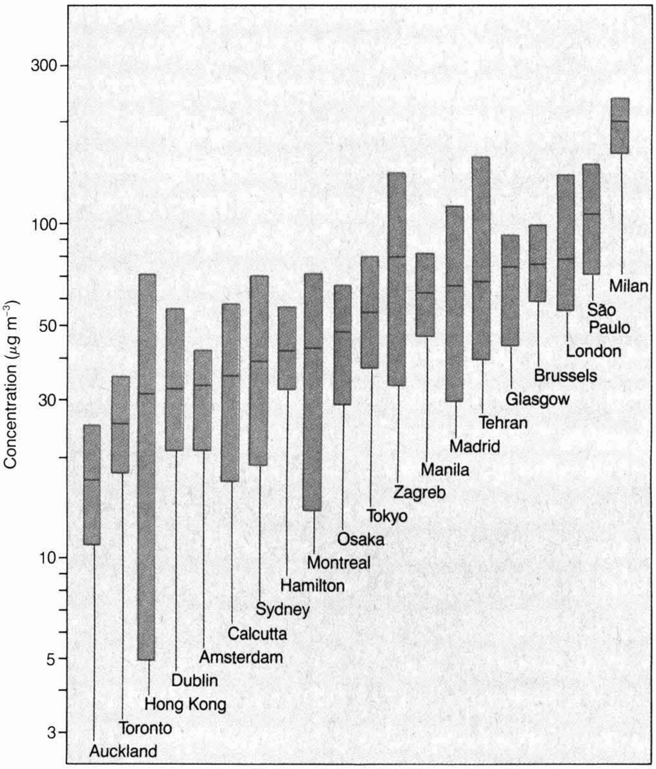


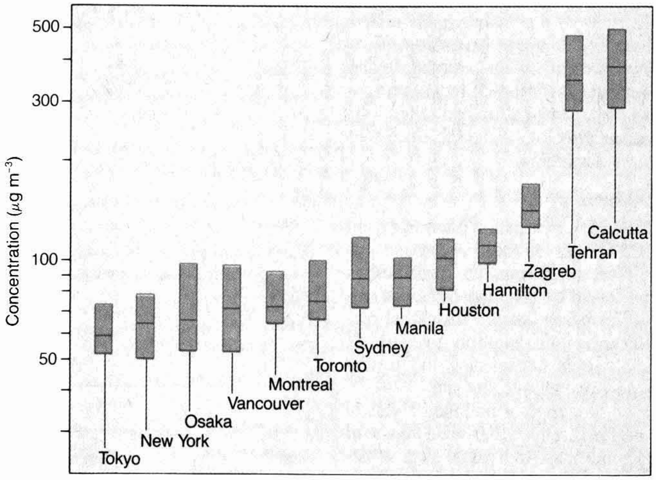
FIGURE 2

SO_2 in cities of the GEMS monitoring network, 1976–80[a]



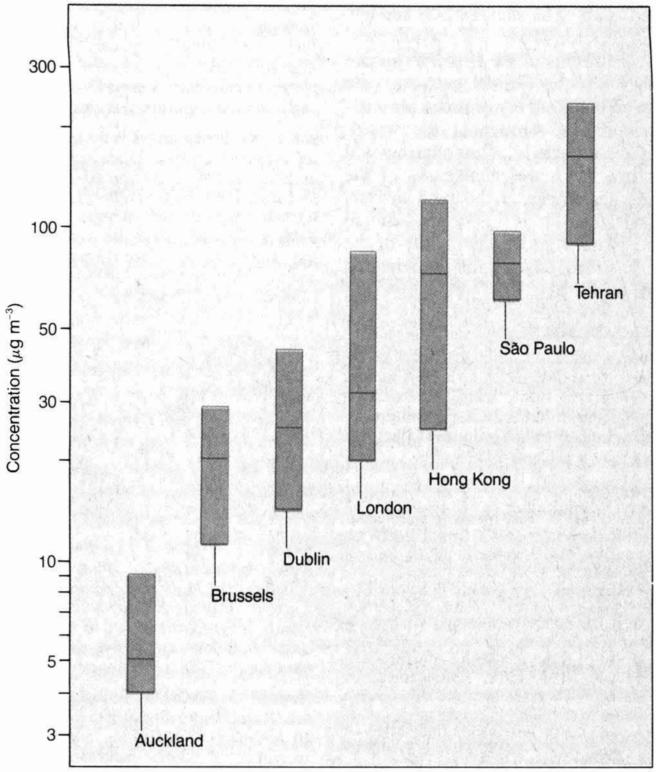
[a]Range of annual averages at individual sites and composite average for each city

FIGURE 3
Suspended particulate matter in cities of the GEMS air monitoring network, 1976–80[a]



[a]Range of annual averages at individual sites and composite average for each city

FIGURE 4
Smoke in cities of the GEMS air monitoring network, 1976–80[a]



[a]Range of annual averages at individual sites and composite average for each city

between a pollutant measured at different sites within a city and between different pollutants measured at the same site (*9*). The diversity of sites and the variable influence of localized sources limit the general correlation of air pollution monitoring results. This applies also to different sites in the same urban area. However, more widely prevailing meteorological features give greater uniformity in variations, providing, for example, generally recognizable seasonal cycles in pollutant levels.

The correlations of SO_2 at different sites in the same urban area span a wide range. The same variability is also found for the particulate levels, determined either gravimetrically or as smoke levels. At about 30% of the paired sites in the same city, SO_2 and SPM concentrations were more highly correlated ($r > 0.7$). For the remainder of sites within a given city, the results for a particular pollutant were less significantly correlated ($r < 0.7$). Abrupt changes in general intersite relationships can be used to draw attention to unusual local changes in source emissions or perhaps to abnormal monitoring operations.

Correlations of SO_2 and particulate measurements at the same site also have been investigated (*9*). In general, when SO_2 levels are elevated, SPM levels also are higher. But this relationship is variable, covering a wide range of significance (from $r = 0$ to $r > 0.9$). The general seasonal cycles strongly influence the observed correlations. Details of the correlation analyses are given in the interpretive report of the GEMS data (*9*).

Comparisons of guidelines

To limit the effects of exposure of the general public, guidelines for SO_2 and particulate levels in air have been suggested by WHO (*11*). For annual average concentrations relevant to long-term effects, the guideline values are 40–60 $\mu g\ m^{-3}$ for SO_2 and smoke, and 60–90 $\mu g\ m^{-3}$ for gravimetrically determined particulate levels.

Most sites in the GEMS network with average concentrations taken from 1975 to 1980 are below or within the guideline values. About one-quarter of the sites are above the upper guideline for SO_2. A somewhat greater proportion, just over 40% of all sites, is above the upper guideline for SPM, including smoke. City center, industrial, and commercial sites are more frequently above the upper guideline and suburban residential sites are usually below the lower guideline value.

For limiting acute effects from short-term exposure to air pollutants, the guideline values applied to the 98th percentile of the daily averages are 100–150 $\mu g\ m^{-3}$ for SO_2 and smoke and 150–230 $\mu g\ m^{-3}$ for SPM (high-volume determination). The upper guidelines are exceeded by nearly one-third of all sites for SO_2 and by nearly one-half of the sites for SPM. Residential sites are more frequently below the guideline values than are commercial or industrial sites.

Further comparisons of the monitoring results with regional or national air quality standards may be made. These are best accomplished by the local investigator with the specific and relevant regulatory limits. Examples of such standards are the European Community Directive (*12*) and the U.S. National Ambient Air Quality Standards (*13*). The air concentrations of SO_2 and SPM or smoke in these standards are approximately comparable to the upper values of the WHO-suggested guidelines.

Air quality trends

The determination of trends in urban air quality is an important objective of the air monitoring project. Because of the changing composition of the network, it has been possible to look at trends only at the individual sites. The major limitation of the trend analysis is that the period is still quite short, up to eight years.

A semiquantitative procedure has been used for the trend analysis. Comparisons are made in the changes in average levels from the first half of the monitoring period to the second half. For classification purposes the trend is said to be downward if the change is at least −3% per year. An upward trend requires at least +3% average change per year. More complicated trend analysis methods, such as linear regression or rank correlation techniques, generally confirm the findings of the semiquantitative procedure when they are applied to data sets extended with supplementary data for up to 10 successive years (*9*).

All sites with data for five or more years are included in the trend analysis. This includes 63 sites with SO_2 data and 62 sites with SPM data (both gravimetric and smoke results).

The predominant trend in the annual average data for SO_2 and SPM is downward. Downward trends are noted at 54% of the sites for SO_2 and 43% of the sites for particulates. Most of the changes are in the range of 3–9% per year with fewer ranging from 9% to 15% or more per year. Upward trends occur at 16% of the sites for SO_2 and 10% for particulates. However, at none of the sites do SO_2 and particulate levels increase simultaneously. Similar observations are made with regard to trends in the maximum (98th percentile) values (*9*).

The causes of these trends can be investigated only with additional information from the local areas. Upward trends may be due to increased industrial activity or urban expansion. Generally, lower urban air pollutant levels are attributed to emission reduction systems, use of low-sulfur fuel, fuel conservation policies, and high stacks to increase dispersion.

Conclusion

The wide participation of countries in the GEMS air monitoring project ensures that representative distributions of the levels of SO_2 and SPM are obtained for urban areas. This global picture of urban air pollution gives useful perspective in considering the results from any one monitoring site.

The wide range of pollutant levels in the network reflects the wide range of local conditions. Individual sites sometimes show relatively high levels of SO_2 or SPM and comparisons with the WHO guidelines show that improvement is still needed to reduce annual average levels and peak daily concentrations. Although the majority of sites in the trend analysis show downward or stationary trends, upward trends were noted at 10 of 63 sites for SO_2 and at 6 of 62 sites for SPM.

These results of the first interpretive analysis of the GEMS network data form an initial survey of urban air quality conditions throughout the world. Additional periods of monitoring will improve the representativeness of the results and strengthen the trend analysis in particular. It is important now to continue to improve the quality of the results and to maintain full participation of all countries.

Acknowledgment

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Burton G. Bennett *(l.) is a senior programme officer of the United Nations Environment Programme and associate director of the Monitoring and Assessment Research Centre in London, U.K. His technical speciality is in pathways analysis and pollutant exposure synthesis.*

Jan G. Kretzschmar *(r.) is an environmental research scientist specializing in air pollution modeling, measurement methods, and data analysis and interpretation. He has worked in the nuclear and nonnuclear fields at the Nuclear Energy Research Centre, in Mol, Belgium, for the past 10 years and is currently at Janssen Pharmaceutica, Beerse, Belgium.*

Gerald G. Akland *(l.) is director of the Data Management and Analysis Division of EPA's Environmental Monitoring Systems Laboratory. His work involves data management and analysis of air pollution data. He is in charge of operating the data bank for the GEMS air monitoring project.*

Henk W. de Koning *(r.) is a staff member of the World Health Organization in Geneva. He joined WHO in 1974 as an air pollution specialist. His work concerns the development of air pollution prevention and control programs and implementation of the GEMS air monitoring project.*

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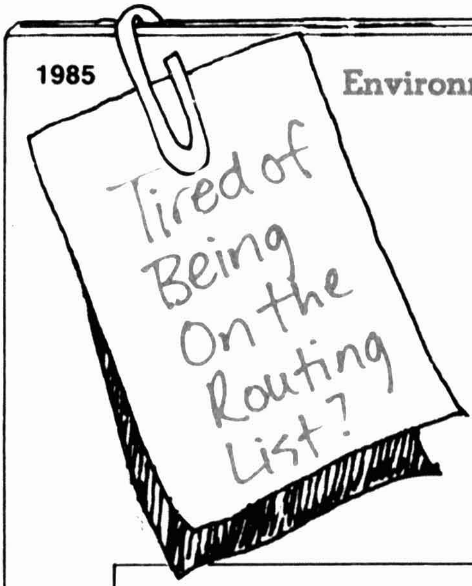

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Safeguarding indoor air quality

California's lawmakers and health experts have a program to address the problem

Ken Sexton
Health Effects Institute
215 First Street
Cambridge, Mass. 02142

Jerome J. Wesolowski
California Department
of Health Services
Air and Industrial Hygiene Laboratory
2151 Berkeley Way
Berkeley, Calif. 94704

Concern over the adverse health consequences of air pollution has focused traditionally on outdoor and occupational (primarily industrial) exposures. In response, federal and state programs have been created to protect public health from outdoor air pollution and to protect workers from dangerous air pollutants in the industrial workplace. The EPA is responsible for setting and enforcing National Ambient Air Quality Standards (NAAQS), which are designed to protect the general public from outdoor air pollutants to within an adequate margin of safety. The Occupational Safety and Health Administration (OSHA) enforces consensus standards for industrial work environments, which are designed so that no employee will suffer material impairment of health or functional capacity. But no one federal agency has responsibility or authority for indoor air quality other than in the industrial workplace (*1*).

It is now recognized that nonindustrial indoor environments, such as private residences, offices, schools, and commercial and public buildings, are important places of air pollutant exposure. Although the magnitude of indoor health hazards is not now known, evidence continues to mount that measurement of indoor exposures is critical for the realistic assessment of air pollution's effect on health (*2–5*). It is known that indoor contaminant concentrations make significant contributions to time-weighted, integrated exposures. The implications of this finding for government efforts to protect public health through enforcement of NAAQS (outdoor air) and permissible exposure limits (workplace air) have not been explored fully.

The issue of unhealthful indoor air has received expanded attention in recent years as scientists (*2, 3, 6*), professional organizations (*7, 8*), environmental and health groups (*9*), industrial associations (*10*), and the government (*10, 11*) have come to recognize the potential hazards. Despite accelerating interest in general, formal and comprehensive efforts have not been mounted by federal or state governments to determine the seriousness of potential health risks. An exception is the state of California, which has created and implemented the first state program devoted exclusively to the investigation of nonindustrial indoor air quality.

Impediments to action

Several reasons account for society's tardy response to the issue of indoor air quality. First, the discovery of contaminated air in nonindustrial indoor environments is relatively recent. There are insufficient data on the number of people exposed, the pattern and severity of exposures, and the related health consequences. Until adequate data are accumulated to allow accurate estimates of health risks, decisions about appropriate public responses are not likely to

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represent balanced choices between costs and benefits. The lack of a firm scientific basis for action is a major obstacle to the development of effective and reasonable government programs.

Second, because the scientific community has only recently recognized the potential hazards of indoor air pollution, the public is poorly informed about the issue. With the possible exception of antismoking groups, no organized constituency has formed to champion the cause of clean indoor air. The absence of such a coalition to lobby for healthful indoor environments means that there is little political urgency associated with legislation on indoor air quality. It is likely that an increase in public awareness and media attention would generate political pressure to provide legislators and regulatory officials with more incentive to take action.

Third, although they agree that indoor air pollution poses a potentially serious health problem, federal and state officials have been reluctant to act without specific statutory authority. The absence of clearly defined responsibility has caused a number of problems. These include a fragmented approach, with each agency addressing only that aspect of the issue within its purview; separate agencies instituting redundant research programs to suit their specific needs; and federal agencies assuming adversarial roles when they assess the effect of federal actions on indoor air quality (*1*). These problems should diminish as EPA assumes the lead in coordinating federal efforts to address the issues surrounding indoor air quality (*12*).

Adequate federal funding for indoor air research has not been available in the past, despite laudable efforts by the Department of Energy and the Consumer Product Safety Commission. Although the issue of indoor exposure is gaining increasing prominence, the prevailing climate is one of fiscal retrenchment and reducing regulatory burdens. It is little wonder that agencies have not been clamoring to take on added responsibility, because new programs inevitably mean additional demands on already shrinking budgets. The lack of federal money specifically for indoor air quality projects limits prospects for financial support, which in turn discourages new researchers from entering the field.

In addition, regulators are averse to being drawn into the nettlesome debate over whether government should intervene in private indoor spaces, especially residences. The question of the proper role of government in dealing with air pollution hazards inside public and private buildings and the implications of voluntary vs. nonvoluntary risks have not been addressed adequately (*13*). Irrespective of the salient policy issues, the practicality of dealing with indoor air pollution through a regulatory approach is arguable (*3, 13*).

Why is safeguarding indoor air quality important?

On the basis of current knowledge, there are five major reasons that the investigation of indoor air quality is essential for the adequate evaluation of air pollution health risks:

- Most urban residents spend 80–90% of their time indoors; some groups, such as the elderly, the infirm, and infants, are inside almost all the time.
- Concentrations of some pollutants, such as asbestos, radon, tobacco smoke, formaldehyde, respirable particles, microorganisms, and many volatile organic compounds, are commonly higher indoors than outdoors.
- Monitoring studies have shown that because personal exposure to many pollutants is not characterized adequately by outdoor measurements, indoor values are consistently the best estimator of individual exposure.
- Indoor air quality may be adversely affected by trends toward reduced ventilation in buildings, increased use of synthetic materials, and increased reliance on unvented combustion appliances for space heating.
- Reports of inadequate indoor air quality and building-related illnesses from homeowners and office workers are a burgeoning problem for local, state, and federal health agencies.

Finally, some regulatory officials and environmentalists fear that explicitly acknowledging the importance of indoor exposures in assessing health risks will weaken the case for ambient air quality standards. The industry argument goes like this: Because NAAQS are set to protect public health and because indoor sources of pollutants such as carbon monoxide, nitrogen dioxide, and respirable particles account for a substantial fraction of population exposure, efforts to reduce exposure should focus on indoor sources, rather than on requiring expensive controls on outdoor sources. One primary justification for more research is the need to evaluate the seriousness of indoor health hazards so that policy makers can more readily assess the effectiveness of existing control strategies.

Justification for action

There is ample precedent for government authority and responsibility to protect public health and welfare inside buildings. For instance, it is common practice to regulate construction and operation of public buildings. Government inspectors routinely enforce building codes, health regulations, safety rules, and fire ordinances. Although the government has an obligation to protect public health in indoor as well as outdoor environments, society cannot make informed choices about indoor air quality until adequate information is available.

The recognition that indoor air pollution may be a serious health hazard leaves policy makers with a familiar dilemma: How can government best fulfill its responsibility to safeguard citizens' health when the information on hand is incomplete and sometimes contradictory? Or more simply, now that we have discovered indoor air pollution, what do we do about it? The scientific basis of decisions about public action is weakened by a lack of data on the distributions of sources, building characteristics, daily activity and exposure patterns, indoor concentrations, and effects on health. Nevertheless, because data from several studies indicate that indoor exposure to some pollutants represents a significant health risk (*2, 3*), government efforts to define the magnitude of public health consequences are justified.

Justification for California's program focusing exclusively on nonindustrial indoor air quality is based on several factors. First, indoor air pollution can no longer be termed an emerging public health problem. Unhealthful indoor air is a fact of life for many people in California, and the situation may be worsening because of energy conservation measures and the increased use of synthetic building materials (*2, 3, 6*). Moreover, the federal response has been woefully inadequate, with efforts devoted primarily to dealing with crises caused by the use of asbestos in schools, formaldehyde emissions from urea–formaldehyde foam insulation, and elevated radon concentrations in homes built on phosphate lands in Florida and mining areas in Montana (*2*). There is a critical need in California for research to assess the nature of potential indoor environmental hazards.

Complaints about building-related illnesses in private and public buildings are a growing concern of many local and state health officials (*14*). In California, an increasing number of homeowners and office workers are reporting problems with air quality. Yet because air quality in private residences, offices, schools, and public and commercial buildings is an institutional gray area, in which authority and responsibility at the state level are ill-defined, complainants are frequently told that little or nothing can be done. In general, states lack the authority, funding, and knowledge to present an adequate response to complaints about indoor air quality.

Indoor air quality program

A budget change proposal (BCP) to establish an indoor air quality (IAQ) program within the Department of Health Services was approved by the governor of California for inclusion in his budget for the fiscal year beginning in July 1982. The BCP appropriated funds for eight permanent technical positions within the department's Air and Industrial Hygiene Laboratory. The IAQ program is the nucleus of a multidisciplinary effort to carry out investigations of identified and potential problems with the quality of indoor air.

In addition to the BCP, Assembly Bill 3200, which gives the Department of Health Services explicit responsibility for coordinating state efforts to assess, protect, and enhance indoor environmental quality, was approved by the governor in September 1982. As part of the California Health and Safety Code (*15*), this act established a legislative mandate for the IAQ program. It declares, "The people of the state of California have a primary interest in the quality of the indoor environment in which they live." The act also states that "the public interest shall be safeguarded by a coordinated, coherent state effort to protect and enhance the indoor environmental quality."

The California IAQ program is responsible for promoting and conducting research on the determining factors of healthful indoor environments. Among the professional disciplines represented by our program staff members are chemistry, engineering, epidemiology, microbiology, psychology, and public health sciences. As part of the California public health effort, we have established strong ties with other state government groups, including the Human Monitoring Program, the Epidemiological Studies Section, and the California Occupational Safety and Health Program (Cal/OSHA).

The IAQ program is structured to obtain information about emission sources, ventilation effects, indoor concentrations, human activity patterns, exposures, health risks, control measures, and public policy options, so that informed policy decisions can be made about the need for government action. The process by which the issue of safeguarding indoor air quality is being addressed in the state is summarized in Figure 1.

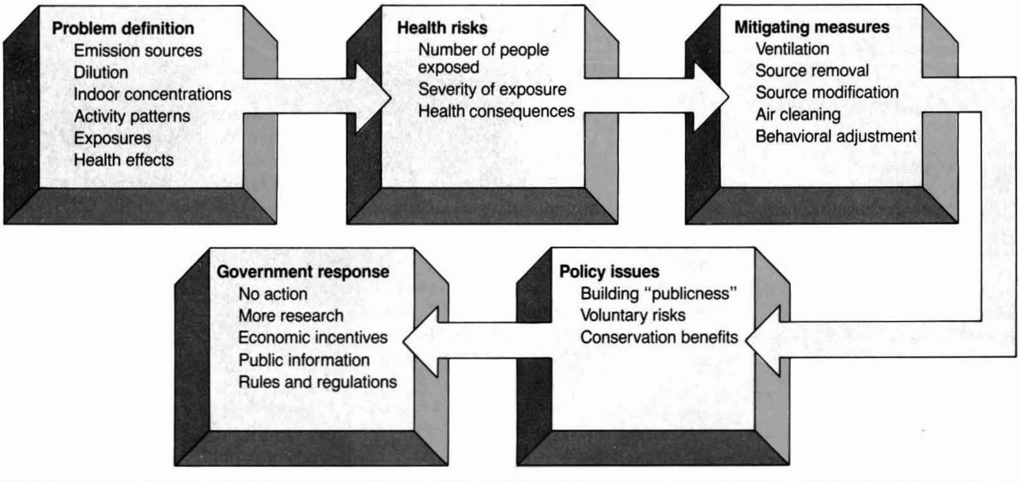
The data are gathered by a variety of methods, including research conducted by staff members, review of the available scientific literature, participation in technical meetings, contractual agreements with outside agencies, cooperative research projects with other groups, and consultation with experts inside and outside the Department of Health Services. The aim is to assess the nature and extent of potential indoor hazards in the state so that health risks can be evaluated adequately.

Priorities

The IAQ program was not created as a knee jerk reaction to yet another newly recognized environmental problem. It was established without undue attention from the media or widespread public outcry about the need for government action. The program has no regulatory authority. Rather, its purpose is to initiate research necessary to define the essential components of healthful nonindustrial indoor environments. The program's goal is the timely acquisition of information to serve as the basis for a determination of the need for government response and appropriate forms of intervention (Figure 1).

Given the broad mandate outlined in Article 9.5 of the California Health and Safety Code and the paucity of data on hand, it is obvious that the current levels of funding and the number of professional staff are insufficient to address the spectrum of indoor health issues. It is therefore important to establish priorities so that available resources are focused on those issues likely to be of greatest concern. Important considerations in determining resource allocation include potential health risks (number of people exposed, severity of exposure, and health consequences), ongoing research by academic and government scientists outside the California health department (to avoid duplication), availability and suitability of sampling and analytical methods for important indoor contaminants, and the likelihood that identified indoor contaminants are a threat to the

FIGURE 1
Addressing indoor air quality issues



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health of citizens (based on assessment of building stock, demographics, and time-activity patterns).

Research on indoor exposures to selected gas phase and particulate phase organics, respirable particles, radon, and airborne microorganisms will be the major focus of our efforts for the next two to three years. In conjunction with attempts to define exposure distributions, data will be obtained on emissions from indoor sources and on the effects of ventilation on indoor contaminant concentrations. We also expect to carry out cooperative studies to investigate the relationship between indoor exposure and body burden (the amount of a given toxin in the bloodstream) for selected toxic chemicals. Because most people spend an average of 16 hours each day at home, and because in-home pollutant levels have been shown to exceed outdoor values for many contaminants, most of this research will be conducted in residential indoor environments.

Current resources also will be used to address the issue of building-related illnesses, especially in modern office buildings. Complaints from office workers about inadequate indoor air quality and associated symptoms, such as eye and throat irritation, headache, skin rash, and nausea, are a continuing source of study for California health officials. Because funds to carry out a systematic, multidisciplinary investigation of this issue are not now available, the program staff are working with Cal/OSHA to develop a coordinated mechanism for receiving and documenting building-related health complaints.

Resources also will be devoted to public education that fosters awareness of potential indoor air hazards and possible mitigating measures. Pamphlets and handbooks will be made available to consumers and homeowners about important indoor air issues. Furthermore, we have instituted a series of instructional presentations to professional groups, including building managers, physicians, architects, and industrial hygienists.

Continuing activities

A major aspect of the IAQ program's task is to coordinate state activities affecting nonindustrial indoor environments. As shown in Table 1, many state agencies have jurisdiction over some part of the problem.

To ensure that the diverse groups deal with indoor air quality issues in a coherent and harmonious manner, the California Working Group on Indoor Air Quality was established. Representatives from concerned state agencies, primarily mid-level managers familiar with IAQ issues, meet periodically to discuss mutual interests and assess the needs of individual agencies. Discussions so far have focused on three major topics:

- the development of a coordinated system within the state to receive, document, and respond to building-related health complaints,
- the need to distribute information on important indoor air quality problems to individuals and groups, and
- the development of a standardized protocol that state, county, and local health officials can use to investigate building-related health complaints.

An important issue in addressing the health complaints of building occupants is the availability of private laboratories. As Sexton and Repetto point out, "Because air pollution levels in one building have virtually no effect on adjacent structures, the value as well as the cost of information remains largely private" (*13*). For example, the costs and benefits of maintaining adequate indoor air quality in private dwellings are borne by the occupants. The closed-loop cost-benefit cycle suggests the possibility of a private demand for air-monitoring services, air-cleaning devices, and easy-to-use pollution monitors (*13, 16*).

TABLE 1
California state agencies concerned with indoor air issues

Agency	Jurisdiction
Department of Health Services	Lead agency for indoor air quality issues
California Energy Commission	Residential and nonresidential building standards
Cal/OSHA	Enforcement of OSHA standards in the workplace
Department of Food and Agriculture	Regulation of pesticide applications
California Air Resources Board	Outdoor air quality standards
Department of Consumer Affairs	Consumer products that are sources of air pollution
Office of the State Architect	Indoor air quality in state buildings
Department of Housing and Community Development	Indoor air quality in conventional and manufactured homes
State Department of Education	Asbestos in schools
Department of General Services	Indoor air quality in state buildings

The California IAQ program has neither the staff nor the resources to respond adequately to all, or even most, of the complaints by office workers and homeowners. To assess existing indoor air-monitoring capabilities within the private sector, a list of private companies and public agencies that routinely make contaminant measurements in nonindustrial indoor environments has been compiled. The list is available to all interested parties (*16*).

A number of research projects have started to address specific indoor air quality issues. Several investigations of air quality inside office buildings have been conducted in response to complaints about building-related illnesses (*17, 18*). When adequate funding is obtained, we hope to conduct a systematic study, in cooperation with Cal/OSHA, of the relationship between air quality in office buildings and workers' health.

There are a number of studies that focus on indoor residential environments. Among them are an investigation of airborne asbestos levels in homes with asbestos-lined furnaces, a comparison of two widely used methods to measure formaldehyde (*19*), and measurements of formaldehyde concentrations in 50 conventional homes in the San Francisco Bay area (*20*).

Other current studies include an indoor air monitoring project in 750 randomly selected mobile homes, focusing on measurement of formaldehyde and nitrogen dioxide concentrations (*20, 21*), and an investigation of the relative contributions of indoor and outdoor sources to in-home respirable particle concentrations. An environmental chamber study is currently under way in cooperation with Lawrence Berkeley Laboratory. Its purpose is to characterize particulate and organic emissions from major indoor sources (*22, 23*). In addition, indoor and outdoor particle samples from selected buildings are being analyzed for mutagenicity by means of a modified Ames test that uses special strains of histidine-dependent *Salmonella typhimurium* (*18, 23*).

Determining success

As the field of indoor air quality research matures and the issues become more sharply defined, awareness of the necessity for an integrated approach to air pollution control will become more widespread. Findings from indoor air studies will come to the attention of the scientific, regulatory, and environmental communities, altering the perception that this is a peripheral issue and that indoor air quality is somehow separate from current government actions to limit exposures to outdoor air pollution.

All other factors being equal, the health effects of breathing air pollutants, such as carbon monoxide and nitrogen dioxide, are the same whether exposure occurs indoors or outdoors. Therefore, the justification for current control strategies, which focus almost exclusively on outdoor sources, is at odds with documented studies showing that elevated concentrations of both pollutants are common inside many residences and office buildings (*3, 4*). Ultimately, the success of the program will be determined by the degree to which safeguarding air quality in nonindustrial indoor environments becomes an integral part of the California Public Health System.

Complex policy issues

We expect the program to evolve as our knowledge about the determinants of healthful indoor environments expands. Emphasis will gradually shift from collecting data on exposure and body burden to applying accumulated information toward the mitigation of indoor air problems. More attention also will be directed to justifying direct government action to reduce indoor exposure, as well as to the effectiveness and suitability of alternative forms of intervention.

Maintaining healthful air quality in nonindustrial indoor environments is more than just a complex technical issue. It also raises complicated public policy questions about the proper role of government in safeguarding public health in private and public buildings (Figure 1) (*13*).

The compilation of information about pollutant concentrations, human exposure, and associated health hazards is not in itself sufficient to determine the appropriateness of government intervention. It is equally important to obtain data on individual perceptions of air quality, public awareness of health risks, and the extent to which this information influences private choices. A workable policy on indoor air quality must balance the need to protect individual privacy against government's responsibility to protect public health and safety.

Decisions about the need for public action to abate indoor air pollution must address several major policy issues: Does the role of government depend on the degree of public access to, and occupancy of, a particular building? If so, what is an appropriate response to air quality problems in private buildings? Is consideration of the difference between voluntary and involuntary risks important for choices about government intervention? What are the tradeoffs between energy conservation measures and indoor air quality? Should the emphasis be on protecting building occupants from long-term chronic exposures or short-term peak exposures? If government intervention is justified, what forms are appropriate?

California has begun to address the entire range of technical and policy issues by establishing a permanent IAQ program. Its goal is to acquire data necessary to define the components of healthful indoor air, to evaluate the applicability of available mitigating measures, and to assess the relative merit of policy alternatives.

Acknowledgment

Assemblywoman Sally Tanner, chairperson of the California Assembly Committee on Consumer Protection and Toxic Materials, was instrumental in creating California's IAQ program. She and other members of the committee have been influential in drawing public attention to the need for safeguarding indoor air quality. We also thank J. Heslep, D. Lyman, and C. Langston of the California Department of Health Services for their invaluable support in setting up the program, and members of the staff who assisted in implementing the program, including P. Flessel, R. Stanley, L. Pierce, S. Twiss, M. Petreas, K. Liu, L. Webber, S. Hayward, H. Okomoto, J. Stratton, G. Kulasingam, A. Kelter, and R. Neutra.

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Ken Sexton *(r.) is the director of California's indoor air quality program. He received a doctorate in environmental health sciences from Harvard University and a master's degree in environmental engineering from Washington State University. Sexton has extensive experience in environmental research, including ambient air measurements, pollution transport, source apportionment, atmospheric chemistry, indoor and personal monitoring, and exposure assessment. His current interests are environmental policy and the measurement and modeling of human exposure to toxic air pollutants.*

Jerome J. Wesolowski *(l.) is chief of the Air and Industrial Hygiene Laboratory of the California Department of Health Services and a lecturer at the University of California, Berkeley. He received a doctorate in nuclear physics. Wesolowski's research on the use of nuclear techniques, particularly neutron activation analysis, to measure trace elements in ambient air led to his present career in environmental science. He is the founder of California's indoor air quality program.*

Reagan's EPA budget request

Richard M. Dowd

The president's proposed budget for fiscal year 1986 includes a request of $1.37 billion for EPA operations and $900 million for Superfund cleanups of abandoned hazardous waste dump sites. These figures are increases from $1.31 billion and $620 million, respectively, in fiscal year 1985. If the budget is adopted, the 45% increase for Superfund will be the largest change in any program.

Additionally, funding for the Resource Conservation and Recovery Act (RCRA) would rise by $54 million, to $247 million. These increases, however, must be viewed in light of the recently enacted RCRA legislation and likely changes in the Superfund law, both of which may require major additional funding.

Under the Reagan proposal, the agency's enforcement program would increase by some 20% to $193 million, which some observers regard as an indication of the administration's intent to increase the use of enforcement as a tool to ensure compliance with RCRA's provisions.

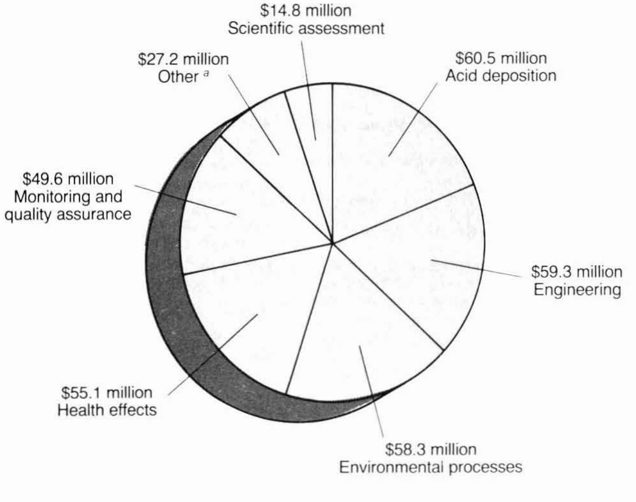
Research and development

The president's proposed budget of $325 million for EPA's Office of Research and Development (ORD) signals marginal changes in research priorities, with some programs receiving increases and others showing significant decreases.

The largest increase is an additional $30 million for the agency's acid rain research program. At a total of slightly more than $60 million, this figure constitutes about 20% of EPA's research effort. The additional funds are to be spent in three areas. The first is a survey and study of the effects of acid deposition on lakes. The second project is a study of the effects of acid deposition on forests. Finally, the dry deposition monitoring program would be accelerated.

Reagan administration's proposed budget for EPA research and development

Total $324.8 million



[a] Includes grants program and management and support

Hazardous waste research would be increased by about $8 million, or 20%, mostly for extramural support to improve monitoring methodologies for hazardous waste disposal facilities.

The administration proposes to increase funds for research on toxic substances by about $14 million, to nearly $50 million. The money would be used for risk assessment of pesticides and genetically engineered organisms and for improving control technology assessment of genetically engineered organisms. A portion of this money is slated for increased research on reproductive toxicity, health effects of biotechnology, and consequences of human exposure to toxic chemicals.

Areas of decreased funding

Some of the funding increases are the result of reductions in other areas. These include eliminating research on the health effects of nonionizing radiation, eliminating research on indoor air pollution, and further reducing extramural grants and funds for Centers of Excellence. Some scientists predict that this move will compromise the viability of the centers.

Research on limestone injected multistage burner (LIMB) technology will be phased out. A proposed decrease in LIMB funding from $12 million to $3 million would close out the program with a 1988 demonstration of this control technology. Research would be discontinued on developing the technology for the many boilers now in use. This will curtail investigations of a promising option for reducing the precursors of acid deposition.

Perhaps the most significant area of reduction is in ORD's salaries and expenses budget, which has been reduced by 4% from last year. Because expenses under this account are essentially fixed, this may translate (taking inflation into consideration) into a real cut of more than 15% for intramural research.

Richard M. Dowd, Ph.D., is a Washington, D.C., consultant to Environmental Research and Technology, Inc.

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ES&T RESEARCH

Degradation of Polycyclic Aromatic Hydrocarbons during Simulated Stack Gas Sampling

Eva Brorström-Lundén* and Anne Lindskog

Swedish Environmental Research Institute, S-402 24 Gothenburg, Sweden

■ The formation of sampling artifacts due to exposure to NO, NO_2, SO_2, and SO_3 has been studied. The sampling method was tested in a thermostatic oven attached to a smoke generator and involves filtration of particles at stack gas temperature, condensation, and adsorption on Amberlite XAD-2. A substantial degradation of reactive PAH took place in all steps during sampling. The reactivity increased in the presence of acid. The reaction products formed included 9-nitroanthracene, 1-nitropyrene, 10-nitrobenz[*a*]anthracene, nitrobenzo[*a*]pyrene, and several polycyclic ketones, aldehydes, and guinones, but the main reaction products have not been identified so far.

During the last few years several papers have been published concerning reactions between individual polycyclic aromatic hydrocarbons (PAH) and reactive gases like NO_2, HNO_3, SO_2, and SO_3 (*1–6*). Under certain circumstances benz[*a*]anthacene, benzo[*a*]pyrene, and perylene will thus form nitro derivatives by exposure to NO_2, and exposure to SO_3 will cause degradation and formation of unidentified compounds. The reactions are dependent on what kind of carrier the individual compound is adsorbed on (*2–4*) as well as the presence of water (*7*).

During combustion of organic material, NO_x*and* when fossil fuel is used, SO_x will be formed together with PAH. The concentrations of the gases will pass through the collected material for several hours. Under these circumstances it is likely that transformation reactions may take place and thus lead to an underestimation of the PAH content. As some of the transformation products are direct mutagens in Ames' *Salmonella* test (*1*, *8*) the formation of these sampling artifacts would also give rise to an erroneous conception of the mutagenic effect of the stack gas.

A first set of experiments concerning the possibility of artifact formation during stack gas sampling was carried out in our laboratory some years ago. The results obtained indicated that degradation of PAH on exposure to NO_2, SO_2, and SO_3 occurred and that most of the reactions took place during sampling (*9*).

The aim of this expanded study was to find out to what extent and under which circumstances degradation of reactive PAH takes place during sampling and to identify some of the compounds formed.

In order to make a transference of the results to the conditions in full scale feasible, the work had to be carried out in a way that as much as possible imitated realistic operating conditions. This means that the quality of the carrier, the mixture of PAH, the distribution of PAH between gas phase and particles, the humidity of the smoke as well as the mixture, and concentrations of the different gases must be relevant. By working with a smoke generator attached to a thermostatic oven, most of these demands can be met. The PAH and soot are formed by burning propane, and thus the reactivity is dependent on the quality of the carrier, this is a limitation of the method.

Experimental Section

Equipment and Experimental Conditions. Soot and PAH are generated in a smoke generator by combustion of propane with a deficit of air. The smoke generator is attached to a thermostatic oven, 1.5 m long and with an internal diameter of 62 mm. The flow through the oven is about 29 L/min, the residence time about 25 s, and the temperature 150 °C. The system is equipped with two sampling ports (see Figure 1), P1 placed immediately after the smoke generator and P2 after the oven. Reactive gases are introduced to the system between P1 and the oven with a flow of about 2 L/min. NO, NO_2, and SO_2 are supplied from gas bottles, mixed, and diluted to suitable concentrations in a dilution system before entering the oven. SO_3 and gaseous HCl are obtained by letting an air stream pass over glass containers with fuming sulfuric acid and concentrated hydrochloric acid, respectively. The concentrations of NO and NO_2 are measured with a chemiluminescent instrument, and the concentration of SO_2 is measured with an IR instrument. The concentration of HCl(g) is determined by absorption in a weak solution of alkali followed by analysis on an ion chromatograph, while SO_3 is absorbed in a 80% solution of 2-propanol and the concentration determined by titration (*10*).

During the experiments samples are taken in each of the two sampling ports. The sample from P1 constitutes a reference sample to the gas-exposed sample from P2. The sampling method tested includes filtration of particles at stack gas temperature, condensation, and adsorption of vapor-phase compounds on Amberlite XAD-2. The equipment is made of glass. A buffer solution (1 M $K_2H_2PO_4$) is added to the condensate bottle before sampling.

In total, 15 experiments have been accomplished. The test conditions are listed in Table I. The first three experiments were carried out without any addition of reactive gases, to test the reproducibility of the system. In subsequent experiments the different gases were added in concentrations simulating conditions in stack gases. Thus,

Table I. Test Conditions

test	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
sampling time, min	15	60	180	15	60	180	155	60	120	15	60	15	60	15	60
added, ppm															
NO	–	–	–	160	160	160	400	400	400	160	160	400	400	400	400
NO_2	–	–	–	12	12	12	30	30	30	12	12	30	30	30	30
SO_2	–	–	–				350	350	350			350	350	350	350
SO_3	–	–	–											10	10
HCl	–	–	–							29	29	26	26		

Table II. PAH Used in the Calculation of Relative Concentrations

reactive PAH	calculated relative chromatographically closest stable PAH
anthracene	phenanthrene
pyrene	fluoranthene
cyclopenta[*c*,*d*]pyrene + benz[*a*]anthracene	triphenylene
benzo[*e*]pyrene	benzo[*b*]-, benzo[*j*]-, benzo[*k*]fluoranthenes
benzo[*a*]pyrene	benzo[*b*]-, benzo[*j*]-, benzo[*k*]fluoranthenes
perylene	benzo[*b*]-, benzo[*j*]- benzo[*k*]fluoranthenes

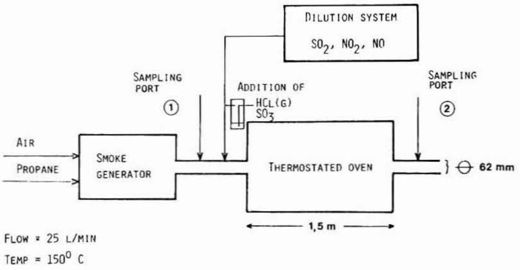

Figure 1. Experimental equipment.

in experiments 4–6 combustion of a fuel not containing sulfur is simulated, and in experiments 7–9, combustion of sulfur-containing fuels is simulated. Since the reactivity of PAH on exposure to NO_2 seems to increase in the presence of acid (*5*), some experiments with addition of SO_3 and HCl(g) were carried out as well. The sampling time (equals exposure time) varied from 15 min to 3 h, but the smoke generator was working during the first 10 min only.

Analysis. Filters and XAD-2 cartridges were Soxhlet extracted with methylene chloride during 24 h. The condensor was rinsed with ethanol which then was added to the condensate. After dilution with distilled water (1:1) the condensate was extracted with methylene chloride. The combined extracts were conconcentrated and analyzed on Carlo Erba Ractovap 2101A gas chromatograph equipped with a 50 m × 0.38 mm i.d. glass capillary column coated with SE-54. Individual PAH were identified by means of retention times. The concentrations of the individual reactive PAH were calculated relative to a stable PAH with adjacent retention time (Table II). The terms reactive and stable refer in this case to a reactivity scale of PAH in electrophilic reactions made up by Nielsen (*11*) and the results obtained in other experiments (*5*–*7*).

In order to identify some of the reaction products formed the three extracts from each sampling point were combined, concentrated, and transferred to a silica column (10% water) for fractionation. The column was eluted with two portions of *n*-hexane, *n*-hexane–methylene chloride (3:1), methylene chloride, and methanol to give five fractions with increasing polarity. The fractions were analyzed on a Carlo Erba Fractovap 4130 with a 25 m × 0.32 mm i.d. glass capillary column coated with JXR, 0.4 μm. Some of the fractions were also analyzed on a Hewlett-Packard 5990A GC-MS with a 25 m × 0.33 mm i.d. fused silica column BP5, 0.5 μm. The masses from 50 to 350 amu were scanned every 0.4 s.

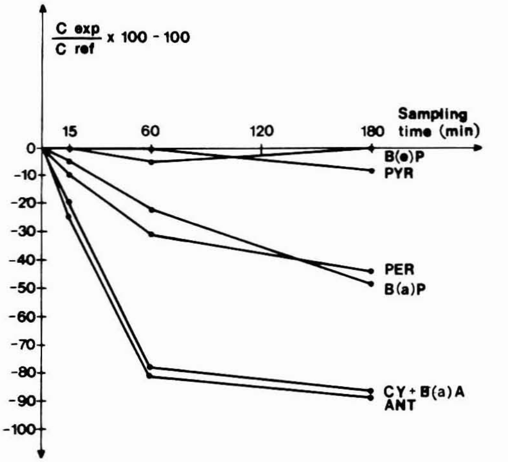

Figure 2. Degradation of individual PAH on exposure to NO (160 ppm) and NO_2 (12 ppm). B(e)P = benzo[*e*]pyrene, PYR = pyrene, PER, = perylene, B(a)P = benzo[*a*]pyrene, CY + B(a)A = cyclopenta[*c*,*d*]pyrene + benz[*a*]anthracene, and ANT = anthracene.

Results and Discussion

Degradation. The reproducibility tests (no. 1–3) demonstrated that the relative concentrations of individual PAH were rather constant with time and also rather accordant at the two sampling points, in spite of the difference in distribution between particles and gas phase. In the exposure experiments the degradation of individual PAH was calculated from the difference in relative concentration at the two sampling points. The experimental uncertainity is estimated to be ±10%. The degradation, in percent, of reactive PAH is demonstrated in Figures 2–6. There was a great difference in reactivity between different PAH, but degradation of reactive PAH took place in all experiments.

The degradation increased with increasing sampling time. An increase of the concentration of NO and NO_2 together with an addition of SO_2 (Figures 2 and 3) had no effect on the total degradation, but anthracene (ANT) and cyclopenta[*c*,*d*]pyrene (CY) reacted faster during the first 15 min. CY coelutes with the less reactive benz[*a*]anthracene (BaA) which is why the degradation somewhat underestimated (*7*). Addition of HCl(g) to the NO–NO_2 mixture (Figures 2 and 4) gave rise to an increased degradation rate. After 1 h 90% of the benzo[*a*]pyrene (BaP) had disappeared compared with 20% without addition of

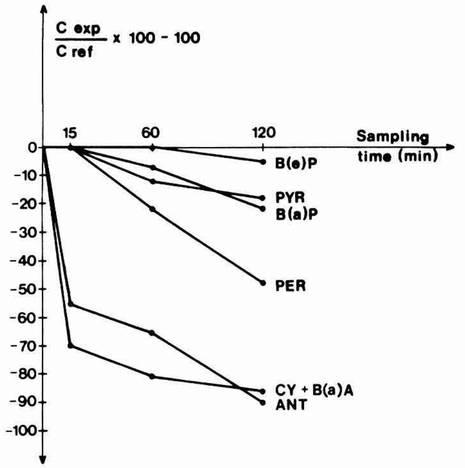

Figure 3. Degradation of individual PAH on exposure to NO (400 ppm), NO_2 (30 ppm), and SO_2 (350 ppm).

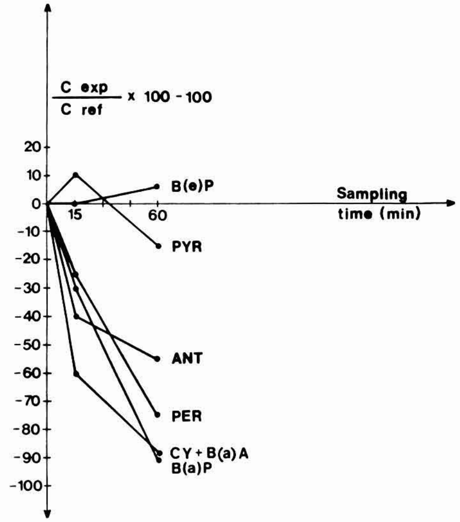

Figure 4. Degradation of individual PAH on exposure to NO (160 ppm), NO_2 (12 ppm), and HCl (29 ppm).

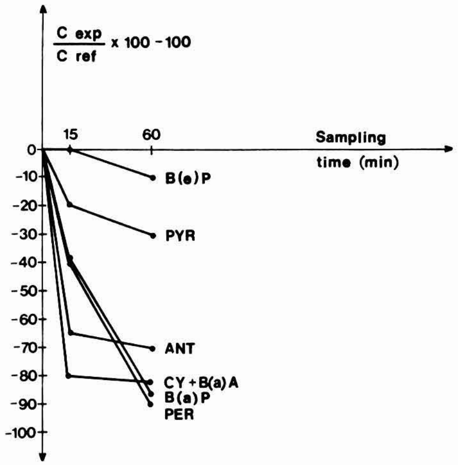

Figure 5. Degradation of individual PAH on exposure to NO (400 ppm), NO_2 (30 ppm), SO_2 (350 ppm), and HCl (26 ppm).

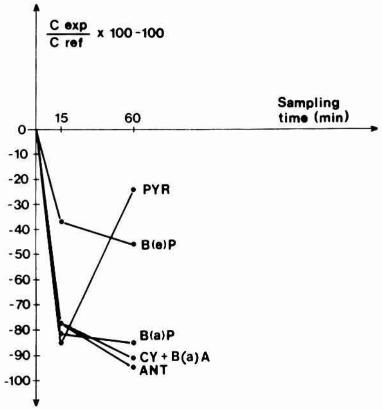

Figure 6. Degradation of individual PAH on exposure to NO (400 ppm), NO_2 (30 ppm), SO_2 (350 ppm), and SO_3 (10 ppm).

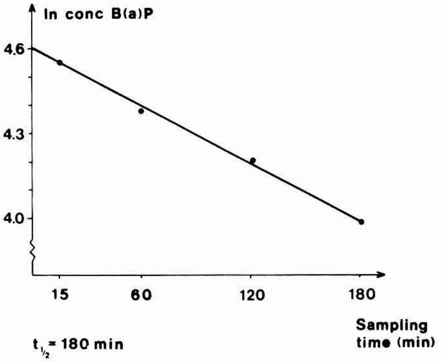

Figure 7. Degradation rate of benzo[*a*]pyrene on exposure to NO (160 ppm) and NO_2 (12 ppm).

HCl(g)9 In the experiments with $NO–NO_2–SO_2$ the addition of HCl (g) had less effect on the degradation of CY and ANT while the degradation rate of BaP and perylene (PER) increased considerably (Figures 3 and 5). The addition of SO_3 affected the degradation rate even more. These were the only experiments where benzo[*e*]pyrene, considered as rather stable by Nielsen (*11*), was degraded: 45% after 1 h.

In the experiments with 160 ppm of NO and 12 ppm of NO_2 the reaction is first order with respect to BaP (Figure 7). The half-life for the degradation would then be 180 min.

Simple Model for Comparison with Full Scale Sampling. Due to the huge amount of soot formed, it was not possible to let the smoke generator work for more than 10 min. As a consequence the obtained percental degradation was greater than it would have been if new PAH had been fed to the sampling train continuously. If we assume that the formation rate of PAH is constant and use the degradation of BaP obtained in the $NO–NO_2$ experiments during the period 15–60 min. The following correlation can be stated:

$$C_t = \frac{M_t}{1 - (2.2 \times 10^{-3})t}$$

where C_t = true amount at time t, M_t = analyzed amount at time t, and t = sampling time. Calculated in this way

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the true degradation of BaP during sampling due to NO_2 exposure would be 29% after 3 h. On the other hand, the degradation would have been greater if a more activating carrier, e.g., fly ash, had been used (*3*).

Reaction Products. A great number of polycyclic ketones, aldehydes, and quinones preferably with two to four rings have been formed due to reactions during sampling. Still the main reaction products of the PAH studied have not been identified so far. The amounts found of NO_2–ANT, NO_2–pyrene, NO_2–BaA, and NO_2–BaP are too small to be the only compounds formed by degradation of the corresponding PAH. Either the nitro-PAH formed in a primary process have reacted further to yield more polar compounds or the large molecules have been decomposed to form smaller molecules, which then have been oxidized.

Registry No. ANT, 120-12-7; PYR, 129-00-0; PER, 198-55-0; CY, 27208-37-3; BaA, 56-55-3; BeP, 192-97-2; BaP, 50-32-8; NO, 10102-43-9; NO_2, 10102-44-0; SO_2, 7446-09-5; SO_3, 7446-11-9; HCl, 7647-01-0.

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Distribution of Mercury during Simulated in Situ Oil Shale Retorting

J. P. Fox*

Lawrence Berkeley Laboratory, Berkeley, California 94720

■ This paper reports the first continuous, real-time measurements of Hg in process gases. Mercury in offgases from a steam/air/N_2 run of a 20-kg laboratory in situ retort was monitored for 78 h by using Zeeman atomic absorption spectroscopy. A good mass balance was obtained, and 95% of the Hg (1391 μg) was recovered; 76% was present in the gases, 13% in the spent shale, 9% in the shale oil, and 3% in the retort water. The offgas Hg was nonuniformly emitted in a series of pulses during the final one-third of the run. Studies of four other incomplete runs revealed that Hg accumulates in unretorted shale ahead of the reaction zone. This Hg travels down the shale bed in advance of the reaction zone and is released into the gases when the temperature at the bottom of the bed reaches about 300 °C.

Introduction

The high volatility of Hg at temperatures encountered in fossil-fuel combustion processes has led to numerous studies of Hg mobilization in coal- and oil-fired power plants (*1–7*). More recently, coal conversion (*8–10*) and oil shale (*10–17*) processes have been investigated. These studies reveal that a significant fraction of the Hg present in the feed is volatilized and partitioned among products. Studies of in situ oil shale processes have used mass balances to estimate the amount of Hg released to product gases (*10–12*). These showed that 45–91% of the Hg is distributed to the gases. However, direct measurements of Hg in the gases indicated that concentrations were up to several orders of magnitude lower (*10*, *17*).

This study, conducted Sept 26–28, 1977, was conceived to resolve the discrepancy between mass balance estimates and direct gaseous measurements. Real-time, continuous measurements of Hg in offgases were made by Zeeman atomic absorption spectroscopy (ZAA) and by an independent method. A mass balance was determined to study the distribution of Hg and to help validate the gas-phase measurements. Four incomplete runs were also studied to help elucidate the mechanisms responsible for the observed emission profile.

Experimental Section

Laboratory Retort. In situ retorts consist of underground, stationary, packed beds of rubblized oil shale. The top of the shale bed is ignited, and a carrier gas is used to propagate a reaction zone through the bed. This was simulated in the present work in a 20-kg controlled-state retort (Figure 1). The facility and its operation have been previously described (*18*).

Operating conditions for the five runs studied in this work are summarized in Table I. Two types of experiments were conducted: "completed" and "interrupted". In the completed run, the entire shale bed was retorted, while in the interrupted runs, heating was stopped after shale within heater zone 13 or 14, about 0.2 m from the top of the retort, reached 540 °C.

Sampling. Raw oil shale, input gases, spent shale, shale oil, retort water, and offgases were sampled. A 50-g aliquot of each solid was split and ground to less than 0.015 mm (100 mesh). In the interrupted run, the inside walls of the retort tube and shale from zones 15–24 were washed with

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* Address correspondence to this author at Fox Consulting, 1988 California Street, Berkeley, CA 94703.

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Table I. Retort Operating Conditions

run	run type	shale grade, L/ton[a]	shale size range, mm	oil yield, % Fischer assay (volume basis)	retorting rate, m/day	maximum temp, °C	sweep gas	gas flow rate, standard $m^3/(m^2 min)$
1	incomplete	125	10–19	43	1.83	540	N_2	0.12
2	incomplete	125	3–10	33	1.83	540	N_2	0.12
3	incomplete	125	3–13	30	0.04	540	N_2	0.12
4	incomplete	123	3–13	46	1.83	540	N_2	0.12
5	complete	118	3–13	98	1.83	760	64.5% N_2, 10.5% O_2, 25% steam	0.15

[a] All shales used in these experiments came from the Anvil Points Mine near Rifle, CO.

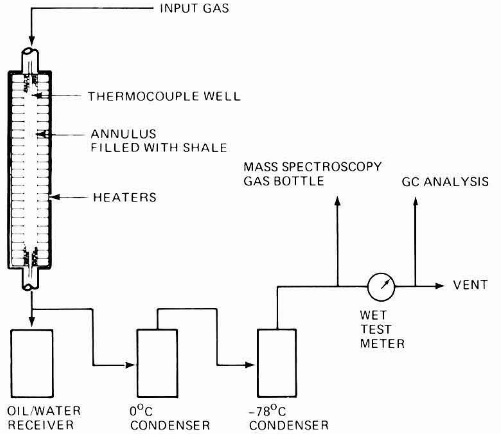

Figure 1. Schematic of laboratory in situ oil shale retort used in this study. The retort is electrically heated, and movement of the reaction zone is simulated by successively activating 24 external, Lindberg-type furnaces surrounding an internal (8 cm i.d. × 4 m) tube packed with crushed shale.

cyclohexane to recover surface oil (washes). Bitumen was recovered from shale by Soxhlet extraction for 48 h with cyclohexane (extracts). The extracted and unextracted spent shale, washes, and extracts were analyzed for Hg.

In the completed run, the oil–water mixture was sampled ahead of the receiver (Figure 1) approximately every 4 h during retorting. Oil and water were separated by centrifugation, and each fraction was analyzed for Hg. At the end of all runs, the water layer was removed with a syringe (retort water), and the condenser contents were mixed with the remaining oil (wet oil). A 25-mL aliquot of retort water and wet oil were collected for analysis. Retort water samples were not acidified (*19*) and were stored in air-tight, acid-washed, polyethylene bottles at 4 °C. The retort water was vacuum filtered through a 0.45-μm Millipore filter to collect particulates.

Mercury. All of the solid, liquid, and oil samples were analyzed in a batch Zeeman atomic absorption spectrometer described elsewhere (*20–22*). The accuracy of this technique for these types of samples has been demonstrated (*12, 15, 23*). All water samples were analyzed by standard additions by using inorganic Hg standards prepared in a 0.1 N HNO_3 matrix. Oil calibration standards were prepared by diluting Conostan petroleum standards with Singer sewing machine oil. Three to 10 replicates of each sample were analyzed.

The product gases were continuously analyzed for total Hg (gaseous plus particulate) by using Zeeman atomic absorption spectroscopy. This application of ZAA has been described elsewhere (*21, 24*). The system was calibrated by injecting Hg-saturated air into the gas line with a syringe pump approximately every 30 min. The syringe pump procedure was validated in the laboratory by using a more elaborate technique (*25*). No differences between the two procedures were found.

The standard sampling procedure for Hg in stack gases (*26*) is based on collecting volatile Hg in a series of impingers containing the aqueous oxidant ICl. Modifications of this procedure were used to provide an independent check on the accuracy of ZAA measurements. Four different impinger train configurations were tested during the completed run: (1) I-I, (2) N-I-I, (3) H-I-I-E-A-N, and (4) E-I-I-A. These included 1 M ICl impingers (*27*) to trap Hg (I), 10% H_2O_2 to oxidize H_2S (H), 6.3 N NaOH to neutralize acidic gases and protect pumps and wet test meters (N), an empty sparger to trap particulates (E), and an acid impinger of 1:1:1 HNO_3–H_2SO_4–H_2O (A). Impingers H, N, A, and E were variously added in an attempt to clean up the gas and increase the life of the ICl solution and sampling equipment. Analytical-grade reagents were used for impinger solutions, and reagent blanks were determined. Impinger sampling times ranged from 1 to 5 h.

Carbon, Hydrogen, Nitrogen, and Sulfur. Two or three replicates of each solid sample were analyzed for total C, H, N, and S, and a single sample was analyzed for inorganic C. Total C, H, and N were determined on a Carlo Erba Model 1104 elemental analyzer gas chromatograph. A 2-mg sample was combusted in 10 mL of O_2, and evolved gases were analyzed for elemental N, CO_2, and H_2O. Inorganic C was determined by reacting a sample of about 100 mg with 20% perchloric acid. The evolved CO_2 was quantitated by coulometric titration. Organic C was calculated by subtracting inorganic C from total C. Total S was determined by combusting a sample of 100–200 mg in an O_2 atmosphere. The evolved SO_2 was titrated automatically with KIO_3. Various NBS standards were used to calibrate these methods.

Major constituents in the gases were determined every 2 h both on-line by gas chromatography and off-line by mass spectrometry. The experimental setup for these measurements is shown in Figures 1 and 2.

Results and Discussion

Mass Balance. The Hg mass balance for the completed run (Table II) indicates that 95% of the Hg was recovered in the oil, water, gas, and spent shale. The good closure corroborates the accuracy of the ZAA gas measurements. The unaccounted for 5% is attributed to analytical error and losses in the unheated sampling lines. Some 76% of the recovered Hg was present in the gas, in agreement with previous estimates calculated indirectly from mass balances (*10–12*).

Gas Analysis. The major compounds in the shale gases were H_2, CO_2, CO, H_2S, and C_1–C_5 hydrocarbons (Table

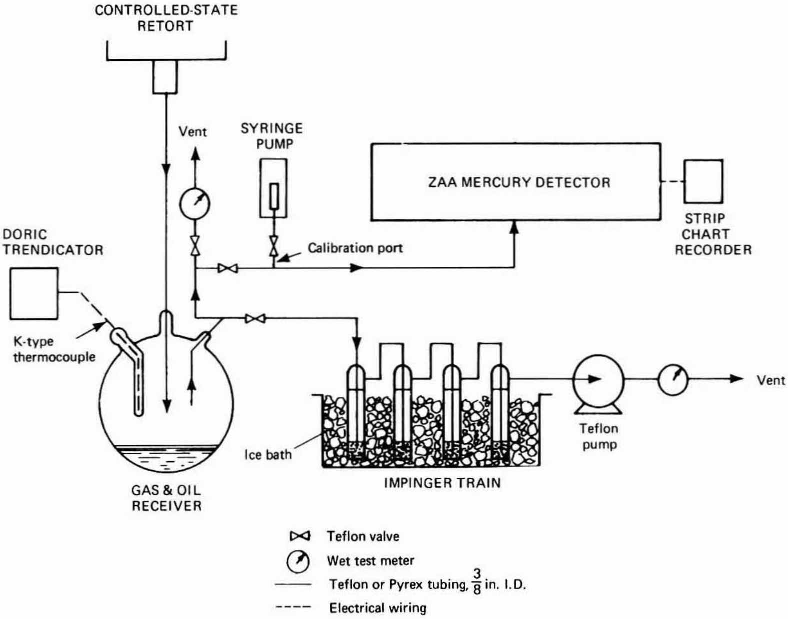

Figure 2. Experimental setup for Hg measurements in offgases from completed run using ZAA and various impinger trains.

Table II. Mercury Mass Balance for Completed Run (Run 5)

	product mass, g	average mercury concn, ppb	mercury mass, μg	mercury distribution, %
inputs				
raw shale	16954	86 ± 20	1458	100
gas	2723	<0.3	<0.9	
total	19677		1458	
outputs				
spent shale	11380	16 ± 8	182	13
shale oil	2233	54 ± 11	121	9
retort water	351	103 ± 13[a]	36	3
offgas	5814	181[b]	1052	76
total	19778		1391	
recovery,[c] %	101		95	

[a] Particulate Hg = 79 ± 4 ppb. [b] Average concentration computed from area under emission curve (Figure 4). Average precision (±1σ) for individual measurements was 10%. [c] Recovery = (total outputs/total inputs) × 100.

Table III. Mass Spectral Analysis of Exit Gases from Interrupted and Completed Experiments (Mole Percent Calculated on a N_2- and Moisture-Free Basis)

	interrupted runs				
	1	2	3	4	completed run
H_2	21.6	29.4	37.2	23.7	22.5
CH_4	11.6	12.8	11.8	14.7	3.3
C_2H_4	1.1	0.8	0.3	0.9	0.2
C_2H_6	3.4	3.8	4.8	4.6	0.8
C_3H_6	0.9	1.0	0.9	1.2	0.2
C_3H_8	1.8	2.0	2.4	2.1	0.4
C_4's	4.8	3.1	5.5	1.8	0.5
C_5's	5.6	2.5	0.7	0.0	0.1
CO	14.4	7.9	0.0	11.3	22.9
CO_2	31.2	32.6	33.5	35.6	47.8
NH_3	0.0	0.0	0.0	0.0	0.0
H_2S	3.6	4.0	2.7	4.1	1.1
COS	0.0	0.0	0.1	0.0	0.01
O_2	0.0	0.0	0.0	0.0	0.01

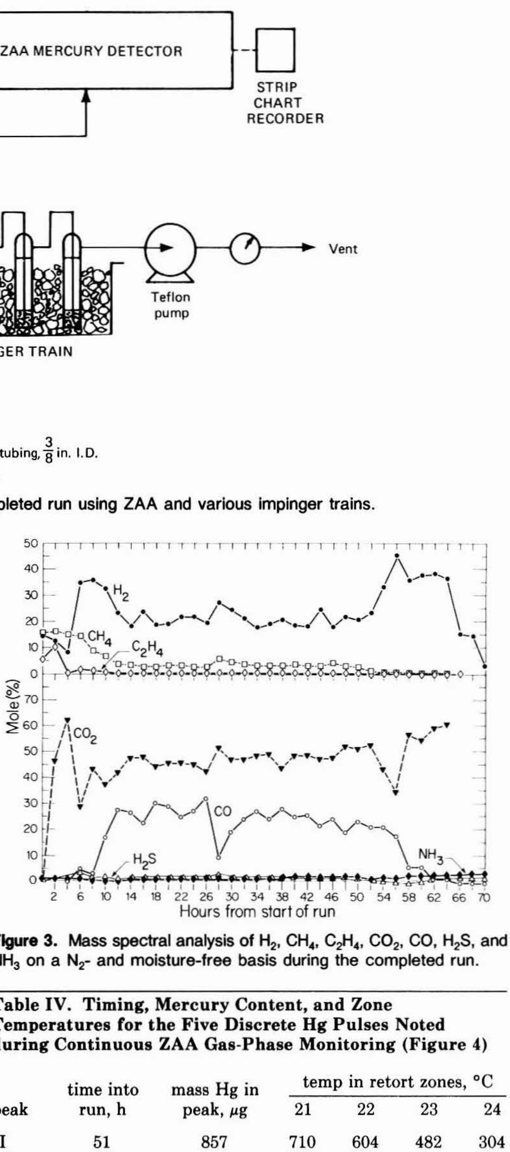

Figure 3. Mass spectral analysis of H_2, CH_4, C_2H_4, CO_2, CO, H_2S, and NH_3 on a N_2- and moisture-free basis during the completed run.

Table IV. Timing, Mercury Content, and Zone Temperatures for the Five Discrete Hg Pulses Noted during Continuous ZAA Gas-Phase Monitoring (Figure 4)

peak	time into run, h	mass Hg in peak, μg	temp in retort zones, °C			
			21	22	23	24
I	51	857	710	604	482	304
II	57	74	710	732	732	771
III	62	20	643	643	671	710
IV	64	23	621	632	649	682
V	67	78	593	649	632	677

III). Measurements made by gas chromatography and mass spectrometry agreed to within ±10%. These constituents were relatively uniform during most of the run, decreasing toward the run's end (Figure 3).

Mercury, on the other hand, was nonuniformly emitted (Figure 4), and concentrations ranged from <0.2 to 8000 μg/m^3. This variability was not due to measurement errors, which were subsequently estimated to be ±10% (±1σ precision) (*24*). Mercury was below the detection limit of

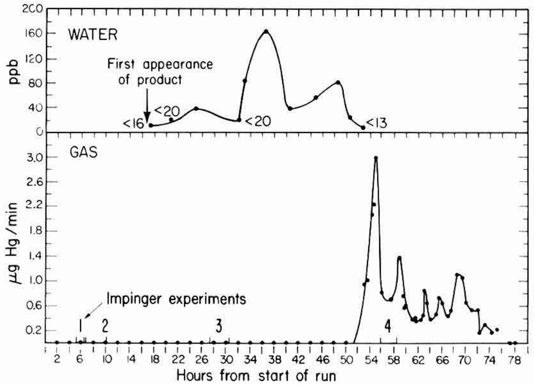

Figure 4. Time variation of total Hg in the offgases and retort water from the completed run. Data points for gas measurements (●) correspond to times when calibration was performed. Data points along the base line were below the detection limit (<0.2 $\mu g/m^3$). Data points for water measurements correspond to times when samples were taken. The average precision ($\pm 1\sigma$) for the water and gas analyses was 10%, approximately the width of the data points.

Table V. Summary of Impinger Measurements of Hg in the Offgas of the Completed Run (Run 5)

expt	train configuration[a]	time into run, h[b]	total Hg collected, μg	Hg emission rate, μg/min	Hg concn, μg/m³
1	I-I	5.2–6.4	<2	<0.03	c
2	N-I-I	6.8–10.2	<9	<0.09	c
3	H-I-I-E-A-N	27.3–30.6	<8	<0.04	<30
4	E-I-I-A	55.8–58.5	119.7	0.74[d]	515

[a] A = 10 mL of 1:1:1 HNO_3–H_2SO_4–H_2O in an impinger; H = 50 mL of 10% H_2O_2 in a sparger; I = 10 mL of 1 M ICl in an impinger; N = 50 mL of 6.3 N NaOH in a sparger; E = empty sparger. [b] The times when these experiments were conducted are shown on Figure 4. [c] Accurate gas volumes were not available for experiments 1 and 2. [d] The total Hg (119.7 μg) found in these impingers was distributed as follows: empty impinger = none detected; ICl impingers = 16.6 μg; acid impinger = 9.5 μg; MIBK wash of ICl impingers = 88.8 μg; MIBK wash of connecting lines = 4.1 μg; MIBK wash of acid impinger = 0.7 μg.

both the ZAA (<0.2 $\mu g/m^3$) and the impingers (<10 $\mu g/m^3$) during the first two-thirds of the run. Mercury release coincided with the end of oil production and a decrease in H_2S (Figure 3) and occurred in five discrete pulses.

Pertinent information on the five Hg pulses is summarized in Table IV. Over 80% of the Hg was released to the gases within 4 h of its initial detection. The temperature of the bottom retort zone (zone 24) when Hg was first detected was 304 °C, in good agreement with the temperature (285–316 °C) at which it was removed from the gas stream in interrupted runs (Figure 5).

Mercury was detected in a single impinger experiment (experiment 4). A total of 119.7 μg of Hg was captured in the four impingers (Table V). Of this total, 105.4 μg or 88.1% was found in the ICl impingers. The majority of this Hg (88.8 μg) was present in rubbery precipitates that formed primarily in the ICl solution. An additional 4.1 μg was found in precipitates within connecting lines. Only 16.6 μg or 17% of the Hg captured in the ICl impingers was in solution.

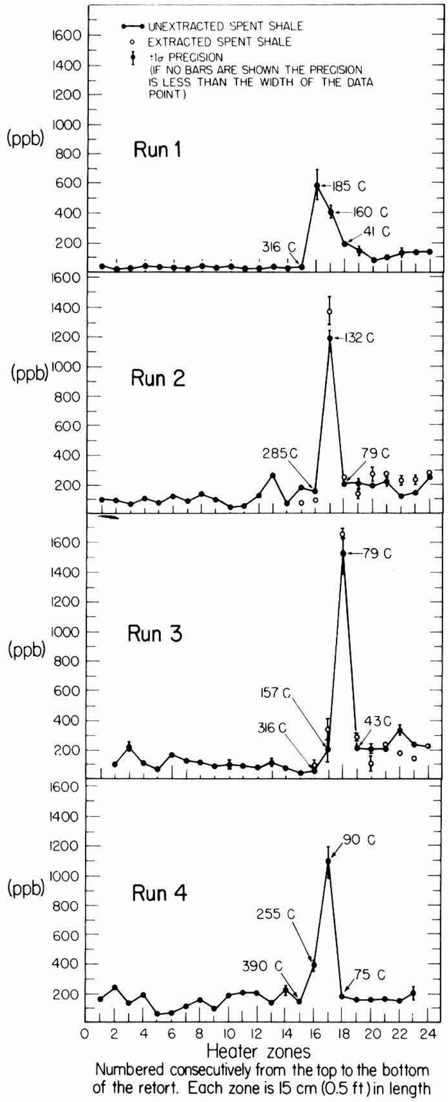

Figure 5. Variation in Hg along the shale bed in four incomplete runs. Retorting was terminated in zones 13 or 14.

The precipitates also were present in ICl impingers in which no Hg was detected and were probably a mixture of S^0 and HgS, the latter occurring only in experiment 4. This is supported by visual observation of yellow beads on impinger walls and the fact that the precipitates were insoluble in distilled water and HCl, slightly soluble in trichloroethane, and dissolved readily in MIBK. The S^0 would form in all impingers according to the following reaction:

$$ICl + H_2S \rightleftharpoons HCl + HI + S^0$$

The HgS may have formed by direct reaction of Hg(g) with S^0 or by reaction of H_2S with $HgCl_2$ or HgI_2 in the impinger solution. Mercury is known to react with ICl, giving $HgCl_2$ and HgI_2 on warming (*28*). One method of preparing HgS is to pass H_2S through a solution of $HgCl_2$ and ICl (*29*, *30*).

The impinger data (Table V) are in good agreement with the ZAA measurements (Figure 4). No Hg was detected by either method during the first two-thirds of the run. The Hg levels measured during experiment 4 by impingers and by ZAA differ by 4% and are 0.74 and 0.71 μg/min, respectively.

Hourly Oil and Water Samples. The Hg in all of the hourly oil samples was below the detection limit (<10–<100 ppb). Since the average Hg concentration of oil in the receiver at the end of the run was 54 ± 11 ppb, either the 4-h sampling regime was not adequate to define the emission profile, Hg originated in the condensates which were mixed with the oil (see end of Sampling section), or Hg was transferred from the gases to the oil in the receiver. The latter is likely in any event because the Hg-containing offgases were in direct contact with the oil at the completion of oil production.

Mercury concentrations in hourly water samples are presented in Figure 4. These data indicate that the Hg emission profile for retort water is similar to that for the gases. Variability in Hg levels is much greater than analytical precision (±1σ), which averaged ±10% for these samples. No Hg (<20 ppb) was detected for 17 h after the first appearance of oil (t = 16.5 h). Thereafter, the Hg was released in pulses, a maximum being reached about 36 h into the run. Similar behavior was noted in a second completed run not reported here (*12*). Oil production terminated about 52 h into the run, coinciding with the appearance of Hg in the gases and the disappearance of Hg in the water.

Interrupted Run. Mercury measurements of shale samples from four interrupted runs are summarized in Figure 5. A Hg pulse occurs between zones 15 and 19, below the point at which retorting was terminated. The shale temperature at the appearance of this peak was 293 ± 29 °C, less than the temperature at which pyrolysis occurs (500 °C). This agrees with the shale temperature (304 °C) at which Hg was first observed in the gases during the completed run (Table IV). The majority of the Hg accumulates where shale temperatures are 79–185 °C.

The mechanism responsible for the accumlation of Hg ahead of the reaction zone is uncertain. It may be physical adsorption, chemical adsorption/complexation, or condensation. Spent shales have previously been reported to sorb SO_2 and H_2S from gases (*31–33*), and soils from oil shale regions adsorb Hg^0 (*34*).

Extracted and unextracted shales, surface oils, and bitumen were analyzed in an attempt to elucidate removal/volatilization mechanisms. A typical distribution of these constituents is shown in Figure 6. These data demonstrate that the Hg peak coincides with the point at which kerogen conversion has ceased (as clearly evidenced by the organic C, H, and bitumen distribution in Figure 6) in an area that is wet with oil.

No Hg was detected (<10–<100 ppb) in the surface oils or bitumens, indicating that they were not sinks for Hg. No statistically significant difference was found in Hg concentrations among extracted and unextracted shales (Figure 5), confirming the extract analyses. Shale sections containing the Hg peak also were examined by scanning electron microscopy. No Hg-containing particles or regions were identified, indicating that the Hg was very diffuse. Elemental Hg can be excluded because it is soluble in cyclohexane (*35*).

The gas profiles (Figure 3) suggest that H_2S plays a role in the emission of Hg. The concentration of H_2S decreased when Hg was first emitted; the average H_2S concentration prior to Hg detection was 1.34 ± 0.59 mol %, and following detection, it was 0.51 ± 0.25 mol %. Thermodynamic calculations (*12*) indicate that the volatilized Hg, which includes Hg^0 as a major component (*10, 16*), may be removed from the gas stream by the following reaction:

$$Hg(g) + H_2S \rightleftharpoons HgS + H_2$$

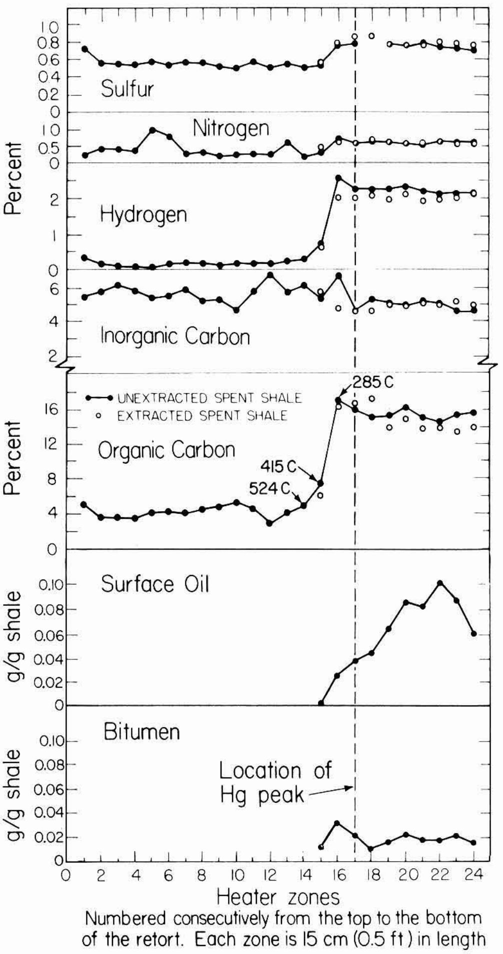

Figure 6. Variation in S, N, H, inorganic C, organic C, surface oil, and bitumen along the shale bed in incomplete run 2. The average analytical precision (±1σ) was the following: N, 5.0%; S, 1.5%; total C, 2.4%; H, 3.2%.

The HgS thus formed may be subsequently revolatilized by

$$HgS + H_2 \rightleftharpoons Hg(g) + H_2S$$

$$HgS + CO \rightleftharpoons Hg(g) + COS$$

An equally tenable explaination of these data is that Hg is removed from the gas stream by interaction with kerogen, perhaps through S or other heteroatom functional groups such as $-SH$, $-NH_2$, or $-COO^-$. This Hg may be subsequently revolatilized and transported in an organic form, as suggested by the data of Hogdson et al. (*15, 16*). Alternatively, both mechanisms may occur simultaneously.

Conclusions

This work is the first known application of ZAA to real-time monitoring of Hg in complex gases. This study demonstrated that ZAA is well suited for continuously measuring Hg in shale gases with high concentrations of organic molecules and H_2S. It was subsequently demonstrated for continuous on-line analyses of Hg in other oil shale gases (*15, 16*). The technique allowed precise (±10%)

measurement of Hg with up to 95% extinction of the 2537 Å analytical line by broad-band UV absorption and agreed to within 4% with independent measurements by ICl impingers.

The ZAA has several important advantages over ICl impingers, the standard method (*26*). It is capable of nearly continuous, real-time monitoring and has a large dynamic range, low detection limit (<0.2 $\mu g/m^3$), and good precision and accuracy. The ICl impinger method is not recommended for routine monitoring of shale gases because the ICl solution is rapidly exhausted, Hg-containing deposits form in the impingers and sampling lines, and the method is laborious, particularly for long-term monitoring required of in situ retorts.

This study demonstrates that a good mass balance can be obtained around an in situ retort by continuously measuring Hg in offgases. The poor mass balances obtained in previous studies (*10–12*) and the low concentrations of Hg reported in shale gases (*10, 17*) are partially explained by the nonuniform emission of Hg from in situ retorts. To adequately characterize gaseous Hg emissions from in situ retorts, either Hg must be continuously measured or a large number of discrete measurements must be made throughout a run, which may last many months.

Mercury is nonuniformly emitted from in situ retorts in pulses toward the end of a run. This type of emission profile was subsequently confirmed in small-scale experiments in the author's laboratory (*15*). Similar emission profiles have been observed recently at two large field in situ retorts (*14*), and highly variable offgas Hg concentrations have been reported at another field in situ experiment (*16*).

This type of distribution may be qualitatively explained by considering the operation of an in situ retort. Such a retort consists of a packed bed of shale through which a reaction zone is propagated. Pyrolysis products are carried out of the reaction zone by the sweep gas and travel ahead of it. Mercury present in the raw shale is released at 160–320 °C (*15*), well in advance of pyrolysis products. This Hg travels down the bed and is removed from the gases in areas where no pyrolysis has occurred and where the bed temperatures are less than 300 °C. The deposited Hg may be reduced by CO, H_2, or organics in the gases and is revolatilized when bed temperatures exceed 300 °C. This process of successive volatilization and condensation continues until the majority of the Hg accumulates near the bottom of the retort. When the reaction zone reaches this area, the Hg is volatilized and swept out of the retort in a series of discrete pulses which may correspond to different chemical forms of Hg.

In a commercial retort, which may be 100–200 m high, raw shale Hg concentrations may vary by a factor of 10 over the length of the retort (*11*). This, together with nonuniform retorting conditions, may superimpose significant variability on the pulsing behavior noted in this study.

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Groundwater Contamination by Volatile Halogenated Alkanes: Abiotic Formation of Volatile Sulfur Compounds under Anaerobic Conditions

René P. Schwarzenbach,* Walter Giger, Christian Schaffner, and Oskar Wanner

Swiss Federal Institute for Water Resources and Water Pollution Control (EAWAG), CH-8600 Dübendorf, Switzerland

■ The investigation of a groundwater contamination caused by a leaking wastewater tank of a chemical plant revealed that in groundwaters, under highly reducing conditions in the presence of hydrogen sulfide, certain volatile bromo- and chloroalkanes may undergo second-order nucleophilic substitution reactions yielding very persistent and hazardous volatile sulfur-containing compounds including dialkyl sulfides. Rate constants determined in the laboratory indicate that these nucleophilic substitution reactions may compete with hydrolysis, even at the low hydrogen sulfide concentrations typically encountered in the aquatic environment.

Volatile halogenated hydrocarbons (i.e., halogenated alkanes, alkenes, and benzenes are ubiquitous groundwater pollutants (*1–5*). The major causes of groundwater contamination by such chemicals include leachates from chemical waste dumps (*6*), spills (*7*), infiltration of polluted surface waters (*8,9*), and leaching from the ground surface (e.g., pesticides (*4*)). Recent studies have shown that volatile halogenated hydrocarbons are rapidly transported in the ground and that many of these compounds are quite resistant to chemical and/or biological transformation under conditions typical for the subsurface (*8–12*). However, for some volatile halogenated hydrocarbons, chemical reactions (e.g., hydrolysis (*13*)) and/or biological transformation (*9, 11, 12*) may be important. In such cases, the crucial question is whether possibly harmful chemicals are formed which may accumulate in the subsurface.

In this paper, we present evidence that in groundwater, in the presence of hydrogen sulfide, certain volatile halogenated alkanes can undergo nucleophilic substitution reactions, leading to the formation of persistent and hazardous sulfur-containing compounds. The data originate from the investigation of a groundwater contamination caused by a leaking wastewater tank of a chemical plant (see also preliminary report in ref 14). We report here the results of a field investigation and of laboratory experiments conducted to support the hypotheses postulated for the reaction mechanisms responsible for the formation of the sulfur-containing compounds detected in the ground.

Case History

After the operation of a chemical plant (which manufactured predomiantly intermediates for chemical synthesis) had ceased, it was discovered that a large portion of the underlying aquifer was heavily polluted. A substantial leak was found in one of the factory's wastewater tanks, indicating that infiltrating wastewater had been the most probable cause of this groundwater pollution. Among the chemicals that were manufactured in this plant in substantial amounts, and that were likely to have been present in the wastewater, were various volatile halogenated hydrocarbons including a series of halogenated alkanes (see Table I). Our investigation of this case was carried out 7 years after the plant's operations had been terminated and after an extensive cleanup of the area including the removal of soil and aquifer material as well as continuous pumping of groundwater from two cleanup wells. At that time, the water from the cleanup wells still had a very bad smell and contained no oxygen. Hydrogen sulfide at concentrations of up to 2×10^{-5} M was detected in this water. The pH of the water was typically between 7.6 and 8. The major objective of this investigation was to determine whether the groundwater in this area was still

Table I. Alkyl Halides Which Were Manufactured by the Chemical Plant and Which Were Likely to Have Been Present in the Wastewater

compound name	molecular formula	abbreviation	production[a]
methyl iodide	CH_3I	MeI	I
ethyl bromide	CH_3CH_2Br	EtBr	I
n-propyl bromide	$CH_3CH_2CH_2Br$	*n*-PrBr	I
isopropyl bromide	$(CH_3)_2CHBr$	*i*-PrBr	I
n-butyl bromide	$CH_3CH_2CH_2CH_2Br$	*n*-BuBr	I
isobutyl bromide	$(CH_3)_2CHCH_2Br$	*i*-BuBr	I
sec-butyl bromide	$CH_3CH_2CH(CH_3)Br$	*sec*-BuBr	I
n-amyl bromide	$CH_3CH_2CH_2CH_2CH_2Br$	*n*-AmBr	III
isoamyl bromide	$(CH_3)_2CHCH_2CH_2Br$	*i*-AmBr	II
sec-amyl bromide	$CH_3CH_2CH_2CH(CH_3)Br$	*sec*-AmBr	I
3-bromopropene	$CH_2{=}CHCH_2Br$		I
1-bromo-3-chloropropane	$BrCH_2CH_2CH_2Cl$		I
1-chloro-2-bromopropane	$CH_3CHBrCH_2Cl$		III
1,4-dibromobutane	$BrCH_2CH_2CH_2CH_2Br$		II

[a] I = major product (>5 tons $year^{-1}$); II = significant amounts produced (>0.5 ton $year^{-1}$); III = minor product (<0.5 ton $year^{-1}$).

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contaminated with compounds related to those manufactured by the plant.

Experimental Section

Field Measurements

Sampling. Samples were taken from the two cleanup wells by gently filling 1-L glass bottles completely. The bottles were closed without headspace and the samples were analyzed within 48 h of collection.

Determination of Volatile Organic Compounds in the Groundwater Samples. The volatile organic compounds were concentrated from the groundwater samples by the closed-loop gaseous stripping/adsorption/elution procedure developed by Grob (*15, 16*). This method permits the analysis of low boiling, nonpolar trace components in water at the nanogram per liter level (*17*). The groundwater samples (typically 1 L) were stripped for 90 min at 30 °C, and the organic compounds were trapped by adsorption on a filter of 1.5 mg of activated charcoal. The filter was then extracted with a total of 20 μL of dichloromethane.

High-resolution gas chromatographic analyses (HRGC) were performed on a Carlo Erba gas chromatograph (Model 2400 T) equipped with a 50 m × 0.31 mm i.d. glass capillary column coated with Pluronics 121, according to the procedure described by Grob (*18, 19*). The conditions were the following: gas (H_2) 0.8 atm, oven temperature 5 min at ambient, then 3 °C/min to 180 °C.

HRGC/MS measurements were carried out on a Finnigan mass spectrometer (Model 1015 D) equipped with a data system (Model 6000) and coupled to a Carlo Erba gas chromatograph (Model 2150). The glass capillary column (Pluronics 121; see above) was directly connected with the mass spectrometer by means of a glass capillary. Helium was used as carrier gas. The mass spectra were recorded under electron impact ionization at 70 eV.

Laboratory Study

Materials. The organic chemicals, i.e., 1-bromohexane, 3-bromohexane, hexane-1-thiol, and hexane-3-thiol, were all purchased from Fluka, Buchs, Switzerland, and used as received. The pH buffer solutions (pH 8 (borate/HCl), 9, 10(boric acid/KCl/NaOH)) were obtained from Merck, Darmstadt, West Germany. To avoid oxidation of the mercaptans, a solution of titanium(III) citrate, prepared as described by Zehnder and Wuhrmann (*20*), was used as redox buffer. The water used for the experiments was doubly distilled in quartz.

Kinetic Experiments. Kinetic experiments were performed to determine if mercaptans and dialkyl sulfides could be produced from alkyl halides under anaerobic environmental conditions and, if so, to roughly calibrate how fast such processes might occur. It should be emphasized that it was not the aim of these experiments to derive precise kinetic data for these reactions. All experiments were carried out in 100-mL volumetric glass flasks. The flasks were filled with approximately 95 mL of pH buffer solution which had been purged with nitrogen for 1 h (removal of oxygen). One milliliter of the titanium(III) citrate buffer and, in some of the experiments, 1 mL of a 10^{-2} M hydrogen sulfide solution were added (see Table II). The resulting redox buffer concentration was 10^{-3} M. The organic compounds were dissolved in methanol and added by using a microliter syringe. The flasks were then completely filled with buffer solution and closed with a glass stopper without headspace. During the experiments the flasks were gently shaken at 25 °C.

After a given time period, the flasks were opened and 2 μL of a methanolic solution of two internal standards (1-chloro-*n*-heptane, 1-chloro-*n*-undecane) was added; 5 mL of the water was then removed from the flask, and the remainder was acidified with concentrated hydrochloric acid and extracted twice with 1.5 mL of pentane. The pentane extracts were combined and subjected to gas chromatographic analysis using the same equipment as for the field measurements.

Table II. Laboratory Experiments with 1-Bromohexane: Concentrations of the Various Species as a Function of Time

			parameter[a,b]				
expt	time, h	pH[c]	H_2S_{tot},[d] μmol/L	RBr, μmol/L	ROH, μmol/L	RSH_{tot}, μmol/L	RSR, μmol/L
1	0	8.0	100	6.5	ND	ND	ND
	360			3.2	1.2	0.5	ND
2	0	9.0	100	6.5	ND	ND	ND
	360			3.1	1.2	0.5	0.003
3	0	8.0	0	6.5	ND	4.8	ND
	192			4.4	0.8	4.3	0.008
4	0	8.0	0	7.4	ND	49.0	ND
	192			5.4	0.9	55.0	0.06
5	0	7.9	100	6.5	ND	ND	ND
	288			3.5	1.0	0.5	ND
	504			2.5	1.6	0.7	ND
6	0	9.7	110	6.5	ND	9.1	ND
	288			3.1	1.0	8.4	0.26
	504			1.9	1.5	8.0	0.33
7[e]	0	7.6	0	6.5	ND	ND	ND
	288			4.8	0.9	ND	ND
	504			3.7	1.6	ND	ND

[a] R = *n*-C_6H_{13}. [b] ND = not detectable. [c] pH varied by ±0.05 pH unit; for calculations pH was assumed constant for a given experiment. [d] For calculations $[H_2S]_{tot}$ was assumed constant for a given experiment. [e] No redox buffer added; pH buffer 50 times diluted.

The pH of the water was measured at the beginning and end of each experiment with a standard glass electrode. Hydrogen sulfide concentrations were determined colorimetrically according to the Swiss Standard Methods (*21*).

Determination of the Rate Constants. Because of competing processes occurring and because of the small number of experiments, the rate constants were not determined one by one but by a simultaneous evaluation of all experiments in order to make optimal use of the information contained in the experimental data. This evaluation was done by the help of a computer simulation of the kinetics of the chemical system (nucleophilic substitution on 1-bromohexane) as described below. The simulation was based on the following reactions assumed to be irreversible:

$$\mathrm{RBr} + \mathrm{H_2O} \xrightarrow{k_{\mathrm{H_2O}}} \mathrm{ROH} + \mathrm{Br^-} + \mathrm{H^+} \tag{1}$$

$$\mathrm{RBr} + \mathrm{OH^-} \xrightarrow{k_{\mathrm{OH^-}}} \mathrm{ROH} + \mathrm{Br^-} \tag{2}$$

$$\mathrm{RBr} + \mathrm{HS^-} \xrightarrow{k_{\mathrm{HS^-}}} \mathrm{RSH} + \mathrm{Br^-} \tag{3}$$

$$\mathrm{RBr} + \mathrm{RS^-} \xrightarrow{k_{\mathrm{RS^-}}} \mathrm{RSR} + \mathrm{Br^-} \tag{4}$$

The associated acid–base reactions were taken to be rapid equilibria:

$$\begin{aligned} \frac{[\mathrm{HS^-}][\mathrm{H^+}]}{[\mathrm{H_2S}]} &= K_{e1} & \frac{[\mathrm{RS^-}][\mathrm{H^+}]}{[\mathrm{RSH}]} &= K_{e3} \\ \frac{[\mathrm{S^{2-}}][\mathrm{H^+}]}{[\mathrm{HS^-}]} &= K_{e2} & [\mathrm{H^+}][\mathrm{OH^-}] &= 10^{-14} \end{aligned} \tag{5}$$

The values of the equilibrium constants $k_{e1} = 1.26 \times 10^{-7}$ mol/L and $K_{e2} = 2.0 \times 10^{-13}$ mol/L were taken from the

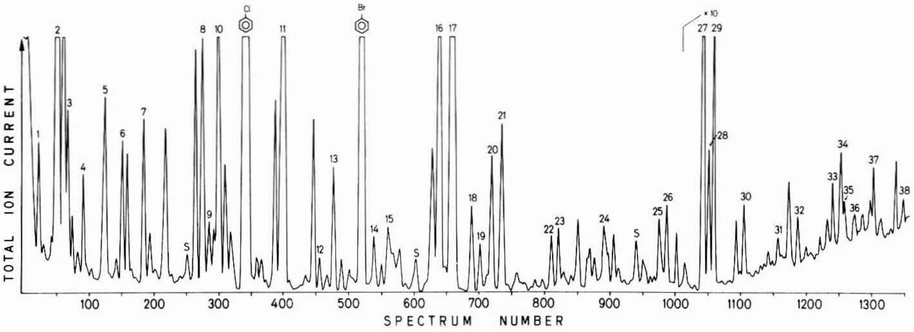


Figure 1. Total ion chromatogram of the volatile organic compounds present in a water sample from a cleanup well. For peak identification see Tables IV and V.

literature (22), $K_{e3} = 2.5 \times 10^{-11}$ mol/L was determine by Haag (23), and the rate constants $k_h = k_{H_2O} + k_{OH^-}[OH^-]$, k_{HS^-}, and k_{RS^-} were determined by a parameter optimization computer program (NLP; see ref 24) which searches for a local minimum of a nonlinear function of one or several parameters. This program was added to a Fortran program that, given a first estimate of the unknown values of the kinetic constants, performed the following regression steps:

(1) Values C_{comp} are computed for all reactants listed in Table II by integration of the kinetic eq 1–4 using the initial values taken from Table II and the equilibrium eq 5.

(2) For all experiments and all reactants with experimental concentrations C_{exp} above the detection limit, the deviation $d = (C_{comp} - C_{exp})/C_{exp}$ is calculated.

(3) The sum of all d^2, taken as a measure for the quality of the approximation of the experimental data by the model computations, is determined.

(4) A new set of values for the kinetics constants is chosen by the optimization program, and steps 1–3 are repeated until the sum of d^2 has reached a minimum.

As can be seen from Table II R_{tot} = RBr + ROH + RSH_{tot} + 2RSR shows a tendency to decrease during the experiments. This decrease was probably due to evaporation of RBr from the flasks. It cannot be taken into account by the simulation and leads to a systematic error. Therefore, another "kinetic reaction" was added in order to simulate the loss of R, which was assumed to be proportional to the concentration of RBr. With this improved description of the experiment the minimum for the sum of errors was lowered by a factor of 2. The standard deviations of the optimized parameter values were calculated by the use of sensitivity analysis and the laws of error propagation. They were below 10% with an estimated standard deviation of the experimental data of 15% for ROH and 10% for RBr, RSR, and RSH. However, since this calculation was exclusively based on the analytical errors in the experimental data, it is valid only insofar as the hypotheses formulated in eq 1–5 provide a correct and complete description of the chemical system.

Table III. Hydrolysis Rate Constants and Estimated Half-Lives of Some Volatile Bromoalkanes under Environmental Conditions (pH 7, 298 K)

compound name	formula	k_h, h^{-1} [a]	$t_{1/2}$ [b]
ethyl bromide	CH_3CH_2Br	9.4×10^{-4}	30 days[c]
n-propyl bromide	$CH_3CH_2CH_2Br$	1.1×10^{-3}	26 days[c]
isopropyl bromide	$(CH_3)_2CHBr$	1.4×10^{-2}	2 days[c]
isobutyl bromide	$(CH_3)_2CHCH_2Br$	6.6×10^{-4}	44 days[c]
n-hexyl bromide	$CH_3(CH_2)_4CH_2Br$	7×10^{-4}	40 days[d]
3-bromohexane	$CH_3CH_2CH(Br)$- $CH_2CH_2CH_3$	6×10^{-2}	12 hours[d]

[a] $k_h = k_N$ since $k_B[OH^-]$ and $k_A[H_3O^+]$ are not important below pH 10 (see ref 13). [b] $t_{1/2} = \ln(2)/k_h$. [c] Data derived from ref 13. [d] This work.

Table IV. Dialkyl Sulfides Detected in Water Samples from the Two Cleanup Wells

peak no.[a]	elemental composition	structure[b]	identification[c]
1	$C_4H_{10}S$	MeS-*i*-Pr	MS(R)
2	$C_4H_{10}S$	EtSEt	MS(R), GC
3	$C_4H_{10}S$	MeS-*n*-Pr	MS(R), GC
4	$C_5H_{12}S$	EtS-*i*-Pr	MS(R), GC
5	$C_5H_{12}S$	MeS-*i*-Bu	MS(R), GC
6	$C_5H_{12}S$	EtSPr	MS(R), GC
7	$C_5H_{12}S$	MeS-*n*-Bu	MS(R), GC
8	$C_6H_{14}S$	MeS-?-Am	MS
9	$C_6H_{14}S$	*n*-PrS-*n*-Pr	MS(R), GC
10	$C_6H_{14}S$	EtS-*n*-Bu	MS(R)
11	$C_7H_{16}S$	EtS-?-Am	MS
12	$C_7H_{16}S$	EtS-?-Am	MS
13	$C_7H_{16}S$	EtS-*n*-Am	MS(R)
14	$C_8H_{18}S$	?-BuS-?-Bu	MS
15	$C_8H_{18}S$	?-PrS-?-Am	MS
16	$C_8H_{18}S$	*n*-BuS-*n*-Bu	MS(R), GC
21	$C_9H_{20}S$	?-BuS-?-Am	MS
22	$C_9H_{20}S$	?-BuS-?-Am	MS
23	$C_{10}H_{22}S$	*i*-AmS-*i*-Am	MS(R)
24	$C_{10}H_{22}S$	?-AmS-?-Am	MS

[a] See Figure 1. [b] Tentative structure; for abbreviations see Table I. [c] MS = identification based on mass spectra; (R) = reference spectrum available (25). GC = identification by coinjection with authentic standards.

Results and Discussion

Volatile Organic Compounds Present in the Water from the Two Cleanup Wells. Figure 1 shows the total ion chromatogram of the HRGC/MS analysis of the volatile compounds detected in a representative water sample from one of the two cleanup wells. Among the major components were bromobenzene which has been manufactured by the plant and chlorobenzene which had been used as a solvent (14). Other than the halogenated benzenes, none of the chemicals listed in Table I were detected at significant concentrations, which is not surprising, since, in particular, the alkyl bromides undergo hydrolysis at significant rates (see examples given in Table III). It should be noted that with the analytical technique used in the field investigation, the hydrolysis products, i.e., the corresponding alcohols, could not be detected. However, numerous sulfur-containing compounds were identified which could clearly be related to the chemicals listed

Table V. Volatile Sulfur-Containing Compounds Detected in the Water Samples from the Two Cleanup Wells

peak no.[a]	elemental composition	structure[b]	identification[c]
17	$C_3H_6S_2$	$\overline{CH_2CH_2CH_2SS}$	MS
18	$C_5H_{12}S_2$	$EtSCH_2SEt$	MS(R)
19	$C_5H_{11}S\ Cl$	$EtSCH_2CH_2CH_2Cl$	MS
20	$C_4H_8S_2$	$\overline{CH_2CH_2CH_2CH_2SS}$	MS
25	$C_6H_{14}S_2$	$EtSCH_2CH_2CH_2SMe$	MS
26	$C_7H_{15}S\ Cl$	?-$BuSCH_2CH_2CH_2Cl$	MS
27	$C_3H_6S_3$	$\overline{CH_2CH_2CH_2SSS}$?	MS
28	$C_8H_{17}S\ Cl$	?-$AmSCH_2CH_2CH_2Cl$	MS
29	$C_7H_{16}S_2$	$EtSCH_2CH_2CH_2SEt$	MS(R)
30	$C_8H_{17}S\ Cl$	?-$AmSCH_2CH_2CH_2Cl$	MS
31	$C_8H_{18}S_2$	?-$PrSCH_2CH_2CH_2SEt$	MS
32	$C_8H_{18}S_2$	?-$BuSCH_2CH_2CH_2SMe$	MS
33	$C_9H_{20}S_2$	*i*-$AmSCH_2CH_2CH_2SMe$	MS
34	$C_9H_{20}S_2$	?-$BuSCH_2CH_2CH_2SEt$	MS
35	$C_6H_{12}S\ Cl_2$	$ClCH_2CH_2CH_2SCH_2CH_2CH_2Cl$	MS
36	$C_9H_{20}S_2$	*sec*-$AmSCH_2CH_2CH_2SEt$	MS
37	$C_{10}H_{22}S_2$	*i*-$AmSCH_2CH_2CH_2SEt$	MS
38	$C_{10}H_{22}S_2$	*sec*-$AmSCH_2CH_2CH_2SEt$	MS

[a] See Figure 1. [b] Tentative structure; for abbreviations see Table I. [c] MS = identification based on mass spectra; (R) = reference spectrum available (*25*).

in Table I. The tentative structures of these compounds are summarized in Tables IV and V.

The compounds in Table IV are all dialkyl sulfides which were most likely formed by nucleophilic substitution reactions of the alkyl bromides (Table I) with hydrogen sulfide and alkyl mercaptans (see eq 3 and 4). For the identification of many of these compounds reference mass spectra and authentic standards were available. In contrast, almost no reference data were found in the literature for the compounds summarized in Table V. The tentative structures are therefore based solely on our interpretation of the mass spectra. Some of these mass spectra as well as their interpretations are given in Figures 2–4. The structures proposed from these spectra indicate that all of these compounds were most probably formed from nucleophilic substitution reactions involving 1-bromo-3-chloropropane, a major product manufactured by the chemical plant. Note that some of the compounds contain sulfur as well as chlorine atoms (e.g., compound 35, Figure 2). This is not surprising since, for the alkyl chlorides, reaction rates more than an order of magnitude smaller than for the corresponding bromides can be assumed (*13, 26*).

With respect to the mass spectra shown in Figures 3 and 4, some of the key fragments may be interpreted as in Scheme I (see also the fragmentations indicated in the two figures). Unfortunately, no transitions of metastable ions could be observed to support the proposed fragmentation pattern due to the fact that the spectra were obtained from a quadrupole mass spectrometer. Compounds 33 and 37 are assumed to contain an isoamyl group because of the relatively high abundance of m/z 43. Furthermore, a secondary amyl group was assigned to compounds 36 and 38 because of the relative abundance of the fragments m/z 45 compared to m/z 47 and m/z 59 compared to m/z 61, suggesting that one of the sulfur atoms is bound to a secondary carbon atom.

Reaction Mechanisms and Reaction Rates. The rate constants derived from the laboratory studies (see Experimental Section) for the reactions of a representative primary alkyl bromide (1-bromohexane) are given in Figure 5. The reaction of a secondary alkyl bromide (3-bromohexane) with hydrogen sulfide yielded no sulfur-containing compounds. The observed hydrolysis rate constant is given in Table III.

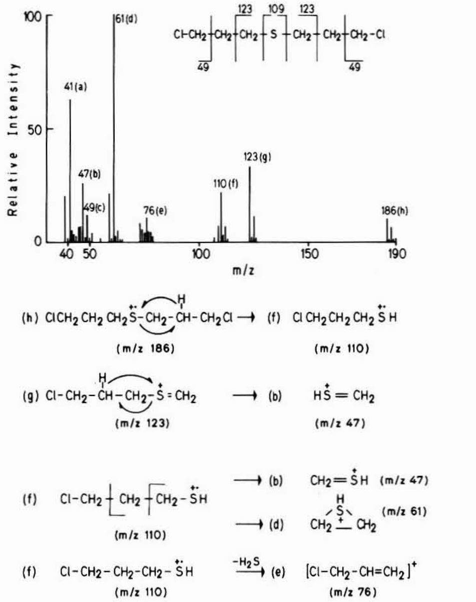


Figure 2. Mass spectrum, proposed fragmentation pattern, and tentative structure of compound 35.

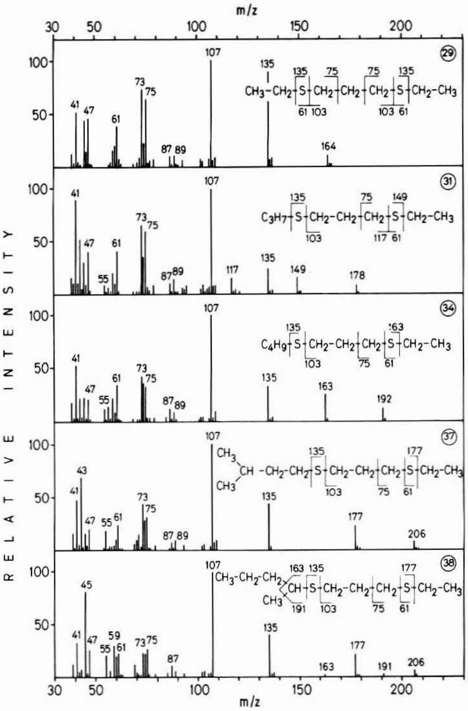


Figure 3. Mass spectra and tentative structures of products from reactions involving 1-bromo-3-chloropropane: Compounds with m/z 107 as base peak (see Scheme I).

The results of the laboratory experiments are consistent with the general theory of nucleophilic substitution reactions of halogenated alkanes (see e.g., ref 27). Accordingly, primary alkyl bromides should react in water with HS^- or

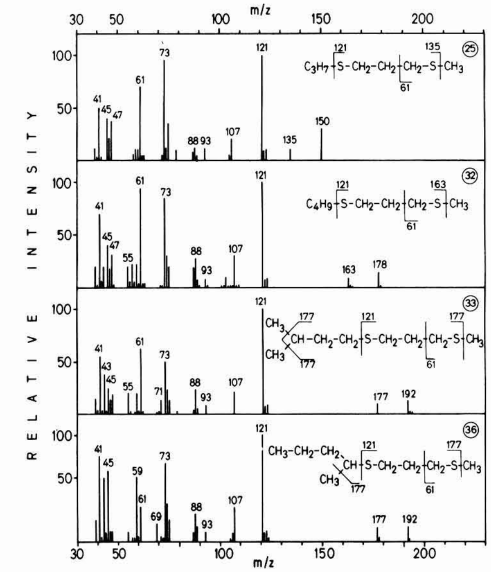
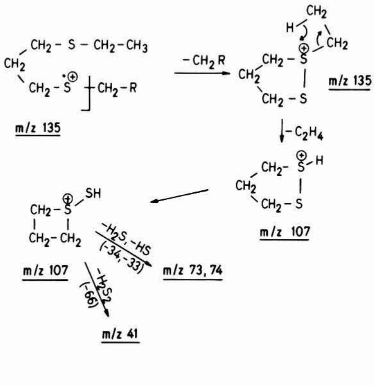


Figure 4. Mass spectra and tentative structures of products from reactions involving 1-bromo-3-chloropropane: Compounds with *m/z* 121 as base peak (see Scheme I).

Scheme I



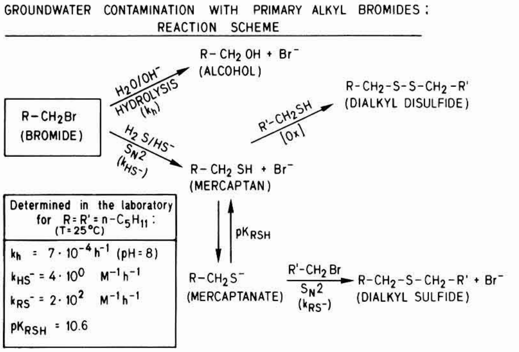


Figure 5. Formation of dialkyl sulfides from alkyl bromides under anaerobic conditions. Proposed reaction scheme and rate constants for the reactions of 1-bromohexane.

RS$^-$ by a true S_N2 (substitution, nucleophilic, biomolecular) mechanism, whereas tertiary halides react by a S_N1 (substitution, nucleophilic, unimolecular) mechanism. The secondary halides probably undergo "borderline reactions" (reactions that exhibit properties intermediate between S_N1 and S_N2 mechanisms (*28*)). At the low hydrogen sulfide concentrations typical for the groundwater environment ($\leq 10^{-4}$ M), significant amounts of alkyl mercaptans and consequently of dialkyl sulfides and related compounds should only be formed if the reactions proceed predominantly by an S_N2 mechanism. Thus, mainly primary and, as shown in Tables III and IV, also some secondary alkyl halides may lead to such products in groundwater. Note that no dialkyl sulfides containing two secondary alkyl groups were found, which may be explained by the hypothesis that secondary alkyl bromides such as the 3-bromohexane used in our laboratory study undergo S_N2 reactions with RS$^-$ but not with HS$^-$ which is a less "soft" nucleophile than RS$^-$ (*29*).

Since it is not possible to reconstruct the actual field situation of the case study reported in this paper, a simple calculation using the rate constants derived from the laboratory experiments may serve to demonstrate that nucleophilic substitution reactions of primary alkyl bromides with hdyrogen sulfide and with alkyl mercaptans may yield dialkyl sulfides in appreciable concentrations under typical sulfate reducing groundwater conditions. Starting with an initial concentration of RBr in the infiltrating wastewater of 1×10^{-5} M and assuming a constant concentration of total H_2S of 5×10^{-5} M (maintained by sulfate-reducing bacteria) and a pH of 8, the calculation predicts the following product distribution after about 1 year (when practically all RBr has reacted): ROH ~75%, RSH ~25%, and RSR ~0.2%, which corresponds to a dialkyl sulfide concentration of about 10^{-8} M or 2 μg/L. Thus, although only a small fraction of the alkyl bromide is ultimately converted to dialkyl sulfide, such products may accumulate to concentrations that may cause concern, since these compounds seem to be very persistent in the subsurface. It should be noted that the above calculations are based on rate constants derived at 25 °C. Since HS$^-$ and RS$^-$ are much "softer" nucleophiles than OH$^-$ and H_2O (*29*), the activation energies of the reactions of alkyl halides with HS$^-$ and RS$^-$ can be assumed to be significantly smaller than those of hydrolysis. The relative importance of these reactions increases therefore with decreasing temperature, which is important when considering that the temperature of the groundwater is usually much lower than 25 °C (i.e., around 10 °C).

Finally, with respect to the major products, i.e., the alcohols and mercaptans, it might be worth mentioning that these compounds are transported much faster in the groundwater and are probably much less resistant to microbial and possibly chemical (e.g., oxidation of mercaptans) transformation reactions compared to the sulfur compounds detected at our field site. In addition, the applied analytical technique (closed-loop gaseous anaysis) was not optimized for these chemicals.

Conclusions

The results of this investigation clearly show that, in groundwater under reducing conditions in the presence of hydrogen sulfide, brominated and chlorinated alkanes may undergo nucleophilic substitution reactions leading to a variety of aliphatic sulfur-containing products which seem to be very persistent in the subsurface. Those compounds, in particlar those containing sulfur as well as chlorine atoms, are of great concern from a hygienic and possibly also from a toxicological point of view. Thus, given the great number of halogenated hydrocarbons continuously released to the environment, the types of reactions reported in this paper should be considered in any risk and hazard assessment. The majority of environmentally important halogenated hydrocarbons have, however, aromatic, vinylic, or geminal-polyhalogenated structures and are therefore less susceptible to nucleophilic substitution reactions. Nevertheless, the formation of sulfur-containing compounds in anaerobic groundwater environments, as reported in this paper, can certainly occur in other similar situations. Clearly, more work is needed to evaluate the kinetics of such nucleophilic substitution reactions, in particular, reactions involving polyhalogenated alkanes.

Acknowledgments

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Registry No. RBr, 111-25-1; ROH, 111-27-3; RSH, 111-31-9; RSR, 6294-31-1; H_2S, 7783-06-4; CH_3CH_2Br, 74-96-4; $CH_3CH_2CH_2Br$, 106-94-5; $(CH_3)_2CHBr$, 75-26-3; $(CH_3)_2CHCH_2Br$, 78-77-3; $CH_3CH_2CH(Br)CH_2CH_2CH_3$, 3377-87-5.

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Concentrations of Six Metals in the Air of Eight Cities

Bernard E. Saltzman,* Jacob Cholak, Lawrence J. Schafer,† David W. Yeager, Bernard G. Meiners, and Jozef Svetlik

Department of Environmental Health, University of Cincinnati Medical Center, Cincinnati, Ohio 45267

■ During 1968–1971, 8763 samples were collected at 59 sites in U.S. cities for a study of particulate lead concentrations in air. Each site was sampled continuously for a full year. These samples have been analyzed for total suspended particulate matter and for cadmium, chromium, lead, manganese, nickel, and zinc. Results of over 42 000 analyses are summarized in convenient graphical form, showing geometric means, geometric standard deviations, maxima, and minima. Supplementary tables present these data and cumulative frequency distributions. This historical data base should be a useful reference to determine effects of changes in fuel consumption patterns and trends. It presents a uniquely extensive cross-sectional picture of trace metal concentrations determined by a single highly experienced laboratory. Results were compared with available recent data for 17 identical sites. Recent lead concentrations averaged 35% of the older values, and some reductions occurred in concentrations of other metals.

During the past decade a substantial change has occurred in the world energy picture. Changes in fuel composition and consumption have altered air pollution patterns. The hazards from lead emissions from automobiles have remained a long standing controversial subject. Two extensive lead studies were reported. From June 1961 through May 1962, 3400 samples of particulate lead from the atmosphere were obtained at 20 sites in three cities (*1*). From Dec 1968 through Feb 1971, 8763 samples of particulate matter were collected at 59 sites in eight cities in widely different sections of the country, including the cities in the previous study for purposes of comparison, and were analyzed for lead (*2*). Since these samples were suitable for other analyses, they also were analyzed for cadmium, chromium, manganese, nickel, zinc, and total particulate because the effects of these substances were believed to be of biological and economic importance.

The environmental significance of most trace metals in air is not yet fully understood, and data on their concentrations are essentially for archival purposes for future interpretation. There are no current air quality standards for metals except for lead. Comparisons are difficult because most data are for only a few sites in each city for relatively few samples per year, and frequently for only a few metals. Analyses have been conducted by laboratories of variable qualifications using a variety of methods, none of which have been collaboratively tested. Thus, one can expect substantial interlaboratory variations, and some data confirm this. This comprehensive study was conducted at numerous sites in each of eight cities, continuously for a full year at each location, and all samples were analyzed by a single highly experienced laboratory. Thus, these data present a uniquely extensive cross-sectional picture permitting relative comparisons of different sites. They also should be valuable as historical background levels for future studies of trends and changes.

Collection of Samples

The cities sampled were selected to reflect a wide range of geographic and climatological characteristics. Cincinnati, Philadelphia, and Los Angeles were included for comparisons with an earlier lead study (*1*). New York City, Chicago, and Houston represented large northern, midwestern, and southern cities. Washington, DC, represented a large city without industrialization. Los Alamos and Okeana, OH, represented background areas with low pollution. Table I provides a summary of the sampling sites and analytical data. Figure 1 presents map outlines of the seven major cities and shows the positions of all sites. More detailed information on the sites is presented in the tables of the supplementary material (see paragraph at end of paper regarding supplementary material.)

The sampling equipment consisted of a filter holder, a 106-mm mixed cellulose ester membrane filter of 3-μm pore diameter, efficiency >99% (Millipore, type WS), a vane pump and motor unit drawing a nominal free air flow of 0.17 m^3/min, a cooling fan, and suitable electrical and air connections. A plywood housing with a gable roof permitted the necessary ventilation and noise attenuation. Initial and final air flows through each filter were determined from calibrated orifice meter measurements. The units were operated continuously for 12 months at each site. Filters were changed at most locations on Monday, Wednesday, and Friday. However, at high traffic sites in Los Angeles, it was necessary in order to avoid filter obstruction to install tandem automatic switch-over units which collected 24-h samples. In low traffic and rural sites the filters were changed weekly.

Analytical Methods

Before use, the filters were conditioned in a controlled atmosphere and weighed in Cincinnati. Each was then shipped in a numbered plastic Petri dish to the sampling site. The monitors returned the filters in the same dishes with the necessary sampling information. The filters were again conditioned and weighed to determine the total particulate weights by difference.

Half of each filter was cut off and placed in a 100-mL beaker. The filters collected during 1968–1969 (in Cincinnati, Los Alamos, Los Angeles, Okeana, and Philadelphia) were combined so that one sample was analyzed for each week for each site. These samples were not analyzed for manganese and nickel. The filters collected during 1970–1971 were analyzed individually. Each composite or individual sample was wetted with 2–3 mL of concentrated nitric acid. It was then heated to dryness on a hot plate and ashed in a muffle furnace at 500 °C. The ash was dissolved in 10% (v/v) nitric acid and transferred into a 10-mL glass-stoppered cylinder. After the final volume was adjusted to 10 mL, the solution or an appropriate dilution was aspirated directly into the burner of a Perkin-Elmer Model 403 atomic absorption spectrophotometer with a three-slot Boling burner. The instrument settings and resonance lines used were those recommended in the manufacturer's analytical methods manual (*3*).

In analyses for Cd, Cr, Ni, and Mn, portions of the original solution were aspirated into the burner, whereas for Pb and Zn an aliquot of the original solution diluted 1:9 with 10% v/v nitric acid was employed. For a similar preparation with the volumes and dilutions employed, studies indicated that analysis of half of a filter representing an air volume of approximately 100 m^3 could detect

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† Deceased.

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Table I. Summary of Sampling Sites and Results

area	no. of sites	dates of sampling, from–thru	total no. of samples	geometric mean concentration, $\mu g/m^3$ PM	Cd	Cr	Pb	Mn	Ni	Zn
Chicago	9	3/70–2/71	1298	80	0.005	0.012	1.44	0.075	0.018	0.47
Cincinnati	4	12/68–11/69	384	62	0.005	0.011	1.45			0.61
Houston	7	3/70–2/71	1070	56	0.001	0.009	1.14	0.044	0.015	0.17
Los Alamos	2	12/68–11/69	91	10	0.001	0.005	0.17			0.02
Los Angeles	8	12/68–11/69	1841	70	0.002	0.012	3.40			0.26
New York	9	3/70–2/71	998	67	0.007	0.013	1.40	0.031	0.042	0.36
Okeana, OH	2	12/68–11/69	125	44	0.002	0.005	0.30			0.16
Philadelphia	10	12/68–11/69	1744	69	0.006	0.009	1.53			0.62
Washington, DC	8	10/70–9/71	1213	53	0.003	0.010	1.36	0.033	0.023	0.17
totals	59		8763							

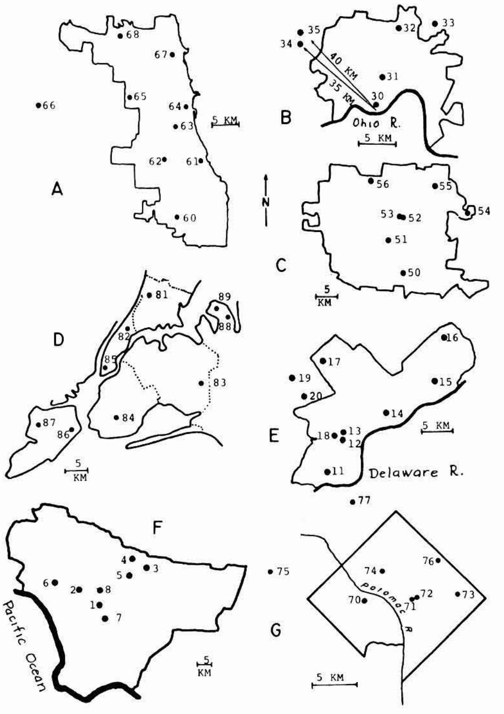

Figure 1. Maps of cities showing locations of sampling sites: A, Chicago; B, Cincinnati and Okeana; C, Houston; D, New York City; E, Philadelphia; F, Los Angeles; G, Washington, DC.

as little as 0.1 μg of Pb/m^3, 0.01 $\mu g/m^3$ each of Zn, Cr, Ni, and Mn, and 0.001 μg of Cd/m^3. The sensitivities of detection for samples of course improved in proportion to the ratio of the actual sample air volume to that assumed. However, nils or values below the detectable limits indicated above were recorded merely as less than the detectable limit for the specific metal. In the case of particulate matter, the limit of significance by weight was 10 $\mu g/m^3$. Studies with known quantities of the metals added to filters carried through the preparatory procedure yielded recoveries of approximately 95% for Pb, Zn, Cr, Ni, and Mn and approximately 85% for cadmium. However, the values reported here do not include any corrections for recoveries.

Results

The sampling periods, numbers of sites, numbers of samples collected, and geometric mean concentrations in each city for this study are given in Table I. Plots were made of the data for each sampling site of frequencies for each concentration interval (each covering $^1/_{50}$ of the range). In the statistical calculations each sample was weighted according to its sampling period. Although practical considerations in running a large scale sampling program required different periods for some samples, as explained below the statistical effects were expected to be minor. Even though these plots each represented over 150 samples, the curves were not smooth. The bumps in the frequency curves at the high concentration ends suggested that these frequencies might be substantially underestimated from a log-normal concentration model. Cumulative distributions also were plotted. From these curves the concentrations for each tenth percentile were interpolated. A summary of the mass of data obtained for this 1968–1971 study is presented graphically in Figure 2, in a form to permit ready comparisons. These represent for each site the minimum, maximum, geometric mean, and geometric standard deviation for the concentrations of each metal. For the calculations of geometric mean, values below the detection limits were assigned values of 50% of the limit, in order to calculate the necessary logarithms. Since usually only a small fraction of the samples were in this category, this approximation involved little error. More exact calculations are complex (*4*).

Discussion

The zinc concentrations showed the greatest range of geometric mean concentrations and geometric standard deviations, whereas the particulate concentrations showed one of the smallest ranges for both of these variables. As expected, commercial and industrial sites usually showed higher concentrations of particulate pollutants. Although the sampling time does not affect the observed arithmetic mean, it does slightly affect the geometric standard deviation. A study (*5*) of continuous monitoring data for sulfur dioxide during 1962–1964 showed empirically that the geometric standard deviation varied with the sampling time raised to an exponent which was −0.02 for Chicago, −0.04 for Los Angeles, −0.05 for Washington, DC, −0.07 for Philadelphia, and −0.10 for both Cincinnati and San Francisco. This study theoretically explained some of the complexities of the effects of sampling times on resulting data. Although the figures cited are only for sulfur dioxide, in the absence of better information, they may be applied for estimating effects for particulate matter. In the data reported here, samples for Cincinnati, Los Alamos, Los Angeles, Okeana, and Philadelphia were weekly composites, whereas those for the other cities, generally two 2-day samples and one 3-day sample each week, were analyzed individually. If a worst case estimate of an exponent of −0.1 is used, the differences in geometric standard deviations between 3-day and 2-day samples would be only 4% and between 7-day and 2-day samples 13%. For the latter case if the exponent were −0.02, the difference would be

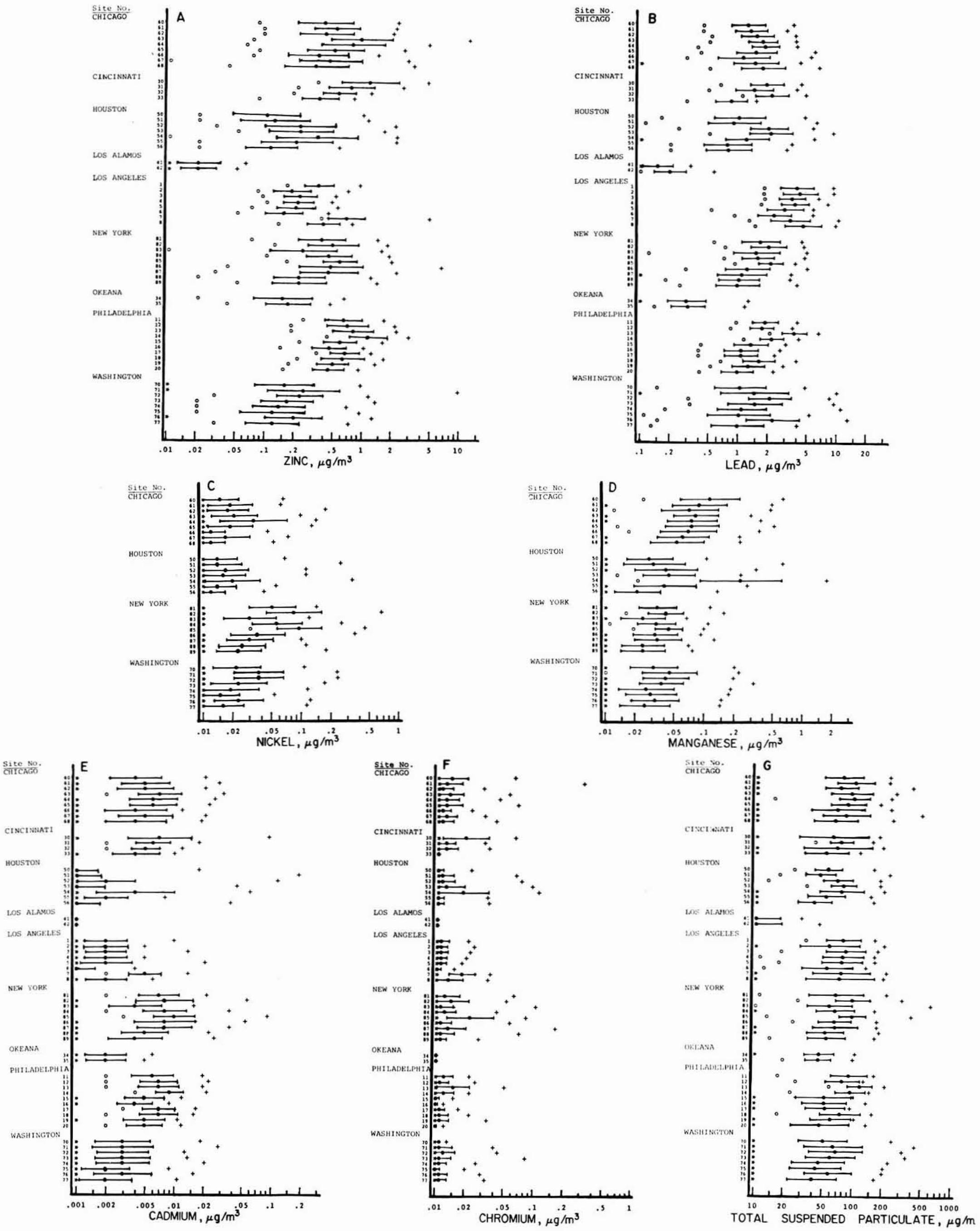

Figure 2. Summary of the 1968–1971 data for the 59 sites: A, Zinc; B, lead; C, nickel; D, manganese; E, cadmium; F, chromium; G, total suspended particulate. (O) Minimum; (*) less than nominal detection limit; (+) maximum; (⊢●⊣) geometric mean ± 1 geometric standard deviation.

only 3%. The geometric mean and geometric standard deviation may be applied for designing sampling programs and for estimating extreme values. Simplified nomographic methods have been presented (*6*) for these purposes.

The current EPA air quality standards are promulgated for only two particulate pollutants: particulate matter 75 (primary) and 60 μg/m³ (secondary) annual geometric mean; lead 1.5 μg/m³ (primary and secondary) 3-month arithmetic mean. Criteria documents (*7, 8*) discuss the sources and significance of these pollutants. About 60% of the sites exceeded the 60 μg/m³ secondary EPA standard for total particulate, but only 15 of the 59 sites exceeded the primary standard of 75 μg/m³. The annual arithmetic mean concentration of particulate lead exceeded 1.5 μg/m³ for 33 sites, including all those in Los Angeles,

Table II. Comparison of Analyses of Samples from the Same Sites[a]

		NADB[b]	geometric mean concentration[c]						
site no.[a]	NADB[b] periods	no. of samples	PM, $\mu g/m^3$	Cd, ng/m^3	Cr, ng/m^3	Pb, $\mu g/m^3$	Mn, ng/m^3	Ni, ng/m^3	Zn, $\mu g/m^3$
Chicago (3/70–2/71)[d]									
10H01/60	82/70	57/70	57/95/75			0.249/–/1.21			
7H01/62	79/70	108/140	71/93/71						
5H01/64	79/70	115/134	85/24/97						
6H01/65	75/70	15/130	96/103/84						
4H01/67	82/70	57/132	55/104/80			0.261/–/1.44			
3H01/68	79/70	112/138	60/79/63						
Cincinnati (12/68–11/69)[d]									
1A01/30	79/68	28/26	75/99/60	4/3/7	–/13/19	0.87/1.28/1.87	–/50/–	24.8/9/–	
14G01/32	82/69	59/18	71/98/66						
Houston (3/70–2/71)[d]									
7H01/51	79/–	55/–	54/–/144			0.349/–/0.88	5/–/31		
1A01/53	80/68	9/26	69/74/76	1/1/<1	12.8/8/12	0.57/1.49/2.07	27.1/20/44	4.8/8/16	0.10/–/0.22
Los Angeles (12/68–11/69)[d]									
1A01/1	80/60	16/26	99/129/77	1/2/2	6/12/11	0.57/2.64/3.82	22.8/–/<10	7.4/–/–	
New York (3/70–2/71)[d]									
6H01/81	79/71	26/153	52/91/66						
14A01/82	79/–	11/–	75/–/97	4/–/8		0.872/–/1.99		24.8/–/85	
Philadelphia (12/68–11/69)[d]									
3H01/12	82/68	80/365	58/109/78			0.22/–/1.71			
Washington, DC (10/70–9/71)[d]									
1P01/71	76/68	9/26	50/86/65	–/2/3	–/5/11	–/0.61/1.46	–/10/45	–/16/37	
3I02/72	78/71	42/18	98/102/69						
7I02/73	79/71	33/28	71/62/61			1.34/–/1.48			
mean ratio recent/old[a]			0.75/0.99	0.94/0.89	1.05/0.81	0.43/0.35	1.36/1.78	1.68/0.30	–/0.46
N[a]			15/17	3/4	2/2	3/9	1/3	2/2	–/1

[a] NADB/this study. [b] Recent/old. [c] Recent NADB/old NADB/this study, generally from 150 samples. [d] Sampling period for this study.

6 of the 9 in Chicago, 5 of the 9 in New York, and 5 of the 10 in Philadelphia. With the more recent reduction of the lead content of gasoline, the current lead levels are decreasing (*9–11*). Standards for industrial workers for metals also are available (*12*).

Before these values are compared with those of other studies, certain differences in evolving sampling and analytical methodologies must be considered. The only current regulatory requirement, that for lead instituted after the publication of the criteria document (*8*) in 1977, is for 3-month arithmetic mean values. Since future applications of trace metal data are unclear, the strategy has been to collect as much information as practicable. Advances in technology during the past decade have resulted in the current adoption of the inductively coupled argon plasma atomic emission spectrometer, which provides analyses of multiple elements simultaneously at a reasonable cost. This has partly displaced the atomic absorption spectrometer (which replaced the older spectrophotometric methods). The differences between the results of these methods have never been fully characterized. Examination of recent EPA National Aerometric Data Bank data for metals in samples collected in the same place and time, however, shows substantial differences between results by the atomic emission and atomic absorption methods. Also, the values in the NADB listed for the 1968–1971 period of this study were obtained by an earlier hi-vol emission spectra (low-temperature ash) method. The recent proposal of an inhalable particulate (<10 μm) standard will result in replacement of the high volume sampler with new devices with sharply different sampling efficiencies for different particle sizes. When sampling from air at varying velocities, the inertial, viscous, and gravitational forces affect large and small particles differently. High volume sampler inlets do not sample isokinetically and, thus, collect large and small particles with different efficiencies. The nonrepresentativeness of the samples varies with wind velocities and directions and thus cannot be accurately characterized. All of these changes are being adopted to improve the quality and scope of the information collected. Statistical difficulties obviously result when comparisons over a time period are made, since exact effects of changing methodologies are not known, but the advantages overrule the objections. Thus, the available historical data must be compared with newer data with appropriate allowances as far as possible.

This comprehensive study was initiated during the early development of sampling networks, before EPA was formally established in 1970. The high volume sampler utilized in other studies employed an 8 in. × 10 in. flash fired glass-fiber filter as a compromise adapted for both organic an inorganic analyses. For this study a mixed cellulose ester membrane filter with a 3-μm pore diameter was selected in preference because it was better suited for trace metal analysis. Sample extraction before ashing and possible extraction of interfering silica was eliminated, and blanks were very low. It was also the method used in the earlier 1961–1962 lead study which was being followed up. The efficiency of the membrane filters was at least as good as that of glass-fiber filters. The ashing procedure was less likely to suffer from loss of metals in possible insoluble material than the EPA extraction method with dilute nitric acid.

In order to compare the particulate size selective characteristics of the sampler used in this study with those of the widely used high volume sampler, the minimal areas between the gabled roofs of the sampling boxes and the filter housings were determined as 670 and 645 cm^2, respectively. The related air flow rates of 0.17 and 1.6 m^3/min thus produced upward air velocities of 4.3 and 40 cm/s. The unit density aerodynamic particle diameters which settle at those rates in still air were calculated according to Stoke's law. These sizes, 37.5 μm for this study and 116 μm for the standard high volume sampler, approximate their sampling cutoff diameters. Unless one samples near a dust source, particles larger than 37.5 μm would be uncommon because of their rapid fall out. In any event, the 37.5-μm cutoff size is closer to the now recognized 10-μm inhalable particle size, and the data should be more relevant to the new standard.

In comparing maximum values of data sets the numbers of samples must be taken into consideration. If 150 samples per year are collected, one can expect a higher maximum than if only 20 are collected. The numbers of trace metal samples per year in the EPA data file are highly variable but are rarely as large as in this study.

Despite these statistical difficulties, it is useful to compare these data with the corresponding recent ones in the EPA National Aerometric Data Bank file from 1975 to 1983 and with the older ones from 1968 to 1971. There were no data from Okeana in this file. Most of the recent data were for particulate matter. There were no other data from Los Alamos. There were some data for lead, and very little for the other metals from the other seven cities. The current method used for samples from all these cities for five metals was the Jarrell-Ash Emission Spectra ICAP, for which the minimum detectable concentrations (in $\mu g/m^3$) were listed as follows: Cd, 0.001; Pb, 0.01; Mn, 0.0408; Ni, 0.0056; Zn, 0.0133. Neutron activation was generally the method used for Cr, with a sensitivity of 0.0104 $\mu g/m^3$. These sensitivities were about the same as those of the present study for Cd, Cr, and Zn, more sensitive for Pb and Ni, and less sensitive for Mn. Five cities also analyzed for lead by atomic absorption, with a detection limit of 0.002 $\mu g/m^3$. This method was also applied to four other metals in Houston samples, with detection limits (in $\mu g/m^3$) as follows: Cd, 0.002; Cr, 0.002; Mn, 0.001 $\mu g/m^3$; Ni, 0.004. Houston also analyzed for the six metals by X-ray fluorescence, which exhibited much poorer sensitivities ($\mu g/m^3$): Cd, 0.06, Cr, 0.05, Pb, 0.05; Mn, 0.04; Ni, 0.02; Zn, 0.01. The samples for trace metals were usually 24-h samples collected at frequencies varying from bimonthly to semimonthly. Where several analytical methods were applied at the same site, there were often substantial differences between the results for the same metal. In some cases the differences might be related to random variations among the differing numbers of samples collected at the same sites and/or work done by a different agency.

Seventeen sites in the present study appeared to be at the locations identical with those in the EPA data bank file. Table II shows the data comparisons. When the listed geometric mean was below the detection limit of the method, it was not regarded as accurate enough for listing here. Results for this study are the geometric means for about 150 samples at each site. The data bank results were based on far fewer samples, as given in the third column. The comparative data selected were the most complete data during 1968–1971 and most recently on or after 1976. In all cases the lead concentrations declined substantially. The average ratio of the recent/old values was 35%. The particulate matter declined at most sites. Most of the values for Cd, Cr, Mn, and Ni also showed declines.

Comparison of geometric mean values found in this study for each city with recent data collected by others at different sites is difficult. Recent data were collected generally at more sites in each city for particulate matter and generally at fewer sites for the metals. Similar relationships were found.

A number of other studies have been made of suspended particulates in some of the same or nearby cities such as New York City (*11*, *13–15*), Los Angeles (*10*), and Pasadena, CA (*16*). Sources of trace metals have been tracked by calculating the enrichment factors of their concentrations over those encountered in soil (*17*) and also from their concentrations in fuels and in industrial materials and emissions (*18*). Lead has been shown to be mainly from automobile emissions and vanadium in Northeastern U.S. from combustion of fuel oil. Cadmium and zinc may come from some incinerators. Chromium, manganese, and nickel do not show any significant urban enrichment.

The large mass of data presented here should serve as a useful historical reference point. Recent studies have not provided data for these cities of comparable completeness for most of these metals.

Acknowledgments

The analyses reported here were performed upon samples collected by the Department of Environmental Health, University of Cincinnati, for the lead survey previously cited (2). That project was directed by Lloyd B. Tepper, M.D., under the guidance of the Subcommittee for the Surveillance of Air and Population Lead Levels, which included representatives from the American Petroleum Institute, Automobile Manufacturers Association (now Motor Vehicle Manufacturers Association), E. I. du Pont de Nemours & Co., Ethyl Corp., International Lead Zinc Research Organization, and the Office of Air Programs, U. S. Environmental Protection Agency. Local governmental agencies cooperating were Chicago Department of Air Pollution Control, District of Columbia Department of Public Health, Houston Department of Public Health, Los Alamos Scientific Laboratory, Los Angeles County Air Pollution Control District, New York City Department of Air Resources, Philadelphia Health Department, and City of Vernon Health Department.

Supplementary Material Available

Eight tables with one listing the classification and location of sampling sites and with seven summarizing the concentrations of total suspended particulate and six metals (Cd, Cr, Pb, Mn, Ni, and Zn) (28 pages) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper or microfiche (105 × 148 mm, 24X reduction, negatives) may be obtained from Microforms Office, American Chemical Society, 1155 16th St., N.W., Washington, DC 20036. Full bibliographic citation (journal, title of article, author, page number) and prepayment, check or money order for $43.50 for photocopy ($45.50 foreign) or $6.00 for microfiche ($7.00 foreign), are required.

Registry No. Cd, 7440-43-9; Cr, 7440-47-3; Pb, 7439-92-1; Mn, 7439-96-5; Ni, 7440-02-0; Zn, 7440-66-6.

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Continuous Removal of Both Mutagens and Mutagen-Forming Potential by an Experimental Full-Scale Granular Activated Carbon Treatment System

John C. Loper,*[†,‡] M. Wilson Tabor,[‡] Laura Rosenblum,[†] and Jack DeMarco[§]

Department of Microbiology and Molecular Genetics and Department of Environmental Health, College of Medicine, University of Cincinnati, Cincinnati, Ohio 45267-0524, and Cincinnati Water Works, Cincinnati, Ohio 45228

■ Trends in the removal of mutagens and of total organic carbon (TOC) were measured for granular activated carbon (GAC) in use at the Cincinnati Water Works. Fourteen sets were analyzed, one set for each of the first 3 weeks beginning Nov 29, 1982, and 11 others at 2–4-week intervals during the next 32 weeks. Sample points per set were settled river water, chlorinated sand filtered water, GAC-treated water, water from these two latter points stored 3 days in the presence of a free chlorine residual, and distributed water. Residues were extracted by using XAD-2 resin and bioassayed by using the Ames test strains TA98 and TA100. No mutagens were detected from the settled water, so the great majority of mutagens entering GAC treatment were products of the chlorination step. These mutagens were preferentially removed by GAC treatment, and GAC effluent was greatly reduced in its potential to form mutagens upon rechlorination, even when the GAC was used several months beyond normal use for TOC removal. Analyses of residues extracted from the used GAC also indicated the efficient removal of waterborne mutagens.

Introduction

Drinking water sources, particularly surface waters of major river systems, may be burdened with a broad range of natural and man-made chemicals. Most of these are unknown compounds of low volatility that are present at low concentrations. Nevertheless, known mutagens and carcinogens have been detected among organics extracted from such waters (*1*), and bioassays conducted on subfractions of extracted organics have documented the presence of additional as yet unidentified mutagens (*2–4*). Some of these genotoxic compounds originate from industrial sources while others are known to arise as products of disinfection during the treatment process (*5–8*). These discoveries have raised concerns of possible adverse health affects, particularly in relation to the long-term exposure possible from drinking water.

Such concerns have stimulated a number of responses in regulation and in research. For known genotoxic compounds, regulations have been developed or proposed that limit their presence in public water supplies (*9, 10*). For the unidentified contaminants, research has been conducted on methods for extraction and concentration to obtain residue organics as complex mixtures (*11*). Additionally, surrogate mixtures of nonvolatile mutagens have been obtained by chlorination of humic substances (*4, 6, 12–15*). Such mixtures have been examined for short-term and long-term toxicological effects and by the use of short-term bioassays in conjunction with chemical fractionation for compound identification (*17–20*). We have developed a general preparative procedure for the isolation (*21*), separation (*17*), and chemical characterization (*22*) of mutagenic components from drinking water. This procedure features the extraction of nonvolatile residues by using XAD resins and the subfractionation of mutagenic mixtures by high-performance liquid chromatography (HPLC) on the basis of activity for *Salmonella* strains TA98 and TA100. The *Salmonella* mutagenesis assay is used both for its convenience as a short-term test and for its utility based on extensive use in detecting potential carcinogens (*23*).

Meanwhile, treatment plant procedures are being examined for the removal of such products. Adsorption by granular activated carbon (GAC) is an effective method for removal of many water contaminants (*24*) and has proven successful in pilot scale experiments for the removal of mutagens (*25, 26*). In recent years an experimental full scale GAC system for water treatment has been developed at the Cincinnati Water Works (*27*). A preliminary test of this system by Monarca et al. (*28*) indicated an efficient removal of drinking water mutagens, on the basis of single

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[†] Department of Microbiology and Molecular Genetics.
[‡] Department of Environmental Health.
[§] Cincinnati Water Works.

Table I. Characteristics of Granular Activated Carbon (GAC) Adsorbers

GAC data		hydraulic data	
manufacturer and type	Westvaco, WV-G	diameter, ft	11
mesh size	12 × 40	bed height, ft	14.8
total BET surface area, $m^2\ g^{-1}$	1100 minimum	surface loading, gal $min^{-1}\ ft^{-2}$	6.94
mean particle diameter, mm	0.90–1.20	flow per day, mgd	1
carbon weight, lbs	42 000	residence time, min	15

sets of samples obtained at two time points in GAC use, one at the start and one after continuous use for 3 months.

The work reported here was designed to further test the same GAC system during the effective adsorptive life of the GAC. Prior reported data (*27, 29*) prove that, at the beginning of service for postfiltration adsorption, these contactors remove >90% of the total organic material as indicated by measurements of total organic carbon (TOC) in influent and effluent water. Adsorption efficiency progressively decreases during use until only about 30% of the influent level of TOC is removed. This reduced adsorptive capacity is maintained for TOC for up to 6–12 months of operation. Plots of TOC in influent and effluent water vs. time eventually tend to parallel each other. In practice the GAC is considered exhausted for TOC adsorption once such a parallel pattern of residual TOC appears. In the study reported here, samples were taken up to and well beyond that point. Multiple samples from six separate stages or conditions of water treatment or distribution were taken over an 8-month period. For each sample, residue organics were obtained and bioassayed by our general procedure by using XAD-2 and *Salmonella* mutagenesis. After this phase of the study, carbon removed from the exhausted GAC contactor was extracted. Mutagenic and chromatographic properties of the resulting organic residues were compared to those obtained for the recurrent water samples.

Experimental Section

Facilities. Ohio River water at the California Plant of the Cincinnati Water Works, Cincinnati, OH, is considered to be representative of water supplies which might require GAC treatment. The plant normally processes 135 million gallons a day (mgd) by using long-term presettling in the presence of added aluminum sulfate followed by coagulation–flocculation, sedimentation, and rapid sand filtration. Chlorine, lime, fluoride, and ferric sulfate are applied between the presettling basins and the flocculation/sedimentation basins. In addition the plant has installed a system of four 1-mgd GAC adsorbers to treat sand-filtered water. A schematic diagram of the plant and treatment procedures appears in Figure 1. Specific features of these adsorbers are summarized in Table I, and other physical configuration and performance characteristics are described in earlier publications (*27, 29*). One of these adsorbers filled with fresh carbon was connected to influent chlorinated sand-filtered water to inaugurate this study.

Reagents. Solvents were nanograde (Mallinckrodt), HPLC grade (Fisher Scientific), or distilled-in-glass (Burdick & Jackson). Other chemicals were purchased as reagent grade from commercial sources and were used as obtained.

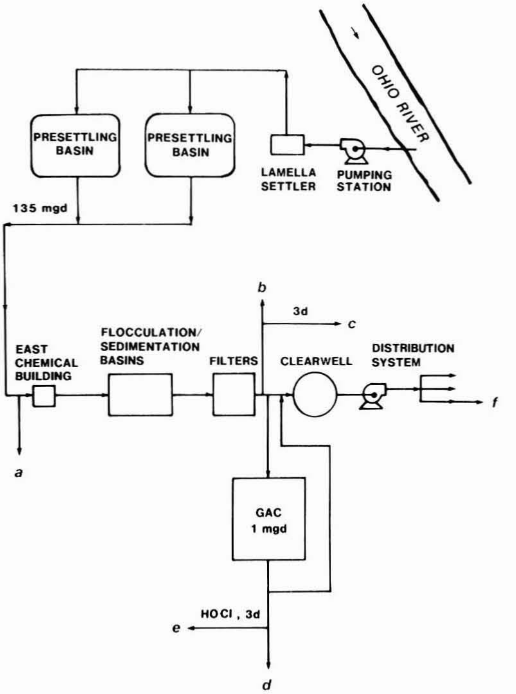

Figure 1. Schematic of the water plant and the six water sample points. The process diagramed was in use at the Cincinnati Water Works–California Plant throughout this study.

XAD-2 Resin Columns. Water samples were processed over 25-cm^3 XAD-2 bed volumes contained in stainless steel columns with internal dimensions of 1 cm × 31 cm. Reagent XAD resins prepared according to U.S. EPA criteria (*30*) were obtained from the Applied Science Division of the Milton-Roy Co. They were stored until use in amber bottles under methanol, and columns were formed by gravity from slurries in the same solvent.

Columns were eluted separately by using 4 column volumes of an 85:15 (v/v) mixture of hexane–acetone based on a method of LeBel et al. (*31*). Eluates were concentrated to 10^{-4} × the original water volume by rotary evaporation under reduced pressure at 30 °C. Concentrates were bioassayed immediately or were stored at 4 °C under nitrogen in Teflon-sealed amber glass vials.

Column configuration and bed volumes were designed to accommodate 150 L of water containing TOC levels typical of these sources on the basis of theoretical performance properties of XAD resins as discussed by Leenheer and Huffman (*32*). The columns were then tested for mutagen recovery using laboratory tap water in a series of preliminary experiments conducted during the 2 months prior to starting the GAC adsorber. Columns of XAD-2 were found to retain mutagenic organics from 270 L of tap water, a volume equal to 10 times that intended for the major study. Sample flow rates of 4–16 bed volumes per minute were comparably effective in permitting adsorption and recovery of mutagenic residues. Use of a similarly sized column of XAD-7 subsequent to the XAD-2 column adsorbed no additional mutagens from this drinking water. Previous experiments had demonstrated that type 1 water without or with chlorination to 2 mg/L did not yield mutagens when processed in this fashion with XAD-2 or XAD-7 (*21*).

Sample Sets and Sampling Protocol. Each sample set consisted of 27 L volumes of water from six points described here and diagrammed in Figure 1: (a) settled unchlorinated water; (b) chlorinated sand-filtered water, finished and ready for distribution or for use as influent to the GAC adsorber; (c) chlorinated sand-filtered water collected and stored 3 days to simulate distributions; (d) GAC bed effluent; (e) GAC bed effluent water rechlorinated to 2 mg of chlorine/L and stored 3 days; (f) chlorinated finished water distributed to the tap in the university laboratory. Since GAC removes free chlorine residual, the GAC effluent water samples that were stored for 3 days (point e) were first dosed with a 0.4–0.6% sodium hypochlorite solution. Approximately 17 mL of the solution was required to achieve an initial free chlorine residual of 2.0 mg/L and a stored free chlorine residual of at least 0.5 mg/L, as measured by the amperometric titration method (*33*). Each sample was forced at 140 mL/min through a 0.45-μm Durapore (Millipore) filter and then directly over a 25-cm^3 XAD-2 column. In the case of the distributed tap water samples (point f) this was done by employing 35 lbs/in^2 of pressure at the water line as described previously (*21*). Settled unchlorinated water samples were pumped over the filtration and adsorption assembly by using a Milton-Roy Model MR-117S TFE diaphragm pump. All other samples were processed under nitrogen pressure by using a 20-L pressure reservoir (Amicon). The following sampling procedure was established for these sample volumes and column flow rates to provide for routine collection and assay within a 1-week work period:

Day 1: a.m., process point a water; p.m., process water for points b and d, collect water for points c and e, chlorinate water of point e, store samples c and e in covered glass bottles, cap, and store XAD-2 columns at 4 °C.

Day 2: elute XAD-2 columns and concentrate residues, bioassay samples a, b, and d.

Day 4: p.m., process samples c and e at Waterworks and sample f in the university laboratory and store columns at 4 °C.

Day 5: as day 2 for samples c, e, and *f*. Since previous samples of water from points b and f had shown typical levels of drinking water mutagens (unpublished results of Loper et al. and ref 21), this procedure was expected to provide for at least 1 mutagenically active sample in each trio of unknowns being assayed.

Mutagenicity Assay. The *Salmonella* mammalian microsome mutagenicity assay using strains TA98 and TA100 was employed essentially as described by Ames et al. (*34*). Cultures of these tester strains were prepared on day of use by inoculating 9-mL stocks of nutrient broth with a thawed 3-mL aliquot of each stock culture which had been frozen (−80 °C) in log phase in the presence of 8.8% dimethyl sulfoxide (Me_2SO) and the inoculated broths were incubated with shaking at 37 °C until cell densities of (1–2) $\times 10^9$/mL were reached (ca. 2.5 h). Dose–response data were obtained from assays which incorporated four doses of the test residue dissolved in 25–200 μL of Me_2SO examined in the absence (−S9) and presence of microsomal activation mix containing the polychlorinated biphenyl mixture Arochlor 1254 (PCB) induced rat liver S9, 20 μL/plate (+S9). Residue doses per plate chosen were representative of 0.25, 0.5, 1.0, and 1.5 L of original water except in specifically cited cases where doses up to 3 L/plate were employed. Experimental plates were prepared in duplicate while spontaneous plates containing Me_2SO as the solvent control were prepared in triplicate in the absence and presence of S9. Each assay incorporated both direct-acting (i.e., assayed minus S9) and S9-dependent control mutagens appropriate for each tester strain. For these experiments, the mean revertant colony counts, ±SE obtained for each group of spontaneous plates and positive control plates were the following (the number of plates appears in parentheses): TA98 spontaneous −S9, 17 ± 3 (93), and +S9, 31 ± 6 (92); TA98 with 2 μg of 2 aminoanthracene (2-AA) and 20 μL of PCB-induced S9, 1622 ± 394 (62); TA98 with 50 μg of 1-amino-2-carboxy-4-nitroanthraquinone, 1645 ± 284 (64); TA100 spontaneous −S9, 128 ± 19 (96), and +S9, 127 ± 16 (96); TA100 with 2 μg of 2-AA and 20 μL of PCB-induced S9, 1491 ± 342 (61); TA100 with 1 μL of methyl methanesulfonate, 1277 ± 241 (62). Specific mutagenic activities were expressed as net revertant colonies per liter equivalent of original sample volume, calculated by least-squares regression analyses of the linear portion of the dose–response curves. A mutagenic response was defined as a dose-related response with at least a 2-fold increase in the number of colonies per experimental plate over the number of colonies per spontaneous plate.

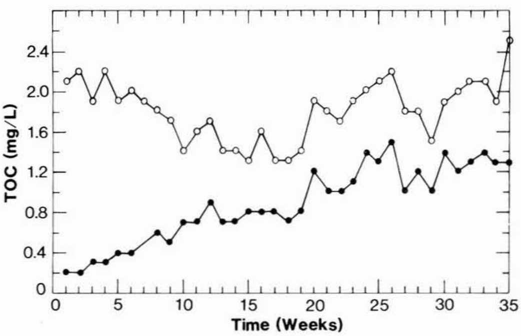

Figure 2. Levels of total organic carbon (TOC) in water before and after GAC treatment. Water samples were of chlorinated water and GAC-treated water from points b and d as diagramed in Figure 1.

Extraction of GAC. Samples of the carbon were taken from the GAC adsorber prior to its use and again at the end of the experiment. Aliquots (50–100 g) of the damp carbon sample were extracted with methylene chloride for 24 h by using a large Soxhlet apparatus. The extract was passed through sodium sulfate (previously muffled at 500 °C for 4 h) to remove any water, and residues were concentrated by rotary evaporation.

HPLC Separation. Analytical scale separations by high-performance liquid chromatography (HPLC) were performed on a Waters Associates ALC/GPC 205 system using a prepacked, 3.9 mm by 30 cm column of 10-μm silica particles bonded to octadecylsilane (*17*). Separations were accomplished by using a water to acetonitrile linear gradient solvent system flowing at 2.0 mL/min, and the effluent was monitored by absorbance at 254 nm.

Results

Total Organic Carbon and Performance of this GAC Contactor in TOC Removal. Throughout this study TOC values were obtained from grab samples collected weekly from chlorinated sand-filtered finished water (b) and GAC effluent water (c). These values are presented in graph form in Figure 2. The TOC of sand-filtered finished water ranged between 1.3 and 2.5 mg/L during the study. As shown in Figure 2, performance of this GAC bed for TOC removal was consistent with that reported in previous studies (*27, 29*). Effluent water sampled early in the study showed TOC levels typical of the low levels normally found at the start of adsorption cycles (*29*). These levels in effluent water increased during the first 15 weeks of the study and then maintained a pattern of about 65% of the influent TOC level. Thus, by conventional practice this GAC was considered exhausted for TOC adsorption at 15 weeks.

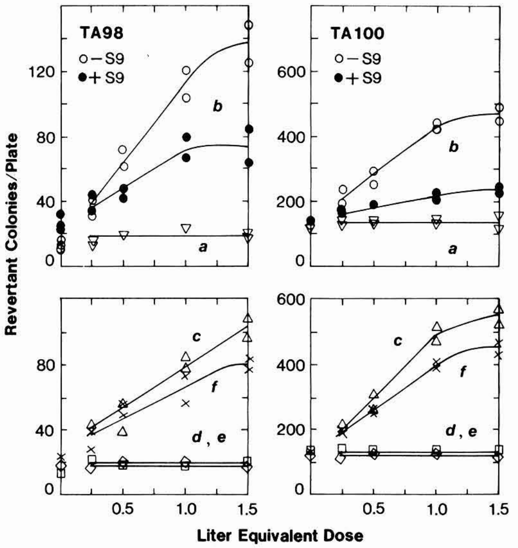

Figure 3. Mutagenic responses of residues from water samples collected during week 1. Residues from sample points a–f as diagramed in Figure 1 were assayed with strains TA98 and TA100 both −S9 and +S9. Data presented here are −S9, open symbols, and +S9, closed symbols, for sample points a (▽), b (○), c (△), d (□), e (◇), and f (×). Data points for d and e are averages of duplicate plate counts.

Sampling Schedule, Lack of Mutagenesis in Settled Nonchlorinated Water, and Mutagenicity of Samples from Points b, c, and f. Weekly sample sets were processed for the 3 weeks beginning Nov 29, 1982, and 11 additional sets were processed at 2–4-week intervals through the week of July 25, 1983. No mutagenicity was detected in assays of each of the 14 samples of settled nonchlorinated water taken at sample point a. As was to be predicted on the basis of published studies of drinking water mutagenesis (*5*, *21*), the most consistently active samples were those of sample point b, the recently chlorinated sand-filtered finished water. Representative data for all sample points are those of week 1, presented in Figure 3. As documented in Figure 4, each of the 14 samples of chlorinated water taken from point b was shown to be mutagenic, indicating the rapid production of mutagens in this water following chlorine treatment.

For both strains, the presence of S9 in the assay mix reduced the level or eliminated detection of mutagenicity. As presented in Figure 4, for residues from point b, throughout this study the levels of TA98 mutagenesis −S9 varied over 12-fold, yielding specific activity values of net revertant colonies per liter equivalent of from 134 to 11. For strain TA100 −S9, assays of 13 of these 14 samples showed values of net revertant colonies per liter equivalent which varied from 297 to 112 (see Figure 4). Data for week 14 showed a rising dose response which failed to attain a 2-fold response at the maximum dose tested, 1.5 L equiv/plate.

Point c samples, the chlorinated sand-filtered water stored for 3 days before nonvolatile organics were extracted for bioassay, showed the same pattern of direct-acting mutagenic activity, with decreased activity for either strain when tested in the presence of S9. Mutagenicity for strain TA98 −S9 was detected in 13 of the 14 point c samples. Activity for this strain tended to decrease slightly with this storage, yielding values of net revertant colonies per liter equivalent which ranged from a high of 119 (in week 9) to undetected (in week 28) (data not shown). Activity for strain TA100 −S9 increased somewhat, up to 60% in the most extreme case, for 8 of the 14 samples. The range of specific activity values for TA100 −S9 in net revertant colonies per liter equivalent was from 364 (in week 3) to undetected (in weeks 22 and 28) (data not shown).

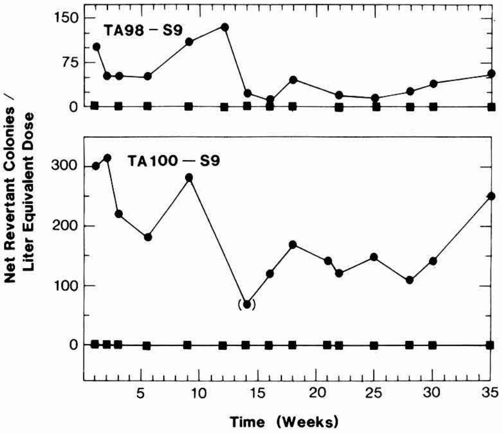

Figure 4. Mutagenesis produced following chlorination was removed by GAC treatment. Data are for residues found to be mutagenic by the criteria described under Experimental Section, except for the strain TA100 −S9 response for week 14 indicated by ((●)). This residue showed a dose response which rose to just short of a 2-fold response. (●) Chlorinated water from sample point b diagramed in Figure 1, assayed with strains TA98 and TA100 in the absence of microsomal activation (−S9). Plots of (■) are presented to emphasize that none of the residues from paired samples of unchlorinated water (from point a, Figure 1) or of GAC-treated water (from point d, Figure 1) showed mutagenic activity.

Because of unpredictable changes in demand on the municipal water system, water distributed to the laboratory (point f) is only generally related to the actual point b samples taken at the Waterworks. Nevertheless, tap water at the laboratory gave findings similar to stored nondistributed finished water (point c). Most of the samples were mutagenic for both strains when assayed −S9, and mutagenic activity was decreased in the presence of S9. The range of direct-acting mutagenicity in net revertant colonies per liter equivalent for TA98 was 76 to undetected and for TA100 was 320 to undetected.

Removal by GAC of Chlorination Product Mutagens and of Chlorine Mutagen-Forming Potential. This chlorinated sand-filtered finished water, sampled at point b, is the influent water stream to the GAC. In contrast to this mutagenic influent water, each of the 14 samples of water collected immediately effluent to the GAC (point d) was not mutagenic in our assays (indicated by the flat lines in Figure 4). In fact none of these samples showed even a rising dose response which might suggest a real but low level of mutagenesis (less than a doubling with 1.5-L residue equivalent/plate; see Experimental Section).

Moreover, none of these water samples developed detectable mutagens following the readdition of chlorine and storage for 3 days, a period of time generally required for disinfection prior to distribution. Data for week 25 is cited as a possible exception since in this case a rising dose response was apparent. For this sample set the TOC values (mg/L) influent and effluent to the GAC were 1.8 and 1.2, respectively. Effluent water (point d) was treated with chlorine to 2.6 mg/L and stored 3 days (point e) at which time the residual chlorine measured 2.0 mg/L. For

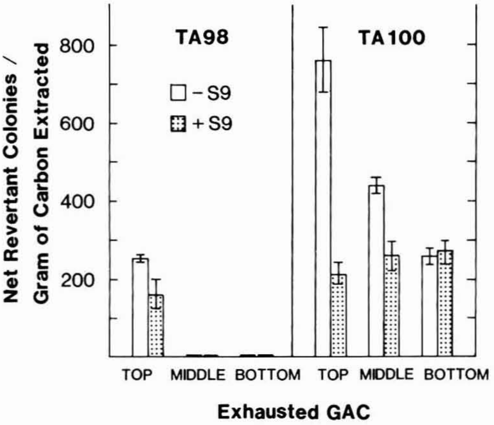

Figure 5. Mutagenic activity recovered from GAC used in water treatment. Following 9 months of use in the adsorber, carbon samples were removed from the top, middle, and bottom and were extracted as described under Experimental Section. The data show the range of specific mutagenicity values for replicate assays using strains TA98 and TA100 in the absence of S9 (open bars) and +S9 (stippled bars).

three of our four assay conditions, by use of strain TA98 ±S9, and strain TA100 +S9, these samples from points d and e showed neither a doubling of revertant colonies relative to spontaneous values nor a pattern of rising dose response in assays up to 2 L equiv/plate. When residues from sample point e were assayed with TA100 −S9 in four doses up to 3 L equiv/plate, data for duplicate plates suggested the presence of a rising dose response. On the hypothetical assumption that this slope was an accurate indication of low level mutagenesis, extrapolation of the slope to a dose of 8 L equiv/plate would be required to yield a doubling of total revertants per plate relative to the spontaneous reversion value in that experiment. If actually representative, such a level of mutagenesis would indicate that GAC treatment yielded a reduction of mutagen-forming potential to a level that still was less than 13% of that measured for the unadsorbed water.

Extraction of Mutagens from the GAC. After the GAC had been backwashed and settled and on the day it was put in service, a sample of carbon was taken from the top. This carbon, consisting of fine particles of nonuniform size, was stored in a glass-stoppered bottle at 4 °C. In Dec 1982 and again in Nov 1983 aliquots of this sample were extracted with methylene chloride as described under Experimental Procedures. The extracted residues were assayed with TA98 and TA100 ±S9 by using residue doses obtained from 0.1, 0.2, 0.5, and 1.0 g of the GAC. For both GAC aliquots, neither mutagenicity nor toxicity was observed.

Although the last regular water sampling was conducted during the week of July 25, water flow was maintained through the GAC during the month of August. Additional carbon samples were removed at the end of that month. Three sampling levels were selected, the top, middle, and near the bottom of the contactor. Soxhlet extractions were performed on each of these carbon samples, and the resultant extract residues were subjected to bioassay and to characterization as to their 254-nm absorbance profile during analytical separations by reverse-phase HPLC.

The mutagenic response data are presented as average specific mutagenicity values in Figure 5. Qualitative and quantitative differences were evident for all three sampling levels. All activity for TA98-assayed ±S9 was present in residues extracted from the top sample. While activity for TA100 was most pronounced in those residues, appreciable mutagenic activity was also detected for residues extracted from GAC samples removed from the lower levels. For TA100 mutagens at decending levels in the adsorber there was decreasing sensitivity to inactivation by S9. In effect this resulted in the level of TA100 mutagenesis assayed +S9 being constant for the three samples while the activity −S9 decreased nearly 3-fold. Assessing the significance of this pattern will require further compound separation, but clearly different mutagenic compounds are present in these mixtures.

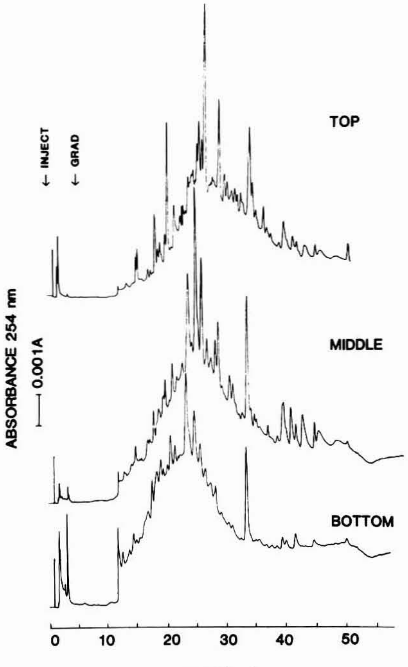

Figure 6. Absorption profiles from reverse-phase HPLC of residues extracted from GAC used in water treatment. Residues were prepared as described in Figure 5. Chromatographs were of the residues extracted from 35, 100, and 23 mg of carbon from the top, middle, and bottom of the adsorber, respectively.

Comparative reverse-phase HPLC profiles presented in Figure 6 are for residues extracted from carbon taken from the three levels of the adsorber. The patterns show that numerous 254-nm absorbing compounds are contained in each of these residue mixtures. By this assay, increasingly polar compounds were recovered from descending levels of the GAC bed. In Figure 7 the HPLC profile for residue from carbon taken from the top of the GAC bed at the end of the experiment is contrasted with the HPLC profile for residue from 10 times as much carbon, removed from the top at the beginning of the experiment 9 months earlier. The sample of regenerated GAC was essentially free of extractable compounds, both when it was collected at the beginning of the experiment and after it had been stored unused for several months at 4 °C.

Discussion

In addition to its use for control of organic compounds in drinking water that cause taste, odor, and color problems, GAC has received increasing attention as a treatment for the removal of compounds known or suspected to be of toxicological importance. Assessment of the performance of GAC for removal of toxic substances is complicated

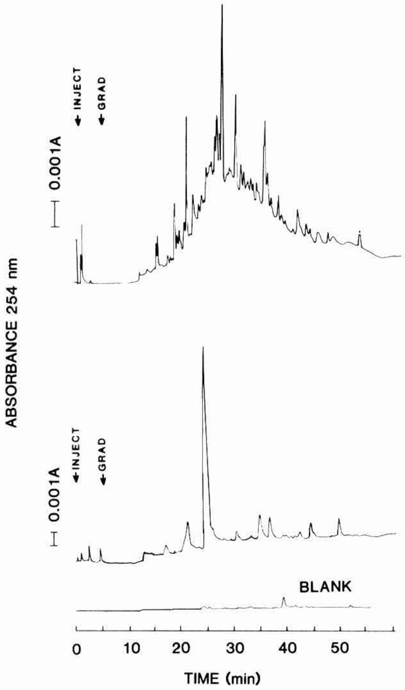

Figure 7. Absorption profiles from reverse-phase HPLC of residues extracted from carbon before and after its use in water treatment. Chromatographs were of residues extracted from 350 mg of carbon from the top of the adsorber collected on the initial day of use and from 35 mg of carbon from the top collected 9 months later.

both by limitations of knowledge as to the identity of bioactive compounds likely to be present and by the necessity for their concentration prior to bioassay or chemical identification. As discussed in ref 24, the compounds of interest may be classified as (1) industrial chemicals entering source waters from point discharge or spills and from agricultural runoff, (2) organic compounds that react with chlorine disinfectants to form disinfection byproducts, (*3*) these chlorination byproducts themselves, and (4) natural humic products that typically constitute the major portion of the TOC in the water. This latter category is of interest primarily because its constituents may compete for adsorption sites on the GAC, preventing the removal of more toxic compounds or perhaps displacing previously adsorbed ones back into the water.

In a recent study, Monarca et al. (*28*) conducted an assessment of GAC treatment at this water facility by measuring *Salmonella* TA98 and TA100 mutagenesis induced by nonvolatile organic mixtures. In that study the mixtures had been concentrated from the water by a procedure which used reverse osmosis followed by liquid–liquid extraction and XAD-2 resin adsorption. Four 7570-L water samples were examined, one each from water influent and effluent to GAC that had been in use the preceding 3 months and one each collected 2 weeks later from water influent and effluent to freshly regenerated GAC. Analysis of the effects of GAC treatment was based upon both the mutagenic activity and the mass of the recovered residues. Mutagenesis was detected by both tester strains, and the levels of activity decreased in the presence of S9, results that are typical for studies of such waters (*35*). Comparison of mutagenic activity/mass of residue for influent and effluent samples indicated that for these two time points in operational age of the GAC, the GAC efficiently and preferentially removed mutagenic compounds from among the TOC of the effluent waters.

Our study was conducted to measure trends in mutagen removal relative to levels of TOC removal throughout extended use of one of these adsorbers and to monitor both for the presence of mutagenic activity in settled unchlorinated water and for effects upon mutagenic activity caused by rechlorination of water effluent to GAC treatment. Consequently, our protocol had several differences from that of Monarca et al. Resin adsorption using our XAD-2 procedure was chosen for extraction of residues since it lends itself to frequent collection and processing of multiple samples. No attempt was made to determine the mass of residues recovered, but rather the entire residue was used for bioassay. For repetitive collection of water from multiple points it was necessary to work with samples of appropriate small volumes. Previous analysis of chlorinated water from this facility using our XAD-2 procedure indicated that dose ranges with residue levels representative of up to 1.5 L/plate would yield colony counts severalfold the spontaneous level with no problem of cell toxicity (*21*). This turned out to be generally the case, although the activities of mutagenic samples were lower for samples taken in spring and early summer than at the beginning and the end of the study. Presumably some of the samples found to be nonmutagenic by our assay criteria would have appeared active if measured at higher doses. The extent of the quantitative difference between mutagenic and nonmutagenic determinations among paired samples is considerable, however, on the basis of the characteristic absence of even low levels of rising dose response for nonmutagenic samples, as exemplified in Figure 4. In the one case where a low level dose response marginally was apparent, a hypothetical extrapolation to a significant dose indicated that sample was only 13% as active as its pair which received alternate treatment. Clearly to establish quantitative values for residual mutagenesis in most of the samples which we assayed as inactive would have required collection of sample volumes so large as to be incompatible with the object of the study.

Within the detection limits of our assay, several major trends were evident. (1) No mutagenic activity was detected in residues from the 14 samples of settled water collected prior to chlorination, at point a as diagram in Figure 1. In earlier unpublished experiments, our analysis of 10 random samples of unchlorinated water from this facility had identified one sample as mutagenically active. Those findings together with the data for these 14 samles indicate the presence of mutagens in the settled water is a relatively rare event. Thus, the majority of mutagens entering the GAC were products resulting from the chlorination treatment effected at the immediately preceding step (point b). (2) The levels of mutagenic activity detected in this chlorinated drinking water (point b) were similar to those generally measured for such waters (*35*), and these activities were selectively removed by GAC treatment. No mutagenic activity was detected in residues from GAC effluent (point d), even though the adsorber was kept in use for several months beyond the time that effluent TOC levels stabilized at approximately 0.65 times those of influent water. (3) Mutagen-forming potential was selectively removed by GAC treatment. It is standard practice in the United States that drinking water entering distribution from the treatment facility retain a low level of chlorine or similar disinfectant. Since the mutagenic activity being followed in this study became apparent upon chlorination of the settled water, it was of particular interest to measure the activity in GAC effluent water which had been rechlorinated and stored 3 days to simulate distribution (point e). No mutagenicity was found even though the last several samples contained appreciable levels of TOC. As recorded in Figure 2, the fluctuation in TOC of influent waters was such that on more than one occasion, GAC effluent water had TOC levels greater than those recorded for influent water in previous weeks. Thus, our assays demonstrate that GAC effluent waters of comparable TOC content were qualitatively different in having been stripped of their mutagen-forming potential. (4) The results of analyses of residues from the GAC used in this adsorber were consistent with the efficient removal by GAC of chemicals including mutagens. Organic residues recovered from the unused GAC were not mutagenic and showed a simple 254-nm absorption profile when separated by reverse-phase HPLC. By contrast, similar extractions of used GAC from the top near the water intake, from the middle, and from the bottom near the water effluent yielded residues with appreciable mutagenic activity. Reverse-phase HPLC gradient elutions showed these samples to be complex in that numerous 254-nm absorbing compounds were separable into subfractions on the basis of their polarity. All of the activity for TA98 and most of the TA100 −S9 activity recovered was in residues extracted from the topmost sample. Nevertheless, some mutagenic activity for strain TA100 was detected from GAC taken from the bottom of the column, indicating this column was nearly exhausted in its capacity for removal of those mutagens.

On the basis of these findings, this experimental full-scale GAC treatment system continues to be effective for removal of *Salmonella* mutagens long after removal of TOC has reached a steady state. Even as the adsorber approaches its capacity for removing mutagens, the TOC in effluent water remains greatly reduced in its capacity to yield mutagens upon rechlorination for distribution.

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Reaction of Dissolved Chlorine with Surficial Sediment: Oxidant Demand and Production of Trihalomethanes[†]

Allen D. Uhler[‡] and Jay C. Means*

Chesapeake Biological Laboratory and Department of Chemistry, University of Maryland, Solomons, Maryland 20688-0038

■ Reactions between dissolved HOCl and surficial sediments from the Potomac River, MD, are reported. All sediment samples showed a tendency to react with HOCl under a range of pH (5–10) and salinity (0–30 mg/L) conditions. At pH 7.0 and 0‰ salinity, the average HOCl demand was approximately 0.07 mol of HOCl/mol of adsorbed organic carbon. The only purgeable organic compounds produced by the chlorination of these sediments were trihalomethanes. The speciation and yield of trihalomethanes were found to be a sensitive function of salinity. Along the salinity gradient 0–30‰ at pH 7.0, trihalomethane production reached a maximum at about 5‰ salinity and then rapidly fell off with increasing salinity. It is proposed that increasing salinity alters the reactivity of adsorbed organic matter, resulting in a less reactive material at high salinities.

Introduction

Chlorine is used routinely on a worldwide basis as a disinfectant of potable water and as a biocide in the pretreatment of power plant and industrial cooling waters. Interest in the fate of chlorine and its byproducts in the aqueous environment has grown in the last decade as concerns for the environmental and health effects of dissolved chlorine have increased (*1–6*).

There is considerable interest in trihalomethanes (THM) in natural waters because of their potential carcinogenicity. Concern over low level human exposure to THMs (*7, 8*) has led the U.S. Environmental Protection Agency (EPA) to propose maximum THM levels in finished drinking water. Rook (*9*) was the first of a number of investigators to report the production of volatile trihalomethanes upon the chlorination of a variety of different natural waters. Since these early discoveries, considerable effort has been expended attempting to pinpoint sources of THM precursors (*10–12*). In particular, much has been accomplished in detailing the reactivity of dissolved and colloidal organic matter with chlorine, yet little attention has been focused on the reactions of organic matter adsorbed to suspended sediment. Recent laboratory work (*13, 14*) demonstrated that selected organic compounds sorbed to activated carbon yielded significantly different chlorination products than did chlorination of the same compounds in solution. This suggests that chlorination of sediment-bound organic matter may have substantially different reaction pathways than organic matter dissolved in natural waters. Carpenter and Smith (*15*) suggested that organic matter adsorbed to suspended sediment represented a reactive fraction of organic carbon in natural water. Typical sediment loads in natural waters are about 5–25 mg/L, and sediments can contain sorbed organic carbon on the average of 5% by weight (about 10% organic matter). Thus, adsorbed organic carbon could make a significant contribution to the total organic carbon load in solution and perhaps be a potential source of reactive THM precursors in the aqueous environment. Additionally, organics sorbed to surficial sediments could react with residual chlorine from water treatment outfalls at the sediment/solution interface, resulting in formation of halogenated organics in sediment pore waters.

In this paper we describe the reactivity of surficial sediment samples collected from the Potomac River, an estuarine tributary of the Chesapeake Bay, and detail the production of volatile halocarbons during these reactions. The effects that solution conditions exhibit on the distribution of halocarbon species and the amount of total halocarbon produced are described.

Table I. Chemical and Physical Properties of Sediments

sample	% sand	% silt	% clay	% OM	% C	% N
PT-1	21	26	53	3.5	1.7	0.25
PT-2	85	6	9	0.6	0.23	0.06
PT-3	62	11	27	1.7	1.07	0.15
PT-4	56	11	33	2.7	1.40	0.18
PT-5	17	26	57	3.2	1.23	0.18

Table II. Composition of Instant Ocean[a]

component	ppm at 34‰ concn	component	ppm at 34‰ concn
Br^-	65	K^+	371
Ca^{2+}	398	Mg^{2+}	1 265
Cl^-	18 788	Na^+	10 424
HCO_3^-	145	SO_4^{2-}	2 577

[a] Manufacturer analysis.

Experimental Section

Sediments were collected from the Potomac River on Oct 28, 1983. Figure 1, a map of the Potomac River, shows the locations of the five sampling sites. Sediment samples were obtained with a Van Veen sampling device. Temperature, dissolved oxygen, and pH measurements were made of the water column directly above the sediment–water interface. The top 2 cm of each sample was sectioned off and stored in an acid-washed bottle. These bottles were stored at 4 °C in a dark, cold room until used.

Distilled water was passed through a Millipore Milli-Q ion-exchange/carbon adsorption system. The resulting water was found to be chlorine demand free. In order to remove dissolved organic matter and salts from the interstitial water of the sediments, the samples were cleaned in the laboratory. Approximately 25 g of sediment was placed in a centrifuge tube with 50 mL of distilled water. This slurry was stirred and then centrifuged at 7000 rpm to separate the suspended matter from the water. This step was repeated 6 times. Mechanical analysis and weight loss on combustion assays of the sediment were performed by the Soils Testing Center at the University of Maryland. Carbon and nitrogen compositions of the sediments were determined with a Perkin-Elmer 240B elemental analyzer. Table I lists some chemical and physical properties of the sediment samples.

Experiments at salinities of 1, 5, 15, and 30‰ were carried out in solutions of Instant Ocean (Aquarium

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[†] Contribution No. 1573 of the University of Maryland Center for Environmental and Estuarine Studies.

[‡] Present address: Division of Chemical Technology, Food and Drug Administration, Washington, DC 20204.

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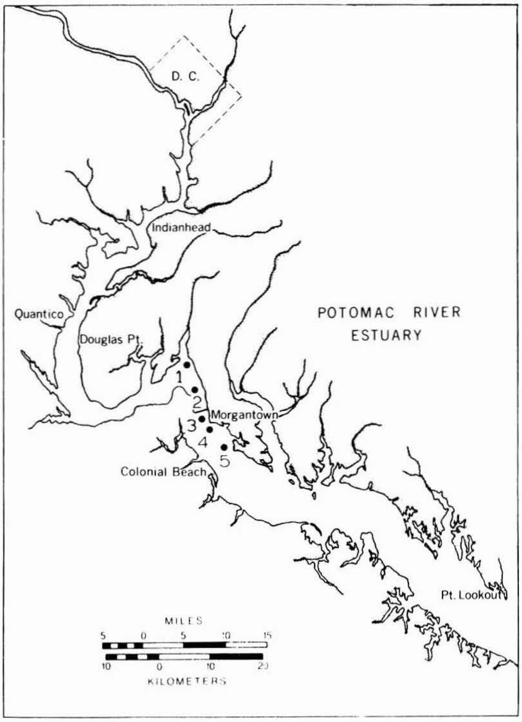

Figure 1. Map of lower Potomac River, MD. Sampling sites are marked with solid circles.

Systems, Inc.). Table II lists the chemical compositions of Instant Ocean. Strictly speaking, the 0‰ salinity solutions did have a salinity calculated to be, at most, 0.1‰ due to the presence of buffer. At higher salinities (>1‰) the buffer contribution to overall salinity was negligible. Sediment suspensions were allowed to equilibrate for 24 h before being used. The salinities of the solutions were then determined conductimetrically.

The rate of HOCl consumption by the sediments was examined at several different pH and salinity values at room temperature. Selected sediments were individually mixed with 1.0 L of distilled water in a round-bottom flask and agitated with a magnetic stir bar. The pH of the solution was maintained with a 0.001 M buffer [acetate for pH 5; phosphate for pH 7; borate for pH 9; $Ca(OH)_2$ for pH 10 and 11]. The flask was covered to exclude light from the reaction mixture, since there is some preliminary evidence for a photocatalytic enhancement of HOCl decay reactions (*15*). To start the reaction, an aliquot of 0.50 M NaOCl was rapidly injected. At predetermined time intervals, 10-mL aliquots were removed from the flask, filtered through a 0.4-μm Nuclepore filter, and analyzed for total residual oxidant ampereometrically (*16*). Control reactions were carried out concurrently with the actual rate experiments to determine how much, if any, HOCl was lost over time due to other processes such as volatilization or reaction with buffer.

Table III. Ion Fragments Monitored for SIM determination

THM	ion fragments (m/e)
$CDCl_3$	84,[a] 86, 88
$CHCl_3$	83,[a] 85, 87
$CHBrCl_2$	85,[a] 127, 129
$CHClBr_2$	127,[a] 206, 208
$CHBr_3$	171,[a] 173, 175

[a] Quantitation ion. Mass spectrometer settings: 70 eV (positive electron impact). Ion dewll time: 30 ms/ion.

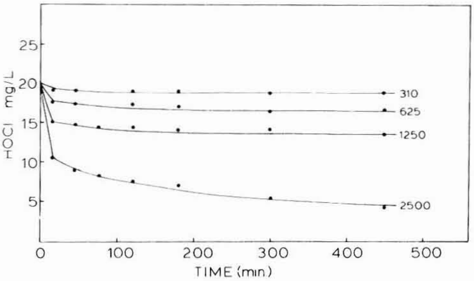

Figure 2. Effect of sediment concentration on HOCl consumption rate. Initial HOCl in all experiments is 20 mg/L, while the pH was maintained at 7.0. Initial sediment concentrations of sample PT-1 are given milligrams per liter.

The production of volatile halocarbons upon the chlorination of sediment was monitored by a coupled purge and trap gas chromatography/mass spectrometry (Hewlett-Packard 5985B) (GC/MS) method. The THMs produced were quantified by using an internal standard technique, with chloroform-*d* as the internal standard. Trihalomethane standards were prepared according to the method of Nicholson et al. (*11*). Fifteen milliliters of a buffered sediment suspension was pipetted into a purge tube and attached to the purge and trap unit. Next, the internal standard followed by an aliquot of NaOCl was injected into the solution via a septum-sealed side arm. The solution was mixed with a magnetic stir bar. After a predetermined time had passed, a 0.5-mL aliquot of 1.0 M sodium sulfite solution was injected to dechlorinate the solution. Next, the solution was purged with helium at a flow rate of 20 mL min^{-1} for 10 min onto a Tenax-GC (Supelco, Inc.) column. The Tenax was desorbed at 200 °C for 2 min onto the head of a 6 ft × 0.25 in. i.d. 1.5% OV-101 on 60/80 mesh Chromosorb G column. The GC column was held at 35 °C for 4 min and then programmed at 10 °C min^{-1} to 200 °C. The mass spectrometer was operated in the electron impact mode at 70 eV. The source temperature was 200 °C, and the source pressure was (2–5) × 10^{-6} torr. Semiquantitative GC/MS experiments were carried out with the mass spectrometer scanning the mass range 30–350 amu. Quantitation of the THMs was performed by using selected ion monitoring (SIM). Table III lists the THMs quantified, along with the respective ion fragments monitored during the SIM procedure.

Results and Discussion

The sediment samples all showed a tendency to react with dissolved chlorine; however, reasonably high sediment loads were necessary to observe a significant chlorine demand (>100 mg/L sediment). The rate of stirring was found not to effect the rate of HOCl consumption, suggesting that the rate of reaction was not limited by mass transport of reactants. Figure 2 shows a series of chlorine decay curves for the sample PT-1 at pH 7. In these experiments, the initial HOCl dose was fixed at 20 mg/L, while the sediment concentration among the trials ranged from about 300 to 2500 mg/L. A concomitant increase in rate and magnitude of HOCl consumed with increasing sediment concentration can be seen.

Figure 3 shows a family of chlorine decay curves for the five samples collected from the Potomac River. Each point

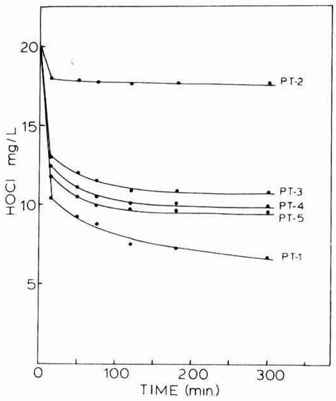

Figure 3. HOCl consumption rates of surficial sediment samples from the Potomac River. All experiments were conducted at pH 7.0 with an initial HOCl dose of 20 mg/L and a sediment concentration of 2500 mg/L.

Table IV. Oxidant Consumed by Sediment Samples after 24 h[a]

sample	% OC	mmol of OC added	mmol of HOCl consumed	mol of HOCl/ mol of OC
PT-1	1.72	3.5	0.25	0.071
PT-2	0.23	0.50	0.03	0.060
PT-3	1.07	2.2	0.17	0.077
PT-4	1.40	2.9	0.19	0.065
PT-5	1.23	2.6	0.20	0.077
				0.070[b]
				0.007[c]

[a] OC, organic carbon. [b] Average. [c] Standard deviation.

on a curve represents one measurement. The reproducibility for these experiments is in the 15–30% range. In this experiment, the initial chlorine concentration was 20 mg/L (as HOCl), and the sediment concentration was fixed at 2500 mg/L. One of the most striking features of these decay curves is the apparent two-stage decay of chlorine. This process is most obvious among the faster reacting sediment samples. There appears to be a rapid chlorine decay during the initial contact period (<15 min) followed by a slower decay phase. The organic carbon consumed during the rapid phase is apparently a more reactive fraction of the sorbed organic material. Note in Figure 3 that the total amount of oxidant consumed by the sediment samples is proportional to the percent organic carbon of the samples.

The decay curves in Figure 3 indicate that the bulk of the organic matter sorbed to the sediment either is quite refractory with respect to reaction with HOCl or is unavailable for reaction. Table IV a compilation of the consumption of HOCl after 24 h by the sediment samples. an average demand of 0.07 ($\sigma = 0.07$) mol of HOCl/mol of organic carbon is seen.

The effect of changing the pH and salinity on the amount and rate of chlorine consumed by the sediments was investigated. Over the pH range 7–11, there was virtually no change in the rate of chlorine consumption. At higher pH (>10), there was evidence for slightly faster chlorine decay, but this was not investigated in detail, since pHs in excess of 8.5 are very rare in natural waters. Changing the salinity from 0 to 30‰ had no measurable effect on the rate or amount of oxidant consumed by sediments.

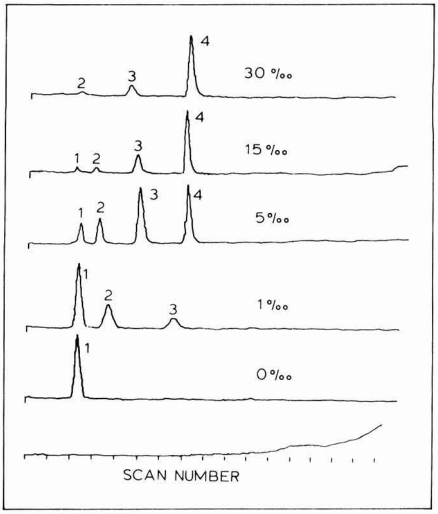

Figure 4. Reconstructed total ion chromatograms of volatile THMs produced upon the chlorination of sample PT-1 at pH 7.0. The bottom trace is an unchlorinated sample, with sediment concentration of 2500 mg/L. Remaining traces are of experiments where initial HOCl dose was 20 mg/L, sediment concentration was 2500 mg/L, and salinity was varied from 0 to 30‰. Peak 1, $CHCl_3$; peak 2, $CHBrCl_2$; peak 3, $CHBr_2Cl$; peak 4, $CHBr_3$.

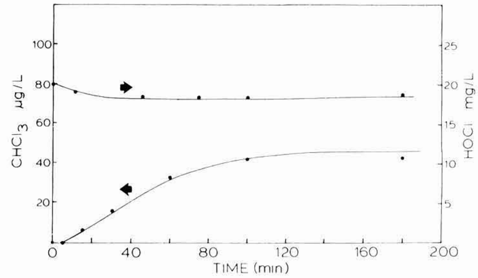

Figure 5. Composite diagram of HOCl consumption vs. chloroform production upon the chlorination of samplet PT-2 in fresh water (salinity = 0‰). Arrows on graph indicate ordinate scale for associated curve. Initial solution conditions: 2500 mg/L sediment, 20 mg/L HOCl, pH 7.0.

The purgeable organic compounds produced by the chlorination of these sediments appear to be restricted solely to trihalomethanes. Figure 4 shows six reconstructed total ion chromatograms of purge and trap experiments with sample PT-1 at pH 7, where the sediment concentration is 2500 mg/L and the initial HOCl concentration is 20 ppm. The bottom trace is of an unchlorinated sample, while the next five are GC/MS traces of experiments where the salinity is increased incrementally from 0 to 30‰.

No evidence for any volatiles in the untreated sample exists. However, in the chlorinated samples low molecular weight THMs are observed. Chloroform ($CHCl_3$) is the sole volatile product in the 0‰ salinity sample, but bromoform ($CHBr_3$) and mixed chloro-bromomethanes become dominant in the higher salinity samples. No other volatile organic compounds were detected in any of these experiments.

Figure 5 is a composite diagram of chlorine decay and chloroform production curves for sample PT-2 in fresh water (0‰ salinity) at pH 7, with a sediment concentration of 2500 mg/L and initial HOCl of 20 mg/L. Very similar

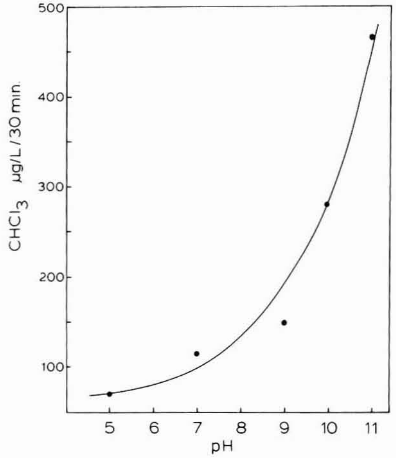

Figure 6. Effect of pH on chloroform yield. Experimental conditions: 2500 mg/L sample MT-1, 20 mg/L HOCl. Contact time: 30 min.

chlorine decay/chloroform production curves exist for all five samples. Chloroform production appears to be complete in less than 2 h. It is not surprising to note that there is a slight delay between the time that chlorine is introduced into the sample ($t = 0$ min) and the time chloroform appears in solution ($t = 15$ min). The HOCl decay curve reaches a plateau value of about 18 mg/L residual in 30 min, while the chloroform production curve requires about 100 min to reach a plateau value of about 45 ppb. This observation supports a reaction pathway for chloroform production which has been described by Morris and Baum (*17*). The first phase involves the production of haloform precursor followed by a second slower step involving the release of the volatile THM via a hydrolysis reaction.

Figure 6 shows the effect of increasing pH on rate of chloroform production. A dramatic increase in chloroform production is seen at pH greater than 8. This is consistent with a mechanism involving hydrolysis of the chlorinated methyl group (as suggested by the above mechanism) and/or OH^- catalyzed aromatic ring rupturing during the chlorination step of aromatic compounds (*12*).

Brominated organic compounds are formed in saline solution by reaction with hypobromous acid. Hypobromous acid, a Br^{1+} species, is produced rapidly in saline solution by oxidation of Br^- ion by HOCl:

$$HOCl + Br^- \rightarrow HOBr + Cl^-$$

The second-order rate constant for this reaction is a rapid $2.95 \times 10^3\ M^{-1}\ s^{-1}$ at 298 K (*18*). Figure 7 is a speciation diagram of the THMs produced at pH 7 as a function of salinity. Note that the total halomethane production ($CHCl_3 + CHCl_2Br + CHClBr_2 + CHBr_3$) appears to reach a maximum in the 5‰ salinity range. Total halomethane production then steadily declines as a function of salinity. At 30‰ salinity, the total halomethane produced is only 40% of that produced at 5‰ salinity. This trend in amount of total halomethane produced as a function of salinity has also been observed in the chlorination of estuarine water (*19*).

An hypothesis for the observed total THM production as a function of salinity is that ions in solution (with increasing salinity) alter the reactivity of the sorbed organic matter. An experiment was performed in which only NaBr was added to the sediment suspensions. Thus, no other solution ions were present, except for the pH buffer. Total THM produced as a function of Br^- concentration at pH 7 is shown in Figure 8. On the same graph, total THM vs. Br^- concentration in artificial seawater is shown. Note that, in the NaBr-only experiments, the total THM vs. Br^- curve has empirically the same shape as that in artificial seawater, except that the total THM yield is more than twice as great at all bromide concentrations in the NaBr-only experiments. The offset in total THM between the two experiments likely reflects the effect of solution ionic strength on the reactivity of sorbed organic matter. An increase in ionic strength likely changes the conformational and electrostatic nature of the sorbed organic matter (through ion pairing), making the material more hydrophobic and less reactive with increasing ionic strength. This effect has been noted with dissolved humic matter (*20–22*).

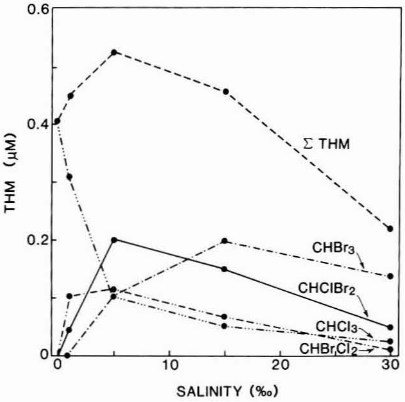

Figure 7. Effect of salinity on THM speciation and yield at pH 7.0. Experimental conditions: 2500 mg/L sample PT-1, 20 mg/L HOCl. Contact time: 30 min.

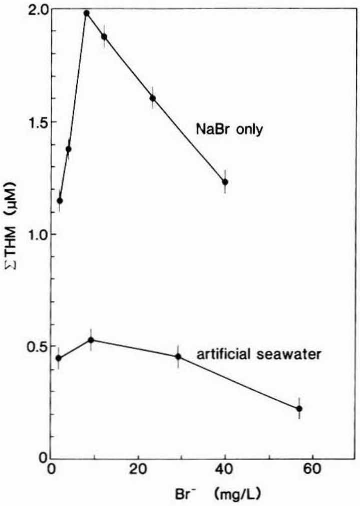

Figure 8. Total THM yield as a function of Br^- concentration in solutions of artificial seawater and NaBr at pH 7.0. Error bars represent standard deviation of three experments. Experimental conditions: 2500 mg/L sample MT-1, 20 mg/L HOCl. Contact time: 30 min.

The following interpretation of the trend in total THM production as a function of Br^- concentration is offered. Luon et al. (*23*) have shown that HOBr forms more substitution compounds than an equivalent amount of HOCl, because HOCl is a stronger oxidant and tends to fully oxidize organic carbon. Hence, in the experiments described in this paper, as HOBr concentration increases (via oxidation of Br^-), it would be predicted that an increase in total THM production would be observed with increasing Br^- concentration. This is seen in experiments at low bromide concentration, but as bromide concentration increases beyond 10 mg/L, total THM production decreases. This may be the result of the fact that HOBr, a weaker oxidant than HOCl, is less capable of forming THM precursors via oxidation reactions (perhaps a ring rupturing mechanism). At low bromide concentration, HOCl can still react fast enough to produce THM precursors for subsequent reaction with both Br^{1+} and Cl^{1+} oxidants. At higher bromide concentrations, the HOCl is consumed more rapidly in the formation of HOBr, and precursor production drops off, resulting in a decrease in overall THM production.

Conclusions

Surficial sediments from the Potomac River exhibit a measurable chlorine demand under normal conditions of pH (5–10) and salinity (0–30‰). At pH 7 and 0‰ salinity, this demand is approximately 0.07 mol of HOCl/mol of adsorbed organic carbon. No measurable change in oxidant demand is seen with change in pH over the range 5–10 or with change in salinity over the range 0–30‰.

Volatile trihalomethanes are produced upon the chlorination of Potomac River sediments. At pH 7 and with a 20 mg/L HOCl dose, THM production ranges from an average of 120 μmol of THM/mol of adsorbed organic carbon (0‰ salinity) to about 70 μmol of THM/mol of adsorbed organic carbon (30‰ salinity). THM production increases steadily with pH and rises dramatically at about pH 9. Brominated THMs rapidly become the dominant species with increasing salinity. Above salinity of 5‰, the brominated THMs comprise at least 85% of the total THM.

The total THMs produced in the reactions described in this paper rarely represented more than 1% of the oxidant consumed. A significant portion of the oxidant undoubtedly was consumed during the production of CO_2. Nonetheless, a substantial amount of oxidant is producing compounds unaccounted for in this work. Rook (*24*) has shown that nonvolatile organohalides generated by chlorination of natural water are at least a factor of 5 more concentrated than THMs. Likely products include both soluble compounds such as halogenated organic acids and phenols and halogenated, macromolecular compounds still adsorbed to the sediment particles. These nonvolatile organohalides will have a substantially longer residence time in natural waters and could well be deleterious to organisms thriving in such environments. Current research in this laboratory is now focusing on the identification of nonvolatile reaction products of dissolved chlorine and sediment-bound organic matter.

Registry No. HOCl, 7790-92-3; $CHCl_3$, 67-66-3; $CHBrCl_2$, 75-27-4; $CHClBr_2$, 124-48-1; $CHBr_3$, 75-25-2; Cl_2, 7782-50-5.

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Determination of Chromium Speciation in Environmental Particles. Multitechnique Study of Ferrochrome Smelter Dust

X. B. Cox, III, and Richard W. Linton*

Department of Chemistry, Venable and Kenan Laboratories of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27514

Frank E. Butler

U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711

■ The chemical speciation of particulate Cr has a significant influence on its environmental impact, with Cr^{6+} compounds of greatest current concern. A novel analytical regimen was evaluated for the determination of the concentration, speciation, and potential bioavailability of environmental Cr by using the example of ferrochrome smelter dust. Various wet chemical extractions were compared for possible use in the routine environmental monitoring of "bioavailable" Cr and Cr^{6+}. Complementary nondestructive instrumental methods included bulk elemental analysis via instrumental neutron activation (INAA), microscopic studies via scanning electron microscopy–energy dispersive X-ray microanalysis (SEM–EDX), and surface chemical analysis via X-ray photoelectron spectroscopy (XPS). Roughly half of the total Cr in the primary smelter dust was extractable by routine acid/base leaching (bioavailable), of which about 40% was Cr^{6+}. The Cr^{6+} exists as $Cr_2O_7^{2-}$ or CrO_4^{2-} and predominates in submicron particles probably formed during smelting. The remainder of the Cr is primarily insoluble Cr_2O_3 which is located in large particles similar to the original chromite ore.

Introduction

As a current focus on the environmental importance of Cr, two comprehensive surveys for Cr were completed in 1983 (*1, 2*) summarizing potential sources and hazards. These studies indicate the importance of the determination of specific chemical states of environmental Cr. Although Cr in inorganic compounds may occur in valence states ranging from −2 to +6, the Cr^{3+} and Cr^{6+} species are of primary environmental interest (*3, 4*). Compounds containing Cr^{6+}, present largely from anthropogenic processes (*1*), are believed to be responsible for most of the health problems associated with all Cr compounds. The toxicity and carcinogenicity of Cr^{6+} compounds also are reported to be much higer than that for Cr^{3+} compounds (*5, 6*). Therefore, a more complete understanding of the health effects of Cr source emissions requires information on Cr concentration, speciation, and bioavailability.

There are a number of pollutant Cr sources, including kilns, smelting furnaces, boilers, and leaching and plating tanks. The burning of oil, coal, and wood and the incineration of municipal refuse and sewage sludge also contribute to atmospheric Cr. Cement production, asbestos mining, and the routine wear of Cr-containing products such as vehicular brake linings are additional contributors to the environmental mobilization of Cr.

The source of Cr chosen for this initial investigation is a ferrochrome smelter that processes mixtures of Cr-containing ores and lime ($CaCO_3$) in an electric arc furnace. Both Cr^{3+} and Cr^{6+} species are present in the dust captured by pollution control devices, in this case a baghouse. As baghouse dusts are disposed of in landfills, where leaching mechanisms can extract species into the environment, the dust provides a useful analytical sample to determine the amount and chemical state of Cr potentially available for biological uptake (operationally designated as "bioavailable" Cr). The main goal of this study is to use nondestructive instrumental techniques in concert with conventional wet chemical analysis (*6–10*) to establish the fraction of bioavailable Cr present as Cr^{6+}. An additional objective is the evaluation of various wet chemical techniques to help establish a reliable, routine approach to environmental source monitoring of particulate Cr species, ultimately to include ambient particle samples. Supplemental information on inter- and intraparticle Cr distribution is provided by specialized surface and microprobe analytical techniques.

Wet chemical techniques, as applied to routine environmental monitoring, have many potential advantages including high sample throughput, low cost, low detection limits, and the ability to determine both elemental concentration and chemical state. The latter aspects are complicated in that a particulate sample is physically altered (extracted, dissolved, etc.) with the possibility of induced chemical changes, matrix effects, and differential solubility artifacts.

Particularly well suited to complement the wet chemical techniques used in this study is X-ray photoelectron spectroscopy (XPS). The XPS experiment (*11*) allows for essentially nondestructive analysis of Cr on the surface of the smelter dust. Surface specificity is important in that it is the particle surface which comes in direct contact with the environment. Changes in chemical speciation and/or concentration in the surface region may cause an element to have an environmental importance far greater than its bulk concentration would indicate (*12*). Furthermore, particle surfaces may show a high concentration of water-soluble compounds (*12*) which can be accessed by the environmental leaching actions of atmospheric water or groundwater or by biological fluids following particle ingestion or inhalation. Chemical state information also is provided in XPS via shifts in binding energies of photoelectrons, enabling a comparison of the relative proportion of surface region Cr^{3+} vs. Cr^{6+} in the specific instance of the smelter dust sample.

In addition to the intraparticle (surface vs. bulk) Cr chemistry, it is of interest to establish the interparticle distribution of Cr; i.e., is the Cr localized in Cr-rich particles? Scanning electron microscopy–energy dispersive X-ray analysis (SEM–EDX) provides both morphological information (secondary or backscattered electron imaging) and X-ray maps of the distribution of elements among particles (*13*). Correlating the characteristic X-ray emission with the position of the electron beam allows for spatially resolved elemental analysis with a resolution on the order of 1 μm. Because of the inherent X-ray line width and the energy resolution of the EDX detector, little

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Table I. Wet Chemical Methods Employed in the Analysis of Extractable Cr^{6+} and Total Extractable Cr in Ferrochrome Smelter Dusts (*14*)[a]

description	results[e]
(1) borate fusion[b] (ASTM D3682)	45.6–48.1 mg/g of total Cr; spike recovery 18–55%
(2) mild acid[b] (method 3020)	0.009–0.01 mg/g of Cr^{6+}; spike recovery <1%
(3) mild acid[c] (method 3020)	0.33–0.71 mg/g of Cr^{6+}; spike recovery <1–2.7%
(4) acid digestion[c] (method 3020, method 3020 with H_2O_2, or method 3050.)	21.3–23.8 mg/g of total Cr; spike recovery 96–116%
(5) EP toxicity[b] (method 1310)	8.4–8.5 mg/g of Cr^{6+}; spike recovery 89–103%
(6) EP toxicity[c] (method 1310)	8.5–12.7 mg/g of Cr^{6+}; spike recovery 112–114%
(7) EP toxicity[c] (method 1310 or method 1310 with H_2O_2)	7.6–7.8 mg/g of total Cr; spike recovery 93–98%
(8) strong acid, sonication[c] (ASTM D3683)	22.0–27.5 mg/g of total Cr; spike recovery 107–114%
(9) alkaline digestion[c] (method 3060 or method 3060 with H_2O_2)	5.8–6.0 mg/g of total Cr; spike recovery 157–242%
(10) alkaline digestion[c] (method 3060)	5.8–6.0 mg/g of Cr^{6+}; spike recovery 144–328%
(11) alkaline extract[b] (method 3060) followed by HF/H_2SO_4 followed by H_2SO_4[d]	10.3–10.5 mg/g of Cr^{6+}; 25.0–26.6 mg/g; total Cr spike recovery 109.6–114.9%

[a] Total Cr determined by INAA was 55 mg/g. [b] Analysis by colorimetric analysis method 7196. [c] Analysis by atomic absorption coprecipitation, method 7195. [d] Analysis by flame atomic absorption spectroscopy, method 7190. [e] Spike recovery based on percent of added Cr^{6+} spike recovered on parallel sample analysis.

chemical state information is available directly from this technique (*13*).

Experimental Section

Materials. The primary dust samples for this study were taken from the hopper catch of a positive pressure baghouse serving several electric arc ferroalloy furnaces. These furnaces were used to melt ores containing 40–50% Cr and burnt lime to produce low carbon ferrochrome. In addition to Cr, these chromite type ores contain Fe, Al, and Si, as oxides. The dust was collected in 5-gal plastic containers, mixed by shaking, and then stored in smaller batches in screw-cap polyethylene bottles. This dust served as the principal sample for this study and was analyzed extensively by each of the analytical techniques. Particles from this site were also collected in size-resolved fractions by way of an in-stack Andersen Mark III cascade impactor, placed at the entrance of one of the ferroalloy plant furnace baghouse collectors. The size-resolved particles were analyzed by wet chemical methods only.

In order to further evaluate the analytical methods developed in this study, dust samples were obtained from a second type of ferrochrome smelter. The smelter operated in a manner similar to the first but employed less lime. This dust (designated as smelter dust II) was collected and stored in the same manner as the primary dust sample but was analyzed by INAA, wet chemistry, and XPS only.

Methods. Wet chemical analysis was performed by PEDCo, Inc., using extraction and analysis procedures derived from EPA-approved methods (*14*) (Table I). The goals of the wet chemical analysis were to determine the total Cr content of the sample, the amount present as bioavailable Cr, and the fraction of bioavailable Cr present as Cr^{6+}. Extensive testing of acid and base extraction procedures, analysis methods, and sampling handling requirements were undertaken, verifying results by standard addition to monitor recovery efficiency and effects of Cr speciation. The wet chemical extraction procedure of choice (Table I, no. 11) provided information on Cr^{6+} content and gave the highest yield for acid/base-soluble Cr. This extraction technique utilized a basic solution of 3% Na_2CO_3–2% NaOH with heating to just below the boiling point for 30–45 min for the extraction of Cr^{6+}. To extract the remainder of the bioavailable Cr, an acidic solution of 1:1 H_2SO_4 and concentrated HF was used. The sample and solution were heated in a water bath to ensure dissolution before heating over a hot plate until SO_3 fumes were given off; after cooling the residue was extracted with 9 M H_2SO_4.

Analysis methods were chosen following the blind analysis of nine liquid samples, prepared to contain known concentrations of Cr^{6+} and/or Cr^{3+}, by personnel at PEDCo, EPA, and the Research Triangle Institute (RTI, Research Triangle Park, NC) using several analytical techniques (atomic absorption spectrometry, inductively coupled plasma atomic emission specrometry, pulse polarography, and colorimetric analysis). The techniques yielded similar results for total Cr and total Cr^{6+} in solution. However, the colorimetric procedure (method 7196) and the AA procedure (method 7190) were deemed preferable for eventual routine environmental monitoring applications due to lower costs and general availability to most analytical labs. In addition to wet chemical extraction approaches, a lithium borate fusion technique (ASTM D3682) was tried for total Cr (*15*).

The instrumental neutron activation analysis (INAA) was performed by the Trace Element Analysis group of the EPA in Research Triangle Park, NC. Samples of 10–40 mg of dust were irradiated for 4 h at a flux of 10^{13} neutrons/s and then allowed to decay for 10 days before counting for 700 s on a 25% efficiency Ge(Li) detector and/or a 38% efficiency high-purity Ge detector. All work was done in triplicate, with standardization being by two NBS chromium standards.

The SEM-EDX work was performed at RTI on an ETEC scanning electron microscope, equipped with a Kevex 5100 Si(Li) energy dispersive X-ray analyzer. Samples were prepared by lightly dusting particles onto a carbon paint coated carbon stub and then evaporatively coating with carbon to help reduce charging effects. Analysis was with a 20-kV electron beam with a 30° tilt.

The XPS was performed at the University of North Carolina on a Perkin-Elmer Physical Electronics Model 548 XPS-Auger spectrometer with a Mg Kα X-ray source. Data acquisition and reduction were handled by an inhouse built microcomputer based on the Intel Z-80 microprocessor (*16*). A low-resolution (100 eV analyzer pass energy) survey scan (0–1000 eV binding energy) was acquired for each sample to determine elemental composition. For quantitation and speciation purposes, higher resolution (25 or 50 eV pass energy) "window" scans (25 eV in width, scan rate of 1 eV/s) were then acquired for elements of interest. The Cr window was typically acquired by coaddition of 20 spectral scans of the Cr $2p_{3/2}$ and $2p_{1/2}$ photoelectron peaks (nominal binding energies of 576 and 581 eV, respectively).

For XPS sample preparation, a small portion of the dust was ground in an agate mortar and then burnished onto In foil. The aqueous extraction procedure used in conjunction with XPS entailed sonicating 1.0 g of dust in two 100-mL aliquots of doubly distilled deionized water for 15 min each. Following centrifugation to remove the solid residue, the two aliquots were mixed together to form a clear yellow pH 10 extract and then divided into two portions. To one portion was added 40 mL of spectral grade 2-propanol and 10 mL of ACS grade glacial acetic acid. This pH 4 solution was stirred and heated (<80 °C) for 18 h during which time the color changed from yellow to green. The reacted solution was then rotary evaporated to remove the excess 2-propanol and to reduce the volume to 10 mL of a cloudy green solution. Aliquots of this solution were removed and placed on In foil in a 100 °C oven and evaporated to dryness. The solid residue was analyzed by XPS. The nonreacted portion of the extract was also rotary evaporated to reduce its volume, and aliquots of the milky-yellow mixture were placed on both Al and In foils in a 100 °C oven to dry. The solid residues were analyzed by XPS.

Results and Discussion

Results of each analytical technique as applied to the primary dust sample will be discussed independently and then integrated to obtain an overview of the physiochemical aspects of Cr speciation in the ferrochrome smelter dust. Subsequently, the results from the application of the derived analytical procedures to smelter dust II will be presented and discussed.

INAA. Instrumental neutron activation analysis was performed on the initial primary dust sample, giving a value of 55 ± 2 mg/g (all uncertainties expressed as one standard deviation) total Cr for three randomly selected samples. Smelter dust which had been subjected to leaching by an alkaline solution (method 3060) followed by leaching with a 9 M H_2SO_4 solution (see Wet Chemistry) had a Cr concentration equivalent to 27.7 mg/g in the original sample. The INAA results, therefore, indicate that only about 50% of the total chromium is readily removed by harsh acid/base leaching conditions. As a working definition, this is considered to be the upper limit to the bioavailable Cr fraction.

Wet Chemistry. The lithium borate fusion method gave the highest yield for total Cr compared to the various wet chemical extraction techniques (48 mg/g). This value is within 13% of the total Cr concentration indicated by INAA. Because of sample alteration during fusion, no chemical state information was available. In addition, the fusion technique was deemed to be inappropriate for routine environmental total Cr analysis primarily due to the expense of sample preparation and the low recovery rates of added Cr^{6+} spikes (Table I).

Wet methods for the determination of total Cr (method 3020, method 3050, method 1310, and ASTM D3683; Table I) gave much lower concentration values than were obtained by fusion or INAA, indicating that these acid extraction techniques do not access all Cr species. This is expected as chromite ore is known to be particularly resistant to acid/base leaching (*17*). The acid extraction procedures also do not preserve speciation information, since oxidizable matrix components leached into solution during the extraction procedure can rapidly reduce Cr^{6+} to Cr^{3+} in an acidic medium.

Speciation information of Cr^{6+} was retained by a method 3060 alkaline extraction. For three replicate measurements 10.2 ± 0.1 mg/g of Cr^{6+} was detected in the alkaline leachate by colorimetric analysis. Standard addition and control sample experiments indicate that negligible Cr^{3+} is extracted during the alkaline leaching process. Colorimetric analysis is the analytical technique of choice for determining Cr^{6+} in alkaline solution, even though atomic absorption (AA) coprecipitation (method 7195) indicated higher concentrations of Cr^{6+} in alkaline extracts during control sample tests. Recovery rates of added Cr^{6+} spikes (Table I) indicate that the AA results are biased by matrix interferences, perhaps due to the high Na concentration in the alkaline extract.

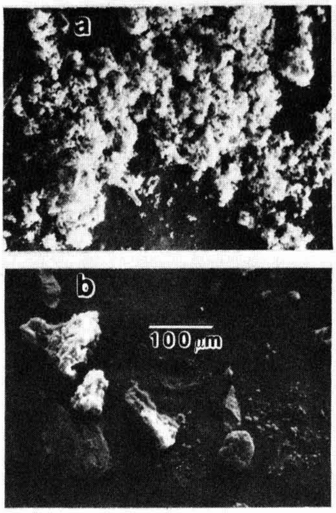

Figure 1. SEM micrographs of ferrochrome smelter dust before (a) and after (b) leaching with base followed by acid.

Following alkaline extraction, some of the Cr^{3+} and other acid-soluble Cr species were removed with the acidic solution of HF/H_2SO_4 followed by H_2SO_4. Three replicate samples yielded an average of 15.4 ± 0.7 mg/g of Cr, determined by flame AA (method 7190), bringing the total acid/base extractable Cr to 25.6 ± 0.7 mg/g for the three replicate samples, or 47% of the total Cr content found by INAA. This is in good agreement with the 50% value obtained directly by INAA. Similar results for total extractable Cr also were obtained by methods 3020 and 3050 and ASTM D3683 (Table I). Repeated leaching with the various extracting solutions was found to extract little additional Cr.

The total Cr extracted by acid and base reaction is considered to be the maximum amount of bioavailable Cr. Thus, of the total bioavailable Cr (25.6 mg/g), an estimated 42% is Cr^{6+} (10.2 mg/g) on the basis of wet chemical techniques.

SEM–EDX. Two samples were analyzed by SEM–EDX: the smelter dust and the smelter dust residue following leaching by both alkaline and acidic solutions. The smelter dust appears (Figure 1a) to contain two main types of particles: small (largely submicron) particles forming "fluffy" aggregates and large, angular particles. The aggregates dominate in number and contain mainly Si and Ca, with detectable amounts of S, Cr, and Fe. These smaller particles may be formed at least in part from a condensation of vapors containing S and Cr during the smelting process as well as from adsorption or reaction with $CaCO_3$ added to the ore mixtures. The enrichment of Cr on particle surfaces during high-temperature processes has been previously established by other methods (*18*). The larger, angular particles, however, contain primarily Cr,

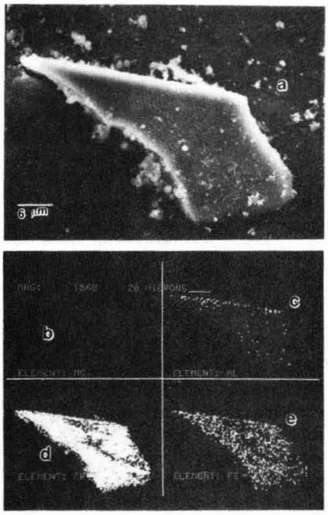

Figure 2. SEM micrograph (a) of unleached ferrochrome smelter dust and corresponding X-ray maps for (b) Mg, (c) Al, (d) Cr, and (e) Fe, showing correlations expected of chromite ore in the large particle.

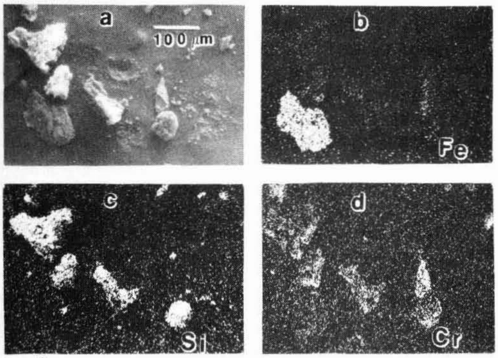

Figure 3. SEM micrograph (a) of ferrochrome smelter dust following base/acid leaching, and corresponding X-ray maps for (b) Fe, (c) Si, and (d) Cr.

Fe, Mg, and Al, as evidenced in the X-ray maps in Figure 2, and appear chemically more similar to chromite ore. Since several different types of Cr-containing ores may be used during the smelting procedure and each collected particle is subject to possible differences in its time–temperature history in the smelter, large variations in particle morphology and composition are expected. The samples which were alkaline/acid leached were highly depleted in the small particle aggregates (Figure 1b) relative to the unleached sample, suggesting that a large fraction of the bioavailable Cr is present in the smaller particles. Wet chemical analysis of size-resolved samples confirmed this point as will be discussed subsequently. In addition, some elements in some chemical forms, Fe in FeO (as found in chromite ore), for example, are preferentially extracted by the acid solutions (*17*), leaving the leached chromite particles enriched in Cr and Si, as suggested by the X-ray maps in Figure 3.

Table II. Estimated Surface Concentrations (Atomic Percents) of Elements Detected by XPS on Smelter Dust before and after Various Extraction Procedures

element	atomic %[a]			
	dust[b]	alkaline[c]	acid[d]	aqueous[e]
Al	7.8	4.7	ND[f]	8.8
C	10.8	16.5	9.2	24.0
Ca	4.4	4.4	3.5	6.7
Cr	2.4	ND	0.8	1.1
Cl	1.2	0.5	ND	0.5
F	1.3	0.5	ND	0.9
K	1.5	ND	ND	ND
Na	5.6	3.2	ND	ND
O	54.5	63.8	70.4	49.8
S	2.1	ND	5.0	0.3
Si	6.3	6.0	11.2	6.6
Zn	2.0	0.5	ND	1.2

[a] Atomic percents based on detectable elements adding up to 100%; quantitation using sensitivity factors of Wagner et al. (*21*). [b] Unleached smelter dust. [c] Alkaline leached (method 3060) smelter dust. [d] Smelter dust alkaline leached (method 3060), followed by acid leach (Table I). [e] Smelter dust leached by water (see Experimental Section. [f] Not Detected.

Table III. Elements Detected by XPS in Ferrochrome Smelter Dust, Including Their Binding Energies (BE, in eV) and Probable Chemical State

element[a]	BE, eV[b]	Chemical state
Al 2p	72.8	Al^{3+} as in Al_2O_3
C 1s	284.6	adsorbed hydrocarbons
	289.0	CO_3^{2-}
Ca $2p_{3/2}$	346.7	Ca^{2+}
Cl 2p	198.3	Cl^-
Cr $2p_{3/2}$	576–579	Cr^{3+}, Cr^{6+}
F 1s	684.2	F^-
K $2p_{3/2}$	292.6	K^+
Na 1s	1071.5	Na^+
O 1s	531.4	various oxides, carbonates, etc.
S 2p	168.9	SO_4^{2-}
Si 2p	101.8	Si^{4+} as in SiO_2
Zn $2p_{3/2}$	1021.9	Zn^{2+}

[a] Element identity and photoelectron line measured. [b] Spectra taken at 50 eV pass energy; all peaks charge corrected to C at 284.6 eV. Uncertainty in peak position estimated at ±0.2 eV, except for Cr which is in the range indicated with an uncertainty of ±0.2 eV for any specific compound.

XPS. The original smelter dust sample was analyzed by XPS as were samples subjected to alkaline leaching, alkaline/acid leaching, and aqueous leaching. As indicated in Table II, the extraction procedures alter the estimated surface region concentrations of various elements including Cr. Elements including the alkali metals (Na, K), halides (F, Cl), sulfur, and transition metals (Zn, Cr) appear preferentially leached from the surface during any of the various extraction procedures. (One exception is the acid-leached particles that apparently show artifactual deposition of surface sulfate from the acid solution upon drying.) The above behavior may reflect surface enrichment of more volatile elements as has been observed in depth profiling measurements of other high-temperature particle source emissions such as coal fly ash (*19*). Elements resistant to extraction in XPS studies (Table II) include Si, Al, and O which are expected to form relatively insoluble, nonvolatile components of bulk oxide phases. This behavior also is similar to XPS studies of coal fly ash (*19*). (One exception is the high extractability of Al in acid media consistent with enhanced Al_2O_3 solubility at lower pH.) Interpretation of the quantitative Ca and C results (Table II) is difficult in part because it involves the chemistry of $CaCO_3$ added to the chromite ore during smelting. Additional discussion of C results will be presented in a later section.

The photoelectron binding energies (BE) established by XPS for various detectable elements are listed in Table

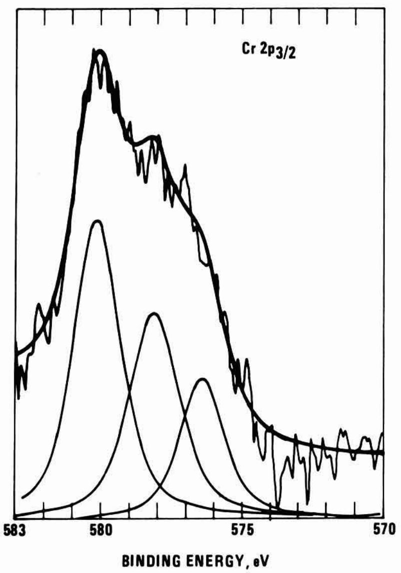

Figure 4. Three-component curve fit of Cr $2p_{3/2}$ photoelectron peak from spectrum of primary ferrochrome smelter dust. The three components represent (a) $Cr_2O_7^{2-}$ or CrO_4^{2-} at high binding energy, (b) CrO_3 or a Cr^{3+} salt such as $Cr_2(SO_4)_3$ at intermediate binding energy, and (c) Cr_2O_3 at low binding energy.

Table IV. Binding Energies (BE) of Some Standard Cr Compounds

compound	Cr $2p_{3/2}$ peak BE, eV
Cr metal[a]	575.0
Cr^{3+} oxide[a,b]	576.0–576.5
$CrCl_3$[b]	577.2–577.6
$Cr_2(SO_4)_3$[a]	578.6[c]
CrO_3[b]	578.1
$K_2Cr_2O_7$[a,b]	579.2–579.8
K_2CrO_4[b]	579.3

[a] Experimentally determined. [b] From handbook (*22*). [c] Broad peak (~3 eV in width) may reflect surface oxide contamination or the presence of hydrated salt species.

III. The measured BE corrected for any electrical charging (*19*) is an indication of a chemical state. Surface sulfur, for example, is present predominately in a sulfate state as is characteristic of many pollutant particles produced in high-temperature processes (*12*).

Of most interest in this study is the XPS indication of multiple oxidation states for Cr. Mathematical curve fitting by using a least-squares fit of Gaussian–Lorentzian line shapes (*20*) suggests, for eight replicate samples of the unleached dust, the presence of three main Cr components (Figure 4). Comparison of these binding energies to the peak positions of standard spectra (Table IV) suggests that the low BE component (576.3 ± 0.3 eV) is a Cr^{3+} oxide while the high BE component (579.6 ± 0.2 eV) is a $Cr_2O_7^{2-}$ or CrO_4^{2-} compound. The intermediate BE component (577.9 ± 0.4 eV) could be either the Cr^{6+} oxide CrO_3 or a Cr^{3+} salt species such as $Cr_2(SO_4)_3$. A more definitive identification of the chemical state of this Cr component required a concerted application of wet chemical and instrumental techniques as follows.

The Cr^{6+} oxides are water soluble, as are several hydrated Cr^{3+} salts, while Cr^{3+} oxides are not; therefore, an aqueous solution extract of the dust should contain only the two higher BE components of Cr. Since Cr^{6+} compounds are strong oxidants, reaction of the aqueous solution with an excess of a primary or secondary alcohol (*21*) should reduce the Cr^{6+} to Cr^{3+} (eq 1). If the reaction

$$2e^- + 4H^+ + 2\ R\text{–}CHOH\text{–}R + Cr_2O_7^{2-} \rightarrow 2\ R\text{–}C(=O)\text{–}R + Cr_2O_3 + 4\ H_2O \quad (1)$$

is done in aqueous solution, Cr hydroxide may also be produced; however, either product will result in a BE shift for the Cr^{6+} component in a solid residue of the solution extract to a lower BE. The fraction of leached components that contains a Cr^{3+} compound should not be affected by the alcohol, and the XPS BE in a solid residue of the solution extract should experience no shift.

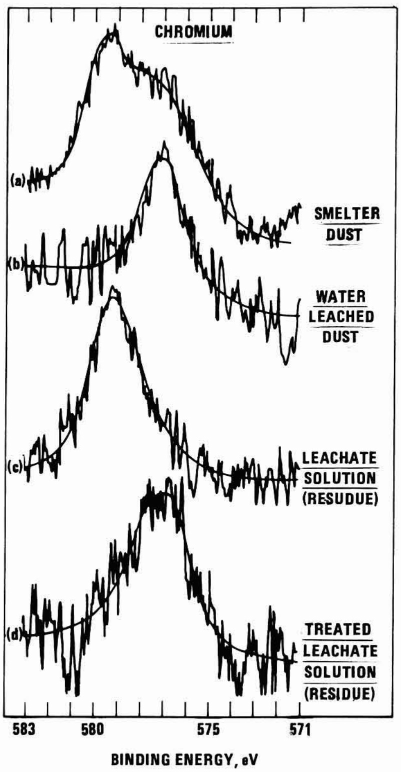

Figure 5. Cr $2p_{3/2}$ photoelectron peak for (a) the ferrochrome smelter dust initially, (b) the ferrochrome smelter dust following aqueous leaching, (c) the residue from the water leachate solution evaporated to dryness, and (d) the residue from the water leachate solution treated with 2-propanol/acetic acid and evaporated to dryness.

The results of this analysis are summarized in Figures 5 (data and calculated curve fits) and 6 (quantitative results derived from curve fits). The Cr $2p_{3/2}$ peak of the smelter dust is shown before (Figure 5a) and after (Figure 5b) extracting with water. The water-leached dust particles contain only a low binding energy Cr^{3+} oxide peak (BE = 576.3 eV) (Figure 6b), with the two higher BE components having been removed into the aqueous leachate (Figures 5c and 6c). Thus, the bioavailable Cr appears by XPS to include $Cr_2O_7^{2-}$, CrO_4^{2-}, and a possible CrO_3 and/or a soluble Cr^{3+} salt component such as $Cr_2(SO_4)_3$. When the leachate solution is treated with 2-propanol and acetic acid, the highest BE component (BE = 579.6 eV) decreases, leaving the intermediate 577.9 eV component relatively unchanged (Figures 5d and 6d). However, the low BE component is enhanced as the result of newly formed Cr^{3+} oxides or hydroxides. The relatively constant

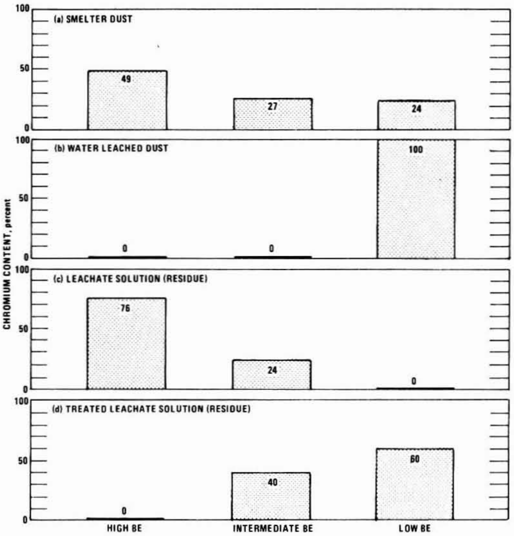

Figure 6. Percent Cr in each of the three chemical states as determined by curve fitting the Cr $2p_{3/2}$ photoelectron peak for (a) the ferrochrome smelter dust, (b) the ferrochrome smelter dust following aqueous leaching, (c) the residue from the water leachate solution evaporated to dryness, and (d) the residue from the water leachate solution treated with 2-propanol/acetic acid and evaporated to dryness.

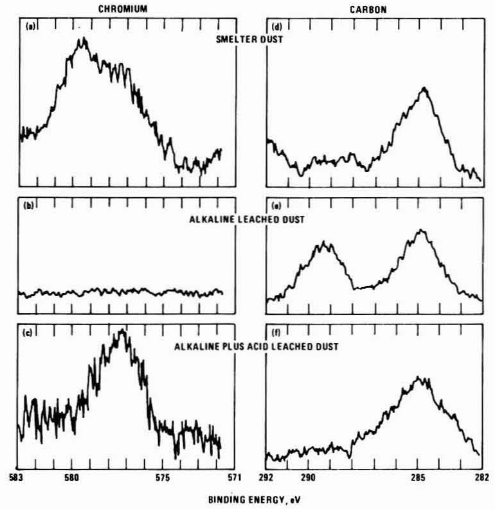

Figure 7. Photoelectron peaks for Cr and C in the ferrochrome smelter dust before and after base/acid leaching. The Cr $2p_{3/2}$ peak is shown for (a) the dust, (b) the dust following leaching by alkaline solution, and (c) the dust following alkaline and then acid leaching. The C 1s peak is shown for (d) the dust, (e) the dust following leaching by alkaline solution, and (f) the dust following alkaline and then acid leaching.

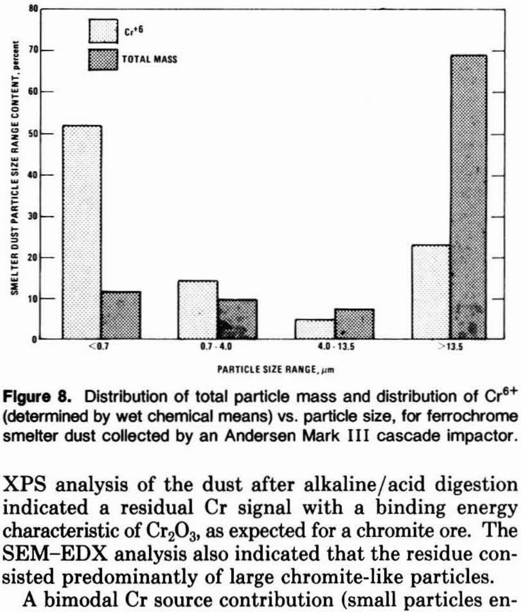

Figure 8. Distribution of total particle mass and distribution of Cr^{6+} (determined by wet chemical means) vs. particle size, for ferrochrome smelter dust collected by an Andersen Mark III cascade impactor.

contribution of the extractable component located near 578 eV (Figures 6c, 6d) helps to substantiate that it is not CrO_3 and is likely to be primarily from a soluble Cr^{3+} salt, perhaps $Cr_2(SO_4)_3$, in the primary dust sample.

Knowledge of the Cr oxidation state of the three components allowed the relative proportions of Cr^{6+} and Cr^{3+} to be estimated. From the curve fitting data for eight replicates of the original dust sample, it was determined that 41% (±8) of the estimated 2.4% surface region atomic concentration of Cr is Cr^{6+}. It is likely to be present as water-soluble $Cr_2O_7^{2-}$ and/or CrO_4^{2-} but not CrO_3.

Similar XPS studies of alkaline-extracted dust particles indicate the absence of detectable surface concentrations (part a vs. part b of Figure 7) of Cr. However, INAA suggests 73% of the total Cr is still present after alkaline extraction. This may reflect a surface enrichment of the alkaline-extractable Cr species on the dust particles. However, a concomitant increase in the atomic percent concentration of C (Table II) and a change in the C 1s peak shape (Figure 7d,e) indicate that there is a surface deposition of carbonate during the alkaline extraction workup procedure. The surface carbonate may attenuate the Cr photoelectron signals from underlying layers. Indeed, leaching with acid removes the carbonate (Figure 7f), exposing some detectable Cr (0.8% atomic) present predominantly at the Cr^{3+} oxide BE (Figure 7c). This is consistent with residual chromite type particles which apparently comprise much of the Cr that is not bioavailable.

Intertechnique Correlations. Chromite ore is known to be resistant to acid or base extractions (*17*). Therefore, the Cr within the chromite ore is largely inaccessible by standard acid/base wet chemical extraction methods, and chromite-like particles in the smelter dust are not bioavailable. The Cr obtained by wet chemical extractions originates primarily from the small, flocculent particles (as determined by SEM of unextracted and extracted dust particles) and accounts for only about 47% of the total chromium (measured by INAA). In qualitative agreement, XPS analysis of the dust after alkaline/acid digestion indicated a residual Cr signal with a binding energy characteristic of Cr_2O_3, as expected for a chromite ore. The SEM–EDX analysis also indicated that the residue consisted predominantly of large chromite-like particles.

A bimodal Cr source contribution (small particles enriched in bioavailable Cr^{6+} and large chromite-like particles containing primarily insoluble Cr^{3+}) is supported by the results of wet chemical analysis performed on size-resolved dust particles. Although particles less than 10 μm in diameter comprise only 28% of the total particle mass, over 75% of the total Cr^{6+} comes from particles in this size range (Figure 8). Furthermore, 55% of the Cr^{6+} detected is concentrated in particles less than 0.7 μm in diameter, which comprise only about 12% of the total particle mass. It is apparent that the small soluble particles and aggregates resulting from the smelting process contain the majority of the Cr^{6+}.

Wet chemical manipulations coupled directly to XPS lead to the identification of the three Cr components: Cr^{6+}

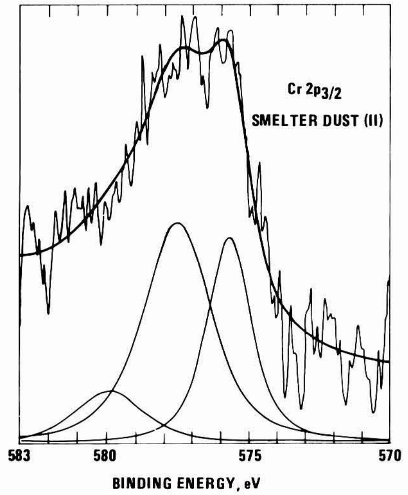

Figure 9. Three-component curve fit of Cr $2p_{3/2}$ photoelectron peak from spectrum of smelter dust II. The three components represent (a) $Cr_2O_7^{2-}$ or CrO_4^{2-} at high binding energy, (b) Cr^{3+} salts such as $Cr_2(SO_4)_3$ at intermediate binding energy, and (c) Cr_2O_3 at low binding energy.

oxide ($Cr_2O_7^{2-}$ or CrO_4^{2-}, but not CrO_3), Cr^{3+} salts (such as $Cr_2(SO_4)_3$), and Cr^{3+} oxide (Cr_2O_3). The Cr^{6+} was estimated by curve fitting to be 41% of the total detectable surface Cr. The above value is similar to the value of 42% of bioavailable Cr being Cr^{6+} determined solely by wet chemical acid/base extraction techniques. However, it should be stressed that these two values should not necessarily agree, as they are derived from different analytical volumes within the sample. While wet chemical extractions access the soluble fraction of the smelter dust made up principally of the small particle fraction, XPS analyzes only the surface layer (50 Å) of all particles irrespective of size. The similarity of the XPS and wet chemical results for the Cr^{6+} fraction does suggest that the bioavailable Cr is confined largely to particle surfaces and/or to the soluble small particle fraction. Analogous to the results of the wet chemical extractions, XPS will derive a high percentage of the total analytical signal from the small particle fraction. This is the consequence of the fact that the smaller particles predominate in number and have much larger apparent surface area to volume ratios as was shown qualitatively by SEM (Figure 1). In short, the small particles probably contribute a very large percentage of the total surface area sampled by XPS. Although the wet chemical extractions and XPS studies are, in principle, measuring different analytical volumes, the agreement in the above results suggests that the XPS experiment is sampling the particles in a manner that reflects the total Cr^{6+} contribution to the total bioavailable Cr. The disappearance of detectable Cr^{6+} in XPS studies of water-extracted smelter dust substantiated that Cr^{6+} present as $Cr_2O_7^{2-}$ or CrO_4^{2-} is bioavailable.

Smelter Dust II. To test the utility of the above analytical regimen, a second Cr source was characterized. Ferrochrome smelter dust II was found to contain more total Cr (109 ± 8 mg/g, by INAA) but less Cr^{6+} (4.30 ± 0.03 mg/g, colorimetric analysis, and 4.31 ± 0.06 mg/g, AA) than the primary dust sample. In addition, the amount of total extractable Cr (36 ± 1 mg/g) was a smaller percent of the total Cr (33%) and included a smaller percentage of Cr^{6+} (12%) than was found in the primary smelter dust. The lower relative concentration of Cr^{6+} was substantiated by XPS, as curve fitting showed 13% of the surface Cr to be Cr^{6+} (for a single determination). Although a low signal-to-noise ratio hinders analytical precision for the minor Cr^{6+} component (Figure 9), the answer obtained by XPS is again close to the wet chemical results for Cr^{6+}. This is a further indication that the two techniques measure closely related analytical volumes. Further research is required to evaluate the general utility of the above techniques for determining the concentration and speciation of bioavailable Cr in other Cr-containing environmental particles.

Acknowledgments

We thank members of the Trace Element Analysis section of the EPA for their work on the INAA and Peter Ingram, Research Triangle Institute, Research Triangle Park, NC, for the SEM–EDX analysis. In addition, thanks go to the personnel of PEDCo, Inc., for the wet chemical analysis work.

Registry No. Cr_2O_3, 1308-38-9; Cr, 7440-47-3; Al, 7429-90-5; C, 7440-44-0; Ca, 7440-70-2; Cl_2, 7782-50-5; F_2, 7782-41-4; K, 7440-09-7; Na, 7440-23-5; O_2, 7782-44-7; S, 7704-34-9; Si, 7440-21-3; Zn, 7440-66-6; ferrochrome, 11114-46-8.

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Environmental Implications of Methylation of Tin(II) and Methyltin(IV) Ions in the Presence of Manganese Dioxide

Spyridon Rapsomanikis and James H. Weber*

Chemistry Department, University of New Hampshire, Durham, New Hampshire 03824

■ This paper examines formation of mono-, di-, tri-, and tetramethyltin compounds from aqueous Sn(II) and relates the processes to possible environmental ones. Factorially designed experiments allowed us to understand separate and combined effects of a dimethylcobalt complex carbanion donor, the carbocation donor iodomethane, and oxidizing agent manganese dioxide. The following are the range of yields: monomethyltin ions, 0–14.4%; dimethyltin ion, 0.8–8.8%; trimethyltin ion, 0–2.65%; tetramethyltin, 0–3.32%; total methyltin compounds, 0–20.5%. Results of the experimental design clarify the role of each reactant and verify various methylation mechanisms. This research also includes studies on the formation of tetramethyltin in 7.3–36.7% yields from reactions of the dimethylcobalt carbanion donor with mono-, di-, and trimethyltin ions.

Introduction

A large increase in the use of organotin compounds from 5500 tons in 1965 to 33 000 tons in 1980 (*1*) has initiated research into the fate of these compounds in the environment. Concern arises because of toxicity of lower alkyltins in comparison with their inorganic counterparts and higher alkyltin derivatives (*2*, *3*). For example, the oral LD_{50} (mg kg^{-1}) values for rats are 10 for Me_3SnCl, 9 for Et_3SnCl, 350 for Bu_3SnCl, and >4000 for Oct_3SnCl (*3*). Methylation of inorganic or partially alkylated tin compounds in the environment would produce more toxic species. Methyltin compounds occur in environmental fresh water, saline water, river water, rain water, tap water, and urine samples (*4*), in Canadian lake samples (*5*), in U.S. and German river and estuarine water samples (*6*), and various water, sediment, and organism samples (*7*). Relative concentrations of $MeSn^{3+}$, Me_2Sn^{2+}, and Me_3Sn^+ depend on the origin of the sample. Human production of methyltin compounds does not account for their ubiquitous presence in the environment (*6*).

Environmental methylation of tin may explain methyltin compound detection in natural water and sediment samples. Maguire (*8*) contributed to this conclusion by observing in freshwater sediments $(n\text{-}C_4H_9)_3(CH_3)Sn$ and $(n\text{-}C_4H_9)_2(CH_3)_2Sn$ moieties, which are unlikely to have an anthropogenic origin. Additional evidence for environmental methylation is transformation of $SnCl_4{\cdot}5H_2O$ to Me_2Sn^{2+} and Me_3Sn^+ (*9*) and Me_3SnOH to Me_4Sn (*10*) by estuarine sediments. Sediment sulfide content and biological activity influence the yields.

Environmental methylation of tin, which has two positive oxidation states, can proceed by diverse reactions. These include oxidative addition of carbocation (Me^+) donors, nucleophilic attack by carbanion Me^- donors, dismutation, and disproportionation. For clarity the following equations contain tin oxidation states, but not ionic charges. Divalent tin(II) can react with Me^+ and Me^- donors (eq 1 and 2). Methyltin(II) compounds can disproportionate into Sn(IV) and Sn(0) (eq 3 and 4). Resulting Sn^0 can react with Me^+ in two steps (eq 5). Furthermore, inorganic Sn(IV) reacts successively with $4Me^-$ and ultimately forms $Me_4Sn(IV)$ (eq 6). The mono-, di-, or trimethyltin(IV) species of eq 1, 3, 5, or 6 can dismutate as shown in eq 7–9.

$$\mathrm{Sn(II)} + \mathrm{Me}^+ \rightarrow \mathrm{MeSn(IV)} \qquad (1)$$

$$\mathrm{Sn(II)} \xrightarrow{\mathrm{Me}^-} \mathrm{MeSn(II)} \xrightarrow{\mathrm{Me}^-} \mathrm{Me_2Sn(II)} \qquad (2)$$

$$2\mathrm{MeSn(II)} \rightarrow \mathrm{Me_2Sn(IV)} + \mathrm{Sn}^0 \qquad (3)$$

$$2\mathrm{Me_2Sn(II)} \rightarrow \mathrm{Me_4Sn(IV)} + \mathrm{Sn}^0 \qquad (4)$$

$$\mathrm{Sn}^0 \xrightarrow{\mathrm{Me}^+} \mathrm{MeSn(II)} \xrightarrow{\mathrm{Me}^+} \mathrm{Me_2Sn(IV)} \qquad (5)$$

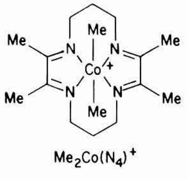
$$\mathrm{Sn(IV)} \xrightarrow[1]{\mathrm{Me}^-} \mathrm{MeSn(IV)} \xrightarrow[2]{\mathrm{Me}^-} \mathrm{Me_2Sn(IV)} \xrightarrow[3]{\mathrm{Me}^-} \mathrm{Me_3Sn(IV)} \xrightarrow[4]{\mathrm{Me}^-} \mathrm{Me_4Sn(IV)} \qquad (6)$$

$$2\mathrm{MeSn(IV)} \rightarrow \mathrm{Me_2Sn(IV)} + \mathrm{Sn(IV)} \qquad (7)$$

$$2\mathrm{Me_2Sn(IV)} \rightarrow \mathrm{Me_3Sn(IV)} + \mathrm{MeSn(IV)} \qquad (8)$$

$$2\mathrm{Me_3Sn(IV)} \rightarrow \mathrm{Me_4Sn(IV)} + \mathrm{Me_2Sn(IV)} \qquad (9)$$

Several laboratory experiments are pertinent to possible environmental formation of methylated tin compounds. Two groups (*11*, *12*) agree that reactions of Sn(II) with MeI form $MeSn^{3+}$, Me_2Sn^{2+}, and Me_3Sn^+ but disagree on formation of Me_4Sn. The first step of the reaction is eq 1, and other products probably occur by dismutation (eq 7–9). In addition methylcobalamin forms MeSn(IV) from Sn(II) in the presence of an oxidizing agent (*13*). Certain ligands also promote dismutation reactions of methyltin compounds (*11*, *14*). Related previous studies (*15*) show that in acetonitrile reaction of a dimethylcobalt Me^- donor with Pb(II) quantitatively forms Pb^0 and Me_4Pb (eq 2, step 4 with Pb(II)), and $Me_2Co(N_4)^+$



$Me_2Co(N_4)^+$

(in $Me_2Co(N_4)^+$, (N_4) is 2,3,9,10-tetramethyl-1,4,8,11-tet-

Table I. Experimental Design and Yields of Methyltin Compounds[a]

	variables[b]			% yield[c] (μg)				
expt	A	B	C	$MeSn^{3+}$	Me_2Sn^{2+}	Me_3Sn^+	Me_4Sn	total
1	+	+	+	3.4 (81)	3.7 (88)	1.0 (23)	0.6 (13)	8.6 (206)
2	+	+	–	1.0 (24)	3.7 (88)	1.0 (22)	0.6 (13)	6.2 (147)
3	+	–	+	5.0 (118)	8.8 (209)	2.6 (63)	1.6 (37)	18.0 (428)
4	–	+	+	7.4 (176)	0.3 (8)	0.0 (0)	0.0 (0)	7.7 (184)
5	+	–	–	0.0 (0)	3.6 (85)	1.9 (46)	3.3 (79)	8.9 (210)
6	–	+	–	0.0 (0)	0.0 (0)	0.0 (0)	0.0 (0)	0.0 (0)
7	–	–	+	10.7 (255)	0.3 (8)	0. (0)	0.0 (0)	11.0 (263)
8	–	–	–	0.0 (0)	0.0 (0)	0.0 (0)	0.0 (0)	0.0 (0)
9	0	0	0	8.2 (195)	2.8 (65)	0.9 (21)	0.7 (17)	12.6 (298)
10	0	0	0	13.6 (323)	4.6 (109)	0.8 (18)	0.7 (17)	19.7 (468)
11	0	0	0	8.8 (208)	4.4 (104)	0.8 (18)	0.8 (18)	14.7 (348)
12	0	0	0	14.4 (341)	4.8 (113)	0.6 (13)	0.7 (17)	20.5 (486)

[a] Each experiment contained 20 μmol of $SnCl_2$. [b] A = $[Me_2Co(N_4)^+]$ (μmol) at a level of 25(+), 12.5 (0) and 0(–). B = $[MnO_2]$ (μmol) at a level of 20(+), 10 (0), and 0(–). C = [MeI] (μmol) at a level of 80(+), 40 (0), 0(–). [c] Based on amount of $SnCl_2$ added.

raazacyclotetradeca-1,3,8,10-tetraene) quantitatively forms Me_4Pb from Me_3Pb^+ and Me_2Pb^{2+} in acetonitrile (eq 6, steps 3 and 4 with Pb(IV)). Other work by our group (*16*, *17*) shows that $Me_2Co(N_4)^+$ reacts with Pb(II) in water forming small amounts of Me_4Pb (eq. 2, step 4 with Pb(II)) and with Me_3Pb^+ and Me_2Pb^{2+} forming larger amounts of Me_4Pb (eq 6, steps 3 and 4 with Pb(IV)).

Previous results are incomplete, and uncertainty still exists about mechanisms of methyl transfer to Sn(II) or Sn(IV) species in aqueous media. Lack of knowledge includes laboratory and environmental processes, and extensive study of possible pathways is required. The present work emphasizes separate and combined effects of carbanion donor $Me_2Co(N_4)^+$ and carbocation donor MeI on methylation of Sn(II) in the presence or absence of the oxidizing agent MnO_2. Me_4Sn formation from reactions of $Me_2Co(N_4)^+$ with $MeSnCl_3$, Me_2SnCl_2, and Me_3SnCl was also determined. These reactions demonstrate the possibility of nucleophilic attack on Sn(IV) species (eq 6, steps 2–4) by naturally occurring carbanion donors and ultimate production of air-transportable, hydrophobic and toxic Me_4Sn. Such processes would complement dismutation reactions of Me_3Sn^+ (eq 9) induced by sulfide ion and oxygen-donor ligands (*11*, *14*).

Experimental Section

Materials. All reagents were obtained commerically and used without further purification unless otherwise stated.

Synthesis and Purification. The synthesis of $[Me_2Co(N_4)]ClO_4{\cdot}H_2O$ has been described previously (*17*), and its aqueous concentrations were determined with a Cary 219 UV–visible spectrophotometer (λ_{max} 436 nm; ϵ = 6800 cm^{-1} M^{-1}) (*17*). MnO_2 suspension in water was prepared according to a literature method (*18*). Dimethyltin dichloride was purified by high vacuum sublimation, and monomethyltin trichloride was purified by three successive recrystallizations from petroleum ether (bp = 60–110 °C).

Reactions. All reactions were carried out in darkness at room temperature by using 50-cm^3 aqueous solutions in 60-cm^3 vials sealed with "crimp on" Teflon-lined silicon rubber septa (Pierce Chemical Co.). Ionic strength of the reaction media was 0.1 M KCl. For the factorial experiments 0.100 mL of a 0.2 M $SnCl_2{\cdot}2H_2O$ stock solution in 2 M HCl containing tin shot was used. Concentrations of $Me_2Co(N_4)^+$, MeI, and MnO_2 are recorded in Table I. Reaction vials containing $SnCl_2$ were always adjusted to pH 7 and sealed under N_2 atmosphere after addition of the required reagents.

Table II. Yields of Me_4Sn from Mono-, Di-, and Trimethyltin Ions and $Me_2Co(N_4)^+$[a]

		Me_4Sn yields[b]	
methyltin ion	μmol added	μg of Sn	% yield
$MeSn^{3+}$	1.0	30	25.4
$MeSn^{3+}$	2.0	28	11.6
Me_2Sn^{2+}	1.5	26	14.7
Me_2Sn^{2+}	3.0	26	7.3
Me_3Sn^+	3.0	131	36.7
Me_3Sn^+	6.0	123	17.2

[a] All reactions contained 5.5 μmol of $Me_2Co(N_4)^+$. [b] Based on the amount of Sn added.

Experiments involving methylation of $MeSn^{3+}$, Me_2Sn^{2+}, and Me_3Sn^+ (Cl^- salts) by $Me_2Co(N_4)^+$ were carried out in similar fashion except that factorial experiments were not done. Table II contains also the concentration of reagents in micromoles.

Analyses. Head-space gases were analyzed after 3 h by sampling with a 0.5-cm^3 gas-tight syringe and injecting into a Varian 3700 gas chromatograph with flame ionization detector (GC–FID), coupled with a Hewlett-Packard 3990 peak area integrator. Quantitation of Me_4Sn was carried out by injecting head space of standards and comparing retention times and peak areas. After Me_4Sn was determined, the vials were opened and N_2 was bubbled through the solutions for 2 min to expel residual volatile CH_3I and Me_4Sn that interfered with analyses of Me_nSnH_{4-n} (n = 1–3). A 10-cm^3 aliquot from each vial was placed in a 120-cm^3 vial and diluted to 20 cm^3 after addition of 50 μL of 0.5 M tris(hydroxymethyl)aminomethane hydrochloride (Tris-HCl) buffer. Injection of 2 cm^3 of 1% w/v $NaBH_4$ through the septum produced volatile methyltin hydrides which were analyzed by sampling with a gas-tight syringe and injecting into the GC–FID. Quantitation of the hydrides was carried out by preparing standards containing the appropriate amount of each Me_nSnCl_{4-n} and treating them like the analyte samples.

Limits of detection for the above method (3σ) were established as 50, 40, 30, and 10μg L^{-1} for $MeSnCl_3$, Me_2SnCl_2, Me_3SnCl, and Me_4Sn, respectively. All analyte responses fell within linear calibration graphs of 0.5–10 mgL^{-1} standards. The graphs had linear correlation coefficients >0.98, and their goodness of fit was determined by using the χ^2 test. Linear regression, residuals, and analysis of variance of those graphs were computed by using the RS/1 package (BBN Research Systems) on a VAX computer. Relative standard deviations for center point analyses were the following: $MeSnH_3$, ±25%;

Me_2SnH_2, ±20%; Me_3SnH, ±15%; Me_4Sn, ±2%.

Adsorption and reactions of $Me_nSn^{(4-n)+}$ compounds on the surface of particulate matter may be one source of error because adsorption of $MeSn^{3+}$ is greater than Me_2Sn^{2+} which is greater than Me_3Sn^+ (*21*).

A glass column (1.8 m length, 4 mm i.d.) packed with 10% SP-2100 on Supelcoport 80–100 mesh W-AW-DMCS support, and a 30 cm^3 min^{-1} carrier gas flow rate were used for all analyses. The column oven was kept at 60 °C with the injection port and detector temperatures at 100 °C for Me_4Sn determinations. For Me_nSnH_{4-n} analyses the column oven was kept at 25 °C with the injection port and detector temperatures at 50 °C. With the above conditions retention times were the following: $MeSnH_3$, 1.46 min; Me_2SnH_2, 2.82 min; Me_3SnH, 5.50 min; Me_4Sn, 3.03 min.

Experimental Design

We used a factorial experimental design to investigate the effect of three-independent variables on methylation of $SnCl_2$. This design, which also measures the effect of all possible combinations of variables, requires 2^3 experiments plus four replicate center points. Center point experiments contain all three variables at half reagent concentrations (Table I) for measurement of random error. Estimation of the statistical effect of each variable and variable interaction is carried out by analysis of variance (ANOVA) calculations and by comparing variable F values to the F value of random error at the 95% confidence level (*19, 20*). All above calculations were carried out utilizing a custom made computer program ("TABGEN") incorporated in the RS/1 package, but for reasons of clarity only their interpretations are discussed.

Variables in this study are a carbanion donor ($Me_2Co(N_4)^+$), a carbocation donor (MeI), and an oxidizing agent (MnO_2). Their separate and combined effects facilitates the examination of several pathways possible for environmental methylation of tin. These include oxidative addition reactions of Sn(II) by naturally occurring Me^+ donors (eq 1) followed by Me^- donation (eq 6, steps 2–4) or by oxidation of Sn(II) to Sn(IV) followed by Me^- donations (eq 6, all steps). Thus, the above experiments model processes for environmental methylation of tin. Sn(II) concentrations are as low as possible for detection of $MeSnH_3$, Me_2SnH_2, Me_3SnH, and Me_4Sn by GC–FID. The solubility of $[Me_2Co(N_4)]ClO_4{\cdot}H_2O$ limits its maximum concentration to 0.5 mM.

Results

Reactions of Sn(II) in Factorial Experiment. Table I summarizes the results of reactions of $SnCl_2$ in the factorial experiment containing methylating agents $Me_2Co(N_4)^+$ and MeI and MnO_2. Yields of products were calculated as percentage Sn converted to $MeSn^{3+}$, Me_2Sn^{2+}, Me_3Sn^+, Me_4Sn, and total methyltin products. In some cases the limiting reagent was $Me_2Co(N_4)^+$, and yields could be based on the percentage methyl transfer from it. However, such treatment would complicate interpretation of the rest of the results.

Yields of $MeSn^{3+}$ are zero or nearly so when MeI is absent and are generally highest in center point experiments. Comparison of experiments 1 and 3, for example, demonstrates that MnO_2 decreases $MeSn^{3+}$ yields. A similar decrease occurs for all methyltin products in the presence of MnO_2.

As expected in sequential reactions, relative yields are generally: $MeSn^{3+} > Me_2Sn^{2+} > Me_3Sn^+ > Me_4Sn$. In most cases Me_2Sn^{2+} yields are highest with the center points. An exception with an 8.8% Me_2Sn^{2+} yield (experiment 3) occurs with high concentrations of $Me_2Co(N_4)^+$ and MeI in the absence of MnO_2. With few exceptions yields of Me_3Sn^+ and Me_4Sn are less than 1%.

Total yields for conversion of $SnCl_2$ to methyltin compounds ranges from 0% (experiments 6 and 8, no methylating agent) to 13–20% (experiment 3, center points). In all cases the highest yields occur in the presence of both Me^+ (MeI) and Me^- ($Me_2Co(N_4)^+$) donors.

Reactions of Methyltin Ions with $Me_2Co(N_4)^+$. Table II contains Me_4Sn yields from reactions of $MeSn^{3+}$, Me_2Sn^{2+}, and Me_3Sn^+ with $Me_2Co(N_4)^+$. Each methyltin ion reacts with $Me_2Co(N_4)^+$ in approximate Co/Sn molar ratios of 1/1 and 2/1. Percent yields of Me_4Sn are 14.7–36.7% for 1/1 reactions. In each case the percent yield for the 2/1 reaction is about double that of the 1/1 reaction for the same methyltin ion. Significant amounts of CH_4 also form in these experiments.

Discussion

Results of the factorial experiments are discussed by comparing the effect of one variable in the presence or absence of a second variable (e.g., effect of MeI in the presence or absence of MnO_2) on the production of each methyltin compound. Consideration of combined effects of two variables in the presence or absence of a third variable (e.g., effects of $Me_2Co(N_4)^+$ and MeI in the presence or absence of MnO_2) on the production of each methyltin compound follows the initial discussions.

Effect of MeI on Production of Methyltin Compounds. Comparison of yields of methyltin compounds in experiment 7 with MeI alone to ones containing MeI and MnO_2 (experiment 4) or MeI and $Me_2Co(N_4)^+$ (experiment 3) adds considerably to our understanding of mechanisms involved. Consider first the effect of MnO_2. The yield of $MeSn^{3+}$ is 10.7% in the absence of MnO_2 (experiment 7) and 7.4% in its presence (experiment 4). The probable reason for decreased yield in the presence of MnO_2 is absorption of Sn(II) on its surface, as observed in analogous Pb(II) experiments (*17*). Experiments in the presence of $Me_2Co(N_4)^+$ and the absence of MnO_2 are similarly enlightening. The presence of $Me_2Co(N_4)^+$ and MeI (expt. 3) greatly decreases $MeSn^{3+}$ yields. The larger 7.4% yield in the absence of $Me_2Co(N_4)^+$ compared to 5.0% in its presence is due to further methylation of MeSn(IV) by a Me^- mechanism (eq 6).

MnO_2 does not play a significant role in Me_2Sn^{2+} production because yields are 0.3% both in its presence (experiment 4) and in its absence (experiment 7). The presence of $Me_2Co(N_4)^+$ along with MeI (experiment 3) increases the Me_2Sn^{2+} yield to 8.8% as a consequence of step 2 in eq 6. The Me_2Sn^{2+} formed in experiment 7 may originate from dismutation of $MeSn^{3+}$ (eq 7) formed after the oxidative addition of MeI to Sn(II) (eq 1).

Similar arguments apply to the effect of MeI on Me_3Sn^+ and Me_4Sn yields. The above compounds are not formed in the presence of MeI alone because the Me^- donor $Me_2Co(N_4)^+$ is necessary to react with the MeSn(IV) initial product. The combined presence of MeI and $Me_2Co(N_4)^+$ (experiment 3) results in significant Me_3Sn^+ and Me_4Sn yields from reaction 1 followed by reaction 6 (steps 3 and 4).

The absence of MnO_2 enhances total methyltin yields. This result is evidence in experiments 4 and 7. Total yields are 11.0% in the absence of MnO_2 (experiment 7) and 7.7% in its presence (experiment 4). This effect occurs because of decreased methylation of Sn(II) in reaction 1 due to its adsorption on MnO_2.

Effect of $Me_2Co(N_4)^+$ on Production of Methyltin Compounds. Yields of methyltin compounds in the presence of $Me_2Co(N_4)^+$ alone (experiment 5) are affected by the presence of MeI (experiment 3) or of MnO_2 (experiment 2). $MeSn^{3+}$ production in the presence of $Me_2Co(N_4)^+$ alone (experiment 5) is zero because reaction 2 followed by reactions 3 and 4 of Me^- donation does not result in formation of $MeSn^{3+}$. Increased yield of 1.0% in the presence of both $Me_2Co(N_4)^+$ and MnO_2 (experiment 2) may be due to oxidation of Sn(II) to Sn(IV) followed by methylation by $Me_2Co(N_4)^+$ (eq 6, step 1). The presence of MeI and $Me_2Co(N_4)^+$ increases the yield of $MeSn^{3+}$ more dramatically to 5.0%, indicating that oxidative addition of Sn(II) by MeI (eq 1) occurs prior to Me^- donation (eq 6).

Comparison of Me_2Sn^{2+} yields in the absence (experiment 5, 3.6% yield) and presence (experiment 2, 3.7% yield) of MnO_2 indicates that the latter compound has little effect. Me_2Sn^{2+} formed in experiment 2 may be due to methylation of $MeSn^{3+}$ by $Me_2Co(N_4)^+$ (eq 6, step 2), while that in experiment 5 may result from $MeSn^+$ disproportionation (eq 3).

The reaction of $Me_2Co(N_4)^+$ with Sn(II) in the presence of MnO_2 (experiment 2) has a lower 1.0% Me_3Sn^+ yield than in its absence (experiment 5, 1.9% yield). In contrast the presence of MeI (experiment 3) results in a higher 2.6% yield than its absence (experiment 5, 1.9% yield). The decreased Me_3Sn^+ yield in the presence of MnO_2 is due to Sn(II) adsorption, while the enhanced yield due to MeI results from oxidative addition of Sn(II) (eq 1) and subsequent methylation by $Me_2Co(N_4)^+$ (eq 6, steps 2 and 3). The 3.3% Me_4Sn yield from $Me_2Co(N_4)^+$ alone (experiment 5) is greater than those in the presence of MeI (experiment 3, 1.6%) or MnO_2 (experiment 2, 0.6%). This result shows the importance of reaction 2 (both steps) followed by reaction 4. Again the yield is enhanced by MeI relative to MnO_2, showing that oxidative addition is more effective than MnO_2 oxidation in forming Sn(IV) species.

The total methyltin yield is a dramatic 18.0% in the presence of $Me_2Co(N_4)^+$ and MeI (experiment 3), but only 6.2% with $Me_2Co(N_4)^+$ and MnO_2 (experiment 2). The 18.0% yield occurs because of the synergic effect of Me^+ and Me^- donors. Presumably oxidative addition by MeI preceeds Me^- donation from $Me_2Co(N_4)^+$. The lower 8.9% yield (experiment 5) for $Me_2Co(N_4)^+$ alone emphasizes the importance of oxidative addition before Me^- transfer.

Combined Effect of MeI and $Me_2Co(N_4)^+$ on Production of Methyltin Compounds. The combined effect of MeI and $Me_2Co(N_4)^+$ in the presence (experiment 1) and absence of MnO_2 (experiment 3) shows that MnO_2 decreases yields of all methyltin species. MnO_2 decreases yields by a factor of 2–3 because of Sn(II) adsorption.

Combined Effect of MeI and MnO_2 on Production of Methyltin Compounds. Experiments 1 and 4 allow comparison of the combined effect of MeI and MnO_2 in the presence and absence of $Me_2Co(N_4)^+$. Enhanced $MeSn^{3+}$ formation in the absence of $Me_2Co(N_4)^+$ (experiment 4) occurs because $MeSn^{3+}$ formed by oxidative addition of MeI to Sn(II) (eq 1) reacts little by eq 7 to form Me_2Sn^{2+} while in the presence of $Me_2Co(N_4)^+$ (experiment 1) Me^- transfer to $MeSn^{3+}$ is significant (eq 6, step 2). In the absence of $Me_2Co(N_4)^+$ the yields of Me_3Sn^+ and Me_4Sn are zero and that of Me_2Sn^{2+} decreases from 3.7% (experiment 1) to 0.3% (experiment 4). These results demonstrate that Me^- transfer reactions (eq 6), not dismutation (eq 7–9), are the main route for di-, tri-, and tetramethyltin formation. The exception of enhanced $MeSn^{3+}$ formation in the absence of $Me_2Co(N_4)^+$ occurs because $MeSn^{3+}$ formed by oxidative addition of Sn(II) in the absence of $Me_2Co(N_4)^+$ reacts little by eq 7 to form Me_2Sn^{2+}. In contrast Me^- transfer from $Me_2Co(N_4)^+$ to $MeSn^{3+}$ is significant (eq 6, step 2).

Combined Effect of $Me_2Co(N_4)^+$ and MnO_2 on Production of Methyltin Compounds. Me I presence (experiment 1) or absence (experiment 2) in experiments containing $Me_2Co(N_4)^+$ and MnO_2 usually does not appreciably affect methyltin compound yields. Similar results in the absence or presence of MeI demonstrate that it does not play a significant role in Me_2Sn^{2+}, Me_3Sn^+, or Me_4Sn formation when MnO_2 is present. MeI plays an important role in the absence of MnO_2 because the latter compound strongly decreases oxidative addition reactions to Sn(II). $MeSn^{3+}$ yield is only enhanced by the oxidative addition reactions of MeI to Sn(II) (eq 1).

Reactions of Methyltin Ions with $Me_2Co(N_4)^+$. Experiments 1 and 3 (Table I) strongly suggest that $MeSn^{3+}$ formed by oxidative addition of Sn(II) by MeI reacts with $Me_2Co(N_4)^+$ by Me^- transfer to form significant but decreasing amounts of Me_2Sn^{2+}, Me_3Sn^+, and Me_4Sn. Reactions of methyltin ions with $Me_2Co(N_4)^+$ (Table II) confirm this mechanism. Table II contains yields of Me_4Sn formed from methyltin ions by reactions having approximately 2/1 or 1/1 Co donor/Sn acceptor molar ratios. Significant amounts of CH_4 also form in these experiments. In all cases reactions with 2-fold $Me_2Co(N_4)^+$ excess result in about double the yields of the 1/1 reactions. The explanation for this result is not clear but may originate from relative rates of competitive reactions. In second-order kinetics doubling the concentration of $Me_2Co(N_4)^+$ would double the rate of that path, allowing it to compete with the CH_4 side reaction.

Also puzzling are the relative Me_4Sn yields from the methyltin ion reactants: $Me_3Sn^+ > MeSn^{3+} > Me_2Sn^{2+}$. The mixed trend suggests that different factors favor Me_4Sn formation from Me_3Sn^+ and from $MeSn^{3+}$. Continuing work on this system will further clarify the results.

Conclusions

Table I describes the separate effect of any variable or the combined effect on any combination of variables on the percentage yield of each methyltin compound. Hence, it is possible to explain the mechanism and the role a Me^+ donor, Me^- donor, and oxidizing agent may play in cycling Sn(II) in the environment. Oxidative addition reactions with MeI in the absence of $Me_2Co(N_4)^+$ produce mainly $MeSn^{3+}$ and to a lesser extent Me_2Sn^{2+}, Me_3Sn^+, and Me_4Sn by dismutation or disporportionation reactions. When $Me_2Co(N_4)^+$ is present, successive Me^- transfer steps produce Me_2Sn^{2+}, Me_3Sn^+, and Me_4Sn. Transfers of Me^- to Sn(II) or Sn(IV) oxidized on the surface of MnO_2 form all methyltin products except $MeSn^{3+}$ in the absence of MnO_2. Diminished yields of all products occur from adsorption of Sn(II) on the MnO_2 surface, and combination of MeI and $Me_2Co(N_4)^+$ produces highest yields of methyltin products. These results are important for a better understanding of environmental processes because a Me^- donor methylcobalamin, Me^+ donors MeI and betaines, and oxidizing agents such as MnO_2 are all present.

Preliminary results on the methylation of $MeSn^{3+}$, Me_2Sn^{2+}, and Me_3Sn^+ indicate the possibility of Me^- transfer to them by a naturally occurring donor such as methylcobalamin. This process would form volatile Me_4Sn and account for the worldwide presence of methyltin compounds (*6*).

Acknowledgments

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Registry No. $Me_2Co(N)_4{}^+ClO_4$, 77310-45-3; $MeSn^{3+}$, 16408-15-4; Me_2Sn^{2+}, 16408-14-3; Me_3Sn^+, 5089-96-3; Me_4Sn, 594-27-4; MnO_2, 1313-13-9; MeI, 74-88-4; Sn, 7440-31-5.

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Contemporary Lake Transport Processes Determined from Sedimentary Records of Copper Mining Activity

William Davison, John Hilton,* Jean P. Lishman, and Winifred Pennington[†]

Freshwater Biological Association, The Ferry House, Far Sawrey, Ambleside, Cumbria LA22 0LP, England

■ In the recent past (ca. 1850) copper was mined in the catchment of Coniston Water in the English Lake District. Chemical analysis of sediment cores shows a clear record of this activity. Although the mining effluent entered the lake at one place, elevated concentrations of Cu, Fe, Mg, and Ca were observed at all five sites investigated, showing the domination of random transport processes in distributing sediment material. Other effects such as progressive downstream settling, which play a minor but significant role in the local copper loading, are identified. A constant excess Cu:S ratio of 2:1 indicated that Cu is present in the sediments as chalcopyrite and that it was transported from the mine workings in particulate form. Mn accumulation is mediated by redox processes, and so the final concentration in the sediment depends on the depth of the overlying water and the availability of organic carbon.

Introduction

Coniston Water, which is situated in a rural part of the English Lake District (Figure 1), occupies a glacially excavated basin in Silurian Slate bedrock. It has a maximum depth of 56 m and a mean depth of 24 m (*1*), and from flow data (unpublished results) the mean residence time of the water is estimated to be 0.75 year. Although the water of the lake is of high quality and shows no signs of pollution, historical records (*2*) show that copper was extracted from the catchment from the 17th century onward, with production increasing dramatically to a maximum in the mid-19th century, causing gross pollution of the lake and streams during the latter period. The sediments of the lake should have retained a record of this anthropogenic activity. We have performed detailed chemical analysis of sediments to provide information about the nature of the residual pollutants and the transport processes involved in transferring material to the sediment.

All the mines were concentrated to the north of the village of Coniston (Figure 1), and the Bonser vein, which has been well studied (*3, 4*), provided the main source of ore in this area. Because washings from the mine could only enter the lake at one point, examination of the sediments at different locations in the lake allowed us to assess whether the effects of pollution were localized or widespread. This spatial information was complemented by good temporal resolution. The input of copper occurred over a discrete (10–20-year) period of time so that the resulting well-defined distribution of copper in several sediment cores could be used to provide information about the sedimentation processes at work in the lake.

Materials and Methods

Sediment samples were taken at the five sites indicated in Figure 1 by using a 1-m Mackereth corer (*5*). This pneumatically operated piston corer collects undisturbed samples of sediment. Dating by ^{137}Cs and examination of the annual variations in diatom assemblages has shown that recent annual laminations of near surface sediments are preserved intact (*6, 7*). Core 2 was collected in 1978, core 1 was collected in 1979, and cores 3–5 were collected in 1980. Although the cores were sliced at 1-cm intervals, some slices were recombined prior to chemical analysis. A sample of ore washings was taken from the disused settlement tanks of the Bonser Lower Mill (*2*).

[†] Present address: School of Biology, University of Leicester, Leicester LE1 7RH, England.

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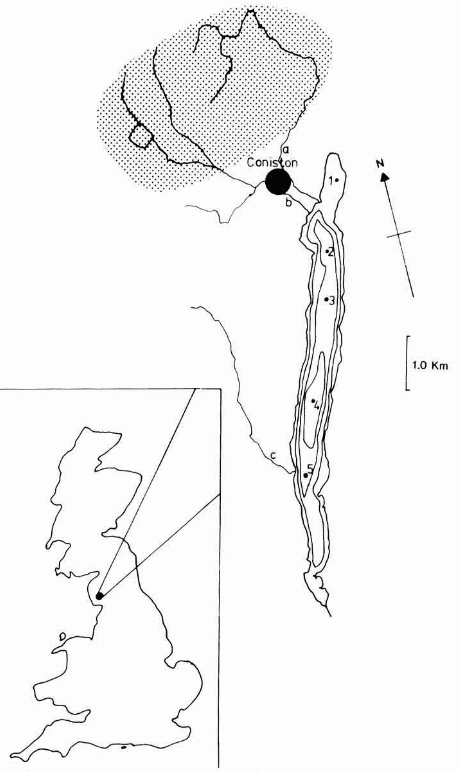

Figure 1. Location of sampling sites on Coniston Water. The shaded area encloses the copper mining region. a = Yewdale Beck; b = Church Beck; c = Torver Beck. Depth contours in 50-ft intervals after Mill (*19*).

CHN concentrations were measured on the dry solids by using a Hewlett-Packard F and M CHN analyzer. Total sulfur analyses were carried out by Carlo Erba using a 1106 elemental analyzer. Cu, Fe, Mg, Ca, and Mn concentrations were obtained on a Perkin-Elmer 303 atomic absorption spectrophotometer after hydrofluoric–perchloric digestion of the dry solid. X-ray diffraction analyses (XRD) were carried out on a Phillips PW1730 instrument at the University of Lancaster. Core 1 was dated by a combination of radiochemical and pollen analysis techniques (*8*).

Results

Stratigraphy. All the cores show the typical features of Lake District sediments (*9*), namely, a 1–2-cm flocculent brown surface layer overlying 10–15 cm of soft black sediment. Below this are dark brown detrital muds. Coniston Water is unusual in having a layer of gray sediment between the black and brown layers. This gray layer, which is 10–15 cm thick, has a low water content, a low carbon content, and a high density (i.e., dry weight per unit volume of wet sediment).

Dating and Environmental History: Core 1. Figure 2 shows the evidence on which the distinct gray layer in the sediments was dated to the period of maximum activity of the copper mines. Changes in the vegetation of the catchment, for which historical records exist, can be recognized in the changing pollen content of these recent sediments (Figure 2). The distribution patterns of ^{137}Cs and unsupported ^{210}Pb, determined at AERE Harwell, provided a depth–time scale for the sediments above the gray layer. ^{210}Pb data were interpreted by using the constant initial concentration (c.i.c.) model (*10, 11*). Approximate dates for the sediments below a depth of 20 cm (Figure 2) were derived from a curve linking the ^{210}Pb depth–time scale that for sediments below a depth of 1 m, provided by 10 ^{14}C dates (SRR-1870 to -79) (as yet unpublished).

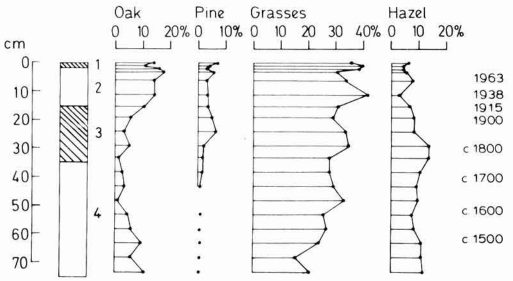

Figure 2. Dating of core 1. Pollen chronology (four selected pollen taxa), sediment stratigraphy, and approximate calendar dates from ^{137}Cs, ^{210}Pb, and ^{14}C measurements. (1) Flocculent oxidized surface layer; (2) black soft sediment; (3) firm gray sediment; (4) dark brown fine-detritus mud. Pollen values are percentages of total pollen.

Historical dates inferred from the pollen chronology are consistent with the radionuclide time scale. The increasing values for oak pollen from the horizon dated to the first decade of the present century reflect the replacement by mature oak woodland (producing much pollen) of former coppices which were cut for charcoal production every 15 years (and so produced much less oak pollen). The inverse correlation with the curve for hazel pollen reflects the same change, since the shrub flowers more freely in coppice than when shaded by mature oaks. Many pine trees were planted locally during the eighteenth century, and its pollen values appear and expand at the corresponding date on the radionuclide time scale. The minimum values for oak and maxima for pollen of grasses and cultivated cereals, which on this time scale fall between ca. A.D. 1500 and 1800, are consistent with the time of local subsistence farming, which preceded the nineteenth century's increasing important of cereals from more climatically favorable regions.

Chemical Analysis. Analytical results from a sediment core (site 2, Figure 1) collected near Church Beck and Yewdale Beck, the main inflows from the mining region, are given in Figure 3. Copper, iron, sulfur, magnesium, and calcium all show large increases above the background in the region 20–35 cm below the surface. The major copper peak can be dated to about 1850, the time of maximum output from the mines. Iron and copper concentration profiles from the cores from all sites (see figure 1 for positions) are given in Figure 4. The clearly defined copper and iron peaks are coincident, not only with each other but with the distinct gray layer which was apparent in all cores. Carbon and manganese profiles (Figure 5) show reduced concentrations coincident with the gray layer.

Discussion

Transport of Copper to the Sediments. The data discussed below suggest that copper and at least a part of the iron were supplied as solid material to the sediments which were formed during the mining period. Conversely, they were not transported in the dissolved form and reprecipitated in the lake water.

The profiles of copper and sulfur for the site at Church Beck (Figure 3) have coincident features, showing a minor

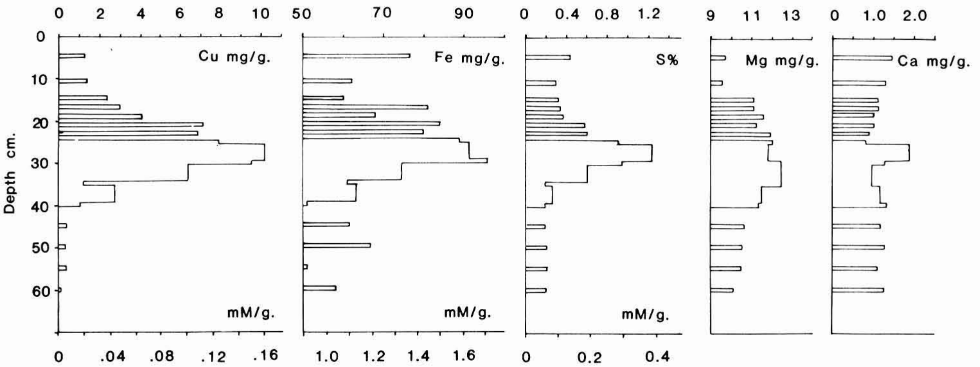

Figure 3. Concentration–depth profiles of the various chemical elements in a core from site 2, near the main source of copper. Note the exceptionally high concentrations of copper.

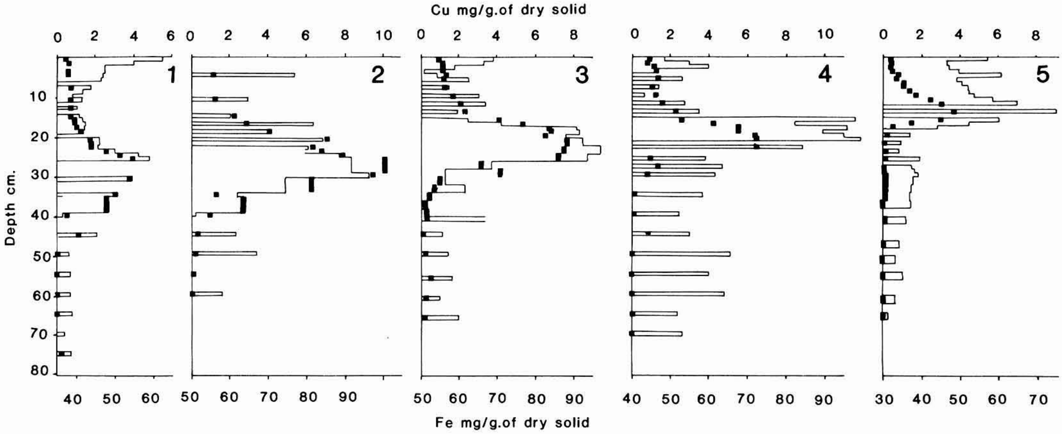

Figure 4. Sedimentary record of copper and iron for five different locations in Coniston Water. Copper concentrations are indicated by black squares and iron by the open histogram.

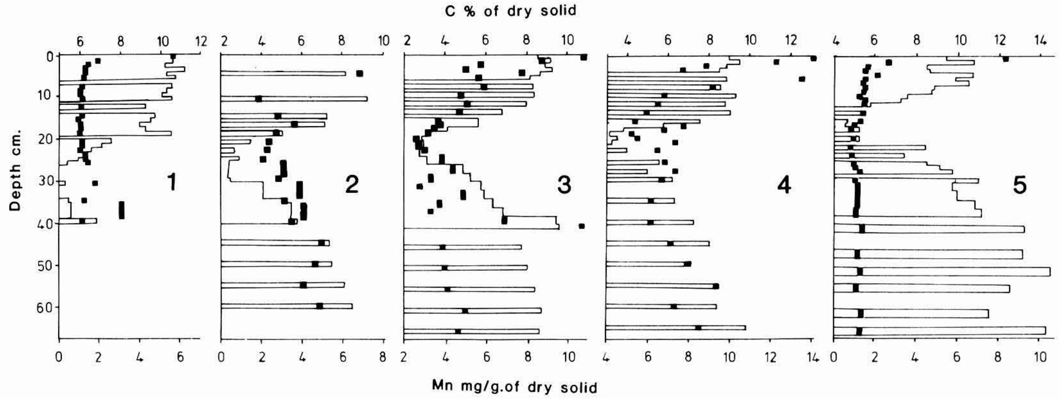

Figure 5. Sedimentary record of manganese and carbon for five different locations in Coniston Water. Manganese concentrations are indicated by black squares and carbon by the open histogram.

peak at 35–39 cm, the maximum at 25–29 cm, and a shoulder at 20–23 cm. The molar ratio of copper in excess of the background to sulfur in excess of the background is about 1:2 throughout the peak. Such a ratio is consistent with chalcopyrite being present. This mineral is the major copper-containing constituent of the ore in the Bonser vein (*3, 4*). Chalcopyrite cannot be detected by XRD measurements performed on the gray sediment, although it is apparent in the XRD spectra of samples of ore washings taken from the disused workings. The concentration of chalcopyrite is sufficiently low in the sediments (~3% of the inorganic matter at the peak) to be below the detection limit of the XRD technique. The ratio of copper to sulfur indicates that material was transported to the sediment in solid form. Had the mineral dissolved, sulfide would have been oxidized to sulfate. Although the latter could have reprecipitated with the copper, the resultant elemental ratio would have been 1:1. The variation in the

Table I. Properties of the Copper Peaks in Each Core

core	water depth, m	depth of maximum concn, cm	maximum concn, mg g^{-1}	peak width at half-height, cm	rel peak area	upper depth limit of peak	depth normalized to 1980
1	8	30	4.4	14	0.47	18	18.3
2	>38	28	10.2	14	1.00	14	14.6
3	>46	22	7.8	12	0.75	11	11
4	>53	19	6.5	10	0.47	12	12
5	34	13	3.8	8	0.18	8.5	8.5

concentration of iron with depth (Figure 3) shows a broadly similar pattern to that exhibited by copper and sulfur. Comparison with the concentrations of copper and sulfur suggests that only 19% of the increase in iron can be accounted for as chalcopyrite. The magnesium concentration also increases in this region of the sediment, indicating an elevated loading by clay minerals. Confirmation of this interpretation is provided by the XRD spectra which show an increase in chlorite, relative to quartz, in the gray mud. Ochsenbein et al. (*12*) have shown that, in a sediment core from a nearby lake, which has the same Silurian slate bedrock, the molar ratio of magnesium to iron associated with chlorite is constant at about 1:2.25. Assuming the same ratio applies to Coniston, we can estimate that a further 21% of the iron excess can be accounted for by the increased chlorite input. There is independent evidence that some of the extra iron in this region of the core is due to an increase in the proportion of chlorite. Using Mössbauer spectroscopy, Coey (*13*) showed a large increase in iron(II) in an equivalent region of a core from Coniston. He interpreted this as an increase in the chlorite content of the sediment.

The remaining iron may well have originated as magnetite since increasing concentrations of this mineral eventually led to the closure of the mines (*3, 4*). Only relatively low concentrations of this mineral would be needed to account for the residual iron, and so it remains undetected by XRD analysis of either the mine washings or the sediment. Coey (*13*) showed that the concentration of iron(III) also increased in this region of the core, but this could be due to either amorphous iron or magnetite.

Calcium concentrations are also enhanced. This is consistent with calcite being transported from the mines in solid form. XRD analysis of the mine washings supports this suggestion because the spectra contain peaks which are indicative of calcite.

All the evidence outlined above indicates that the increase in inorganic matter in the gray layer is largely due to transport of minerals from the source to the sediments in the solid form.

Implications for Transport Processes within the Lake. The old copper workings were based on the Bonser Vein (*3, 4*). Two main groups of mines used water from either Church Beck or Yewdale Beck in the ore-concentration process (*2*). These two streams were the major source of enhanced copper loading to the lake. Copper and iron profiles for five sites in the lake are given in Figure 4. For all localities there is a high degree of association between the copper and iron peaks, indicating that the peaks at different sites represent the same event. We can conclude that the sediment inputs from Church Beck and Yewdale Beck contribute to the accumulating lake sediment throughout the basin. However, a closer study of the data shows that this is not the complete story.

Recent theories of sediment distribution (*14, 15*) suggest that, in small lakes dominated by erosion–transport–accumulation (ETA) processes, maximum accumulation will take place at the deepest point and that the rate of accumulation will decrease in shallower water. The profiles in Figure 4 do not conform to these theories.

In a comparative analysis of the between-site variation of the copper peak three parameters assume importance. These are the following: the peak area, which gives an indication of the total load of copper at such sites; the peak width, which provides information about the total accumulation of material during the period of pollution; the depth of the peak, which provides an assessment of the accumulation rate subsequent to pollution. To provide a standard procedure for obtaining this information, the copper peaks from the different locations were approximated by isosceles triangles. Thus, comparable values for the maximum concentration and the peak width at half-height could be obtained. Relative peak areas were calculated by dividing all the areas by the area of the largest triangle. This semiquantitative estimate of the relative copper loading at each site was preferred to direct integration of the copper profile. The latter option would have involved assumptions and approximations because not only were the concentrations determined on sediment slices of different effective thickness but the concentrations were not determined on all slices (Figure 4). The parameters resulting from the semiquantitative analysis are listed in Table I, along with the maximum concentration of copper and the estimated water depth at each site.

With the exception of site 1 the depth of the concentration maximum decreases progressively down the lake (i.e., from site 2 to site 5). This trend is followed by the maximum concentration itself, the peak width, and, hence, the relative peak area. As the latter measure can be considered as a normalized estimate of the total copper loading to the sediment at each site, it provides evidence for decreasing copper deposition away from the source, i.e., Church Beck–Yewdale Beck. This process can be regarded as being equivalent to settlement of particulate material in a river. The lower quantities of copper recorded at site 1 relative to site 2 are consistent with this notion because it is "upstream" of the copper input.

There is an inconsistency regarding site 1 in that, whereas the copper concentration in the sediment is reduced compared to that at site 2, the amount of sediment accumulating since the cessation of mining activity is increased (Table I). These recent accumulation rates were estimated from the depth at which the extended upper edge of the isosceles triangle intercepts the zero concentration axis. Allowance was made for the extra accumulation which had taken place in cores collected in later years. By use of the accumulation rate of 0.3 cm $year^{-1}$ given by Pennington (*16*), 0.3 cm has been added to core 1 and 0.6 cm to core 2 in order to normalize all the cores to 1980. At the other sites the post-mining accumulation rates, like the width of the copper peak, decrease sequentially down the lake, indicating that deposition at these sites is dominated by the Church Beck–Yewdale Beck inflows. If we assume that copper-containing particles are distributed in the same way as the rest of the sediment load, the high accumulation rate, coupled with the low copper load, of site 1 suggests that there is a substantial alternative source of sediment material other than from Church Beck and Yewdale Beck. The streams flowing into this relatively shallow area at the end of the long narrow lake represent only a small fraction (ca. 7%) of the total catchment. Therefore, to facilitate the enhanced accumulation, this area of the lake must be particularly efficient at trapping sediment brought in by these streams. The shallow sill, which separates the small northern basin from the rest of the lake, may be a contributory factor.

Manganese. Manganese is readily leached from the Silurian slate base rocks of this region, and so all streams and rivers contain reasonable concentrations of the element (*17, 18*).

Consideration of the manganese profiles at the five different sites in the lake can provide further information about transport processes. Figure 5 shows that at sites 1 and 5 the concentration of manganese, for all depths other than the surface, is fairly low and constant at 1–2 mg g^{-1}. At sites 2–4 the manganese profiles have distinct minima which correspond to the period of copper mining, and at other depths, excluding the atypical sediment surface, the concentration of manganese is 4–7 mg g^{-1}. This difference between the sites can be rationalized in terms of the redox chemistry of manganese. Recent work (*18*) has shown that most of the manganese which reaches an anoxic sediment is rapidly reduced and released to the overlying water. The water column of Coniston remains oxygenated throughout the year whereas the sediments, with their high organic carbon content (Figure 5), are strongly reducing. In a neighboring lake which was 15 m deep the manganese released from the anoxic sediment was well mixed with the overlying water so that it was removed via the outflow. Consequently the sediment was impoverished in manganese. This removal mechanism could operate at sites 1 and 5 in Coniston because they are relatively shallow, 8 and 34 (m), respectively. However, the other sites are deeper (Table I), and therefore any Mn^{2+} that is released may be oxidized and reprecipitated so that it returns to the sediment rather than being permanently removed from the lake. Such processes will be intimately dependent on the detailed hydrodynamics of the system and as yet cannot be predicted. They do, however, provide a rationale for the higher concentration in the sediment of the deeper sites. In support of this argument site 4, which has the maximum depth, in excess of 54 m, has the sediment with the highest concentration of manganese.

The carbon profiles at all sites (Figure 5) and the manganese profiles at sites 2–4 all show a pronounced minima during the period of mining activity. This can be attributed to dilution caused by the increased mineral input to the lake at this time. It is interesting that the manganese profiles for sites 1 and 5 are virtually free from this effect. Possibly the diluted manganese input during the mining activity was not so readily mobilized because the sediments had proportionately less organic carbon and so were not as strongly reducing.

Acknowledgments

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Registry No. Cu, 7440-50-8; Fe, 7439-89-6; S, 7704-34-9; Mg, 7439-95-4; Ca, 7440-70-2; Mn, 7439-96-5; chalcopyrite, 1308-56-1.

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NOTES

Tests for Fluorocarbon and Other Organic Vapor Release by Fluorocarbon Film Bags

Nelson A. Kelly,*[†] **Keith L. Olson,**[‡] **and Curtis A. Wong**[‡]

Environmental Science and Analytical Chemistry Departments, General Motors Research Laboratories,
Warren, Michigan 48090

■ Tests were performed on several bags made from fluorinated ethene–propene copolymer film, commonly referred to as FEP–Teflon, to see if they release fluorocarbon vapors, as was recently reported by others. Special attention was given to determining if tetrafluoroethene and hexafluoropropene, the monomer units used to synthesize the film, were released. By use of an instrument that measured total gas-phase carbon, it was determined that at most 0.06 ppm of C of non-methane organic contamination was released into bags of clean air stored outdoors for up to 2 days. A more sophisticated gas chromatography/mass spectrometry technique was used to confirm that neither of the two precursor fluorocarbons was released into the bag at concentrations above the detection limit of ~0.002 ppm for each compound. The latter conclusion applied to bags stored at ~25 °C in a room as well as one stored in an irradiated chamber at 30–40 °C. These findings are contrary to those recently reported by another group who found large releases of fluorocarbon contaminants, especially hexafluoropropene, from similar bags. We conclude that not all FEP–Teflon film releases fluorocarbon vapors.

Introduction

Plastic bags made from fluorocarbon polymers have been widely used in air pollution research (*1–8*). Over the years many virtues and pitfalls for a variety of different films have been investigated by air pollution researchers who employed such bags for the storage of air samples and calibration standards, as well as the irradiation of smog producing mixtures. For the latter purpose, the film most widely used is made of fluorinated ethene–propene copolymer (FEP–Teflon, E. I. du Pont de Nemours & Co., Inc., Wilmington DE), since it is inert, transparent, and photochemically stable (*7*). Even this material, however, has shortcomings that must be considered by scientists using it in smog chamber studies. We have observed that both hydrocarbons and nitrogen oxides contaminated air samples stored in FEP–Teflon bags (*9*). Although we believe that the source of such contaminants was permeation into the bags from outside and that permeability is a characteristic general to all FEP–Teflon film, such problems can be surmounted by simple conditioning procedures (*7*).

Recently, a potentially very serious drawback to the use of FEP–Tefon film for either storage containers or smog chambers was reported by Lonneman and co-workers (*10*). They observed that large amounts of several low molecular weight fluorocarbons were released by FEP–Teflon. The main contaminant was hexafluoropropene, one of the monomer units in FEP–Teflon synthesis. The emitted fluorocarbon vapors also caused ozone formation when irradiated in the presence of NO_x. Although Lonneman et al. speculated that the fluorocarbon emissions from bags might be relatively inefficient as ozone producers, i.e., they state that halogenation of ethene and propene reduces the reaction rate with OH and O_3, there is some evidence to the contrary. For example, C_2F_3Cl, the compound most similar to C_2F_4 for which the reaction rate with OH has been measured (the C_2F_4–OH and C_3F_6–OH reaction rates have not been reported yet), reacts with OH faster than does C_2H_4 (*11*). Furthermore, the peroxy radicals produced in air following OH attack on olefinic fluorocarbons may be even more efficient in converting NO to NO_2 than their hydrocarbon counterparts. By use of the one fluorinated peroxy radical that has been studied, as an example, CF_3O_2, its reaction with NO is twice as fast as CH_3O_2 (*12*). These simple analogies lead us to speculate that if fluorocarbons are released by FEP–Teflon, this is a potentially serious problem for researchers who wish to use Teflon reactors to study free-radical chemistry.

Previous work in our laboratory concerning the contamination of FEP–Teflon bags showed that the bags were contaminated by a myriad of hydrocarbons (*9*). From our previous data, however, we could not be certain that some of the contaminants were not fluorocarbons for two reasons. First, contaminants were not identified beyond noting that they were organic compounds that appeared as peaks on a GC column in the range where C_5–C_{10} hydrocarbons eluted. Second, fluorocarbons could have been present but not detected due to their poor response in a flame ionization detector.

Therefore, it was necessary to test our bags for fluorocarbon release to see if the contamination reported by Lonneman et al. was present in our experiments. The tests were designed to determine the total gas-phase carbon released by the film, as well as the concentration of the two fluorocarbons, tetrafluoroethene and hexafluoropropene, i.e., the two monomers used to make FEP–Teflon film.

Experimental Section

Eight 450-L bags, one 50-L bag, and one 2000-L bag were used for the experiments. All were made of FEP–Teflon, type A. The 450-L bags and the 2000-L bag were purchased from Livingstone Coatings Corporation, Charlotte, NC; the 50-L bag was purchased from Alltech Associates, Deerfield, IL. The heat seals on the Livingstone bags were made by raising the temperature of the film to its melting point (260–280 °C) for as short a time as possible while still yielding an adequate seal. Seven of the 450-L bags were made from 0.05-mm thick film while one 450-L bag, the 2000-L bag, and the 50-L bag were made from 0.12-mm film. All the 450-L bags as well as the 2000-L bag were

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[†] Environmental Science Department.

[‡] Analytical Chemistry Department.

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fitted with FEP–Teflon valves for adding and removing gas samples, as described previously (*7*). For purposes of identification, bags 1, 2, 4, and 6–9 had volumes of 450 L and were made of 0.05-mm film, bag 3 was a 2000-L bag made of 0.12 mm film, bag 5 was a 450-L bag made of 0.12-mm film, and bag 10 was a 50-L bag made of 0.12-mm film.

Two types of experiments were conducted. In the first type, bags 1–6 were flushed once (with ~30 L) and then filled with hydrocarbon-free air (zero air) from Scott Speciality Gases, Troy, MI; they were stored outdoors during Aug 1981 at a site in downtown Detroit, MI. A field study designed to measure the ozone formation properties of Detroit's air was in progress at this site. The bags were suspended ~3 ft above the ground in a field behind the Detroit Science Center which is ~3 km north of the central business district. Measurements of total hydrocarbons (THC), methane (CH_4), and non-methane organic compounds (NMOC) were made in the bags after the zero air was stored for various periods of time. A Byron Model 401 total organic analyzer was used. This analyzer uses a flame ionization detector (FID) to measure THC and CH_4. Unfortunately, the THC measurement is prone to error because different organic compounds have different response factors in a FID. For example, hexafluoropropene and dichlorodifluoromethane gave responses of 0.65 and 0.10 ppm of C relative to methane (1 ppm of C). However, NMOC were measured on the Byron analyzer by chromatographically separating them from CH_4, oxidizing them to CO_2 with a cupric oxide catalyst heated to 700 °C, and then catalytically converting the CO_2 to CH_4 to give a ppm of carbon (ppm of C) response. The detection limits for this instrument were ~0.05 ppm of C for all three components, THC, CH_4, and NMOC.

A second type of experiment, in which specific tests for hexafluoropropene and tetrafluoroethene were conducted, used bags 7–10. Bag 7 was used to prepare a standard containing 0.2 ppm of both hexafluoropropene and tetrafluoroethene; i.e., this bag was not checked for fluorocarbon contamination but rather was used to develop the experimental technique as we will discuss later. The hexafluoropropene and tetrafluoroethene were obtained from PCR Research Chemicals (Gainsville, FL) and were injected into bag 7 with gas-tight syringes as it was being filled with zero air. Bags 8–10 were tested for the presence of fluorocarbon vapors, but slightly different filling and/or handling procedures were used on each one prior to the analysis. Bag 8 was the only one of the three to be preflushed with ~30 L of zero air before it was filled and stored. Bag 9 was irradiated in an indoor smog chamber for 8 h after it was filled and before it was tested for contaminants. The first-order photolysis coefficient for NO_2 in the smog chamber (this is a measure of the light intensity) was ~0.2 min^{-1}. Bag 10 was simply filled with zero air and stored in the laboratory. However, after it was checked for gaseous fluorocarbon contaminants, bag 10 was used to make up 0.01- and 0.2-ppm fluorocarbon standards in order to check the sampling protocol, which we will describe next.

Two different sampling protocols were used, and since both yielded useful data, they will be described. In the initial method, used on bags 7 and 8, gases were sampled by drawing air from each bag into a 30 cm × 3 mm o.d. loop of stainless steel tubing immersed in liquid oxygen. Two liters of air was pumped through the stainless steel trap at 1 L/min with a Bendix Model 44 air sampling pump. An improved sampling technique was used on bags 9 and 10. For this technique, gases were sampled by drawing air from each bag into a 30 cm × 3 mm o.d. loop of stainless steel tubing packed with 60/80 mesh Porapak QS. The trap was immersed in 2-propanol–dry ice coolant. Two liters of air was pumped through the trap at 0.5 L/min with a metal bellows pump. The traps were connected to a 1.3 m × 3 mm o.d. stainless steel column packed with 60/80 mesh silica gel (Applied Science, State College, PA) for analysis by gas chromatography/mass spectrometry (GC/MS). Typically, the helium carrier flow was 30 mL/min, the column was heated to 40 °C, and the coolant was removed from the trap at the start of the analysis.

Table I. Increases in THC, CH_4, and NMOC (As Measured with the Byron Analyzer) in Bags of Zero Air Stored Outdoors for Various Times

bag[a]	storage time before analysis,[b] h	bag condition[c]	ΔTHC, ppm of C	ΔCH_4, ppm	ΔNMOC, ppm of C
1	4	new	0.07	<0.05	0.06
2	6	used	<0.05	<0.05	<0.05
3	6	used	<0.05	<0.05	<0.05
4	7	new	<0.05	<0.05	<0.05
5	7	new	<0.05	<0.05	<0.05
6	47	used	0.09	<0.05	0.06

[a] See Experimental Section for bag dimensions and film thickness. [b] Bags were stored from ~1000 h on a particular day until the time of analysis. [c] New bags were flushed with ~30 L of zero air before they were filled with zero air. Used bags were filled with ambient air and irradiated for one day, pumped out, and filled with zero air overnight, and then pumped out and refilled with zero air, which was stored for the indicated time.

Hexafluoropropene and tetrafluoroethene were detected selectively by monitoring the $C_2F_4^+$ ion current at a mass to charge ratio (m/z) of 100. The $C_2F_4^+$ ion is the molecular ion of tetrafluoroethene and a characteristic fragment ion of hexafluoropropene. The response of the Finnigan-MAT 212 mass spectrometer was calibrated with hexafluoropropene and tetrafluoroethene standards, which were prepared by injecting the pure gases into a glass sampling bulb filled with hydrocarbon-free air. The mass spectrometer detected ~20 nL of C_2F_4 or C_3F_6 which is equivalent to 0.001 ppm in a 2-L air sample. Hydrocarbon standards were also analyzed by GC/MS, so that their retention times could be compared to retention times for hexafluoropropene and tetrafluoroethene.

Attempts were also made to measure hexafluoropropene and tetrafluoroethene by using an electron capture detector (ECD) with a ^{63}Ni source. However, the ECD response was very poor for both compounds, so this technique was abandoned.

Results and Discussion

The results of our analyses for THC, CH_4, and NMOC in bags 1–6 are shown in Table I. The THC and CH_4 increases (ΔTHC and ΔCH_4) suggest that small or negligible quantities of hydrocarbons (<0.09 ppm of C in all cases) were released into the gas phase by either new or used bags. This is consistent with our previous work (*9*). Moreover, the NMOC increases (ΔNMOC) were also small, i.e., <0.06 ppm of C, so the bags were not contaminated significantly by any other carbon-containing compounds, including fluorocarbons. The bags were stored during periods when the ambient temperature was 20–32 °C, and the sunlight probably increased the film temperature a few degrees above this. Therefore, the bags were mildly heated, which should maximize the release of contaminants (*9, 10*). Lonneman et al. (*10*) observed large amounts of contamination within a few hours of storage of clean air in their bags, and concentrations as great as 4.5 ppm of C of

Table II. Increases in Tetrafluoroethene and Hexafluoropropene (As Measured with the GC/MS System) in New Teflon Bags Containing Zero Air or Fluorocarbon Mixtures and Stored Indoors

bag[a]	storage time before analysis,[b] h	mixture	sampling method[c]	no. of trials	C_2F_4, ppm	C_3F_6, ppm
7	–	0.2 ppm of C_2F_4 0.2 ppm of C_3F_6	A	3	0.001	0.2
8	24	zero air	A	2	<0.2	<0.002
9[d]	48	zero air	B	2	<0.002	<0.002
10	24	zero air	B	3	<0.002	<0.002
10	–	0.01 ppm of C_2F_4	B	2	0.006	<0.002
10	–	0.01 ppm of C_3F_6	B	2	<0.002	0.009
10	–	0.2 ppm of C_3F_6	B	1	<0.002	0.2

[a] See Experimental Section for bag dimensions and film thickness. [b] Dash indicates that the analysis was performed immediately after filling. [c] Method A: vapors trapped in an empty sample loop of stainless steel tubing immersed in liquid oxygen. Method B: vapors trapped in tubing packed with Porapak QS and immersed in 2-propanol–dry ice bath. [d] This 450-L bag was exposed to light and higher temperatures in a chamber for 8 h after it was filled (see text).

Table III. Gas Chromatographic Retention Times for Standards Analyzed on the Silica Gel Column Used for This Investigation

	gas chromatographic retention time, min	
standard	column at 40 °C	column at 100 °C
tetrafluoroethene	2.8	1.9
ethene	3.4	*a*
propane	6.9	*a*
hexafluoropropene	21.0	2.7
butane	26.0	*a*
isobutane	27.0	4.3
isopentane	*a*	12.7

[a] Not determined.

equivalent carbon response appeared within 1–2 days of storage. They identified 3.0 ppm of C of the 4.5 ppm of C to be hexafluoropropene. Their bags were made of 0.12-mm FEP–Teflon film and had a volume of 15–40 L; bags made of 0.05-mm film showed far less contamination. We did not observe significant contamination in either 0.05-mm or 0.12-mm bags having volumes from 450 to 2000 L. If the contaminant release rate observed by Lonneman and co-workers for 0.05-mm bags is extrapolated to our 0.05-mm, 450-L bags, we would expect to see ~0.02 ppm of C contamination in 7 h in a new bag. This is below our detection limit for NMOC, so we cannot conclusively rule out some fluorocarbon release based on the results in Table I.

However, the experiments using the GC/MS system were more definitive; the results are shown in Table II. None of the new Teflon bags (bags 8–10) contained hexafluoropropene vapor above a detection limit of 0.002 ppm. Neither bag 9 nor bag 10 contained tetrafluoroethene vapor above the same detection limit of 0.002 ppm. The detection limits are based on the mass spectrometer sensitivity for the compounds, as well as the trapping efficiency determined for each method. These values were determined by the tetrafluoroethene and hexafluoropropene standards in bags 7 and 10. Bag 8 did not contain tetrafluoroethene, but the detection limit of 0.2 ppm was higher than for bags 9 and 10.

The poor detection limit for tetrafluoroethene in bag 8 was due to our original sampling method. Our original trap was a loop of empty stainless steel tubing immersed in liquid oxygen. The results from bag 7 indicate that only 0.5% of the tetrafluoroethene (bp −76 °C) was trapped in the empty tube. The empty trap collected hexafluoropropene (bp −29 °C) effectively. By switching to a packed trap immersed in 2-propanol–dry ice coolant, we were able to collect 60% of the tetrafluoroethene and 90% of the hexafluoropropene at the 0.01-ppm vapor concentration level (Table II, bag 10).

For the GC/MS experiments, we used gas chromatographic conditions that were very similar to those used by Lonneman et al. (*10, 13*). Consequently, we were surprised when hexafluorpropene exhibited a much shorter gas chromatograpic retention time than predicted by Lonneman's data (*10*). Hexafluoropropene eluted from Lonneman's silica gel column after isobutane and just before isopentane. On our silica gel column, hexafluoropropene eluted before isobutane and several minutes before isopentane (Table III). The discrepancy may be explained by the fact that different grades of silica gel can have grossly different chromatographic properties (*14*). On the other hand, it should be pointed out that Lonneman et al. did not analyze an authentic sample of hexafluoropropene.

One other conclusion which we can draw from the retention time data is that light fluorocarbons were not responsible for the contamination observed previously in bags (*9*). The previously observed contaminants had GC retention times similar to C_5–C_{10} hydrocarbons, not C_2–C_5 hydrocarbons where the low molecular weight fluorocarbons would appear (Table III). Thus, for a total of 15 bags constructed from two different rolls of film (9 in this study and 6 in the previous study), none released large amounts of light fluorocarbons.

In conclusion, not all Teflon gas bags contaminate air samples with tetrafluoroethene or hexafluoropropene vapors. Therefore, tetrafluoroethene and hexafluoropropene can be avoided as photochemically reactive interferences in FEP–Teflon bags. In addition, NMOC increases in bags were small, so other fluorocarbons were also not present in large amounts.

Our results do not invalidate the work of Lonneman et al. Some batches of Teflon film may contain more residual starting material than others. However, because tetrafluoroethene (bp −76 °C) and hexafluoropropene (bp −29 °C) are volatile gases, we believe that FEP–Teflon film usually does not contain significant amounts of these chemicals. The volatility of these chemicals also causes us to doubt that they were the "oily deposits" Lonneman and co-workers observed on their bags. Possibly the deposit was some polymer of hexafluoropropene, such as the trimer (which is a viscous liquid), and this substance desorbed the fluorocarbon vapors that they observed. We did not observe such oily deposits on our bags. Another possibility is that our bags were heat sealed differently than Lonneman's. In their review of the use of bags for storing ambient samples, Bullin and Polasek (*6*) state that if the temperature of the heat sealer is raised too high, the polymer decomposes and releases monomers and other light polymers for some time thereafter. Therefore, it may be necessary for every group using bags to perform specific tests on their bags for fluorocarbon and other organic vapor contaminants. Bags can be tested for those two fluorocarbon vapors with the analytical procedure described in this report.

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Registry No. Tetrafluoroethane–hexafluoropropene copolymer, 25067-11-2.

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Monoterpene Hydrocarbons in the Nighttime Troposphere

James M. Roberts,[*,†,‡,§,⊥] **Carole J. Hahn,**[†,§] **Fredrick C. Fehsenfeld,**[†,§] **James M. Warnock,**[†] **Daniel L. Albritton,**[†] **and Robert E. Sievers**[§,⊥]

Aeronomy Laboratory, National Oceanic and Atmospheric Administration/Environmental Research Laboratories, Boulder, Colorado 80303, National Research Council Postdoctoral Associate, Aeronomy Laboratory, NOAA/ERL, Boulder, Colorado 80303, Cooperative Institute for Research in the Environmental Sciences, University of Colorado/NOAA, Boulder, Colorado 80309, and Department of Chemistry, University of Colorado, Boulder, Colorado 80309

■ Monoterpene hydrocarbons were measured during the night at a rural site in the Rocky Mountains. The compounds positively identified and quantified were α-pinene, camphene, β-pinene, Δ^3-carene, and *d*-limonene. The average sum of the mixing ratios of the five compounds measured during the nighttime between July and Oct, 1982, was 0.63 ppb (volume), which was about twice the corresponding daytime average sum. No significant difference was observed between day and night in the relative concentrations of the individual monoterpenes. Increased atmospheric stability, with attendant reduced mixing and dilution during the night, was found to contribute to the larger nighttime vs. daytime monoterpene mixing ratios. Nighttime atmospheric stability was also responsible for the observation of ozone diminution and a corresponding inverse relationship between monoterpene and ozone mixing ratios. The results indicate that, at this site, transport rather than chemistry determines the concentrations of the monoterpenes. The ultimate fate of the monoterpenes is chemical reaction with O_3, OH, or NO_3. Because of the differences in rate constants of reactions between the various monoterpenes and the above species, chemical reaction should cause systematic changes in relative concentrations of monoterpenes, which are characteristic of the reactant species involved.

Introduction

Monoterpene hydrocarbons represent a natural source of reactive organic compounds that are potentially important in the chemistry of the troposphere. Since the monoterpenes react rapidly with ozone and hydroxyl radical, the role of monoterpenes in the daytime production of oxidant has been the subject of much research. Recent measurements of nitrate radical (NO_3) in the nighttime troposphere and rate constants of the reactions of NO_3 with the monoterpenes have raised interest in the possible importance of monoterpenes in the chemistry of the nighttime troposphere.

Since the initial work on emissions of atmospheric monoterpenes from plants by Went (*1, 2*) there have been numerous atmospheric and emission measurements reported in the literature (*3–25*). Reported levels of total monoterpenes have ranged from less than 0.001 to over 10 ppb volume (ppbv) in a variety of deciduous and coniferous forest and grassland environments. The magnitude of global emissions of isoprene and monoterpenes to the atmosphere has been estimated by Zimmerman et al. (*26*) to far exceed that of the emission of anthropogenic organic compounds. There have been several reviews that discuss monoterpenes in the atmosphere (*27–30*).

Reaction rates of monoterpenes with ozone (*31, 32*) and hydroxyl radicals (*33, 34*) indicate that daytime atmospheric lifetimes of the monoterpenes will be several hours or less. Measurements of monoterpene hydrocarbons at night have been made in a forest in Japan by Yokouchi et al. (*25*). The general conclusions from their study were that the nighttime mixing ratios of the monoterpenes were systematically higher than the daytime mixing ratios and that this was due mainly to the absence of OH at night. The relative concentrations of the various monoterpenes were observed to be fairly constant with season and no systematic difference between day and night composition was mentioned. A model study by Peterson and Tingey

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[*] Address correspondence to this author at the Aeronomy Laboratory.

[†] Aeronomy Laboratory.

[‡] National Research Council Postdoctoral Associate.

[§] Cooperative Institute for Research in the Environmental Sciences.

[⊥] Department of Chemistry.

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(*35*) showed that the degree of dilution that biogenic emissions undergo is also an important factor governing ambient concentrations. We will present evidence that suggests that atmospheric dilution is the dominant factor that determines the concentrations of monoterpenes observed in the forest at the Colorado site studied in this work.

Although the reactions between monoterpenes and hydroxyl radicals and ozone initiate chemical reactions that have the potential to produce ozone (*36–42*), measurements of the monoterpenes and NO_x in the daytime at the same site used in this study showed that very little ozone production could be accounted for in this way (*43*). Indeed, a review of the recent literature led Altshuller (*30*) to conclude that natural volatile organic substances do not contribute substantially to the formation of ozone in ambient air.

Measurements of nitrate radicals (*44–47*) indicate that there is a sink, or are several sinks, for NO_3 in both urban and rural areas. The rate constants for the reaction of NO_3 with substituted olefins (*49–52*), and monoterpenes in particular (*52*), have been observed to be fast [$>10^{-12}$ $cm^3/(molecule{\cdot}s)$]. Thus, the monoterpenes may be strong candidates for some contributions to the NO_3 sink (*53*), and NO_3 reaction may lead to significant monoterpene destruction (*24,28*). The mechanism by which the reaction takes place is an important consideration in assessing the effect of monoterpenes on atmospheric odd nitrogen, NO_y ($=NO_x + HNO_3 + PAN + HONO + NO_3 + N_2O_5 + RONO_2$), levels.

In the measurements reported herein, ozone and several meteorological parameters were measured in conjunction with determinations of concentrations of individual monoterpene hydrocarbons, along with several vertical soundings of temperature and humidity. The results are used to discern the relative importance of mixing vs. chemical reaction in governing the ambient concentrations of monoterpene hydrocarbons.

Description of Sampling Site and Experimental Approach

The sampling site used in this study is the Como Creek Site (C-1, 40°2′N, 105°32′W) located at the Mountain Research Station of the University of Colorado. The site is approximately 32 km west of Boulder, CO, and 73 km northwest of Denver, CO, at 3048-m (10 000 ft) elevation, approximately 10 km east of the Continental Divide on the southeast slope of Niwot Ridge.

The monoterpene analysis techniques used in this work have been described in detail elsewhere (*40, 54*). The hydrocarbon samples were collected in the forest approximately 100 m south of the instrument enclosures. The gas chromatograph used for quantitative measurements was a Packard Becker Model 417 with flame ionization detection. The analytical column used was a 25 m × 0.32 mm i.d. fused silica capillary coated with SE-30 methyl silicone (J&W Scientific). The gas chromatography/mass spectrometry (GC/MS) compound identifications were obtained by using a Hewlett-Packard Model 5985 gas chromatography/mass spectrometer/data system. The analytical column used was 30 m × 0.25 mm i.d. fused silica capillary coated with SE-54 methyl, phenyl, and vinyl silicone (Hewlett-Packard). Selected ion monitoring was employed by using the characteristic mass fragments 68, 69, and 93.

Ozone was measured by UV absorption (Dasibi Corp.). Meteorological data were recorded at the site by the National Oceanic and Atmospheric Administration Prototype Regional Observation and Forecasting System (NOAA-PROFS) and the University of Colorado. These data included wind speed, wind direction, temperature, and dew (frost) point.

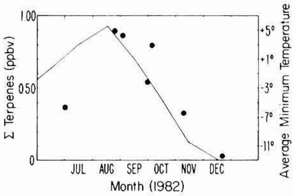

Figure 1. Sum of the mixing ratios of the five major monoterpene hydrocarbons (points) and average minimum temperature (line) measured at Niwot Ridge vs. date.

Measurements of the vertical profiles of temperature and humidity were made by using a radiosonde balloon system (Atmospheric Instrument Research). Soundings were made at times ranging from late afternoon to early morning. The aim of these measurements was to examine the character of the ground-based nocturnal inversion that is often observed at this site.

Results

The nighttime monoterpene measurements were made between July and Dec, 1982. Individual samples were collected 1–2 h apart, often as part of a 24-h sample set. Table I lists the monoterpene hydrocarbon and ozone mixing ratios determined during these nighttime measurements. The average monoterpene mixing ratio of the sum of the five compounds was 0.63 ppbv between July and Oct, 1982. This is approximately twice the average daytime mixing ratio of 0.30 ppbv measured at this site during this period (*43*). The ozone mixing ratios measured varied from 12 to 80 ppbv. Where ranges of ozone mixing ratios are given in Table I, the levels were observed to vary on the time scale of a minute.

The relative abundance of the five major monoterpenes was found to be fairly constant between July and October, as is shown in Table II. The most abundant monoterpene is β-pinene, followed by α-pinene and camphene. The few measurements made in November and December indicate that the relative composition may change slightly with season. The daytime composition found during the months between May and November is also listed in Table II (*43*). The agreement between daytime and nighttime compositions is within one standard deviation about the mean abundance, for each compound. The standard deviations associated with nighttime measurements of α-pinene, camphene, and Δ^3-carene were larger than those of the daytime measurements.

Average monoterpene mixing ratios measured on each night are plotted vs. month in Figure 1. Superimposed on the plot is the average minimum daily temperature at the site (*63*). The trend is similar to that of the daytime measurements, reflecting the dependence of monoterpene emission rates on temperature, which was also observed in laboratory studies by Tingey et al. (*19*).

The plot of ozone mixing ratio vs. monoterpene mixing ratio is shown in Figure 2. The bars attached to some of the ozone measurements again denote observed variations in the mixing ratios on the time scale of a minute or so. With the exception of two points at high ozone and relatively high monoterpene concentration, there appears to be an inverse relationship between the two quantities.

The typical behavior of the ozone concentration relative to the sum of the concentrations of the terpenes during the course of a single set of measurements is shown in

Table I. Monoterpene Hydrocarbon and Ozone Mixing Ratios Measured at Nighttime at Niwot Ridge, CO

		compound mixing ratios, ppbv					
date	time	α-pinene	camphene	β-pinene	Δ^3-carene	*d*-limonene	O_3
7-1-82	17:56	0.12	0.053	0.15	0.12	0.040	43
7-1-82	20:00	0.17	0.087	0.23	0.16	0.080	20–45
7-1-82	22:07	0.035	0.021	0.048	0.019	0.007	48
7-1-82	23:59	0.067	0.020	0.054	0.023	0.012	46
7-2-82	01:51	0.11	0.046	0.14	0.073	0.028	46
7-2-82	03:55	0.077	0.049	0.093	0.043	0.019	34–52
8-24-82	19:00	0.18	0.11	0.26	0.20	0.083	39–48
8-24-82	21:00	0.22	0.18	0.26	0.16	0.081	20–35
8-24-82	22:58	0.26	0.13	0.35	0.23	0.13	12–35
8-25-82	01:00	0.22	0.14	0.21	0.17	0.12	25
8-25-82	03:02	0.19	0.11	0.21	0.13	0.088	25–40
8-25-82	05:05	0.24	0.12	0.28	0.22	0.13	25
9-3-82	19:50	0.23	0.10	0.25	0.18	0.089	50–80
9-3-82	21:36	0.20	0.11	0.25	0.15	0.058	40–70
9-3-82	23:31	0.24	0.10	0.21	0.18	0.096	26–42
9-4-82	01:28	0.17	0.090	0.20	0.15	0.078	22–46
9-4-82	03:30	0.18	0.084	0.17	0.16	0.093	20–40
9-29-82	19:15	0.079	0.096	0.20	0.051	0.068	40
9-29-82	22:52	0.077	0.12	0.18	0.045	0.068	40
9-30-82	00:35	0.079	0.093	0.17	0.051	0.12	36
9-30-82	01:40	0.082	0.11	0.18	0.054	0.071	26
9-30-82	02:35	0.11	0.14	0.24	0.090	0.12	25
10-4-82	22:00	0.15	0.12	0.23	0.072	0.060	23
10-4-82	22:54	0.17	0.17	0.26	0.089	0.089	21
10-4-82	23:45	0.12	0.15	0.22	0.060	0.065	22
10-5-82	00:25	0.18	0.12	0.27	0.095	0.078	27
11-8-82	23:04	0.059	0.073	0.010	0.037	0.044	
11-9-82	00:01	0.056	0.068	0.093	0.036	0.085	
11-9-82	00:47	0.070	0.11	0.093	0.033	0.048	
12-21-82	23:05	0.010	0.009	0.006	0.003	0.002	30
12-21-82	23:45	0.008	0.009	0.002	0.003	0.002	30

Table II. Composition and Average Mixing Ratio of Monoterpene Hydrocarbons Measured Day and Night

	concn, ppbv		% relative abundance ± σ	
compound	day	night	day	night
β-pinene	0.097	0.21	36 ± 3.8	32 ± 4.0
α-pinene	0.054	0.15	20 ± 2.4	24 ± 5.1
Δ^3-carene	0.051	0.10	19 ± 2.2	17 ± 5.1
camphene	0.038	0.10	14 ± 3.7	16 ± 5.1
d-limonene	0.030	0.072	11 ± 3.9	11 ± 3.8
total	0.27	0.63		

Figure 3. The anticorrelation of ozone relative to the terpenes is evident. Near sunset (denoted by the arrow) the ozone concentration declines while the terpene concentration increases. This behavior is attributed to the formation of a near-surface nocturnal inversion layer at the site.

Discussion and Conclusions

Measurements of vertical temperature profiles made at this site at night frequently showed temperature inversions. Such nocturnal inversions are common (*58*), resulting from radiative cooling of the ground surface after sunset. Under inversion conditions, if there is little or no wind, vertical mixing is greatly restricted.

The diminution of O_3 during stable nocturnal conditions is observed at this site and has been observed in several other studies (*59*, *60*). Under these circumstances, the monoterpene mixing ratios measured at this site are usually enhanced. It is clear, however, that the diminution in the ozone as shown in Figure 3 cannot be attributed to chemical destruction by the terpenes. A composition-averaged rate constant for the reaction of O_3 with the monoterpenes (*31*, *32*) combined with a total monoterpene mixing ratio of 1.0 ppbv yields an O_3 lifetime of over 100 h, clearly too long to produce the observed decline in the O_3 concentration. Thus, the lowered ozone concentrations such as those shown in Figure 3 are interpreted to be a result of the destruction of O_3 at surfaces and restricted vertical mixing (*59*, *60*).

Alternatively, the inverse relationship between the ozone mixing ratio and the sum of the monoterpene mixing ratios noted in Figure 3 raises the question of the possible role of the more abundant ozone in regulating the monoterpene concentration at night. In addition to chemical destruction, the monoterpene concentrations are determined by the systematic diurnal variation in meteorological dispersion noted above and by variation of the monoterpene emission rate, which is known to be temperature dependent. The processes are operating in concert, and the changes in ambient mixing ratios should be roughly proportional to the change in emission rate and inversely proportional to changes in the chemical destruction rate and the degree of meteorological dispersion.

In laboratory studies carried out by Tingey et al. (*19*), the emission rate of monoterpenes from slash pine was observed to depend exponentially on temperature with an observed emission rate increase of 7.3% C^{-1}. Therefore, we expect the emission rate of the terpenes to decrease by a factor of approximately 2 between midday and late night due to day/night temperature differences. The relative emission rates of the different terpenes are expected to remain relatively constant.

Given that the emission rates for the terpenes are significantly less at night because of the reduced temperature, the observed increase in the concentration of the terpenes at night must be attributed to a greatly diminished loss rate at night associated with either chemical reaction or dispersion. Considering first the destruction of the terpenes by ozone, if the concentrations of the terpenes are at

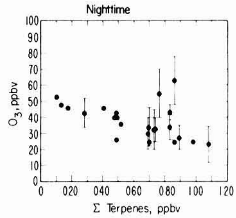

Figure 2. Ozone mixing ratio vs. the sum of the mixing ratios of the five major monoterpene hydrocarbons measured at nighttime at Niwot Ridge. Bars denote variability in measurements with time scales on the order of 1 min.

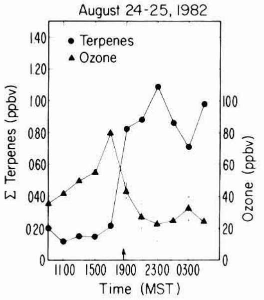

Figure 3. Sum of monoterpene mixing ratios and O_3 mixing ratio vs. time of day, Aug 24–25, 1982. The arrow indicates sunset.

a steady state in which emission is balanced by ozone destruction, then the observed difference in day–night concentration would be

$$\frac{[\text{terpene}]_D}{[\text{terpene}]_N} = \frac{S_D(\text{terpene})[O_3]_N}{S_N(\text{terpene})[O_3]_D} \tag{1}$$

where [terpene] and $[O_3]$ are the measured concentrations of the compounds, S is the emission rate of the terpenes, and the subscripts D and N indicate daytime and nighttime values for these parameters. At our site, the average O_3 concentration during these measurements (cf. Table I) was 32 ppbv at night ($[O_3]_N \approx 6.5 \times 10^{11}$ cm^{-3}) and 45 ppbv during the day ($[O_3]_D \approx 9 \times 10^{11}$ cm^{-3}). It is clear that the daytime increase in ozone concentration relative to the nighttime concentration ($[O_3]_N/[O_3]_D \approx 0.7$) cannot explain the reduced daytime terpene concentration ($[\text{terpene}]_D/[\text{terpene}]_N \approx 0.4$), particularly with the sizably greater daytime emission rate ($S_D/S_N \approx 2$).

Another argument against reaction with ozone alone regulating the terpene concentration can be inferred from the time variations of the mixing ratios of compounds shown in Figure 3, which is typical of the onset of a nocturnal inversion. The concentrations of all the terpenes increase simultaneously. However, the rate constants for the reactions of the terpenes with ozone vary sizably from compound to compound (*31, 32*). Thus, for example, by use of the rate constants for these reactions published most recently by Atkinson et al. (*32*), the time constant for the readjustment of the β-pinene concentration to an instantaneous 30 ppbv change in the ozone concentration would be approximately 10 h, while the time constant for *d*-limonene response would be on the order of 1 h. It is clear that reactions involving ozone cannot alone explain the observed variations in the terpene concentrations.

A reasonably convincing argument can also be made that the consequences of NO_3 and OH on the concentrations of the terpenes at this site must be negligible. Clearly, an additional sink for the terpenes at night created by the reactions of the terpenes with NO_3 would further complicate the rationalization of the observed nighttime increase in the terpene concentration. Since the rate constants for the reaction of α-pinene with O_3 and NO_3 are much larger than the rate constants for the reaction of β-pinene with these compounds (*31, 32, 52*), the chemical reaction of O_3 and NO_3 during the night would enrich β-pinene relative to α-pinene in the ambient air. On the other hand, the rate constant for the reaction of α-pinene with OH is slightly lower than the rate constant for the OH reaction with β-pinene. The work of Tingey et al. (*19*) indicates that the relative emission rates of these compounds remains unchanged through the diurnal cycle. Therefore, reactions of these compounds with OH would tend to increase the concentration of α-pinene relative to β-pinene compared to the nighttime concentrations. For example, the ratio of the concentrations of β-pinene to those of α-pinene at night (cf. Table II) is 1.33. If this composition is maintained by emission balanced by ozone destruction, the ratio of emission of β-pinene to α-pinene would be 0.33. However, if this emission ratio were maintained during the day, an average OH concentration of 1×10^6 cm^{-3} would reduce the ratio of concentrations of β-pinene to α-pinene to 0.46. In fact, this ratio is observed to increase to 1.8 during the day (cf. Table II).

We conclude that emission balanced by photochemical destruction cannot explain the diurnal variations observed in the absolute concentrations and lack of change in relative concentrations of the terpenes. Reaction with ozone cannot by itself reproduce the time variations in the terpene concentration or explain the systematic difference in the absolute concentrations of the terpenes in the absence of altered composition. Significant destruction of monoterpenes due to reaction with OH during the day would lead to a large change in the relative concentrations of the compounds, which is not observed. However, an additional loss of the terpenes during the day is required to offset the expected increase in emission associated with increased temperature. It is clear that dispersion must be the dominant mechanism for regulating the diurnal variation observed in the concentration of the terpenes measured at ground level at this site. At altitudes well above the surface, however, the chemical destruction of the terpenes will become the dominant removal process.

Impact of the monoterpene compounds on the NO_y chemistry of the lower troposphere may have important consequences. The composition-averaged rate constant for the reaction of NO_3 with the monoterpenes measured in this work is 3.3×10^{-12} cm^3/(molecule·s), based on the recent measurements by Atkinson et al. (*52*). A mixing ratio of 0.5 ppbv of the monoterpenes results in a lifetime of NO_3 of about 30 s. Thus, the monoterpenes represent a strong sink for NO_3 in the nighttime boundary layer. These conditions correspond to the high monoterpene emission rate, low NO_3 formation rate conditions noted by Winer et al. (*53*).

The major daytime sinks of NO_3 are photolysis and reaction with NO. A maximum photolysis rate of about 0.2 s^{-1} is predicted under overhead sun conditions (*61*). Mixing ratios of 0.5 ppbv of NO or 3 ppbv of monoterpenes, for example, are required to match the loss rate due to photolysis. Therefore, it is possible that reaction of NO_3 with the monoterpenes may represent the largest loss of NO_3 in the daytime in highly vegetated areas in the remote troposphere such as tropical areas in the southern hemisphere.

Above the surface layer at night, the reaction of NO_3 with the terpenes may constitute the major chemical destruction mechanism for the terpenes (*53*). In rural areas nighttime concentrations of NO_3 above the boundary layer of 0.05 ppbv are common (*44–48*). NO_3 mixing ratios at this level would imply an average monoterpene lifetime of about 5 min. This would make the NO_3 reaction with the monoterpenes a more important loss process for the monoterpenes than the reaction with ozone. It is clear from our previous discussion that since the reactions of monoterpenes with NO_3 proceed at different rates, the removal of monoterpenes by reaction with NO_3 should be accompanied by changes in relative concentration. This provides a way to observe chemical destruction of the monoterpenes and to distinguish between the monoterpene dominant and NO_3 dominant cases noted by Winer et al. (*53*).

The products of the reaction of nitrate radical with propene have been studied by using FT/IR techniques by Bandow et al. (*62*). The reactions of monoterpenes with nitrate radical can be assumed to follow analogous pathways resulting in the loss of one, and possibly two, odd-nitrogen species, with the corresponding formation of dinitrate, peroxy nitrate–nitrate and carbonyl–nitrate organic compounds. These compounds represent a reservoir and possible sink for odd nitrogen and should be present in the nighttime troposphere.

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Calculation of Water Solubility of Organic Compounds with UNIFAC-Derived Parameters

Sujit Banerjee

Safety and Environmental Protection Division, Brookhaven National Laboratory, Upton, New York 11973

■ The application of the UNIFAC method to the calculation of water solubility of organic compounds is reevaluated. It is shown that solubilities calculated directly from UNIFAC-derived activity coefficients at infinite dilution tend to be lower than measured values. A small correction is proposed whereby the molar solubility (S) is related to the solute aqueous phase activity coeff- $(\gamma_{aq}^{\infty})_{\mathrm{UNIFAC}}$ through the equation $\log(S) = 1.20 + 0.782 \log[a_{org}/(\gamma_{aq}^{\infty})_{\mathrm{UNIFAC}}]$. The equation successfully correlates data for 50 representative compounds ranging in hydrophobicity from alcohols and amines to polynuclear aromatics and polychlorobiphenyls.

The water solubility of organic compounds has been correlated with parameters such as boiling point (*1*), the octanol–water partition coefficient K_{ow} (*2*), and molecular surface area (*3*) and volume (*4*), and these relationships have been used for solubility estimations. With the exception of the one involving K_{ow}, these correlations are limited to nonpolar materials and thus exclude a large number of environmentally relevant compounds. The drawback of the relationship with K_{ow} is that partition coefficients may be difficult to measure and must frequently also be estimated. An alternative approach to solubility calculations is the UNIFAC method described by Fredenslund et al. (*5*) where the activity coefficient is first calculated and then related to solubility. The advantage of UNIFAC is that it is based on an increasingly extensive database and can be easily applied to multicomponent mixtures. However, Arbuckle (*6*) recently evaluated the procedure with a number of priority pollutants and concluded that the technique was unreliable when applied to sparingly soluble compounds. In this paper, it is shown that these uncertainties can be overcome with a minor modification and that the UNIFAC method offers an attractive combination of versatility and reliability for solubility calculations.

The water solubility (S) of an organic liquid (in molar units) is approximated by eq 1 where a_{org} represents the

$$S = 55.5a_{org}/\gamma_{aq} \quad (1)$$

activity of the liquid in the organic phase and γ_{aq} is the activity coefficient in the aqueous phase. In the UNIFAC procedure, the solute and solvent are factored into their component groups, and the activity coefficients of these groups are calculated. The activity coefficients of the solute and solvent are then developed from those of the groups. Since several compounds can be assembled from the same groups, activity coefficients of components in a mixture of solutes can be obtained almost as easily as that of a single solute (*7*). For hydrophobic compounds, $a_{org} \approx 1$, since water does not dissolve significantly in the organic phase. In principle, the solubility of the organic material is then available from eq 2, where $(\gamma_{aq}^{\infty})_{\mathrm{UNIFAC}}$ is

$$S = 55.5a_{org}/(\gamma_{aq}^{\infty})_{\mathrm{UNIFAC}} \quad (2)$$

the UNIFAC-derived activity coefficient at infinite dilution. For hydrophilic compounds where the water content in the organic phase is appreciable, a_{org} is typically less than one and can be calculated, as shown by Arbuckle (*6*), if it is assumed that the activity of water in the aqueous phase approximates unity. It follows that at equilibrium, the activity of water in the organic phase must also approximate unity, and the composition of the organic phase which corresponds to this condition can be obtained either from an activity–mole fraction plot or through iterative calculation.

Arbuckle (*6*) has noted that UNIFAC underestimates the solubility of large hydrophobic structures such as acenaphthene. This is not really surprising, since group contribution techniques tend to fail when applied to compounds containing numerous groups, where deviations from simple additivity are compounded. Also, UNIFAC parameters were not derived from compounds such as these, nor were they obtained from solubility data, and these factors undoubtedly contribute to the deviations. It seemed clear that while UNIFAC was inappropriate for the *direct* estimation of solubility, it would be worthwhile to examine whether the deviations were systematic and could be corrected for.

In order to determine the extent to which eq 2 underestimates solubility, activity coefficients were calculated for 50 structurally diverse compounds of widely differing solubilities. The list of compounds was selected to be representative rather than exhaustive, and isomers and other structurally similar compounds were excluded. The calculations were performed with a computer program written in Basic which incorporated the equations of Fredenslund et al. (*5*). Group constants were those of Gmehling et al. (*8*). The results are provided in Table I, and the relationship between $\log S$ and $\log[a_{org}/(\gamma_{aq}^{\infty})_{\mathrm{UNIFAC}}]$ is shown in Figure 1. For the solids in the group, the solubilities provided are those of the corresponding supercooled liquids. These values were obtained from eq 3 (*9*), where mp represents melting point (°C).

$$\log S_{\text{supercooled liquid}} = \log S_{\text{solid}} + 0.01(\text{mp} - 25) \quad (3)$$

Line A in Figure 1 corresponds to eq 2 and reveals that solubilities are generally underestimated by UNIFAC, as expected. However, the differences between measured and computed values are *systematic* and increase with increasing hydrophobicity of the compounds. Correction for

Table I. Water Solubilities of Selected Organic Compounds at 25 °C

compound	mp	$(\gamma_{aq}^{\infty})_{UNIFAC}$	a_{org}[a]	log S[b]	ref
acenaphthene	93	1.40E7		−3.86	4
acetal		3.58E2	0.56	−0.37	10
acrylonitrile		4.53E1	0.93	0.15	10
aniline		9.04E1	0.67	−0.15	10
benzene		2.42E3		−1.68	9
benzo[*a*]pyrene	179	2.80E9		−6.26	4
benzyl alcohol		6.85E2	0.80	−0.40	7
biphenyl	71	1.06E6		−3.88	4
1,3-butadiene		7.19E3		−1.86	10
2-butanol		5.42E1	0.61	0.39	10
2-butanone		3.20E1		0.52	10
carbon tetrachloride		1.04E4		−2.31	11
chlorobenzene		1.92E4		−2.35	7
chloroform		8.64E2		−1.22	11
cyclohexadiene		1.43E4		−1.97	10
cyclohexanol		2.66E2	0.72	−0.42	12
p-cymene		4.30E5		−3.76	11
dibenz[*ah*]anthracene	267	1.86E10		−6.28	4
m-dichlorobenzene		1.73E5		−3.01	7
3,3′-dichlorobenzidine	132	8.79E4		−3.84	11
2,4′-dichlorobiphenyl	43	5.83E7		−5.32	9
1,2-dichloroethane		6.67E2		−1.09	11
diethyl ether		1.62E2	0.75	−0.06	10
7,12-dimethylbenz[*a*]anthracene	122	6.83E9		−5.71	4
2,4-dimethylphenol		1.71E2	0.48	−1.19	11
ethyl acetate		1.50E2		−0.13	7
ethylbenzene		3.40E4		−2.80	9
heptanol		1.32E3	0.76	−1.81	12
hexachlorobenzene	230	9.78E8		−5.48	9
2,2′,4,4′,5,5′-hexachlorobiphenyl	103	2.91E11		−7.66	9
hexanoic acid		1.93E2	0.67	−1.07	10
hexanol		4.73E2	0.73	−1.21	12
methyl acetate		5.36E1		0.45	10
3-methylcholanthrene	179	2.03E10		−6.54	4
methylene chloride		4.23E2		−0.65	10
naphthalene	81	1.39E5		−3.04	4
nitrobenzene		3.34E3		−1.77	11
nitromethane		4.18E1		0.20	10
octanol		3.69E3	0.78	−2.35	12
pentachlorobenzene	86	1.16E8		−4.85	9
phenanthrene	97	7.41E6		−4.42	4
styrene		6.17E4		−2.57	11
1,2,3,5-tetrachlorobenzene	55	1.35E7		−4.33	7
2,2′,5,5′-tetrachlorobiphenyl	87	4.16E9		−6.58	9
1,1,2,2-tetrachloroethane		1.11E4		−1.75	11
toluene		1.21E4		−2.22	9
1,3,5-trichlorobenzene	64	1.54E6		−4.09	7
1,1,1-trichloroethane		2.37E3		−2.00	11
triethylamine		2.00E2		−0.83	10
p-xylene		5.65E4		−2.77	10

[a] Approximated as one unless otherwise noted. [b] For the solids in the series, log S refers to the supercooled liquid and is calculated from eq 3.

the deviations is straightforward and can most easily be made through eq 4 which was derived from regression

$$\log S = 1.20 + 0.782 \log [a_{org}/(\gamma_{aq}^{\infty})_{UNIFAC}] \qquad (r = 0.981) \quad (4)$$

analysis of the data. The correction greatly improves the correlation, as illustrated by line B in Figure 1 which corresponds to eq 4.

Equation 4 is empirical, but the empiricism is justified on two accounts. First, the reasons for the failure of eq 2 are well understood, and it is very unlikely that a nonempirical correction can be devised. Second, the quality of the correlation with eq 4 compares very favorably with others presently available, and the broad range of structures covered exceeds that of most others. A limitation is that several component groups of environmental importance are not included in the UNIFAC database, and compounds such as the phosphate-containing insecticides are well outside the present range of UNIFAC. Despite this constraint, eq 4 is remarkably versatile, and UNIFAC would appear to be well suited for environmental assessment.

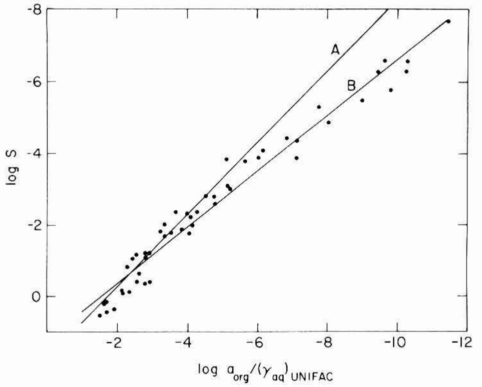

Figure 1. Relationship between log S and UNIFAC-derived parameters. Lines A and B represent eq 2 and 4, respectively.

Registry No. Acenaphthene, 83-32-9; acetal, 105-57-7; acrylonitrile, 107-13-1; aniline, 62-53-3; benzene, 71-43-2; benzo[*a*]pyrene, 50-32-8; benzyl alcohol, 100-51-6; biphenyl, 92-52-4; 1,3-butadiene, 106-99-0; 2-butanol, 78-92-2; 2-butanone, 78-93-3; carbon tetrachloride, 56-23-5; chlorobenzene, 108-90-7; chloroform, 67-66-3; cyclohexadiene, 29797-09-9; cyclohexanol, 108-93-0; *p*-cymene, 99-87-6; dibenz[*ah*]anthracene, 53-70-3; *m*-dichlorobenzene, 541-73-1; 3,3′-dichlorobenzidine, 91-94-1; 2,4′-dichlorobiphenyl, 34883-43-7; 1,2-dichloroethane, 107-06-2; diethyl ether, 60-29-7; 7,12-dimethylbenz[*a*]anthracene, 57-97-6; 2,4-dimethylphenol, 105-67-9; ethyl acetate, 141-78-6; ethylbenzene, 100-41-4; heptanol, 111-70-6; hexachlorobenzene, 118-74-1; 2,2′,4,4′,5,5′-hexachlorobiphenyl, 35065-27-1; hexanoic acid, 142-62-1; hexanol, 111-27-3; methyl acetate, 79-20-9; 3-methylcholanthrene, 56-49-5; methylene chloride, 75-09-2; naphthalene, 91-20-3; nitrobenzene, 98-95-3; nitromethane, 75-52-5; octanol, 111-87-5; pentachlorobenzene, 608-93-5; phenanthrene, 85-01-8; styrene, 100-42-5; 1,2,3,5-tetrachlorobenzene, 634-90-2; 2,2′,5,5′-tetrachlorobiphenyl, 35693-99-3; 1,1,2,2-tetrachloroethane, 79-34-5; toluene, 108-88-3; 1,3,5-trichlorobenzene, 108-70-3; 1,1,1-trichloroethane, 71-55-6; triethylamine, 121-44-8; *p*-xylene, 106-42-3.

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Electrogenerative Reduction of Nitric Oxide for Pollution Abatement

Kevin T. Pate and Stanley H. Langer*

Department of Chemical Engineering, University of Wisconsin—Madison, Madison, Wisconsin 53706

■ Nitric oxide can be electrocatalytically reduced selectively and removed from mixtures of gases which include constituents encountered in stationary power plant effluents. Several of these constituents, including sulfur dioxide and its reduction products, inhibit oxygen reduction in electrogenerative cells while having much less effect on nitric oxide reduction and its removal from simulated effluent-type gas streams. The possibility of utilizing suitable electrochemical cells for removing nitric oxide from effluent gas streams of managed composition in power plants is suggested, together with the possibility of recovering reduced constituents as useful chemicals.

Nitrogen oxides (NO_X) in industrial pollutant gas streams have received special attention in recent years due to concerns about adverse health effects, photochemical smog, and other environmental problems (*1, 2*). The thermodynamically favorable, electrogenerative reduction of nitric oxide for the synthesis of chemicals, namely, ammonia, hydroxylamine, and nitrous oxide, has been described previously (*3, 4*). A high conversion of nitric oxide in both concentrated and dilute feed streams strongly suggests potential application of this or a related reducing system for removal of nitric oxide from effluent streams from stationary power plants. With this in mind, we carried out the following initial study on the performance of the electrogenerative system with simulated flue gas mixtures, that is, dilute nitric oxide in the presence of other competitive oxidant gases such as oxygen and sulfur dioxide as well as with carbon monoxide and carbon dioxide.

The electrogenerative reactor here consists of two high-surface-area, porous, Teflon-backed, gas-permeable, liquid-impermeable, platinum black electrodes separated by an acidic free electrolyte phase as depicted in Figure 1. The cell was operated at room temperature (ca. 25 °C). The external circuit connecting the electrodes consists of a variable resistor load for adjusting current in series with an ammeter. Hydrogen at atmospheric pressure reacts at one electrode, while nitric oxide or a competitive oxidant in a gas mixture reacts at the other with protons from the electrolyte and electrons from the external circuit to generate current at potentials determined by reactions and polarization at each electrode. Electrogenerative reaction potentials are frequently different from those of conventional electrosynthesis. The cathode here is positive relative to the hydrogen electrode. Favorable thermodynamics with catalytic electrodes enable electrogenerative reactions to occur spontaneously to generate current without an external power source. Details of cell construction for constant gas flow at atmospheric pressure are given elsewhere (*4, 5*).

Identified overall electrode reactions for nitric oxide containing gas mixtures (*3–9*) can be represented by

anode:

$$H_2 \rightarrow 2H^+ + 2e \qquad (1)$$

H^+ transported through the electrolyte

cathode:

$$2NO + 2H^+ + 2e \rightarrow N_2O + H_2O \qquad (2)$$

$$2NO + 4H^+ + 4e \rightarrow N_2 + 2H_2O \qquad (3)$$

$$2NO + 6H^+ + 6e \rightarrow 2NH_2OH \qquad (4)$$

$$2NO + 10H^+ + 10e \rightarrow 2NH_3 + 2H_2O \qquad (5)$$

$$2H^+ + 2e \rightarrow H_2 \quad \text{(concentration cell)} \qquad (6)$$

$$O_2 + 4H^+ + 4e \rightarrow 2H_2O \qquad (7)$$

$$SO_2 + 4H^+ + 4e \rightarrow S + 2H_2O \qquad (8)$$

Some results at low potentials for electrogenerative reduction of dilute nitric oxide in the presence of other gases with a platinum cathode of about 5 cm^2 are shown in Table I, which also gives operating details. Both anode and cathode were platinum black electrodes of commercial, American Cyanamid, Teflon-backed LAA-2 (9 mg/cm^2) fuel cell type (*10, 11*). Typical industrial stationary power plant flue gas compositions before treatment are = 180–240 °C, 15 mg/m^3 dust, 9% moisture, 13% O_2, 9% CO_2, 20–60 ppm of CO, 3–7 ppm of hydrocarbons, and 180–240 ppm (0.018–0.024%) each of NO and SO_x (*1*). NO_x and SO_x may be much more dependent on fuel constituents and pretreatment. Actual operation of the electrogenerative cell with low levels of NO, CO, and SO_2 was not possible in this preliminary study because the gas mixtures were manually prepared by bleeding various gases into the stream with needle valves. The minimum concentration level of a gas attained by this method was about 1%. The results of Table I are presented in terms of generated current with chemical conversions. Although not as dilute as in flue gas, these experiments illustrate attractive possibilities for reduction of nitric oxides in polluting air streams.

While we do not report details here, we found that most of the current used for reducing the nitrogen oxides at low potentials resulted in formation of ammonia and hydroxylamine (*3, 4*), in the electrolyte. While ammonia formation is strongly favored in nitrogen diluent alone, there is a trend toward hydroxylamine formation in the presence of carbon monoxide or sulfur dioxide. We have described selectivity studies in these reductions earlier (*4*).

Run 1, which consisted of a cell feed of 1.1% NO in nitrogen, shows that although the NO was at low concentration, its strong adsorption characteristics on noble metal catalysts such as platinum brought about high conversion (97%) of the NO to primarily ammonia. The positive potential at the cathode also results in some hydrogen transfer because of concentration cell effects as illustrated by eq 6, accounting for current not used in nitric oxide reduction.

In run 2, where the feed consisted of dilute NO with 8.6% oxygen, considerable competitive reduction of the oxygen is observed. Most important, however, is that the nitric oxide is selectively reduced; that is, it is apparently adsorbed preferentially and reduced with removal from the gas stream at the platinum cathode. The nitric oxide

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Table I. Electrogenerative Cell Data (Pt Black Cathode and Anode, 5 cm^2, 6 N H_2SO_4 Electrolyte, Hydrogen Anode)

run[a]	cathode feed rate, cm^3/min	measured cell potential, V	current density, mA/cm^2	current fraction, %		$NO \rightarrow NO_2$ conversion before cell, %	NO conversion through cell, %	overall NO conversion, %[b]	overall O_2 conversion, %
				NO_X reduction	O_2 reduction				
1	4.7	0.048	11.1	72.5			96.5	96.5	
2	4.5	0.112	24	13.5	86.5	97.2	>82.1[d]	>99.5	83.5
3	4.8	0.029	7.0	33.3	66.7	93.7	46.0	96.6	14.7
4	4.8	0.054	19	20.7	79.3	94.0	>88.3[d]	>99.3	69.7
5	5.6	0.083	28[c]	5.8	0.8	92.5	60.0	97.0	1.3

[a] Cathode feed composition (vol %): run 1, 1.1% NO, Bal. N_2; run 2, 1.9% NO, 8.6% O_2, Bal. N_2; run 3, 1.9% NO, 9.2% O_2, 1.4% CO, Bal. N_2; run 4, 1.5% NO, 6.3% O_2, 8.1% CO_2, Bal. N_2; run 5, 1.6% NO, 5.3% O_2, 18.3% SO_2, Bal. N_2. [b] Overall NO conversion to NO_2, HNO_3, and electrogenerative cell products (mainly NH_3 and NH_2OH). [c] Substantial SO_2 reduction at the cathode-formed S (solid) and H_2S(g). [d] Final NO concentration in product gas stream was less than 100 ppm (limit of GC detectability) after a single pass through cell.

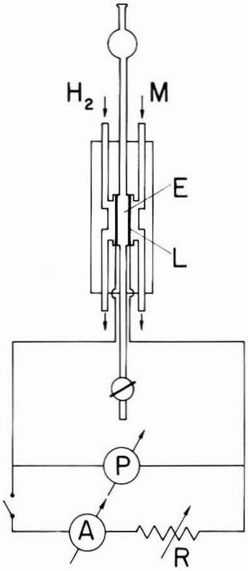

Figure 1. Schematic representation of operating components of electrogenerative system. L, electrodes separated by electrolyte; E, electrolyte compartment, $^1/_4$-in. thick between electrodes, with reservoir and drain; M, mixed gas feed to cathode (see text); P, potentiometer; A, ammeter; R, variable resistive load.

concentration was reduced from 1.9% in the feed to less than 100 ppm (0.01%) in a single pass (greater than 99.5% conversion). The high NO conversion also involved considerable NO oxidation to NO_2 with oxygen in the feed stream before the cell as well as electrogenerative reduction of NO_2 and remaining NO to ammonia combined with current generating oxygen reduction to water (eq 7). When this same feed passed through the cell at open circuit for comparison, nitric oxide concentration was not reduced below 1100 ppm by further O_2 oxidation even further downstream. It should be noted that nitrogen dioxide is also quite soluble in aqueous electrolyte with eventual formation of nitric acid which is readily reduced to ammonia in electrogenerative cells of the type described here. The reduction of nitrate ions to ammonia and hydroxylamine has been reported (*4, 12*).

It is difficult to carry out an exact meaningful material balance in the presence of oxygen because of the nitric oxide oxidation to nitrogen dioxide in the dilute feed stream. However, analyses by gas chromatography for oxygen and nitric oxide before and after entering the cathode compartment of the electrogenerative cell are quite feasible (*4*).

Run 3 illustrates the inhibiting effect of carbon monoxide on the platinum-catalyzed NO/NO_2 and O_2 reduction reactions. There is a significantly greater effect on oxygen reduction which is not readily quantified with respect to carbon monoxide concentration. Extrapolating from the relatively high levels of CO in this experiment (Run 3 at 1.4% CO) to the low level of CO normally found in flue gas (typically 60 ppm), however, suggests that high selective, reductive conversion of NO through the cell might be realized while the oxygen reduction reaction might be inhibited by other flue gas constituents. Carbon dioxide can also compete for adsorption on the platinum catalyst. Run 4, which is at a CO_2 level similar to that in flue gas, shows little effect on the nitric oxide reduction while the oxygen reduction is diminished.

Run 5 consisted of 1.6% NO in the presence of 5.3% oxygen and 18.3% sulfur dioxide. The high feed level of SO_2 occurred because of limited flow control with the SO_2 feed needle valve. This run, although at a much higher level of SO_2 than usually observed in flue gas (typically 200 ppm), shows significant conversion of the nitric oxide in spite of substantial SO_2 reduction to elemental sulfur and some odoriferous hydrogen sulfide at the cathode. The sulfur dioxide reduction nearly completely halted oxygen reduction. The large amount of sulfur deposited (as indicated by yellow solid buildup) would undoubtedly have eventually covered all the platinum catalytic surface. In real effluent streams sulfur dioxide concentration can be controlled by conventional scrubbing where desired. From the result here and earlier, though, it appears that while sulfur dioxide and its reduced derivatives significantly inhibit oxygen reduction (*13, 14*), nitric oxide reduction is much less affected. There is the further possibility that a platinum sulfide complex might be electrocatalytically active for nitric oxide reduction. Similar catalysis of other reduction reactions has been reported (*15*). These results demonstrate that the electrogenerative system may offer an attractive, viable method for NO_x abatement. Very high conversion of NO was maintained under dilute conditions and in the presence of competitive oxidant gases such as O_2 and SO_2. The inhibiting effects of CO and SO_2 on the oxygen reduction can be advantageous since these should still permit selective reduction of the nitrogen oxides, making the electrogenerative system more coulombically efficient for NO_x removal (less hydrogen is consumed for non-NO_x reduction).

A nitric acid–oxygen redox electrode has been proposed as a cathode in a fuel cell earlier (*16*). A nitrogen dioxide–oxygen redox electrode has also been described (*17*). However, these systems were mainly directed to energy generation in a regenerative cell. Nitrogen compounds were not consumed nor were they reduced beyond nitric oxide. Results reported here are different in that significant amounts of ammonia are formed on reduction of nitric oxide.

The goal for pollution abatement then becomes one of controlled electrocatalysis with proper choices of effluent gas stream composition and electrocatalyst composition; it would be desirable to inhibit electrochemical oxygen reduction while allowing nitric oxide reduction. In managing effluent gas streams, efforts could be concentrated on controlled removal of sulfur dioxide without restricting NO_x formation during combustion before the electrochemical cell where it can be readily reduced and removed. There are options in the choice of electrolyte (*4*), and it might be processed for recovery of ammonia and hydroxylamine, both of which have commercial value. Compared to the positive advantage in removing nitric oxide (emphasized here) and the potential value of recovered chemicals from processing of power plant effluents, byproduct electricity would not be important. The implementation of this approach might involve design and adaptation of electrogenerative cells containing large-scale porous catalytic electrodes with high surface area for processing of large volumes of flue gas. Design technology drawn from that develoed for large-scale fuel cells could be applied to the electrogenerative and related electrochemical systems. We are continuing to work on related aspects of nitric oxide reduction.

Acknowledgments

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CORRESPONDENCE

Comment on "Development of a General Kinetic Model for Biodegradation and Its Application to Chlorophenols and Related Compounds"

SIR: Banerjee et al. (*1*) investigated the biodegradation rate of some chlorophenols and related compounds by pure as well as mixed cultures. They found that in most cases rate decreased with increasing lipophilicity (1-octanol–water partition coefficient, K_{ow}) of the substrate. Interpretation of these results was based on a reaction mechanism where penetration of the compound into the organism is rate determining and occurs via two parallel pathways (*2*), i.e., either through the lipid layer (k_3) or through the hydrophilic pores (k_4) of the cell membrane. Banerjee et al. justified their results by assuming that k_3 is inversely related to K_{ow}, while k_4 does not depend on it, and concluded that lipid penetration is dominant for the more lipophilic compounds.

However, it seems difficult to accept that lipid penetration should in any case be *slower* for the compounds with a higher lipophilicity. In addition, Banerjee et al., (*1*) did not consider that chlorophenols are known as inhibitors of bacterial activity (*3*) and in particular of the biodegradation of phenol (*4*), their toxicity being an *increasing* function of K_{ow}.

Therefore, we suggest a different interpretation, based on the idea that enzymatic processes, rather than transport phenomena, are rate determining. In fact, according to the usual kinetic treatment, when chlorophenols act as inhibitors of the phenol degradation, they tend to bind to the enzymes, giving dead-end or slowly reacting complexes. An analogous behavior could be shown when they are subjected to biodegradation. If, along a series where K_{ow} increases, there is (i) an increasing tendency to form complexes with enzymes and (ii) a decreasing reactivity of such complexes, both the inhibition (*4*) and the degradation (*1*) results can be explained. The properties i and ii need not be physically related to lipophilicity; they could actually depend on structural, steric, or electronic factors that are correlated to K_{ow}.

Without aiming at a detailed description of the biodegradation process, a simplified model can be presented to support our interpretation. The degradation of a substrate S in the presence of an enzyme E and an inhibitor I may follow a rate law of the form

$$r_S = \frac{k_S C_S C_E{}^0}{(K_S + C_S)(1 + C_I/K_I)} \qquad (1)$$

where *C*'s are concentrations and k_S refers to the reactivity of the complex ES and K_S to its stability, while K_I refers to the stability of enzymatic complexes including the inhibitor. On the other hand, inhibitor I, if similar to S, may be slowly degraded by the same enzyme E; a rate law such as eq 2 can be written for experiments in the absence of substrate S, where where k_I refers to the reactivity of the complex EI and K_I to its stability, as above.

$$r_I = \frac{k_I C_I C_E{}^0}{K_I + C_I} \qquad (2)$$

Now let us consider a series of inhibitors of increasing complexation ability (i.e., decreasing K_I) and decreasing reactivity of the relevant complexes (decreasing k_I). From eq 1 it comes out that r_S decreases, independently of the reaction order; because of eq 2, r_I is subjected to contradictory influences, but in cases of zero-order processes, i.e., when K_I is negligible in the denominator of eq 2, r_I certainly decreases. These facts, with phenol as S and the chlorophenols as compounds I, have actually been observed (*1, 4*).

It remains to be clarified why enzymatic parameters K_I and k_I should be correlated to K_{ow} values of compounds I. In our opinion, this correlation is a mathematical fact that could mask some different phenomenon, involving physical properties other than lipophilicity. The latter, for instance, is known to increase with molecular size, when aprotic substituents are progressively added into a reference compound: molar refractivity, which is strongly dependent on molecular size, was found significantly correlated to log K_{ow} ($r = 0.73$) for a series of chloro- and nitrophenols (*4*). Within a class of compounds differing only for number and positions of identical substituents, also electronic factors may be correlated to the lipophilicity index: for the 19 chlorophenols, log K_{ow} and Hammett $\sum\sigma$ values (*4*) are linearly related with a correlation coefficient $r = 0.93$.

It should be noted that the model of Banerjee et al. (*1*) did not fit the behavior of some compounds, in particular, two 2,6-chlorine-substituted phenols, for which a different rate-determining step was required. With the present interpretation, these chlorophenols are not exception, but only compounds with lower K_I and k_I values than their isomers, if any, with at least one ortho position free.

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P. Beltrame,* P. L. Beltrame, P. Carniti

Departimento Chimica Fisica ed Elettrochimica
Università di Milano
20133 Milano, Italy

SIR: Beltrame et al. (*1*) postulate that the biodegradability of the various compounds considered in the title study (*2*) is governed by the toxicity of the materials to the organism. They base their proposal on their eq 2 (*1*), which is, in effect, the familiar Michaelis–Menten equation (eq 1) which has no explicit link to toxicity. They contend

$$v = V_{max}[S]/(K_m + [S]) \qquad (1)$$

that under conditions where $[S] > K_m$, the observed zero-order rate, V_{max}, is nominally related to lipophilicity. In our study, the first-order rate data of Yonezawa and Urushigawa (*3,4*) were also interpreted through our model

Table I. Interrelationship between Toxicity and Biodegradability for Chlorophenols

chlorophenol[a]	toxicity (IC_{50}, mM)			biodegradation rate, mol $cell^{-1}$ h^{-1} [e]
	A[b]	*B*[c]	*C*[d]	
2	0.89	5.4	0.812	3.49E–17
3	1.2	3.5	0.525	4.32E–17
4	0.68	3.1	0.552	5.44E–17
2,3	0.94	0.80	0.338	2.66E–18
2,4	0.60	0.46	0.292	3.76E–19
2,5	0.66	0.52	0.308	
2,6	>1.2	3.4	0.400	ND[f]
3,4	0.56	0.32	0.262	6.84E–19
3,5	0.61	0.15	0.358	
2,3,5	0.46	0.051	0.113	
2,4,5	0.29	0.061	0.120	1.43E–20
2,3,4,5		0.017	0.088	7.14E–22

[a] Position of substitution. [b] Reference 7. [c] Reference 8. [d] Reference 9. [e] Reference 2. [f] No measurable degradation.

(*2*). Hence, since $K_m > [S]$ under these conditions, the hypothesis of Beltrame et al. would now require a correlation of V_{max}/K_m with lipophilicity. Given that K_m is a composite quantity of variable mechanistic significance (*5*), the thesis of Beltrame et al. appears to be based on a number of severe assumptions.

Beltrame et al. find it difficult to accept that, within a series of lipophilic compounds, lipid penetration occurs more slowly for the more lipophilic (and usually larger) members in the series. However, other factors being equal, larger molecules diffuse more slowly than smaller ones. For example, the diffusion coefficient of a sphere is inversely related to its radius (*6*). In any case, the hypothesis of Beltrame et al. cannot presumably apply to Yonezawa and Urushigawa's data (*3,4*) where both direct and inverse relationships between lipophilicity and degradability occur.

Contrary to the comment of Beltrame et al. on our apparent disregard of the inhibitory effects of chlorophenols, we had clearly stated (*2*) that experiments were conducted at concentrations below toxic levels of the substrates. These levels were measured at the onset of the study (*7*) and are reported in Table I, along with the measurements of Liu and Kaiser (*8*), the data of Beltrame et al. (*9*), and some of our biodegradation values. The intercorrelation is clearly good. Its meaning, however, is somewhat obscure in view of the differences in organisms and in the toxicity indexes used. The results of Beltrame et al. (*9*) were obtained from the effect of chlorophenols on the degradation rate of phenol in activated sludge, Liu et al. (*8*) measured the inhibition of bacterial dehydrogenase by the test compounds in a *Bacillus* isolated from activated sludge, and our work reflects the effects of the compounds on growth of the organism in a salts medium containing 177 mM phenol (*7*).

As Beltrame et al. recognize (*1*), changes in lipophilicity within the closely related chlorophenol series correlate with several other parameters, including the number of chlorine atoms per molecule. A mechanism inferred from one of these correlations without hard supporting evidence is simplistic at best, especially when it is based on "a mathematical fact that could mask some different phenomenon, involving physical properties other than lipophilicity" (*1*). When the mechanism further requires correlations of both V_{max} and K_m/V_{max} with lipophilicity or a derived parameter, it becomes even more improbable.

We have no difficulty with the importance of toxicity when the substrates are present at toxic levels. However, extension of the toxicity hypothesis to the nontoxic concentrations used in our study is unwarranted, especially on the basis of the evidence provided. It is more likely that the correlation of toxicity with biodegradation is mainly a reflection of the generalization (eg. ref 2 and 8) that both recalcitrance and toxicity increase with increasing chlorine substitution. We would caution against attaching much mechanistic significance to the relationship.

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Sujit Banerjee*

Safety and Environmental Protection Division
Brookhaven National Laboratory
Upton, New York 11973

Philip H. Howard

Life and Environmental Sciences Division
Syracuse Research Corporation
Syracuse, New York 13210

Denzil L. Tullis

Department of Chemistry
University of Arkansas
Little Rock, Arkansas 72204

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ADDITIONS AND CORRECTIONS

1984, Volume 18, Page 168

Robert A. Rapaport and Steven J. Eisenreich*: Chromatographic Determination of Octanol–Water Partition Coefficients (K_{ow}'s) for 58 Polychlorinated Biphenyl Congeners.

Due to further experimental work, it was discovered that 5 of the 58 PCB congeners on page 168 were incorrectly identified. The following list explains these changes. Note that the RPHPLC uncorrected log K_{ow} values are now transferred from the old ID's to the new ones.

old compound ID (systematic no.)	new compound ID (systematic no.)	RPHPLC uncorrected prepd log K_{ow}	"new" final corrected log K_{ow}
2,3,3′ (20)	2′,3,4 (33)	4.99	5.57
3,3′,4,4′ (77)	2,3,3′,4′,6 (110)	5.62	6.53
2,2′,3,4′,6 (91)	2,3′,4,4′ (66)	4.94	5.45
2,3′,4,5,5′ (120)	2,2′,3,3′,4 (82)	5.22	6.14
2,2′,3,3′,5,6,6′ (179)	2,2′,3,4,5,5′ (141)	6.77	7.59

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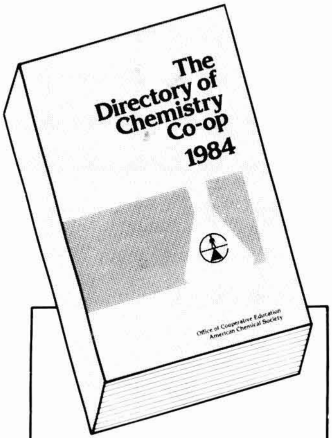

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