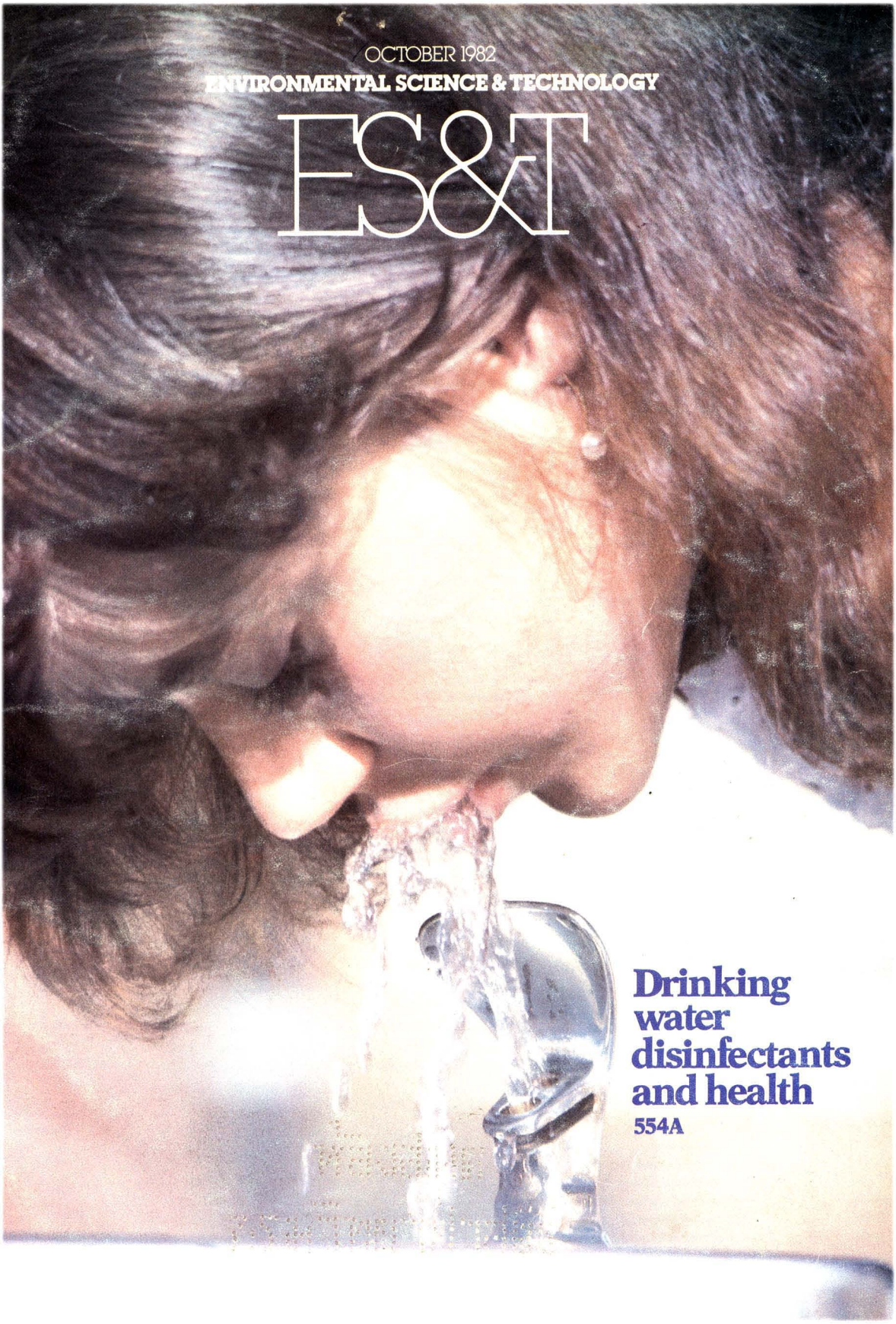
OCTOBER 1982
ENVIRONMENTAL SCIENCE & TECHNOLOGY
ES&T



Drinking water disinfectants and health

554A

"ERT'S PSD PERMITTING STRATEGY PUT OUR NEW MILLER BREWERY ON THE FAST TRACK!"

– Russell Turner, Manager of Environmental Affairs and Energy Conservation, Miller Brewery

"Our new mideast brewery was a key part of our expansion strategy to keep Miller out in front in its competitive market. We needed an environmental consulting firm with solid regional experience, to ensure that we took the fastest and most economical permitting route to start our construction on schedule. We turned to ERT.

"Our best site was located in an area designated as non attainment which made our air permitting requirements particularly tough. ERT had worked extensively in EPA region 5 and had the experience, knowledge of the regulations and sensitivity to the regional issues that enabled them to develop an effective permitting strategy. They determined that the non attainment designation for the area was based on measurements taken well outside the site for our brewery. Using innovative analysis techniques, they were then able to effectively demonstrate a "clean pocket" around the site. EPA 5's acceptance of this clean pocket eliminated the need for emission offsets which could have seriously delayed the project and escalated costs. We then worked closely with ERT to develop detailed modeling data to successfully show that we would not significantly impact this clean pocket area.

"We began our work with ERT on the air quality permits in January of 1979 and we had the permits in-hand by August of that year. I'd call that a good fast track record."

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Russell Turner, Manager of Environmental Affairs and Energy Conservation at Miller Brewery, and Bob Bibbo, ERT Project Manager, review air permitting strategies for Miller's new mideast brewery.

ERT

a step ahead

CIRCLE 5 ON READER SERVICE CARD

ESTHAG 16(10) 533A–590A
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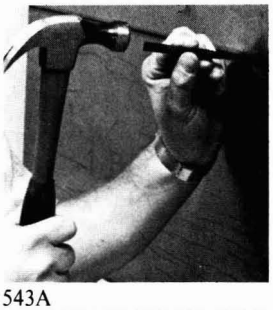

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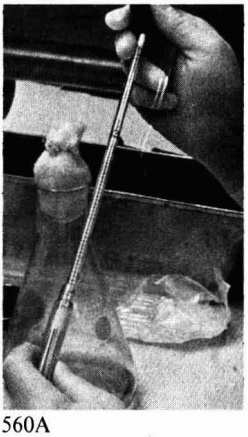

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This issue contains no papers for which there is supplementary material in microform.

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ES&T
LETTERS

Acid deposition

Dear Sir: I would like to take issue with the summary evaluation appearing as the next to last paragraph of the article "Acid Deposition" (*ES&T*, Vol. 16, No. 6, 1982, p. 323A).

There certainly is no question that the issue has become polarized. But to state that one group says, "that we must establish an indisputable cause and effect relationship before we can initiate controls . . ." is setting up a straw man argument. The author herself notes further, "But the very nature of science itself dictates that we will never be able to establish an absolutely certain cause and effect relationship . . . ."

The issue is not proof of cause and effect but rather a reasonable assurance that the remedies proposed do not impose costs on one group that are disproportionately larger than the benefits received by another group. A contractor for the Electric Power Research Institute (EPRI) recently has completed a decision analysis framework integrating the possible control, mitigation, and research options with the uncertainties as to emissions, transport, deposition, effects, and other outcomes. This analytic tool is available from EPRI to all involved in trying to come to grips with this complex problem.

We at EPRI do not advocate which controls and/or mitigation strategies to employ. It is our hope that the structured analysis of the state of the science and the options through the use of this tool will help the polarized groups come toward a consensus.

René H. Malès, Director
Energy Analysis and Environment Division
Electric Power Research Institute
Palo Alto, Calif. 94303

Author's response

In his letter Dr. Malès appears to make two main points. One of these is that indisputable proof of cause and effect is no longer a legitimate acid rain issue. The other is that cost-benefit analysis should be used to determine which control and mitigation strategies to employ.

When Dr. Malès states that my article raises a straw man, he seems to ignore the fact that many industry spokesmen have built up that straw man. They have repeatedly stated before Congress and in numerous acid rain symposia that not enough is known about cause-effect relationships to undertake control or mitigation actions. Typical of such claims is that of William N. Poundstone, an official of the National Coal Association: ". . . let me say that I believe we *should* do something about acid rain. What we should do is determine its causes and its effects *before* deciding how it should be controlled and if, indeed, control is warranted." Dr. Malès and I, however, apparently share a more advanced understanding of acid rain cause-effect relationships than most other industry spokesmen. Furthermore, he seems to recognize implicitly that some controls may be required to avoid adverse effects.

Dr. Malès argues strongly that remedies for the acid rain problem are not appropriate unless they pass a cost-benefit test. Others believe that the cost-benefit relationship is not the only factor that should be taken into account. If it were the only criterion, we could use it to justify many unethical activities. For example, burglary—the costs imposed on the burglarized are no greater than the benefits received by the burglar. But rather than cost-benefit standards, we use ethical standards embodied in law to prohibit burglary.

In our pluralistic society, many insist that a standard of fairness, clearly an ethical standard, is important in regard to acid rain and ask: Do the residents of the Midwest have a right to destroy fish life in the Adirondacks in order to have cheaper electricity rates? Incidentally, even if an amendment such as that recently passed by the Senate Environment Committee becomes law and SO_2 emissions from utilities in the eastern half of the U.S. must be reduced by 8 million tons per year, the electric rates in the Midwest will still be lower than they are in New England.

With respect to international boundaries, representatives of the Canadian government have repeatedly maintained that cost-benefit analysis is particularly inappropriate. It is asserted that U.S. citizens do not have a right to eliminate fish life in thousands of Canadian lakes and possibly damage Canadian forests over the next few decades in order to save a modest fraction of their electric bills.

Participants in this debate have questioned several other important assumptions of cost-benefit analysis that have been applied to acid rain and believe that these should be a matter of public policy discussion and political decision making. Paramount among these assumptions is that a discount rate should be applied to future benefits. Is any discount rate defensible when estimating the value of vital resource bases upon which future generations may have to depend for their livelihood?

Bette Hileman, Assistant Editor
ES&T
Washington, D.C. 20036

ES&T
GUEST EDITORIAL

Fear of hazardous wastes: a self-fulfilling prophecy?

During the past year I had the unique opportunity to visit over 40 hazardous waste facilities in North America and Europe. This project was part of the waste management planning process for the province of Alberta. In my travels, I observed that widespread fear of hazardous wastes is often freezing rational progress toward comprehensive waste management solutions. Both siting of new plants and, to a lesser extent, operation of existing plants have become mired in a swamp of adverse reaction. Problems range from corporate litigation to personal harassment. In many cases, project advocates are finding that the potential rewards are not worth the rising financial and personal costs.

Often, members of the scientific community have, intentionally or unwittingly, promoted adverse public reaction. The basic problem is our frequent failure to maintain perspective. For instance, finding 500 ppm of PCBs in a batch of butter on a supermarket shelf merits rapid action to avoid public exposure. But, finding 500 ppm of PCBs in oil in a sealed transformer merits only reasonable caution. This case does not pose an imminent health hazard unless the transformer is mishandled, allowing the PCBs to reach a target organism.

The above distinction is appreciated by most scientists. However, we are not always careful to explain such realities to the media or the public. When questioned about hazardous wastes, too many of us fail to stress the need for perspective and the importance of circumstances. Imagine talking to a reporter who is in a "cold sweat" about a nearby transformer full of PCBs. He should be advised that in all likelihood he drove to work sitting within 6 ft of a tank of very hazardous material—gasoline. Being both highly flammable and toxic, gasoline has surely killed or injured more people in the last year than PCBs ever have or will. Although one may choose not to drive a car, any form of modern transportation involves hazards. Likewise, meeting countless other needs can be hazardous, for example, cooking meals and heating one's home. In fact, total isolation from exposure to hazardous materials simply is not possible.

Misunderstanding and lack of perspective are particularly likely when discussing carcinogens. The public has a strong fear of cancer. Furthermore, people do not easily comprehend risks of one in a million in terms of their own health. Hence, speculation about the presence of carcinogens in a given waste is certain to produce a compelling fear response regardless of the real degree of risk involved. As a result, carcinogen "name dropping" can quickly destroy any attempt at reasoned discussion.

In reality, most "hazardous wastes" being processed by regulated off-site plants are not classified as highly toxic. Most of them only pose an environmental problem if badly managed—as they usually were before adequate facilities became available. Yet, the fear-induced paralysis of siting adequate new facilities or operating existing ones will eventually ensure that bad waste management occurs more often.

None of us involved in environmental science or engineering can responsibly remain neutral on these issues. But, before becoming involved in public or private debate, we must be sure that we carefully assess the real hazards of a given situation. Fair assessment must consider "accepted" risks in modern society and the "assured" risks of no action.

Steve E. Hrudey

Steve E. Hrudey *is a professor in the Environmental Engineering and Science Program of the Department of Civil Engineering, University of Alberta, Edmonton, Alberta, Canada. He is active in industrial and hazardous waste research and is Canadian regional editor for the rapid communication journal,* Environmental Technology Letters.

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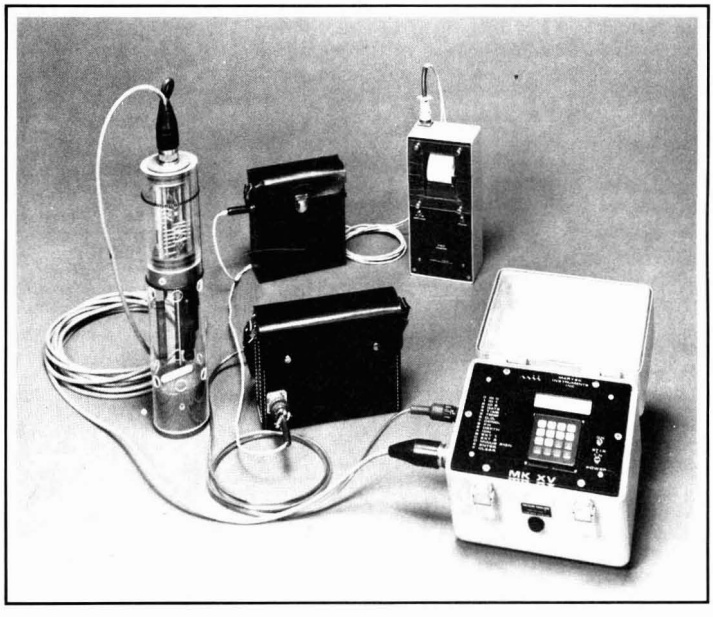

The new Mark XV Water Quality Microprocessor combines the sophistication of digital measurement with the simplicity of rugged field instruments. Designed for direct *in situ* measurement of seven parameters—temperature, salinity or temperature-corrected conductivity, depth, dissolved oxygen, pH, and specific ions—the Mark XV's microprocessor-controlled functions make it the ideal vehicle for operation in remote field environments or in the laboratory.

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The Mark XV power pack is external to the readout module and has its own vinyl carrying case with shoulder strap. While the standard configuration is a digital one, an option for onboard cassette data logging or hard-copy output to the Model AFP Alphanumeric Field Printer is available. The Mark XV is also compatible with computer peripheral equipment.

The combination of easy-to-read digital data, simple operation, and accurate measurement make the Mark XV the microprocessor of choice in water quality monitoring. If you are involved in water quality analysis, whether in lab or field, fresh water or sea water, you owe it to yourself to find out more about the new system from Martek.

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CIRCLE 10 ON READER SERVICE CARD

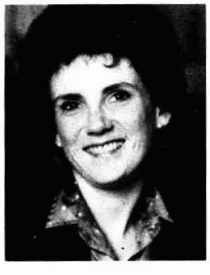
INTERNATIONAL

A cooperative agreement to coordinate acid rain research was signed by officials of the Canadian province of Quebec and the New York State Department of Environmental Conservation. The purpose of the agreement is to avoid duplication in acid rain research in New York and Quebec and to ensure that standardized laboratory procedures are used. A joint committee established by the agreement will publish an annual report on acid rain. Bureaus of information will be set up in New York and Quebec to provide information to the public about acid rain. Quebec previously made similar arrangements with Vermont.

WASHINGTON

By a vote of 352 to 56, the House of Representatives defeated a number of pro-industry amendments and approved a two-year extension of the basic federal pesticide control law, the Federal Insecticide, Fungicide and Rodenticide Act. The most controversial amendment to be defeated was one that would have prevented the states from setting higher pesticide standards than the federal government. This amendment was favored by the Reagan Administration. An amendment allowing private citizens access to federal courts to seek relief from pesticide damage was approved by a voice vote.

The Nuclear Regulatory Commission (NRC) voted 3–1 to approve the start of site preparation work for the Clinch River breeder reactor, a Department of Energy project, in Oak Ridge, Tenn. President Reagans's three appointees to the NRC voted in favor of the project, allowing the DOE to be exempt from certain licensing proceedings. Commissioner John F. Ahearne, a Carter appointee, voted against the project. Commissioner Victor Gilinsky was out of the country and did not vote. Assistant Energy Secretary Shelby T. Brewer said that the NRC decision was an important step in helping the U.S. once again gain a leadership position in the development of nuclear technology. Earlier this year the NRC refused to grant two similar DOE requests to bypass normal licensing requirements.



Bennett: EPA had a sound argument

Stationary sources in nonattainment or "dirty air" areas may no longer use the bubble policy. The U.S. Court of Appeals for the District of Columbia has ruled that EPA acted illegally last October when it extended the bubble policy to areas that do not yet meet clean air standards. The bubble policy was used by the Carter Administration only in attainment areas. EPA Assistant Administrator Kathleen Bennett said, "We are disappointed with the appeals court's decision, as we felt that EPA had a sound legal argument."

An industry-backed amendment on airborne hazardous pollutants was narrowly defeated by the House Energy and Commerce Committee. Instead, an alternate amendment sponsored by Reps. James J. Florio (D–N.J.) and W. J. Tauzin (D–La.) was passed. This amendment sets a four-year deadline for EPA to finish studies on 37 substances that the agency has named as potential airborne carcinogens. These include dioxin, PCBs, coke oven emissions, and formaldehyde. After the vote, Rep. Henry A. Waxman (D–Calif.) said: "The odds are against our doing a clean air bill this year."

Rule changes being considered by the Interior Department's Office of Surface Mining could lead to strip mining on private lands inside 26 national parks, according to the National Park Service. If the changes are adopted, 1.7 million privately owned acres inside the parks could be open to surface coal mining and an undetermined number of acres adjacent to the parks could also be used for mining. The rule change is one of several options being considered by the Office of Surface Mining. Interior Secretary James G. Watt has said repeatedly that he will not allow development in the national parks. The proposed changes are scheduled to take effect by Nov. 15, unless a court injunction delays implementation.

STATES

Acting on EPA's behalf, the Justice Department has filed its first suit under the Superfund law. It has sued 25 companies and individuals to force them to help clean up the now-inactive Chem-Dyne waste facility in Hamilton, Ohio. The department has also reached a $2.4-million out-of-court settlement with 100 other companies that used the facility. Hundreds of thousands of gallons of chemical and industrial wastes including arsenic, benzene, and PCBs are stored there. The Justice Department said that groundwater contaminated with the wastes is believed to be moving toward Hamilton's drinking water wells located three miles southwest of the site and that chemicals at the

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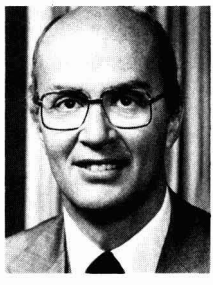
site release poisonous fumes and present a danger of fire and explosion.

Nearly $58 billion in damages has been awarded by a jury to Illinois workers who cleaned up dioxin spilled from a ruptured tank car in January 1979. The workers, present and former employees of the Norfolk and Western Railway Company, complained of ailments ranging from dizziness and fatigue to impotence and loss of memory. Thirty-two of the plaintiffs received an average of at least $1 million each. A veterans' group involved in Agent Orange lawsuits considers this award a major victory because Agent Orange contains dioxin.



Watt: will not cancel leases

In May the Interior Department's Bureau of Land Management issued two leases for oil and gas exploration in a South Carolina federal wilderness area despite the fact that Interior Secretary James G. Watt agreed to ban leasing in wilderness areas until Congress adjourns. Watt said he was not aware until Aug. 14 that the leases had been granted. He has not canceled the leases, however. Instead he telephoned the lessee and obtained a promise that there would be no drilling activity inside the wilderness areas. Drill holes would have to slant in from outside the area. According to the Federal Wilderness Act of 1964, leases in wilderness areas are technically permissible until Dec. 31, 1983, but previous Administrations have granted virtually no leases. The House recently voted 340–58 to pass a bill that permanently bans oil, gas, and mineral exploration in wilderness areas.

The 9th U.S. Circuit Court of Appeals in San Francisco ruled that the state of Washington may not ban out-of-state shipments of low-level radioactive waste. This ruling struck down a 1980 Washington state law forbidding out-of-state shipments. The dump at Richland, Wash., receives 40% of the nation's low-level waste, 95% of which comes from outside the state.

SCIENCE

A new nationwide study headed by the Food and Drug Administration has found that lead levels in the blood of black children are consistently higher than those in white children, and that the difference can not be explained simply by income levels or residential areas. Researchers said that "this difference was found in children and adults, in rural residents and urban dwellers, and in families with low, moderate, and high incomes." Even in central cities, black children had higher lead levels than white children. Overall, 12.2% of black children and 2% of white children had blood lead levels of 30 μg/dL or more—a level considered dangerously high. Lead exposure comes primarily from automobile emissions, chips of lead paint that are ingested, lead dust from smelters, and lead particles carried home on workers' clothing.

Wives of workers most exposed to chemicals in the wastewater treatment plant at an Exxon refinery in Louisiana are five times more likely to have miscarriages or stillborn babies than the average woman, according to a study commissioned by Exxon Corporation. The treatment plant removes a variety of chemicals resulting from the processing of gasoline, oil, waxes, and lubricants. The rate of miscarriage and stillbirth jumped from about 4% before the husbands were exposed to the chemicals to about 20% after exposure. The Environmental Health Associates (EHA) of Berkeley, Calif., performed the research and stressed that the data were too limited to allow firm conclusions. Exxon has turned down an EHA plan to continue the study and has also refused to allow EHA to publish the results.

Hazardous organics in liquid wastes from coal gasification/liquefaction can be identified and quantified through infrared (IR) spectrometry and gas chromatography/mass spectrometry (GCMS) techniques. This work, which involves wastewaters, was done by T. F. Yen et al., of the University of Southern California, for EPA (Cincinnati, Ohio). Macroreticular resins separated organics from wastewaters. Phenolic species predominated, with phenol itself in concentrations sufficient for potential recovery. Polynuclear aromatic hydrocarbons were found in gram quantities at a pilot plant, and *N*-nitrosodimethylamine was present even in kilogram amounts.

Should imported insect pests be fought with natural enemies from their "home countries"? Perhaps, suggests Robert Carlson of the U.S. Department of Agriculture's Asian Parasite Laboratory (Seoul, South Korea). A problem with imported pests is that the natural enemies that keep them in check in their native countries are not available in the U.S. Carlson breeds these enemies and ships them by air to the Beneficial Insects Research Laboratory (Newark, Del.). However, before "imported" enemies can provide biological pest control, their ability to function in their new habitat must be established.

TECHNOLOGY

Passive solar energy will heat a recreational center in St. Paul, Minn., a city noted for rigorous winters. Passive solar devices use the characteristics of the building and its surroundings to make the sun "work," whereas active solar devices use collectors, pumping systems, and the like. The recreation center, built by Acton Construction Company (Hugo, Minn.) will have a greenhouse portion with canisters containing a heat-exchange chemical, kept under vandal-proof glass. Sunlight would melt the chemical, allowing it to store heat, which is given off when the chemical cools and solidifies and is carried through ducts. Summer cooling can be provided by the natural cooling power of the earth.

Heavy-metal removal from water could be done with insoluble starch xanthate (ISX), a grain-based product rendered insoluble in water and then xanthated to form an anionic polymer. The ISX would carry sodium and magnesium ions, and exchange them for heavy-metal cations, according to Pollution Technology Systems, Inc. (PTS, Garland, Tex.). The ISX with heavy metals bound to it could

then be removed from the water by gravity separation or filtration. The heavy-metal-exchange capacity is a function of a single metal's or combination of metals' molecular weights and associated valences. EPA has identified ISX as a type of "best available technology," according to PTS.

Suppose asbestos could have reduced toxicity and yet retain the properties that make it so useful. Flow General Inc. (McLean, Va.) says that Earl Flowers may have found a way to make this possible. He treats asbestos with a solution of metallic salts and forms a surface called "metal–micelle polymer," for which a patent has been issued. Lung cells exposed to this type of asbestos multiplied almost as well as cells never exposed to asbestos, whereas cells exposed to untreated asbestos did not multiply, says Flow General President Joseph Hall. He adds, however, that further animal tests are needed to determine whether asbestos toxicity to humans is indeed reduced.

A computer-based library for water data—the bulk of everything published by the American Water Works Association since 1971—will be found in WATERNET, with indexes and abstracts. This material will be available through the DIALOG Information Retrieval Service, the world's largest on-line information system.

Solid municipal waste will be pyrolyzed to fuel gas in coke ovens at an abandoned coke plant. The ovens will be modified so that pyrolysis occurs in a sealed system. Kem-Solv, Inc. (Bridgeport, Pa.) plans to bale the waste and pyrolyze it at 1800 °F, a high enough temperature to evolve all desirable gas constituents. Gases evolved at 1100 °F will be quenched to 185 °F; at this stage oil with a 10 500-Btu heat content is separated. Benzene and other compounds are then removed and the gas is liquefied, so that CO_2 plus low-boiling fuel gases such as methane are fractionated out. Initially, the plant will handle 3000 tons/d of solid waste from southeastern Pennsylvania.

INDUSTRY

Emerging opportunities for firms to become involved in hazardous waste treatment and disposal are the subject of a proposal by Battelle Columbus Laboratories (Ohio). Battelle believes that while such wastes are an industrial headache, they could present business opportunities for treatment/disposal firms. The study will survey U.S. and European technology and key firms in the business. It will also evaluate business options and opportunities for hazardous waste generators and management firms, including opportunities created by government regulations.

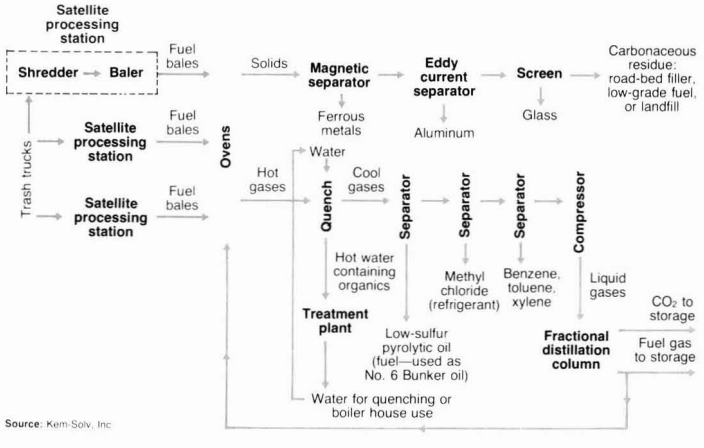
"America needs the Clinch River breeder project," says Aubrey Wagner, retired chairman of the Tennessee Valley Authority (*ES&T*, February 1978, p. 140). He says that energy conservation alone cannot do the job of providing for national needs; solar is too expensive or unproven and hydro is almost completely developed. Wagner looks to coal and nuclear fission, but warns that without breeding, U.S. uranium supplies will be used up soon after the year 2000. He characterizes the Clinch River breeder design as the best technology available in the U.S. and abroad. Wagner's views were stated to the Breeder Reactor Corporation (Oak Ridge, Tenn.).

Long: *contract FGD sludge disposal*

Flue gas desulfurization (FGD) scrubber sludge disposal on contract to utility clients will be offered by Dravo Wellman Company, if plans materialize. Possibly, Dravo Wellman would even own and operate the disposal system under contract to the utilities, says Gary Long, vice-president and general manager. The company surveyed major utilities and gathered information on coal-fired plants due to start up during the next 10 years. Long is confident that the activity expected in the utility business will present Dravo Wellman with a "solid opportunity" in providing waste disposal equipment/systems, and will "mesh very well with current ash-handling activity."

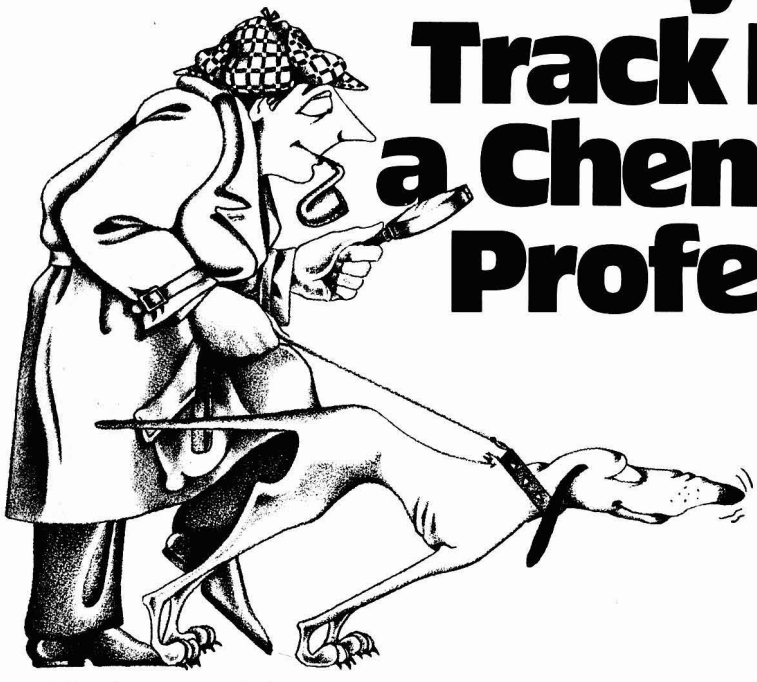
Containing and cleaning up contaminated groundwater can cost $5–10 million per site, David Miller, senior vice-president of Geraghty & Miller, Inc. (Syosset, N.Y.), estimates. The geohydrologic investigations needed to define the extent of a contamination problem can cost $25 000–250 000 alone, he says. Miller told a Senate committee that restoration of a badly contaminated aquifer to potable quality could carry a cost "orders of magnitude higher" than the $5–10 million per site, with time for completion "measured in decades." And even then a partial cleanup would more than likely result because "tremendous volumes" of water would have to be pumped to remove or treat a contaminant plume.

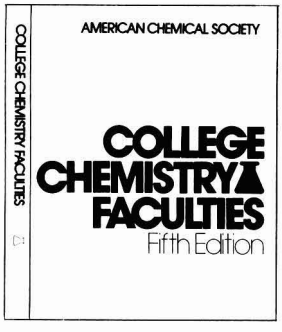
Municipal waste pyrolysis operation



Source: Kem-Solv, Inc.

Trying to Track Down a Chemistry Professor?





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OUTLOOK

Formaldehyde

How did EPA develop its formaldehyde policy?

Exposure to formaldehyde began to receive a great deal of attention as a health risk during the 1970s. The intense concern with this substance coincided with the advent of urea-formaldehyde foam insulation and with rapid growth in the number of mobile homes using particle board and plywood bonded with urea-formaldehyde resins and energy-efficient houses with tightened structures and reduced ventilation rates. Released and trapped formaldehyde became a severe pollution problem especially in mobile homes because they usually have lower air-exchange rates than most conventional houses.

Formaldehyde is one of the most widely used chemicals in American industry with about seven billion pounds produced each year. It is found in so many consumer products that it is reasonable to say there is probably greater exposure to formaldehyde than to any other single chemical with the possible exception of chlorine. The largest applications are in the urea-formaldehyde resin type adhesives for bonding particle board and plywood, but it is also used in urea-formaldehyde insulation, paper products, permanent-press fabrics, hundreds of cosmetics, and many other consumer items. Consumer products are not the only source of human exposure since formaldehyde is emitted in the burning of cigarettes and fossil fuels. It can rarely accumulate at high ambient levels, however, because it is removed by oxidation and by rain.

Those 1.4 million workers who encounter formaldehyde in their daily occupations and those who live in energy-efficient houses or mobile homes with a large quantity of newer plywood, particle board, or urea-formaldehyde insulation are the members of society who receive the greatest exposure. About 1 in 20 Americans inhabits a mobile home in which many of the interior walls are covered with particle board or plywood. These building materials emit formaldehyde for a number of years after the materials are manufactured.

Plywood is an important source of exposure to formaldehyde

During the 1970s and early 1980s, government agencies such as the Consumer Product Safety Commission and the Department of Housing and Urban Development began to hear a great many complaints about formaldehyde presumably released from urea-formaldehyde insulation and particle board and plywood in mobile and energy-efficient homes. For example, the Consumer Product Safety Commission (CPSC) received over 3000 complaints about formaldehyde, 2000 of which involved urea-formaldehyde foam insulation. These complaints raised considerable concern about the health effects caused by formaldehyde—especially because people were being exposed in their homes—and led to two new studies of formaldehyde in 1980 and 1981. Studies carried out by the Chemical Industry Institute of Toxicology (CIIT) and by New York University

0013-936X/82/0916-0543A$01.25/0

TABLE 1

Formaldehyde levels in mobile homes and in houses insulated with urea-formaldehyde foam (UFFI) can be higher than 2 ppm

Type of home	No. of homes	Formaldehyde concentration (ppm) Range	Average
Homes without UFFI	41	0.01–0.08	0.03
Homes with UFFI	636	0.01–3.4	0.12
Mobile homes	431	0.01–2.93	0.38
Ambient	156	0.0–0.08	0.01

Source: Consumer Product Safety Commission, 1982

(NYU) showed that formaldehyde is definitely carcinogenic in rats and perhaps in mice. In the fall of 1980, a federal panel convened by the National Toxicology Program (NTP) concluded that "formaldehyde is an animal carcinogen and should be presumed to be a human carcinogen."

Failure to regulate

As a result, in the spring of 1981, shortly before EPA Administrator Anne Gorsuch came to office, the agency staff recommended that priority attention be given to formaldehyde and drafted a notice to appear in the *Federal Register* saying that formaldehyde would be considered for regulatory assessment under section 4(f) of the Toxic Substances Control Act (TSCA). According to this section of the act, the EPA administrator must act if a chemical "presents or will present a significant risk of serious or widespread harm to human beings from cancer, gene mutations, or birth defects ..." The EPA draft notice stated: "EPA has determined that there may be reasonable basis to conclude that some exposures to formaldehyde present a significant risk of widespread harm to humans. Therefore, the Agency is initiating action to investigate those exposures of greatest concern and determine whether they lead to unreasonable risks."

Anne Gorsuch did not sign the notice and it did not appear in the *Federal Register*. Instead Deputy Administrator John Hernandez convened a series of meetings he called "science courts" on June 19, July 28, and Aug. 14, 1981. In the procedures followed, these meetings only faintly resembled the science court concept recently described in the literature for the resolution of scientifically complex public policy issues such as this one. No public notice was given of the meetings, and they were attended primarily by Formaldehyde Institute representatives and EPA staff. Only three other people were invited to the discussions, two from the National Academy of Sciences and one from the Oak Ridge National Laboratory. This was a change from the usual peer review process. Prior meetings to review extensive scientific data had been announced publicly.

Minutes and transcripts were not made of the discussions. Consequently, it appears that the only ones who know exactly what transpired are those who attended. It cannot be determined what influence, if any, these meetings had on the administrative decision not to regulate formaldehyde. There is no documentation of the decision-making sequence.

But on Sept. 11, 1981, Donald Clay, director of the EPA Office of Toxic Substances, sent a memorandum to John Todhunter, assistant administrator for Pesticides and Toxic Substances, recommending that formaldehyde not be considered a priority chemical under TSCA section 4(f).

Parallel developments occurred at the Occupational Health and Safety Administration. OSHA officials had been planning to release a joint statement on formaldehyde with the National Institute of Occupational Safety and Health, but in July 1981 this decision was reversed. A petition brought by the United Auto Workers requesting an emergency standard for formaldehyde was denied by OSHA on Oct. 26, 1981.

Opposing views

During this same time period, views diametrically opposed to those of the Reagan Administration were being expressed by influential members of academia and the American Cancer Society. On Aug. 17, 1981, Arthur Upton, chairman of the New York University Medical Center Institute of Environmental Medicine, stated in a letter to the heads of federal agencies: "formaldehyde is decisively carcinogenic in animals" and "if the carcinogenicity of formaldehyde is ignored, it would mean that no agent could be regarded as carcinogenic in the absence of positive evidence in humans."

This year, on Feb. 5, the American Cancer Society asked regulatory agencies "to set appropriate standards to minimize occupational and public exposure to the chemical [formaldehyde], its industrial products and applications."

Just five days after this request, on Feb. 10, Todhunter sent a formal memorandum to EPA Administrator Anne Gorsuch which said that formaldehyde should not be considered as a priority chemical for regulation. Terming it "a potential animal carcinogen," he gave three reasons to justify this decision:

- Animal data may not be relevant to humans.
- Positive human data are lacking.
- It has not been "established that, at human exposure levels, the risk [of cancer] is probable and would be high."

This document was reviewed neither by the EPA Science Advisory Board nor by anyone on the EPA staff before it went to the administrator. There are no formal review procedures for documents that support nonregulation. As a result of Todhunter's memorandum, EPA decided not to regulate formaldehyde at the present time. This decision was so controversial that Rep. Albert Gore's Subcommittee on Investigations and Oversight conducted a hearing on May 20, 1982, to examine the scientific basis of the Feb. 10 memorandum and to try to elucidate the decision-making process that led to its formulation.

Twelve days after Todhunter's recommendation, on Feb. 22, the CPSC moved in the opposite direction and decided to ban urea-formaldehyde foam insulation.

Health effects in animals

What evidence is provided by animal tests? The two studies that aroused the greatest concern were the CIIT and NYU studies mentioned earlier. The CIIT study exposed rats for 30 months to airborne formaldehyde at 14.3, 5.6, and 2 ppm, and to charcoal-filtered air. Squamous cell nasal carcinomas (cancer of the nose) were observed in 103 of the 232 rats exposed to 14.3 ppm and in 2 of the 235 rats exposed to 5.6 ppm. No nasal cancers were seen in the rats that inhaled formaldehyde at 2 ppm or in the control animals. Under ordinary conditions, this type of cancer is extremely rare in rats. Other adverse changes in

the respiratory organs of the animals exposed to all levels of formaldehyde were frequently found. These included benign tumors, which usually are an indication of a precancerous state.

A 24-month study at NYU confirmed the results of the CIIT study. Experimenters at NYU exposed male rats to formaldehyde at 14.6 ppm, a mixture of 14.6 ppm formaldehyde and 10.6 ppm hydrogen chloride, and to hydrogen chloride alone at 10.6 ppm. No rats developed nasal carcinomas in the last group, but 10 rats out of each 100 in the groups exposed to formaldehyde developed nasal carcinomas.

When rats and monkeys were exposed to much lower levels of formaldehyde—0, 0.2, 1.0, and 3.0 ppm—for 26 weeks, squamous metaplasia of the nasal passages was evident in all monkeys exposed to 3 ppm and in one out of six exposed to 1 ppm. This means that squamous cells were invading and replacing the cells of the underlying layer, a condition that often indicates a precancerous state. The formaldehyde levels used in this experiment were in precisely the same range that many workers are exposed to and that some people are exposed to in their homes. The OSHA standard for occupational exposure is a time-weighted average of 3 ppm. This standard is currently under review.

In addition to carcinogenicity in animals, formaldehyde is mutagenic in a wide variety of organisms, including some bacteria, fungi, insects, and mouse lymphoma cells. It has caused chromosomal breaks and recombination in intact rats, yeast, and insects, and in cultured mammalian cells. The mechanism of inducing mutations is not known exactly. A report on formaldehyde by the National Academy of Sciences (NAS) states: "Formaldehyde may cause mutations by reacting directly with DNA; by forming mutagenic products on reaction with amino groups in simple amines, amino acids, nucleic acids, or proteins; or by forming peroxides that can react directly with DNA or indirectly by free radical formation." Findings of mutagenicity heighten the suspicion that formaldehyde is carcinogenic since most cancer-causing chemicals are mutagenic.

One controversial question is: What type of cancer-causing agent is formaldehyde? There are basically two types of carcinogenic substances—initiators and promoters. Initiators can act alone by altering the genetic material of the cells. They are therefore called genotoxic. Promoters must act in conjunction with an initiator to enhance or promote the effect of the initiator. The Formaldehyde Institute insists that formaldehyde is a promoter, and consequently believes that there is a threshold level below which it would have no effect. EPA's Office of Toxic Substances, an NTP panel, and the CPSC say that there is a large body of evidence showing formaldehyde is an initiator, or genotoxic. Initiators are commonly believed to have no thresholds. Thus, if there is no threshold, exposure to almost any level can be considered hazardous and should be considered in setting regulations.

On May 20, 1982, Norton Nelson, former director of the NYU Institute of Environmental Medicine, stated in his testimony at a hearing about formaldehyde conducted by Rep. Albert Gore's Subcommittee on Investigations and Oversight: "It [formaldehyde] is genotoxic—that is, it produces alterations in the genetic material of the cell, as determined by direct DNA interaction and as determined by the bacterial revertant tests, such as Ames tests and others."

Carcinogenic effects in humans

So far the direct evidence that formaldehyde causes cancer in humans is very weak. Only a few epidemiological studies that make specific mention of exposure to formaldehyde have been completed. In these experiments, there were increases in several types of cancer, but skin cancer was the only type that showed a statistically significant increase. Because a total of only a few thousand deaths was included in these studies, it was difficult to make meaningful evaluations. Moreover, exposure levels could only be crudely estimated. Several other studies of individuals in occupations where they may be exposed to substantial amounts of formaldehyde suggest increases in cancers of the larynx, oral cavity, nasal cavity, liver, and lung. By 1985, the National Cancer Institute will have completed a survey of the medical records of 17 000 formaldehyde workers. This study should provide much more information than is presently available.

Most scientists and some federal agencies agree that current epidemiological data do not allow conclusions to be drawn about the carcinogenic risks to humans. The International Agency for Research on Cancer is now publishing a monograph that concludes: "The epidemiological studies provide inadequate evidence to assess the carcinogenicity of formaldehyde in man."

However, Todhunter of EPA expressed a different point of view in his Feb. 10, 1982, memorandum: "Three epidemiology studies presented at CIIT are in agreement that there is no excess in nasal or respiratory cancer or even a significant increase in any form of cancer which could be attributed to formaldehyde. Although the individual studies may be limited in scope, when combined they clearly indicate no increased risk in the exposed population."

Other health effects

What is known about other health effects? It is very difficult to discuss these effects because people's responses to different formaldehyde levels are highly variable. Irritation of the eyes and mucous membranes is the principal effect of low concentrations of airborne formaldehyde. In one study, more than 30% of the subjects tested had mild to moderate eye, nose, and throat irritation at 1.5–3 ppm, and 10–20% had strong reactions. Eye, nose, and throat irritation, coughing, wheezing, diarrhea, nausea, vomiting, dizziness, and lethargy are some of the reported symptoms occurring after prolonged exposure at home or at work. Formaldehyde does not usually cause asthma, but it can initiate attacks in those who are already asthmatic.

There is evidence that with prolonged exposure, certain people respond to lower levels of formaldehyde. A number of individuals, most of them living in homes insulated with urea-formaldehyde foam, have developed severe formaldehyde sensitization. In

Evaluation of formaldehyde made by the International Agency for Research on Cancer in Lyon, France[a]

There is *sufficient evidence* that formaldehyde gas is carcinogenic to rats.

The epidemiological studies provide inadequate evidence to assess the carcinogenicity of formaldehyde in man.

[a] The monograph states that this evaluation should be read in conjunction with the following statement:

Sufficient evidence of carcinogenicity is provided by experimental studies that show an increased incidence of malignant tumours: (i) in multiple species or strains, and/or (ii) in multiple experiments (routes and/or doses), and/or (iii) to an unusual degree (with regard to incidence, site, type and/or precocity of onset). Additional evidence may be provided by data concerning dose–response, mutagenicity or structure.

other words, they have acquired a sensitivity to formaldehyde analogous to the acute reaction some individuals have to bee stings. As a result, even very low levels of formaldehyde induce strong effects in these people, and they must isolate themselves from it as much as possible, which is difficult because formaldehyde is ubiquitous in this society.

A variety of problems including irritation and allergic contact dermatitis can result from skin contact with formaldehyde solution. Among dermatitis patients, formaldehyde is the tenth leading cause of skin reaction.

Which members of the population are especially susceptible to formaldehyde? They have not yet been positively identified. Asthmatics and some fraction of those 10 million persons with chronic obstructive lung disease are probably especially susceptible. And there are undoubtedly other groups whose sensitivity is higher than average. The NAS report on formaldehyde concluded that "fewer than 20% but perhaps more than 10% of the general population may be susceptible to formaldehyde and may react acutely at any concentration, particularly if it is greater than 1.5 ppm. People report mild ENT [eye, nose, and throat] discomfort and other symptoms at less than 0.5 ppm, with some noting symptoms at concentrations below 0.25 ppm."

Occupational standard

At the present OSHA standard for occupational exposure—a time-weighted average of 3 ppm over an 8-h period—nearly everyone smells formaldehyde and suffers some irritation. Most people can smell formaldehyde at 1 ppm, and some can sense it as low as 0.05 ppm. Because the 3-ppm standard is not a ceiling, but a time-weighted average, some U.S. workers are exposed to 10 ppm for a part of the working day (for maximum 30-min intervals). At this level, formaldehyde is extremely irritating and unpleasant and has definite adverse effects on almost everyone. The OSHA standard is higher than the occupational standards of all other countries largely because it is an average not a ceiling (see Table 2).

TABLE 2

The U.S. regulations for occupational exposure to formaldehyde are higher than those for any other country

Country	Year	Concentration mg/m³	Concentration ppm	Interpretation [a]	Status
Australia	1978	3	2	Ceiling	Guideline
Belgium	1978	3	2	Ceiling	Regulation
Bulgaria	1971	1	—	Maximum	Regulation
Czechoslovakia	1976	2	—	TWA	Regulation
		5	—	Ceiling (10 min)	
Finland	1975	3	2	Ceiling	Regulation
German Democratic Republic	1979	2	—	Maximum (30 min)	Regulation
		2	—	TWA	
Federal Republic of Germany	1979	1.2	1	TWA [b]	Guideline
Hungary	1974	1	—	TWA [c]	Regulation
Italy	1978	1.2	1	TWA	Guideline
Japan	1978	2.5	2	Ceiling	Guideline
The Netherlands	1978	3	2	Ceiling	Guideline
Poland	1976	2	—	Ceiling	Regulation
Romania	1975	4	—	Maximum	Regulation
Sweden	1978	3	2	Maximum (15 min)	Guideline
Switzerland	1978	1.2	1	TWA	Regulation
U.S.					
OSHA	1980	3.7	3	TWA	Regulation
		6.2	5	Ceiling	Regulation
		12.3	10	Ceiling (30 min)	Regulation
ACGIH [d]	1981	3	2	Ceiling	Guideline
NIOSH	1976	1.2	1	Ceiling (30 min)	Guideline
U.S.S.R.	1977	0.5	—	Maximum	Regulation
Yugoslavia	1971	1	0.8	Ceiling	Regulation

[a] TWA = time-weighted average
[b] Skin irritant
[c] May be exceeded five times per shift as long as average does not exceed value
[d] ACGIH = American Conference of Governmental Industrial Hygienists
Source: "Formaldehyde," Monograph of the International Agency for Research on Cancer, 1982, Vol. 29.

A change in policy?

In summary, a substantial amount is known about the noncarcinogenic effects of formaldehyde on people, but little is known about its carcinogenic effects. Responsible scientists have questioned the apparent unwillingness of federal regulators to act in the absence of conclusive epidemiological data on formaldehyde. Many other substances have been regulated by federal agencies primarily on the basis of animal experiments. Examples are pesticides, hair dyes, food additives, and industrial carcinogens in the workplace. Almost all pesticides and food dyes are regulated in this way.

In the past, the following principles have been widely accepted by toxicologists and by regulators:

- Confirmed positive animal data is presumptive evidence that a chemical is carcinogenic in humans.
- Current information does not allow us to establish threshold levels for carcinogens.
- Positive epidemiological data are not necessary to decide that a chemical poses a significant human risk.

Arthur Upton, and I. B. Weinstein of Columbia University wrote in their Jan. 29, 1982, letter to OSHA and EPA:

> It has come to our attention that EPA, OSHA, and possibly other federal regulatory agencies, may be planning not to take immediate protective action on formaldehyde, in spite of substantial evidence for its carcinogenicity from animal bioassays. We are concerned about the possibility of such a departure from established public health policy. It would conflict with the prevailing views of the scientific community and would set a precedent which could hamper future regulatory action on other carcinogens.
>
> There is general agreement among experts in chemical carcinogenesis that a substance which causes cancer in significant numbers of experimental animals in well-conducted assays poses a presumptive carcinogenic risk to some humans, even in the absence of confirmatory epidemiological data. While negative human data can define the upper limit of risk to man, there is no recognized method as yet for establishing the existence

Statements on formaldehyde given by scientists at the May 20, 1982, hearing on formaldehyde[a]

Norton Nelson: Professor of environmental medicine at the Institute of Environmental Medicine, New York University Medical Center. Director of the Institute for 25 years.

"Formaldehyde is positive in animal tests in several different species, in several different strains, and at dose levels that are not far from those to which people are exposed.

The points brought up in the [Feb. 10, 1982] Todhunter memorandum, which I say in my statement I find unusual and irresponsible, from the standpoint of taking a series of positions which mostly bear on in varying degrees the issue of the significance of formaldehyde and in each instance, contrary to accepted scientific usage, have taken a judgmental position that the evidence is insufficient—I find this inexplicable; I just cannot understand how such conclusions could have been reached."

Roy Albert: Deputy director and vice-chairman of the Institute of Environmental Medicine, New York University Medical Center. Former deputy assistant administrator for Health and Ecology at EPA.

"I believe that the [Todhunter memorandum] to Administrator Gorsuch dated Feb. 10, 1982, in support of the decision not to list formaldehyde under section 4(f) of the Toxic Substances Act, reflects a serious flaw in the EPA's administrative processes."

Richard Griesemer: Director of the Biology Division at Oak Ridge National Laboratory.

"There were in fact so-called benign tumors in all exposure levels in the rat [CIIT] study, in the 2 ppm level. They were described as papillary adenomas [a type of benign tumor], and two malignant counterparts were found in higher doses, so that there appears to be a spectrum of benign to malignant tumors in all the dose levels in the rat study.

"I believe that the data indicate that formaldehyde gas is carcinogenic in rats—exposure levels as low as 2 ppm—for at least four reasons.

"I believe then that in his memorandum Dr. Todhunter has understated the case for the carcinogenicity of formaldehyde and the significance of these findings for humans. Virtually everyone is exposed. We are all exposed to some extent,"

Kenny S. Crump: President of Science Research Systems, Inc. at Ruston, La.

"The details of the risk assessment procedures used in the Todhunter memorandum are not clearly described, and I have not been able to reproduce the risk estimates made in this document. When I used the assumptions that are described in the document, I got larger estimates of risk."

John Todhunter: Assistant administrator for Pesticides and Toxic Substances at EPA.

"Now whether or not a substance may pose any risk of cancer to humans, however, is not the issue under TSCA section 4(f). The question is whether or not the cancer risk is significant. The question is, simply put: Is this a high degree of risk or a low degree of risk?

The answer to that question depends intimately on exposure. The exposure information presently available to OTS [Office of Toxic Substances] indicates that carcinogenic risk for most, if not all, uses of formaldehyde is in a range that regulatory agencies normally would consider low."

[a] This was a hearing to review the scientific basis of the EPA's carcinogenic risk assessment on formaldehyde. It was conducted by the Subcommittee on Investigations and Oversight of the Committee on Science and Technology. The chairman of the subcommittee is Rep. Albert Gore.

> of a threshold for a carcinogen in the human population. These principles, which are accepted throughout the world, have served for many years as the basis for sound public health policy and regulatory action on carcinogens.

The Office of Technology Assessment recently published a report that expresses similar views. It says that all federal agencies accept a "positive bioassay result in a single species as evidence that the substance is a potential human carcinogen." The report goes on to say that all federal agencies "do not accept the idea of thresholds in making decisions about carcinogenic risks" and believe that they "should not wait for epidemiological evidence before taking action to limit human exposure to chemicals considered to be carcinogenic."

In testimony on May 20 before Representative Gore's subcommittee, Todhunter said in defense of his decision not to regulate formaldehyde at this time: "Now whether or not a substance may pose any risk of cancer to humans, however, is not the issue under TSCA section 4(f). The question is whether or not the cancer risk is significant ... The answer to that question depends intimately on exposure. The exposure information presently available to OTS [Office of Toxic Substances] indicates that carcinogenic risk for most, if not all, uses of formaldehyde is in a range that regulatory agencies normally would consider low."

However, several witnesses at the hearing, among them Richard Griesemer, director of the Biology Division, Oak Ridge National Laboratory, took issue with this statement and said that the risk was significant—even when estimated from the exposure levels that Todhunter had noted in his memorandum of Feb. 10. They also pointed out that other chemicals had been regulated at this same level of risk. Because action was not taken on formaldehyde, does this mean that action on other chemicals that are definitely carcinogenic in animals will be postponed until positive epidemiological studies are completed? Many years must often pass, usually several decades, before such studies indicate that a chemical is carcinogenic. Norton Nelson said in his testimony before Representative Gore's subcommittee: "Epidemiological studies must be regarded as a crude and insensitive tool. Only the most violent and intense carcinogens are likely to be detected by epidemiological techniques as normally conducted.... This has led, quite simply, to the policy that we cannot wait for deaths and bodies accumulating before we have regulation."

If EPA is changing the scientific presumptions on which federal health laws are based, should this be done without scientific support and without public review? In the words of Norton Nelson, "Current cancer policy, widely accepted throughout the world ... has been repeatedly expressed, and I think there is now a general consensus among most regulators and scientists throughout the world ... Suddenly we seem to find ourselves in a situation in which this is perhaps quietly, perhaps accurately, but not publicly, being revised."

Part of the problem may stem from the fact that EPA has no formal review procedures or means for public review and comment on documents that support a controversial decision not to regulate. Perhaps the administrator should institute review procedures for these documents analogous to the elaborate review procedures for documents that support regulatory action. Beyond the formaldehyde debate, the administrator should immediately institute proceedings to examine any change in public cancer protection policy the agency has made or intends to make from the previous consensus view mentioned by Dr. Nelson.

—Bette Hileman

Supercritical fluids

Too attenuated to be true liquids and too dense to be true gases, these materials are being evaluated as media for hazardous waste oxidation, coal beneficiation, activated carbon regeneration, and other chemical reactions

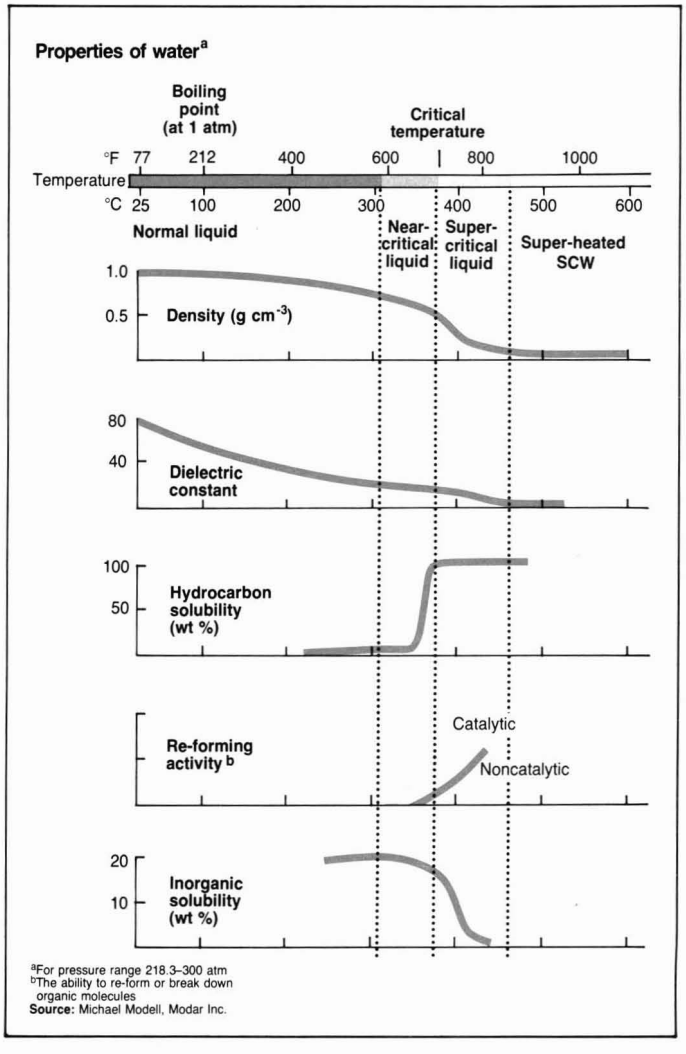
Under certain conditions, water cannot dissolve and ionize inorganic compounds such as sodium chloride, although it is miscible with many organic compounds in all proportions. Yet the same "parcel" of water could mix with enough air or oxygen to oxidize dissolved hazardous organic wastes to simple substances, such as carbon dioxide and water. These phenomena can take place in water in a supercritical fluid (SCF) state.

Possessing properties often far different from conventional liquids and gases, SCFs are characterized as a form of matter in which the liquid and gaseous states are indistinguishable from one another. SCFs are formed when *both* temperatures *and* pressures to which fluids are subjected exceed the critical point (T_c and P_c), and they must be kept in vessels—of strong metals, alloys, or glass, for instance—capable of withstanding the high temperatures and pressures often needed to achieve supercriticality. For example, to bring water to the supercritical state, the temperature and pressure must be raised above 374.2 °C and 218.3 atm, respectively. For carbon dioxide (CO_2), T_c = 31.06 °C and P_c = 72.86 atm.

Even wood can dissolve

In the case of supercritical water (SCW), the density, dielectric constant, hydrogen bonding, and certain other physical properties are so altered that water behaves much as a moderately polar organic liquid would under ambient conditions. Thus, *n*-heptane or benzene, for example, could become miscible in all proportions with SCW, which cannot happen with water under standard conditions. Even some types of wood fully dissolve in SCW. On the other hand, the solubility of sodium chloride (NaCl) could be as low as 100 ppm, and that of calcium chloride can be less than 10 ppm. This is the reverse of the solubilities in water that are encountered under ambient conditions—under which the two salts' solubilities are about 37 wt % and up to 70 wt %, respectively.

When the temperature is raised to any point appreciably above 450 °C, solubilities of inorganics (reckoned in wt %), which with certain notable exceptions increase with temperature, decline precipitously. In addition, the amounts of salts that remain in solution ionize very poorly; for example, for NaCl, at 400–500 °C, with SCW at or below 0.325 g cm^{-3}, the dissociation constant is on the order of 10^{-4}.



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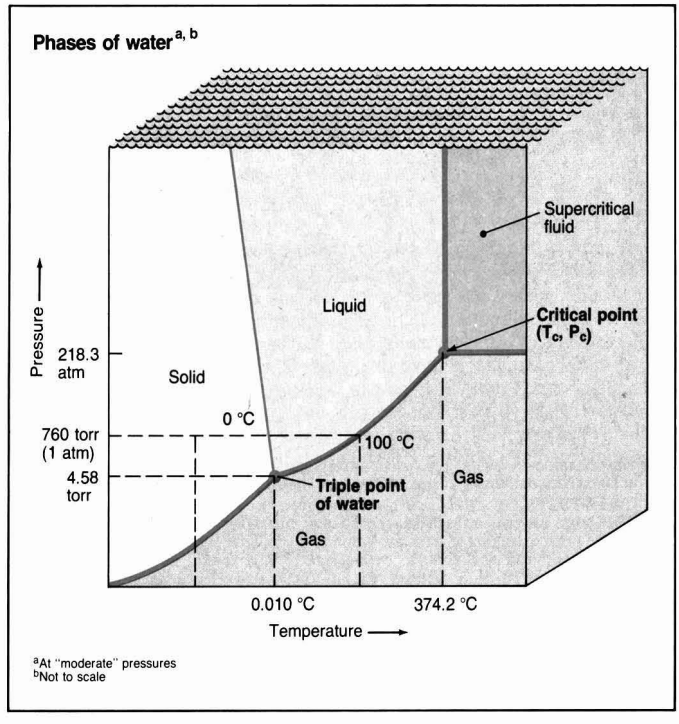
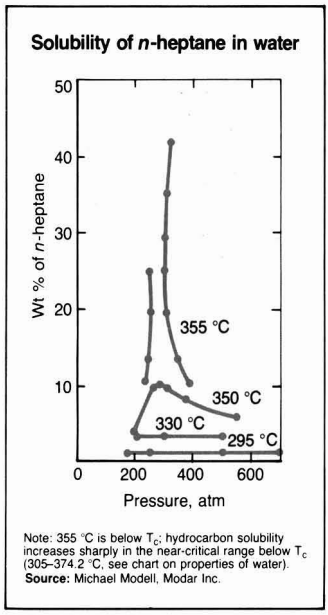
Water itself changes when it is heated from standard temperatures up to and past T_c. Initially, the density decreases slowly from 1.0 g cm^{-3}; it decreases more rapidly as T_c is approached and very sharply just above 372.2 °C. It can go as low as 0.1 g cm^{-3} at 500 °C. At the critical temperature of 374.2 °C and the critical pressure of 218.3 atm, the density of water, known as the critical density (ρ_c), is 0.325 g cm^{-3}.

The high dielectric constant of 80, ascribable to water's 4 kcal mol^{-1} hydrogen bonds, which makes it possible for many inorganics to solvate and ionize, can drop to as little as 2.5, in concert with the weakening and eventual disappearance of the hydrogen bonds. This would explain the difficulties SCW has in dissolving inorganics.

Oxidizing wastes

Another interesting property of SCW above 375 °C is that it is miscible with gases such as nitrogen, oxygen, and air in all proportions; it is this property that could enable SCW to act as a medium for the oxidation of hazardous wastes. Michael Modell, formerly a professor of chemical engineering at the Massachusetts Institute of Technology and now president of Modar Inc. (Natick, Mass.), notes that while the solubility of oxygen or air has not yet been reported in the literature (it has for nitrogen), it stands to reason that nitrogen and oxygen solubilities should be comparable. The same should hold true for air. If so, then supercritical water and oxygen or air would exist in one phase.





Note: 355 °C is below T_c; hydrocarbon solubility increases sharply in the near-critical range below T_c (305–374.2 °C, see chart on properties of water).
Source: Michael Modell, Modar Inc.

The temperature and pressure of the SCW–air or SCW–oxygen mixture can be adjusted to the range in which organic compounds—or wastes—are completely soluble in, or miscible with, water. When this adjustment has been made and the compounds are introduced, what exists, Modell says, is "simply a homogeneous mixture of organics, oxidant, and water in a single phase." Since there is only one phase, no mechanical stirring or agitation is needed to bring about oxidation, he adds.

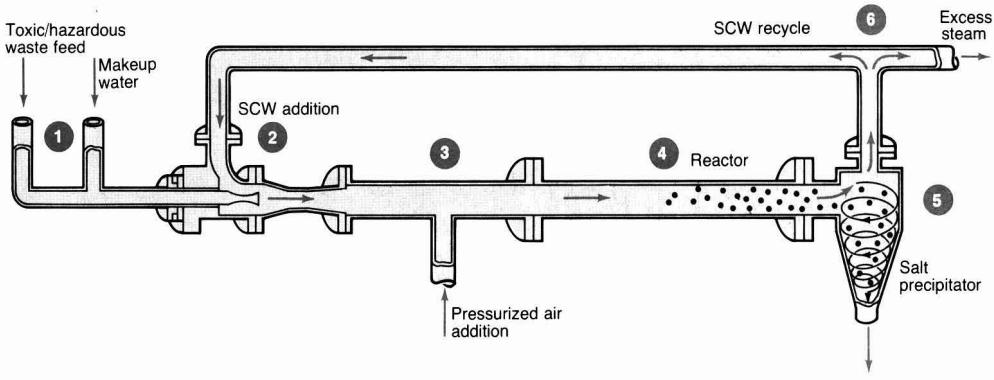
What occurs is a very rapid oxidation that Modell characterizes as a sort of "combustion in water." It takes place, for instance, when toxic wastes and makeup water plus SCW are fed into a tubular reactor along with pressurized air. Heat released by the rapid oxidation of the organic wastes raises the temperature to the point at which any salts formed must precipitate. These are fed, by a cyclone mechanism, to a salt separator that collects the salts. The salts do not interfere with the process. A portion of the SCW effluent is recycled to the process to help provide needed heat; the balance of the heat can be recovered and used for other needs.

Modell notes that with 2% or more of combustible organic wastes, the reaction becomes self-sustaining. Necessary residence time for the waste is usually 1 min, Modell says, adding that because of the high speed of the oxidation process, operation approaches adiabatic conditions; heat losses are extremely small; and the oxidizer keeps "almost all of the enthalpy of oxidation." In essence, then, the reactor effluent temperature is determined by the concentration of organics in the feed, reckoned in wt %.

Modell says that results of his work generally show that if a reactor is supplied with air, SCW, and about 5 wt % of organics at 400 °C and about 250 atm, the heat of oxidation will raise the outlet temperature to 550–600 °C; with oxygen, the outlet temperatures would be higher. Under such severe conditions, most organic molecules should be re-formed to CO_2, water, and other such simple substances. Also, if a temperature of 550–600 °C is attained, any inorganics present—such as chlorine cleaved from organic molecules—will precipitate out (it would form hydrogen chloride, which would be reacted with sodium hydroxide in the system while the temperature was still 400 °C). This can occur because of the inability of SCW to solvate inorganic salts at such high temperatures.

A case in point could involve PCB-laden oils. These oils would be re-formed in the SCW–air reactor to

Supercritical water reactor



1. Toxic/hazardous wastes, in solution, are fed into system automatically and under pressure; then they are mixed with makeup water.
2. SCW heats the solution to initial reaction temperature and adjusts organic content to a concentration of 2–5%, after which pressurized air is added.
3.–4. In the reactor, organics oxidize rapidly in a controlled reaction; heat evolved raises temperature to point at which salts precipitate out.
5. Reactor effluent is fed to salt separator (note cyclone arrangement) that collects the salts.
6. A portion of the SCW is recycled to the reactor; any excess can be converted to steam for other plant operations or energy needs.

Source: Michael Modell, Modar Inc.

CO_2, water, and hydrogen chloride (HCl). To neutralize this HCl, one would introduce sodium hydroxide. Given the temperature increases brought about by oxidation and SCW's extremely poor ability to solvate inorganics above approximately 450 °C, resultant NaCl will "salt out" almost completely, Modell explains.

***Modell:** hazardous waste "combustion" in water*

EPA interim final rules for hazardous waste incineration [*Fed. Regist.* **1982,** *47* (123), 27520] require *at least* 99.99% destruction efficiency. The Chemical Manufacturers Association estimates that probably one-half of the 300 incinerators operated by its member companies for destroying such wastes cannot meet this standard. Modell believes that oxidation in an SCW reactor, given the peculiar properties of that medium and the reactor conditions of temperature and pressure, will decompose hazardous organic wastes with the requisite efficiency and also remove inorganics in solid form for subsequent immobilization or material recovery. Modar Inc., is assembling a 50-gal/d mobile unit to be mounted on a 40-ft trailer, which would treat wastes at a plant site. Modell says that he hopes to have this system ready by January.

"Milder" conditions

If organic hazardous waste decomposition with air or oxygen is enhanced in SCW, one of the reasons would be the relatively severe temperature/pressure conditions in the reactor. Even in an oxygen-free situation, organic molecules would normally break down to very short chain aliphatic hydrocarbons, alcohols, and aldehydes under the severe conditions of SCW. Thus, if one wanted to extract longer chain, higher molecular weight liquid fuels from coal, one might seek SCFs that can work under milder conditions of temperature and pressure, such as CO_2, ethane, and ethylene. These fluids might also serve, for example, as vehicles for the desorption of pesticides from granular activated carbon (GAC), preparatory to subsequent regeneration of the carbon.

A problem with SCF solvents/extractants such as ethane, ethylene, and toluene (used in Britain for experimental coal extraction) is that they could present problems of flammability, toxicity, and other hazards. By contrast, CO_2 does not pose these problems; in addition, it is well-known and inexpensive.

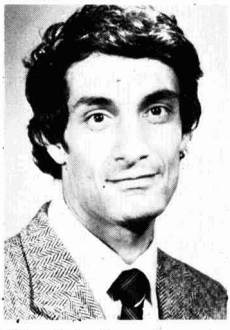
Charles Eckert of the University of Illinois at Urbana points out that it has been known for a long time that various SCFs can dissolve heavy, nonvolatile organic liquids and solids quite efficiently. Suppose that subsequent to dissolution one wanted to separate the SCF solvent from the solute or extract. One would merely decrease the fluid density by expanding the SCF to subcritical pressure. This action would decrease the fluid's dissolving power and lead to "thorough and reversible" separation of the dissolved extract or solute and the SCF, Eckert observes. He and his colleagues have tested solubilities and extractions of heavier organics, principally aromatic hydrocarbons, in CO_2, ethane, and ethylene.

Adsorbent regeneration

Michael Paulaitis of the University of Delaware (now on sabbatical leave at the University of Karlsruhe, West Germany) lists a number of uses of CO_2 in the supercritical state. They include the separation of organic chemicals from water streams (ethanol–water, for example); coffee and tea decaffeination; food and seed oil extractions; low vapor pressure oil processing; solvent and monomer extraction from polymeric materials, especially if they are hazardous; and polymer fractionation.

To regenerate GAC, supercritical

(SC) CO_2 is passed through spent carbon beds, Paulaitis explains. Adsorbed materials are dissolved by the CO_2 during its contact with the carbon bed, which takes advantage of the high solvent capability and enhanced mass transfer properties of the fluid in the SC state. After the CO_2 leaves the carbon bed, it is decompressed, and dissolved materials precipitate, or otherwise separate out. Alternatively, moderate temperature changes can be made to recover dissolved materials from the CO_2. The CO_2 is then heated and recompressed to supercritical state for recycling to the process.



Paulaitis: *cited enhanced mass transfer properties of supercritical CO_2*

Paulaitis cites two problems with this type of extraction. One is the need to feed solids into vessels or reactors constructed to withstand supercritical temperatures and pressures. Thus, treatment with several vessels simultaneously, with some being filled or emptied while others are doing the carbon regeneration, may be required. Another problem is that the buildup of irreversibly adsorbed species on the carbon, which cannot be dissolved by the CO_2, can limit the general applicability of the process.

Nevertheless, SC CO_2 has successfully removed adsorbed pesticides, Richard de Filippi, president of Critical Fluid Systems, Inc. (a subsidiary of Arthur D. Little, Inc., Cambridge, Mass.), told *ES&T*. He said that even after one or two regenerations, by desorption of the pesticide(s) with SC CO_2, the carbon can still be adsorptive up to 70% of its "virgin capacity." He added that this fluid is also being tested as a regenerating medium for certain synthetic resin adsorbents with some, though not all, regenerable to higher percentages of virgin capacity than GAC. Resin regeneration is being evaluated at Illinois Water Treatment Company (Rockford, Ill.).

The pesticide removal work was sponsored by EPA (Cincinnati, Ohio). The agency has now authorized the construction of a pilot-sized unit. That project will be directed by Bruce Tichenor of EPA's Research Triangle Park facility.

Coal extraction

Supercritical CO_2 and certain other fluids could be an alternative for extracting liquid chemicals and fuels from coal. This might be particularly useful with many high-boiling liquids that could be extracted at temperatures lower than the 400 °C or so that would be required for conventional distillation; at such temperatures, some of these liquids could decompose. One reason that SC CO_2 is suitable for such extraction is that its viscosity in the supercritical phase is low, according to Nicholas Vasilakos of the University of Texas at Austin. He adds that the large differences in volatility of the solvent and extracted materials allow easy separation of the coal solution from untreated coal residues, and "virtually complete recovery of the solvent."

Vasilakos's aim is to gain insight into the specific physical and chemical characteristics of supercritical solvents and solvent mixtures that affect the yield and properties of the extraction products. He also hopes to devise combinations of supercritical extraction and chemical treatment methods for the coal that could increase yields of extractable materials with reduced severity of extraction conditions, such as temperature and pressure.

Vasilakos likes SC CO_2 as a component of supercritical coal extraction because of its low T_c and the very reactive, highly porous char it produces in high-pressure gas extractions of coal. Other supercritical solvent "candidates" he is evaluating include ammonia, NO_2, SO_2, boron trifluoride (BF_3), and water. Although water has a much higher T_c than CO_2 or some other simple polar inorganic gases, it can furnish the high solvent density needed for effective supercritical extraction of coal at about 400 °C.

But simple polar inorganic gases are not the only solvent possibilities Vasilakos is scrutinizing. He is looking at polar organic compounds, such as nitrobenzene, methanol and higher alcohols, phenol, and acetone, as well as benzene and certain substituted benzenes. He is also considering some polynuclear aromatic hydrocarbons, such as phenanthrene. Vasilakos finds nitrobenzene and methanol "interesting," because they seem to be efficient solvents for removing organic sulfur—a major SO_x source—from coal under SC conditions. He is also examining two- and three-component solvent systems in his search for maximum extraction yield and high-quality products via what he calls "synergistic effects."

Along with supercritical extraction, chemical methods of extraction are also employed, Vasilakos says. One is hydrogenation, either with hydrogen gas or with hydrogen donor compounds, such as 2-propanol, 2-butanol, tetralin, and the like. Another is alkylation with ethylene or propylene. Still another approach could be the depolymerization of coal with phenol or phenol-related solvents, such as *m*-cresol in the presence of BF_3. Vasilakos points out that catalytic reactions with such catalysts as zinc chloride, alkali metal hydroxides, or alkoxide salts are also possible. He notes that this technique has brought about high conversion percentages of subbituminous coals to cyclohexane- and pyridine-soluble materials at 250 °C, which is well below the normal pyrolysis temperature of coal.

In other trials, Vasilakos tested an SC mixture of toluene and methanol to obtain better extract yields than were apparently possible with each solvent alone. He used an Illinois No. 6 coal (high in sulfur). In future experiments, he plans to study beneficiation reactions of coal under supercritical conditions, with special emphasis on desulfurization. In addition to nitrobenzene, he proposes the use of a methanol–thiophene model system to perform this task.

Supported by the Center for Energy Studies at Austin, Vasilakos is currently involved in the design and construction of a fully automated, continuous pilot-plant unit. This unit is to provide enough flexibility to perform parametric evaluations of supercritical extraction for a wide variety of process materials—including crude oil, coals, lignites, and wastes—on a scale sufficient to interest industrial partners.

—Julian Josephson

Additional reading

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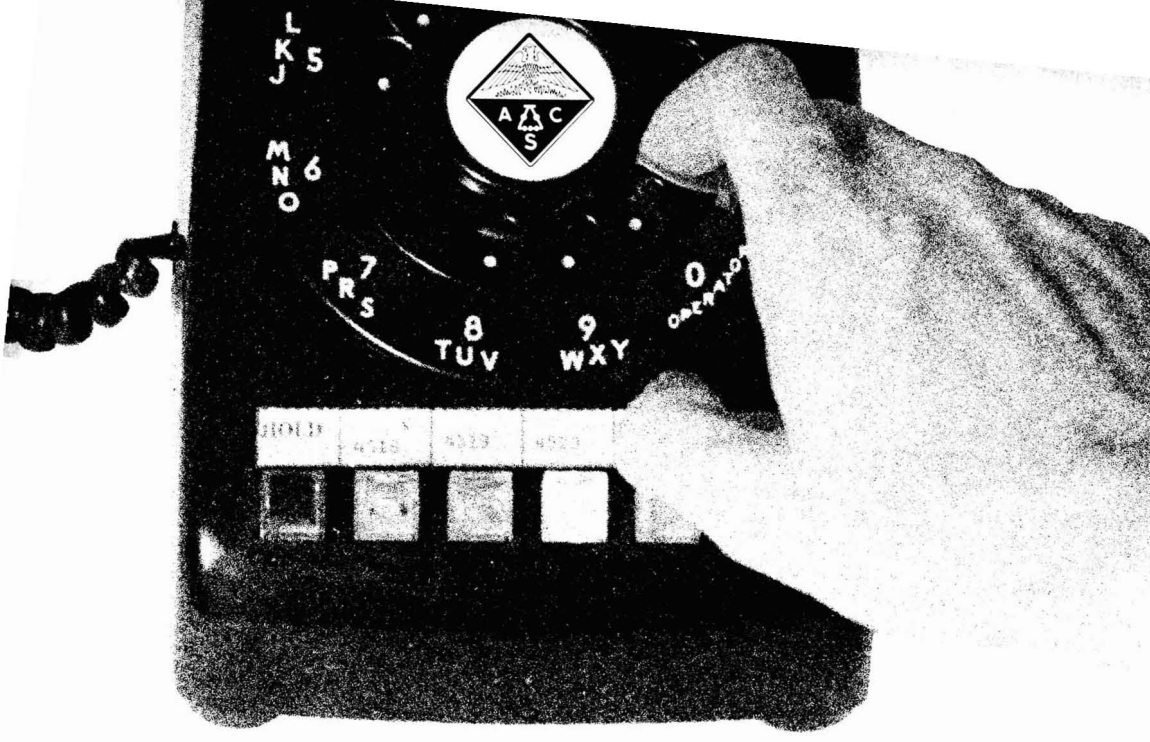

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A compensation fund for hazardous waste injuries

Michael R. Deland

A "Superfund study" just presented to Congress urging the establishment of a fund to provide for "no-fault compensation" for hazardous waste injuries is generating enough interest to guarantee it will be carefully considered by the next Congress. The release of the study could not have been more timely, following closely the announcement of the filing for bankruptcy by the Manville Corporation, the world's largest asbestos mining and manufacturing company. In its filing, Manville cited the burden of more than 16 500 asbestos-related lawsuits; and company consultants estimated that an additional 32 000 suits might be filed in the future. The company treasurer estimated that the litigation could result in awards ranging from $2 billion to many times that amount over the next 20 years.

The Superfund study

The report to Congress, entitled "Injuries and Damages from Hazardous Wastes—Analysis and Improvement of Legal Remedies," is almost 300 pages long, supported by a 400-page appendix. It was mandated by S. 301(e) of the Comprehensive Environmental Response, Compensation and Liability Act of 1980 ("Superfund") and conducted, as required by the statute, by an independent, blue-ribbon panel composed of 12 nationally known attorneys. The study group "reporter," professor Frank Grad of Columbia Law School, describes the hazardous waste problem as presenting "the legal system with a task which is unprecedented in its scientific and medical complexity and in its potential for major health and economic impact."

The study group found that available remedies are inadequate in view of the substantial number of claims that may arise and the factual and legal complexities that will be involved in their litigation. The prime, "almost overwhelming," barrier to recovery is to prove the causal connection between exposure and injury. This is particularly difficult given that adverse health effects from many toxic substances may not appear for 15 or 20 years or even longer following exposure. The study further found that there are no federal statutes that provide remedies for personal injury due to hazardous waste in nonoccupational settings.

Notwithstanding the sweeping nature of these findings, the report's recommendations caught many in the scientific and legal communities by surprise. The study proposes two separate remedies. The "Tier One" remedy would provide for a federal program of no-fault compensation for hazardous waste injuries to be managed by the individual states. The compensation fund would be patterned after Superfund and be established by contributions from or taxes on the producers of hazardous or toxic chemicals and crude oil and by a tax on the deposit of hazardous waste. The compensation plan would be analogous to Worker's Compensation and would provide full recovery for a person's medical expenses and recovery or approximately two-thirds of a person's loss of earnings, as well as death benefits for close surviving dependents.

Among the controversial features of the Tier One proposal are that it reduces a claimant's burden of proof by establishing two kinds of "rebuttable presumptions." The first focuses on the issue of causation and the second includes issues such as the nature and extent of the disease or injury. In the interest of speeding the disposition of the claims, a majority of the study group also decided to leave it to the compensation agency to arbitrate proof of claims, rather than permit the parties allegedly responsible to participate in adversary proceedings. The granting or denial of a compensation award and its amount would then be subject to judicial review in the appropriate state courts.

The "Tier Two" remedy would enable a claimant to proceed concurrently with a personal injury claim under existing tort law with the caveat that the Tier One compensation award be repaid out of any payment obtained from a Tier Two lawsuit.

Ramifications of the report

In 1981 Sen. George Mitchell (D-Maine), feeling strongly that "existing remedies are not adequate," introduced legislation (S. 1486) that would provide a cause of action for compensation for injured parties. The senator, concurring in the report's finding, plans to reintroduce his bill early in the next session. Meanwhile, in the House, Rep. Albert Gore (D-Tenn.) solicited testimony from members of the study group and called on industry to prepare its own proposals for a fund, stating "now is the time for discussion to begin."

The prestige and independence of the study group's individual members, when combined with the thoroughness of their report, give the study instant credibility and ensure that it will be a catalyst for heated congressional debate.

Deland writes this monthly column and is counsel to ERT, Concord, Mass.

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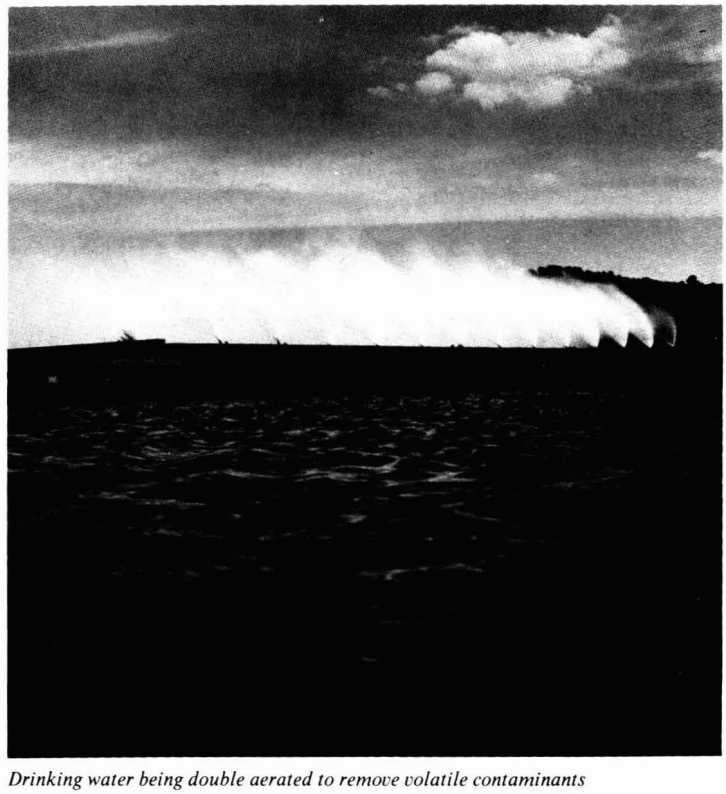
ES&T FEATURE

Health effects of drinking water disinfectants and disinfectant by-products

Not enough is known about the various disinfectants to assess relative health risks

Richard J. Bull
Health Effects Research Laboratory
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268



Drinking water being double aerated to remove volatile contaminants

For drinking water disinfection, the alternatives to chlorine that have been considered most often are chlorine dioxide, ozone, chloramines, UV irradiation, iodination, or some combination of these. The first three have been given the greatest attention because they are effective, relatively inexpensive, and easy to use. In addition to concern over the organic by-products, it has now become clear that some of these chemicals or associated inorganic by-products possess toxic properties of their own.

It is probable that no other public health issue affects a larger proportion of the U.S. population than drinking water disinfection. Proper consideration of the alternatives requires assessing the toxicological hazards of both the disinfectants and their by-products. Final decisions involve weighing acute toxicological hazards against chronic toxicities. Both types of effects have to be considered along with the probability of carcinogenic hazards. This article attempts to review the status of these problems, to discuss some of the more recent data bearing on the issue, and finally to identify those data gaps that currently prevent a clear resolution of this problem.

Toxicology of disinfectants

Prior to 1976, toxicological information relevant to drinking water disinfection was virtually nonexistent. Chlorine (technically a mixture of HOCl and OCl^-, depending upon pH) has received virtually no study: Common use has put it into a category generally regarded as safe. The reduction product of chlorine is Cl^-, which is of no toxicological importance at the levels resulting from drinking water disinfection. Chlorine dioxide (ClO_2) has been studied in recent years and has toxicological properties of concern that will be discussed. Additionally, when used as a disinfectant, ClO_2 produces a substantial amount of chlorite (ClO_2^-) either as a precursor or product. ClO_2^- presents an acute toxicological hazard. There is some evidence that combined chlorine or chloramine (Cl_xNH_y) is also acutely hazardous and that it has a potential for causing chronic toxic effects. Ozone will not be considered in this article because it is not stable in water,

and after ozone treatment, no residual inorganic products of toxicological concern usually remain in the water.

The absence of systematic toxicological data about chlorine is a major gap in the presently available information. The only long-term study of chlorine toxicity is that of Druckrey, which indicates no harmful effects from drinking water containing 100 mg/L of chlorine provided to rats over seven generations (*1*).

It is generally believed that the longer the body takes to excrete a chemical, the greater the potential for toxic effects; excretion times are determined with metabolic studies. More recent work has concentrated on the metabolism of HOCl using ^{36}Cl as a tracer. These studies show that within 72 h, less than 30% of the orally administered dose is excreted in urine and feces (*2*). Similar experiments using ^{36}Cl as a tracer in ClO_2, ClO_2^-, and ClO_3^- indicate that 40% or more of the material is lost in the same time interval. Additionally, with ^{36}Cl as a tracer, HOCl is found to have a greater tendency to concentrate in the bone marrow than do the other three chemicals, and the half-life for elimination of HOCl from plasma is 77 h vs. 35 h for ClO_2, ClO_2^-, and ClO_3^-.

Clear interpretation of these results requires similar studies of the pharmacokinetics of $^{36}Cl^-$ since the chloride ion (Cl^-) is a major by-product and a natural constituent of the body. Nevertheless, it can be concluded that the body handles HOCl quite differently from the way it handles ClO_2, ClO_2^-, and ClO_3^-. The longer half-life of HOCl suggests that it may become more closely associated with cellular components. The toxicological significance of this data is not yet known.

When administered by stomach tube to rats, chlorine dioxide is apparently absorbed primarily as Cl^- and ClO_2^- (*3*). Experiments designed to partition ClO_2, ClO_2^-, ClO_3^-, and Cl^- indicate that 3–4% of the orally administered dose of $^{36}ClO_2$ is recovered as ClO_2^- in the urine over a 72-h period. The major urinary metabolite of either ClO_2, ClO_2^-, or ClO_3^- found in the urine over this period, however, is Cl^-, accounting for 20–30% of the orally administered dose. A critical question is: Where in the body do ClO_2, ClO_2^-, and ClO_3^- become reduced to Cl^-? The oxidative damage done to various cells will be described.

The presence of ClO_2^- systemically following administration of ClO_2 is significant because ClO_2^- has been shown to be capable of oxidizing hemoglobin to a nonfunctional pigment, methemoglobin, a condition known as methemoglobinemia (*4*). More recent studies utilizing ClO_2^- administered in drinking water have revealed that hemolytic anemia is produced at much lower levels of ClO_2^- than those required to produce methemoglobinemia. Although mild in character, relatively clear indications of hemolytic anemia are observed in rats receiving drinking water containing 100 mg/L of ClO_2^- (*5*).

However, subclinical effects (effects not associated with overt diseases such as depleted glutathione and elevated 2,3-diphosphoglycerate) consistently result from water containing ClO_2^- at concentrations of 50 mg/L (*5*) and sometimes at concentrations as low as 10 mg/L (*2*, *6*). Both ClO_2 and ClO_3^- produce depressions of red-cell glutathione concentrations, but these induced decreases tend to disappear with continued exposure, while the ClO_2^- induced decreases in red-cell glutathione concentrations are stable (*7*). These results have also been seen in monkeys, mice, and cats (*8*, *9*). At the relatively low levels found in drinking water, such effects have not been observed, except possibly in one susceptible person with a deficiency of glucose-6-phosphate dehydrogenase (*10*).

The mechanism involved in the hemolytic activity of ClO_2 and its derivatives appears to involve the in vivo production of hydrogen peroxide (*5*, *11*, *12*), a mechanism that is common to most oxidants that cause hemolytic anemia (*13–15*). The creation of hydrogen peroxide by ClO_2, ClO_2^-, and ClO_3^- raises the possibility that HOCl is generated through the activation of myeloperoxidase, an enzyme which catalyzes the formation of HOCl from hydrogen peroxide and Cl^- (*16*). The long-term consequences of this process of producing halogenated chemicals in vivo has yet to be thoroughly investigated.

Chlorine dioxide does appear to possess activity as an antithyroid agent, a property it does not share with ClO_2^- or ClO_3^- (*17*). In African green monkeys, this effect is seen as a depression of serum thyroxine levels following four weeks of exposure to ClO_2 at a concentration of 100 mg/L (about 9 mg ClO_2/kg body weight/d). The perchlorate ion is known to produce goiter and is obviously related to ClO_2 (*18*). The extreme lability of ClO_2 in the gastrointestinal tract raises some interesting issues as to the potential mechanisms involved in this effect (*17*). When ^{36}Cl is used as a tracer, the kinetics of ClO_2 absorption are found to be much more rapid than those observed with the other chlorine compounds including ClO_2^- (*2*). This evidence suggests the possibility that some product of ClO_2, which is formed very rapidly in situ, could be responsible for the antithyroid effect. This is being investigated at our laboratory in Cincinnati.

There are relatively few studies of the effects of the alternate disinfectants or their by-products on other target organs. Abdel-Rahman et al. examined the effects of ClO_2 and ClO_2^- on the turnover of cells in the gastrointestinal tract (*2*). At ClO_2 and ClO_2^- levels of 10 mg/L, there was evidence of increased cell turnover as measured by ^3H-thymidine incorporation. Large changes in DNA synthesis are associated with cell division, and thymidine is a base used exclusively in DNA synthesis (as opposed to RNA synthesis). Therefore, increases in ^3H-thymidine incorporation indicate a higher rate of cell division. Thus, even these low doses of ClO_2 and ClO_2^- appear to cause some minimal level of cell killing and regeneration.

In contrast to findings concerning the gastrointestinal tract, ^3H-thymidine incorporation into the testes is inhibited by ClO_2^- at concentrations of 10 and 100 mg/L in drinking water (*2*). Since a large portion of the DNA synthesis that occurs in the testes is associated with the production of sperm, these data suggest the possibility that ClO_2^- depresses spermatogenesis. Obviously, this effect requires further study.

The use of chloramine in drinking water disinfection has been associated with the production of methemoglobin in dialysis patients (*19*). However, methemoglobinemia and other hematologic effects have not been observed in experimental animals exposed to chloramine by the oral route (*17*, *20*).

A final cause for concern with chloramines is evidence that monochloramine is mutagenic in *B. subtilis*, a bacterium used for mutagenesis testing (*1*). For this reason, the National Toxicology Program (NTP) is investigating the possibility that monochloramine is a carcinogen in mice and rats.

Toxicology of by-products

The problem of disinfection by-products must be discussed in two parts. First, there are the established by-products of disinfection, such as the trihalomethanes, which are created

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from reactions between background organic chemicals and chlorine. Second, a vast group of oxidation and chlorination products can result from the production of new functional groups in the background organic material present in the source water. This results in biological activity in fractions of organic material isolated from water that is distinct from the activity associated with the identified products of disinfection (*21–23*, *24*).

Identified by-products. Of the known products of disinfection, those formed by chlorination have been studied most extensively. The trihalomethanes (THMs) began to receive a great deal of attention after it was learned that chloroform is carcinogenic in both mice and rats (*25*). The other trihalomethanes that occur with a high degree of regularity—bromoform, dibromochloromethane, and dichlorobromomethane—are being examined in the NTP carcinogenesis bioassay program.

In the meantime, a variety of mechanistic questions have been raised concerning the way in which chloroform causes cancer. The basic argument is whether chloroform-induced tumors are produced when chloroform interacts with genetic material of the target cell or whether chloroform acts through an epigenetic mechanism. In other words, is chloroform an initiator or a promoter? Tumor initiators are chemicals that produce an irreversible change in a cell characteristic that is generally believed to involve alteration of cellular DNA. Because the effects of tumor initiators are irreversible, they are commonly believed to act by nonthreshold mechanisms. (That is, any dose of such a chemical possesses a finite probability of causing cancer, although this probability always decreases with decreased exposure.) Tumor promoters are chemicals that can increase the likelihood that an initiated cell will develop into a tumor. To promote permanent damage, however, continuous exposure to such chemicals is often necessary. Therefore, the effects of such chemicals are felt to be reversible and to result from mechanisms that have definite thresholds. One type of mechanism by which such chemicals act is to produce obvious damage to an organ such as the liver. The resulting hyperplastic response to such damage—that is, the stimulation of cell division—can promote the development of tumors in the organ. Clarifying the argument about whether chloroform is an initiator or a promoter could significantly affect the level at which it is regulated in drinking water (*26*).

TABLE 1

Liver fat content and pathology in B6C3F$_1$ mice treated with chloroform in drinking water

Chloroform (mg/L)	Percent liver fat [a]		Number of animals with centrilobular fatty change [a]			
	90 d [b]	180 d [b]	30 d	60 d	90 d	Total
0	3.33	5.82	0	0	0	0
200	3.45	7.93 [c]	0	0	0	0
400	3.89 [d]	6.77	3	0	0	3
600	—	—	0	0	0	0
900	4.51 [d]	7.11 [c]	2	0	0	2
1800	6.36 [d]	10.40 [d]	5	0	4	9
2700	—	—	6	5	2	13

[a] Average value for 10 animals at each dose and time.
[b] Duration of exposure to chloroform at the indicated concentrations.
[c] Statistically significant from control at P <0.05 by ANOVA and t-test.
[d] Statistically significant from control at P <0.01 by ANOVA and t-test.

Thus, a new study of chloroform carcinogenesis was initiated in cooperation with the National Cancer Institute. Preliminary data demonstrate quite clearly that the B6C3F$_1$ mouse is vulnerable to chloroform-induced liver injury (*27*). This effect is most obviously shown as a dose-related increase in liver fat (Table 1). It is clear that a similar dose–response relationship is seen for microscopically observed fatty infiltration of the liver, a clear indication of liver damage. On the other hand, the Osborne–Mendel rat failed to show evidence of the same type of damage except for mild changes at the highest dose tolerated (Table 2). It should be noted that the Osborne–Mendel rat also failed to develop liver tumors as a result of treatment with chloroform (*25*). However, this rat developed kidney tumors after treatment with chloroform, but it is not yet known whether the tumors resulted from kidney damage analogous to liver damage in the B6C3F$_1$ mouse.

In addition to carcinogenicity, other aspects of trihalomethane toxicology have been examined in detail in the past several years (*28*). At doses of either 125 or 250 mg/kg per day for 14 days, the four trihalomethanes of primary concern (chloroform, bromoform, dibromochloromethane, and dichlorobromomethane) all produced enlarged livers and other signs of toxic damage to the liver in CD-1 mice. The four THMs displayed some evidence of interfering with immune function at doses of 50–125 mg/kg per day for 14 days. Given at very high doses (200 mg/kg) intraperitoneally or intratesticularly, both chloroform and bromoform produced depressed DNA synthesis in the testes (*29*). There was

TABLE 2

Liver fat content in Osborne–Mendel rats exposed to chloroform in drinking water

Chloroform (mg/L)	Percent liver fat [a]	
	90 d	180 d
0	3.32	4.49
200	3.31	4.50
400	3.20	4.59
900	3.58	4.77
1800	3.46	5.13 [b]

[a] Average value for 10 animals at each dose and time.
[b] Statistically significant from control at P <0.05 by ANOVA and t-test.

no evidence of such effects with oral administration of either agent, however. When chloroform and bromoform were administered at 100 and 400 mg/kg per day, mice displayed some decreased performance in an operant behavioral task (a task in which an animal must perform successfully to receive a reward), but the authors note that these were near-lethal doses (*30*). Therefore, these data cannot be taken as evidence of specific behavioral dysfunction. It is reasonably clear from this summary that the noncarcinogenic effects of chloroform that have been studied require substantially higher doses than those encountered in drinking water. (In the worst cases, humans are exposed to approximately 10 μg/kg per day of trihalomethanes from drinking water.)

Identifying by-products of chlorination in addition to THMs has been a relatively slow process. The forma-

tion of chlorinated phenols (2-chlorophenol, 2,4-dichlorophenol, and 2,4,6-trichlorophenol) has been known for many years because of the taste and odor problems arising from these chemicals. Of these substances, 2,4,6-trichlorophenol has been demonstrated to be a carcinogen in both mice and rats (*31*). Exon and Koller are presently examining the transplacental toxicity of 2-chlorophenol and 2,4-dichlorophenol (*32*). Their studies contain some evidence that high doses (500 mg/L) of 2-chlorophenol in drinking water are toxic to the fetal rat.

The haloacetonitriles have also been identified as by-products of chlorination (*33*, *34*). This group of chemicals has not yet been characterized toxicologically. The Ames test, however, has shown dichloroacetonitrile to be mutagenic (*35*). We have confirmed this result in our own laboratory as indicated in Table 3. Other members of this group readily available for testing—chloroacetonitrile, trichloroacetonitrile, and dibromoacetonitrile—tested negative under similar circumstances. But it should be noted that cellular killing severely limited the amount of trichloroacetonitrile and dibromoacetonitrile that could be applied to the standard plate assay. We are currently examining the ability of these same chemicals to produce carcinogenic responses in other experimental systems.

More recently, the formation of organic *N*-chloramines following chlorination of surface waters has been postulated (*23*). A model compound, *N*-chloropiperidine, has been shown to be formed in aqueous solution. This chemical possesses direct mutagenic activity in *Salmonella typhimurium* strain TA100 and produces cell transformation of hamster diploid fibroblasts in vitro (*23*). Although the extent to which organic *N*-chloramines occur in chlorinated water is not presently known, these results indicate that the possibility of their formation should be taken seriously.

Unidentified by-products. The organic matter that occurs in surface water sources is quite diverse. Consequently, it is not too surprising that a great variety of products can arise from the use of disinfectants. A major part of the organic material found in drinking water is of quite complicated and heterogeneous structure.

It has been well established that humic and fulvic acids are one source of reaction products such as trihalomethanes (*36*). These naturally occurring substances are complex organic molecules formed from decaying biological matter for which no precise chemical structures have been established. A variety of other products of humic acid chlorination have been identified (*37*), the nature of which depends considerably on pH (*36*).

A key question is whether chemicals produced through disinfection of drinking water have significant biological activity. As a starting point, the EPA laboratory in Cincinnati is studying the formation of mutagenic products following chlorination of humic and fulvic acids. These first experiments were performed in aqueous solution at total organic carbon (TOC) levels of 250 to 1000 mg/L and at a Cl/C ratio of 0.8. In Table 4 are shown specific mutagenic activities of the chlorinated products in the *Salmonella*/microsome assay (Ames test) expressed both in terms of TOC and total organic halogen (TOX) (*38*). Testing the commercial (Fluka) humic acid and humic and fulvic acids isolated from two natural lakes revealed no direct or indirect activity in *Salmonella* strains TA1535, TA1537, TA1538, TA98, and TA100. In contrast, substantial direct-acting mutagenic activity was noted in strains TA98 and TA100 following chlorination of these humic and fulvic acids. No samples showed significant activity in the other *Salmonella* strains. In both qualitative and quantitative terms, the pattern of mutagenicity observed was very similar for all chlorinated samples. The only substantive difference was a tendency toward less activity in TA98 by fulvic acids isolated from aqueous systems relative to

TABLE 3

Mutagenicity of haloacetonitriles in *Salmonella* test strains [a] with (+S9) and without (−S9) metabolic activation

Chemical and highest dose used	TA 1535		TA 1537		TA 1538		TA 98		TA 100	
	−S9	+S9	−S9	+S9	−S9	+S9	−S9	+S9	−S9	+S9
Chloroacetonitrile, 10 μL	−	−	−	−	−	−	−	−	−	−
Dichloroacetonitrile, 1.5 μL	+[b]	+[c]	−	−	−	−	+	+[c]	+	++[d]
Trichloroacetonitrile, 1.2 μL	−	−	−	−	−	−	−	−	−	−
Dibromoacetonitrile, 0.05 μL	−	−	−	−	−	−	−	−	−	−

[a] Standard plate assay as per Ames et al. (1975).
[b] A positive response is defined as a minimum of twice the number of observed revertants on control plates and a clear dose–response relationship. A minimum of six doses.
[c] Revertants/plate were not significantly altered by the addition of S9 mix.
[d] Revertants/plate were significantly altered by the addition of S9 mix.

TABLE 4

Specific mutagenic activities of chlorinated humic and fulvic acids [a,b]

Source	TOC [c] (mg/mL)	TOX [d] (mg/mL)	Net revertants [e]/mg TOC		Net revertants [e]/mg TOX	
			TA 98	TA 100	TA 98	TA 100
Fluka humic	0.92	0.35	309	2323	811	6106
Black lake humic	1.01	0.34	450	2382	1335	7076
Black fulvic	0.69	0.25	181	3003	508	8288
Lake Drummond humic	0.25	0.11	857	2694	1963	6173
Lake Drummond fulvic	0.76	0.26	ND[f]	2367	ND[f]	6919

[a] Data obtained from Bull et al. (1981) with permission.
[b] Nonchlorinated material was uniformly negative at the same TOC concentrations.
[c] Total organic carbon content. Analysis conducted by R. Lingg and R. Kaylor, HERL, U.S. EPA, Cincinnati, Ohio.
[d] Total organic halogen content. Analysis provided by A. Stevens of MERL, U.S. EPA, Cincinnati, Ohio.
[e] Values are based on dose–response data from assays without S9 added.
[f] ND = No detectable mutagenic activity.

humic acids obtained from the same source or commercially.

These data correspond quite closely to what has been observed by Dutch researchers studying the chlorination of drinking water obtained from surface and bank infiltrated waters (*34*, *39*). In Holland, indirect-acting chemicals present in the source water were destroyed by chlorination, and in their place there was a consistent increase in mutagens that act directly in *Salmonella* strains TA98 and TA100. This parallels the nature of mutagenic activity generally identified in samples taken from drinking water, although it is not clear that disinfection is responsible for the activity (*40*).

The degree of risk to human health cannot be estimated through the results of Ames tests alone. Consequently, analogous samples are being studied with higher level tests in mammals. Previous work has shown that treating Ohio River water with either chlorine, ozone, or chloramine increased the numbers of tumors in SENCAR mice when a 1.5-mL total dose of an aqueous reverse osmosis concentrate was injected subcutaneously (beneath the skin) followed by 20 weeks of promotion three times weekly with 2.5 μg of 12-O-tetradecanoylphorbol-13-acetate (TPA) in 0.1 mL acetone (*20*). This low-level response has not been found in two repetitions of the experiment conducted at different times of the year (*41*). Three additional experiments, some of them using samples taken at the same time of the year, are under way. Since the mouse skin system is selective in its response to chemical carcinogens, we are using similar samples in a variety of test systems. Included in these studies are lifetime carcinogenesis bioassays of the disinfection by-products of humic acids in mice.

Finally, it must be pointed out that other toxicological effects of the chemically uncharacterized disinfection by-products have received virtually no attention. Progress in this area has been hampered by the lack of suitable short-term predictive tests for chronic toxicities or, alternatively, by the lack of a model system that could be used as a surrogate for the products of drinking water disinfection. Since the chemicals produced by disinfection are independently quite low in concentration and in general refractory to chemical analysis at the concentrations encountered, they must be concentrated prior to testing. But concentrating samples of water to study the effects of these products is sometimes plagued by questions of recovery and potential artifacts.

The most critical limitation, however, is the cost involved in collecting large enough samples of organic material to perform whole animal studies of chronic effects. Although not directly referrable to toxicological effects other than carcinogenesis and mutagenesis, the Ames test data presented here do suggest that reaction products formed from commercially obtained humic material are quite similar to those from humic and fulvic material recovered from aquatic systems. Testing such commercial materials may, therefore, serve as a model system that could allow better definition of the potential problems associated with by-products found in drinking water. This work would then have to be followed up to establish that the offending chemicals do indeed occur in drinking water as a result of disinfection.

Summary

At this point it is obviously much too early to provide any definitive answer to the question of the relative health risks of the various drinking water disinfectants. That there are problems associated with the use of chlorine is readily apparent. However, neither the dimensions of that risk nor the relative hazards of alternatives can be addressed clearly at this time. Consequently, there is no basis for suggesting that disinfectant alternatives to chlorine are any safer from a toxicological point of view.

Within the context of hazards that have been identified with disinfectants themselves or with simple inorganic by-products, the use of ClO_2 appears to pose a substantially greater problem than the other alternatives. The hazard here would seem to revolve around sensitive populations such as those sensitive to hemolytic anemia, those with endocrine problems, or women of reproductive age. There are indications of potential problems with chlorine and chloramine, however, that need further investigation. The longer half-life of elimination of HOCl compared to ClO_2 and associated products may indicate that chlorine produces endogenous compounds (compounds formed within the body) with which we should be concerned. In the case of chloramine, a major concern is its mutagenic properties. This suggests, but does not prove, the possibility of carcinogenic activity. Traces of ammonia in the source water or the deliberate addition of ammonia to suppress trihalomethane formation results in the formation of chloramines. Neither of these situations is uncommon, and large populations are exposed. Thus, it is important to resolve this issue experimentally.

The formation of disinfectant by-products with organic chemicals in the source water or with chemicals added during treatment remains an extremely complex issue. As long as substantial quantities of background organic material are present in the source water, all disinfectants will produce by-products not present in the source water. In all likelihood the by-products of all disinfectants will include certain chemicals that will be found to possess biological activity of some concern. It should be recognized that the only reason the problem ever came to light was because chlorine produced a group of volatile by-products at the time when the coupled gas chromatograph–mass spectrometry system became the state of the analytical art.

It must be taken as established that treating drinking water with disinfectants produces compounds that have mutagenic activity. Whether disinfectants other than chlorine produce the same levels of mutagenic chemicals as chlorination is likely to depend considerably on local water conditions as demonstrated by Dutch researchers (*34*, *39*). Much of the mutagenic activity found in drinking water appears to result from the reaction of chlorine with naturally occurring organic material in the source water. As a word of caution, it should be noted that these disinfectants are all reactive compounds and can act to destroy toxicologically active chemicals as well (*21*, *34*). In fact, preliminary work in our own laboratory indicates that the level of mutagenic activity generated from humic acid is very dependent upon conditions in the water, such as pH. Therefore, the primary concern in the area should be developing a fundamental understanding of the processes that occur as a result of the reaction of disinfectants with organic material in the water. The key to dealing with this issue should be to determine what conditions of disinfection give rise to potentially harmful products and how production of such by-products can be minimized. At that point, the cost–benefit equations should be used to weigh disinfection efficacy against acute and chronic toxic effects and relative cost in a meaningful way. Within the context of present information, making such judgments does not seem productive and could lead to investment in alternative methods that will prove less advantageous in the reasonably near future.

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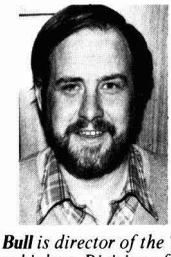

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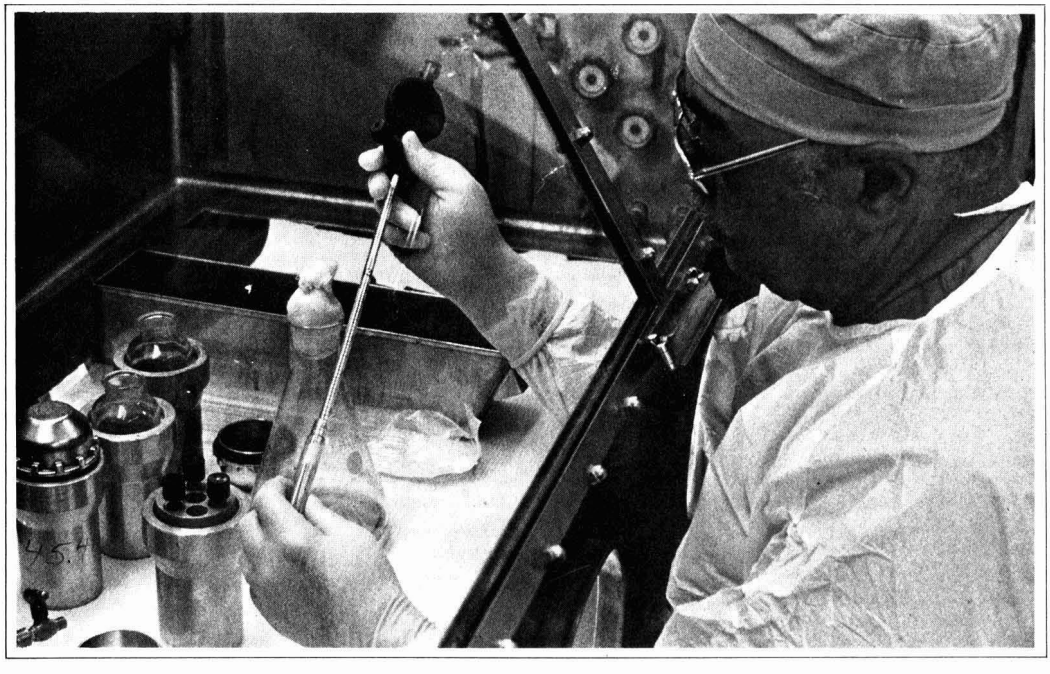
ES&T
CRITICAL REVIEW

Mutagenicity testing in environmental toxicology

The author discusses the nature of genetic damage; tests used for mutagen screening; techniques for detecting mutagens in environmental samples; and monitoring for the effects of mutagens in humans



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During the past decade, genetic effects and particularly mutagenesis have come to occupy a prominent place in toxicology. A great deal of effort has been devoted to the development of sensitive and convenient experimental methods for identifying chemicals that induce mutations, and genetic toxicology tests are now being used to screen large numbers of compounds in order to identify those that may pose a genetic or carcinogenic hazard to humans. Considerations of time and expense necessitate that such screening be done with microorganisms or through other short-term tests. Tests with complex multicellular organisms, which tend to be more costly, are typically reserved for compounds that have yielded interesting results in simpler test systems or that are of great commercial importance.

The task of testing all chemicals to which people are exposed would be enormous. It has been estimated that 70 000 commercial chemicals are in use in the U.S. (*1*, *2*), and that 700 to 3000 new chemicals are introduced each year (*2*, *3*). Not all chemicals are equally important for toxicology testing; thus, priorities must be set so that those chemicals with the greatest potential for causing adverse effects in humans can be most thoroughly examined. Factors that should be considered in setting priorities for testing include volume of production, intended use, likelihood of human exposure, anticipated toxicity, and environmental distribution. Unfortunately, this information is lacking for many chemicals. By any standard, however, the task of testing for mutagens requires simple, inexpensive screening tests that can be applied to large

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numbers of chemicals.

Screening pure compounds is only one aspect of coping with the concern about environmental mutagens, because mutagens also exist as components of complex mixtures. Detecting mutagens in environmental samples introduces complications beyond those encountered in screening pure compounds; mixtures often have variable or inadequately known chemical compositions, and the biological effects of mutagens in complex mixtures are not necessarily additive. Testing complex mixtures and their fractionated components is therefore of current interest in genetic toxicology.

The nature of genetic damage

The major types of genetic alterations are gene mutations, structural changes in chromosomes, and changes in chromosome number. *Gene mutations* are changes in the structure of DNA in individual genes; the term *point mutation* is also used, particularly if it is known that the mutational change is restricted to a single site within a gene. Gene mutations include *base-pair substitutions*, in which one base pair in DNA (such as adenine–thymine) is replaced by another (for example, guanine–cytosine), and *frameshift mutations*, in which one or a few base pairs are added to the structure of DNA or deleted from it (Figure 1).

Some mutagens exhibit specificity for particular mechanisms of mutagenesis. For example, metabolites of benzo[*a*]pyrene induce predominantly frameshift mutations (*4*), whereas diethyl sulfate primarily induces base-pair substitutions (*5*). Other mutagens, such as ultraviolet light, induce a mixture of alterations (*6*). It is therefore important that tests for mutagenicity be able to detect both base-pair substitutions and frameshift mutations.

Structural changes in chromosomes, commonly called *chromosome aberrations*, involve gross rearrangements of the genetic material. Aberrations may involve the deletion of chromosomal segments, the duplication of regions of the chromosome, the inversion of the order of genes in a particular chromosomal region, or the translocation of chromosomal segments to a new location in the same or a different chromosome.

Alterations in chromosome number include *polyploidy* and *aneuploidy*. Polyploidy involves the presence of *extra complete sets* of chromosomes, whereas aneuploidy involves abnormal chromosome numbers that are *not even multiples* of a normal chromosome set. In aneuploids, individual chromosomes may be missing from a normal chromosome set or may be present in excess of the normal number. Examples of the results of aneuploidy in humans include Down's syndrome, in which there are 47 chromosomes per cell because of the presence of an extra chromosome No. 21, and Turner's syndrome, in which there is a missing sex chromosome.

Gene mutations, chromosome aberrations, and aneuploidy all contribute to the burden of human disease. All three are also subject to induction by mutagenic chemicals in experimental organisms. Although there is considerable overlap in the effects of mutagens, and certain mutagens may induce all three types of mutational damage, some agents may show specificity of effect. It is therefore important to have the capability of detecting environmental agents that induce any of these three classes of genetic damage.

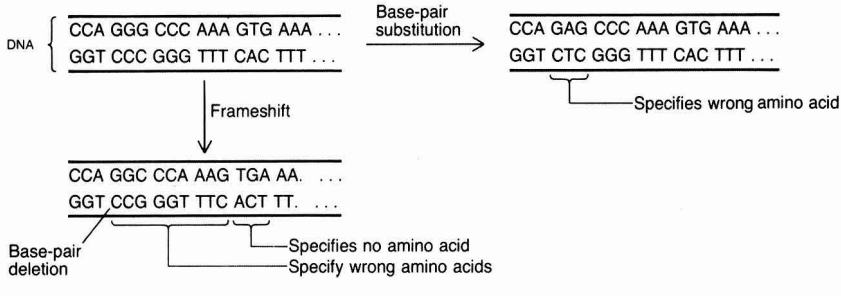
Concern about mutagens

There are two principal reasons for concern about environmental mutagens: an increase in the mutation rate in human germ cells (eggs or sperms) may cause an increased incidence of genetic disease in future generations; and mutations in somatic cells (cells other than germ cells) may lead to an increased cancer incidence in the present generation. Therefore, the induction of mutations both in germ cells and in somatic cells has implications for human health.

The experimental and theoretical bases for associating mutagenesis and carcinogenesis have been reviewed by Straus (*7*). Briefly, the evidence may be summarized as follows:

- Most carcinogenic chemicals are mutagens or give rise to mutagens in

FIGURE 1
Base-pair substitution and frameshift mutations



Effects of base-pair substitutions and frameshift mutations

The altered base sequence that results from a base-pair substitution often leads to a change in amino acid sequence in the protein that is encoded by the gene. The altered protein may function differently from the original protein, thereby causing a difference in the characteristics of the organism.

A frameshift mutation alters all of the genetic information after the point in the DNA at which a base pair is added or deleted. Consequently, frameshift mutations lead to grossly altered and nonfunctional gene products.

Frameshift mutations and some base-pair substitutions can also cause incomplete and nonfunctional gene products because the newly generated base sequence can contain units of genetic information that specify no amino acid at all. The effect of such mutations depends upon the consequences of the missing gene function in the biochemistry of the affected cell or organism.

mammalian metabolism (*1*, *8–10*).

- The sensitivity of different animal strains and organs to carcinogenesis may be related to their ability to metabolize the carcinogens to reactive forms (*11*, *12*) or to repair the induced damage in DNA (*13*).
- People with hereditary defects in DNA repair (*14*, *15*) or chromosome-instability syndromes (*15*) are cancer prone.
- Tumors typically originate as clones from single transformed cells (*16*).
- Several human cancers are associated with defined mutations (*17*) or chromosomal alterations (*18*).

Together, these lines of evidence provide strong support for the hypothesis that mutations in somatic cells are important in carcinogenesis (*7*). Since most chemicals that are known to be carcinogenic in humans or in experimental animals are also mutagenic in laboratory tests, rapid and inexpensive mutagenicity tests are used extensively as predictive indicators of carcinogenesis.

Although it is reasonable to presume that mutagens can contribute to human disease through the induction of gene mutations, chromosomal aberrations, and aneuploidy, the magnitude of the contribution is unknown. About 6% of liveborn infants have genetic defects or malformations (*19*, *20*), but the linkage between environmental agents and such disabilities is less concrete than that between environmental agents and cancer. It is clear, however, that chromosome aberrations and aneuploidy contribute to human disease, in that about 0.6% of infants are chromosomally abnormal (*19*, *20*) and have associated syndromes. Chromosomal abnormalities also contribute to prenatal deaths; about 6% of stillbirths and 50% of spontaneous abortions between weeks 8 and 20 of pregnancy involve chromosomal abnormalities (*20*).

Gene mutations are associated with genetic disease and disability through many disorders that are inherited as simple Mendelian traits. Gene mutations undoubtedly also contribute to the disease burden through their part in diseases that are complex in etiology but that have a genetic component. Although much genetic disease is caused by mutations already present in the population, it is reasonable to presume that environmental mutagens can increase the frequency of these mutations and thereby cause an increased disease incidence.

The pattern of inheritance of a gene mutation can be described as *dominant* or *recessive*. A recessive mutation must be inherited from both parents (that is, must be homozygous) to be expressed, whereas only a single copy of a dominant gene is required for its expression. Therefore, new dominant mutations are expected to be expressed in the first generation after their occurrence, but new recessive mutations may not be expressed for tens or hundreds of generations. Although more than 1000 defined disorders, such as cystic fibrosis, phenylketonuria, and albinism, are inherited as recessive gene mutations (*21*), the great majority of recessive mutations are likely to be inherited from previous generations rather than being new mutations. In contrast, new mutations probably make a larger contribution to the incidence of dominant genetic diseases. Because of their expression in the first generation, induced dominant mutations constitute a greater concern for human welfare for the foreseeable future than do induced recessive mutations. However, recessive genes on the X chromosome are similar to dominant genes with respect to expression, because a single mutation is expressed in males since they have only one X chromosome. About 1% of infants have disorders that are attributable to dominant or X-linked mutations (*19*), but the impact of chemically induced mutation on this incidence is not readily estimated.

A concern about recessive mutations is that many of them may be expressed to a slight extent even in heterozygotes. For example, one of the characteristics of the recessive diseases xeroderma pigmentosum and ataxia telangiectasia is a high incidence of cancer; while heterozygotes for these diseases do not have the high cancer incidence or other symptoms of the diseases, there is some evidence that they nevertheless do have a cancer incidence somewhat higher than that of the general population (*22*, *23*). The suggestion that recessive mutations may show minor effects in heterozygotes is also supported by studies in experimental organisms (*24*). Therefore, even for short-term genetic risk, recessive mutations are not irrelevant.

Fortunately, in mutagen testing it is not necessary to screen separately for the induction of dominant and recessive mutations, because mutagens do not exhibit specificity in this respect. For genetic risk assessment, however, there are practical advantages in studying dominant mutations because they are relatable to the genetic damage that might occur in humans in the first few generations after mutagen exposure. For example, dominant mutations that affect the skeletal system in the mouse have been used to estimate genetic risks posed by ionizing radiation (*19*).

An insidious aspect of exposure to mutagens is the long time between exposure and effect. Because of the latency in carcinogenesis, many more exposures may have occurred before the effect is detected. The problem posed by the temporal separation of exposure and effect is even more pronounced for heritable genetic damage. The consequences of mutagenesis may not be evident for several generations; and even then, it may not be possible to associate an increase in genetic disease incidence with its cause. The goal in genetic toxicology is therefore the identification of mutagens in experimental organisms and prevention of human exposure to them.

Concepts in testing

Throughout toxicology, tests in experimental organisms are used to identify and assess hazards for humans; observations from human exposures are often consistent with data from laboratory studies. For mutagenesis, however, there are virtually no data on human germ cells and very limited data on human somatic cells in vivo. Genetic toxicology is therefore even more heavily dependent on laboratory tests than most other areas of toxicology.

Fortunately, the validity of extrapolating among species in genetic toxicology is supported by the fact that DNA is the hereditary material in all organisms. One can therefore expect most chemicals that interact with DNA as mutagens in one species to be mutagenic in other species as well; experimental observations support this expectation (*1*, *8*). There are also strong correlations between the carcinogenicity of chemicals in mammals and their mutagenicity in short-term tests (*10*, *25–28*). Even pessimistic estimates (*29*) of the strength of short-term mutagenicity tests in identifying carcinogens support their use in the preliminary screening of chemicals.

Besides predicting carcinogenicity, short-term tests can be used to predict mutagenicity in mammalian germ cells. However, because of differences among species in pharmacologic disposition of toxicants, metabolism, and repair of genetic damage, one cannot expect a perfect correspondence between results in short-term tests and genetic effects in mammals. For instance, several chemicals, such as di-

FIGURE 2
Definitions of sensitivity and specificity

$$\text{Sensitivity} = \frac{\text{Number of carcinogens that give a positive result}}{\text{Number of carcinogens tested}} = \text{Proportion of correctly identified carcinogens}$$

$$\text{Specificity} = \frac{\text{Number of noncarcinogens that give a negative result}}{\text{Number of noncarcinogens tested}} = \text{Proportion of correctly identified noncarcinogens}$$

High sensitivity = Few false *negatives*

High specificity = Few false *positives*

ethylnitrosamine, that are mutagenic in short-term tests are reported to be nonmutagenic in mammalian germ cells (*30*, *31*); in this case, the short-term test properly predicts mammalian carcinogenicity but not germinal mutagenicity. Despite such discrepancies, the demonstration that a chemical is mutagenic in other organisms provides some suggestion that it may be mutagenic in humans; the expectation that it is a human mutagen is strengthened if there is independent evidence, such as the alkylation of DNA in germ cells, that the agent reaches germinal tissue in mammals.

Because of limited data, it is not practical to evaluate the performance of short-term tests by their predictiveness for effects in humans. Rather, they must be compared with other laboratory tests. If the intended use of a short-term test is to predict genetic damage in human germ cells, there is no adequate basis of comparison for test results, because the data base on the induction of mutations or defined chromosomal alterations in germ cells of experimental mammals is small. Only about 25 chemicals have been tested in the mouse-specific locus test, and the data permit a confident conclusion on whether the test was positive or negative for only 17 of them (*32*). In the mouse heritable translocation test, there are adequate data for only 14 of 32 chemicals tested (*33*). Therefore one is largely restricted to measuring concordance among submammalian tests. Data from diverse short-term tests can, however, identify compounds that may pose a genetic risk for humans and help to identify those agents that most warrant study in mammalian germ cell tests.

A positive result in a germ cell test provides strong suggestion that a chemical is a mutagen in humans. Negative results in such tests must be interpreted cautiously, however, because only very large-scale experiments can exclude modest increases in mutation frequency. Although such expensive tests are not useful in screening, they can be of paramount importance in assessing genetic risks.

It is easier to evaluate the performance of short-term tests in predicting carcinogenesis than in predicting germinal mutagenesis because of the availability of data on many chemicals in cancer bioassays in rodents. A short-term test is said to exhibit high *sensitivity* in predicting carcinogenesis if a large proportion of carcinogens yield positive results in the test; it is said to exhibit high *specificity* if a large proportion of noncarcinogens yield negative results (*34*, *35*). The term *false positives* is commonly used to denote noncarcinogens that give positive results in a given assay; similarly, undetected carcinogens are called *false negatives*. Although sensitivity is used in other contexts to describe a test's capacity to detect low mutagen concentrations or small changes in mutation rate, the usage

TABLE 1
Relationship between the proportion of carcinogens among test chemicals and the percentage of false positives[a]

Composition of test chemical population		Test performance		Results				False +/
% Carcinogens	% Noncarcinogens	Sensitivity	Specificity	% True positive	% True negative	% False positive	% False negative	Total + (%)
100	0	0.9	0.9	90	0	0	10	0
90	10	0.9	0.9	81	9	1	9	1.2
50	50	0.9	0.9	45	45	5	5	10
10	90	0.9	0.9	9	81	9	1	50
0	100	0.9	0.9	0	90	10	0	100
100	0	0.65	0.65	65	0	0	35	0
90	10	0.65	0.65	58.5	6.5	3.5	31.5	5.6
50	50	0.65	0.65	32.5	32.5	17.5	17.5	35
10	90	0.65	0.65	6.5	58.5	31.5	3.5	82.9
0	100	0.65	0.65	0	65	35	0	100

[a] The terms *sensitivity* and *specificity* are used as defined in Figure 2. Sensitivities of 0.65 and 0.9 were selected as pessimistic and optimistic estimates of the performance of some of the better short-term tests; specificity was set as equal to sensitivity for illustrative purposes. The table shows that the proportion of positive results that are false positives increases as the proportion of carcinogens among test chemicals is decreased.

given in Figure 2 is common in the validation of short-term tests for carcinogens.

Evaluating the capacity of short-term tests to predict carcinogenesis is not without pitfalls. Use of the terms false positive and false negative assumes that the carcinogenesis bioassay permits a correct classification of a chemical as a carcinogen or a noncarcinogen. In fact, however, the carcinogenicity of some chemicals is uncertain even *after* testing. Negative results are particularly troublesome in this respect, because of the possibility that a particular assay failed to detect the activity of a chemical that would have been positive in another test or under other conditions. This concern is supported by the observation that of 98 carcinogens that were tested in both the rat and the mouse, only 44 were carcinogenic in both species (*36*). One should therefore expect that some carcinogens will be scored as negative in carcinogenesis bioassays but will be detected as mutagens in short-term tests. In validation exercises, such chemicals would be regarded as false positives in the short-term test, whereas actually they were incorrectly classified as noncarcinogens.

The difficulty of classifying chemicals as noncarcinogens introduces another complication in test validation—the choice of appropriate noncarcinogens to assess the specificity of a test. Ideally, a short-term test should be able to distinguish a carcinogen from a closely related noncarcinogen. In one validation study (*8*), for example, tests were evaluated for their capacity to differentiate between such pairs of chemicals as ethionine and methionine, 4-nitroquinoline-N-oxide and 3-methyl-4-nitroquinoline-N-oxide, or N-nitrosomorpholine and N-nitrosodiphenylamine. Although the first member of each pair is clearly a carcinogen, the supposed noncarcinogenicity of the other member may be questionable (for example, 3-methyl-4-nitroquinoline-N-oxide) or later found to be incorrect (such as N-nitrosodiphenylamine).

Rather than testing related carcinogens and noncarcinogens, one could test a random selection of putative noncarcinogens or common biochemicals to measure specificity. Doing so on a large scale, however, may waste valuable testing resources. Consequently, a large proportion of the chemicals tested in assay validation typically are carcinogens. In actual testing situations, however, one would expect the proportion of carcinogens to be lower.

As demonstrated by Table 1, the proportion of false positives among all positives becomes larger as the proportion of carcinogens among test

TABLE 2
Genetic toxicology tests

Category of test	Examples	References
Tests for gene mutations		
A. Bacterial tests:		
1. Reversion of auxotrophs	*Salmonella*/mammalian microsome test	*10, 37*
	E. coli WP2 tryptophan reversion test	*38*
2. Forward mutations to drug resistance	Azaguanine resistance in *Salmonella*	*39*
B. Fungal tests:		
1. Reversion of auxotrophs	Adenine mutants in *Neurospora*	*40*
	Multiple auxotrophs in yeast	*41, 42*
2. Forward mutations and small deletions detected by colony color	Red and white adenine mutants in *Neurospora* or yeasts	*42–44*
C. Mammalian cell culture tests:		
1. Forward mutations to drug resistance	Thymidine kinase (TK) mutants selected by resistance to pyrimidine analogues in mouse lymphoma cells or human cells	*45–48*
	Hypoxanthine–guanine phosphoribosyltransferase (HGPRT) mutants selected by resistance to purine analogues in Chinese hamster or human cells	*25, 48–51*
D. Vascular plant tests:		
1. Forward mutations detected in pollen grains	Staining for mutations at the waxy locus in corn	*52, 53*
2. Forward mutations detected in sporophytes	Stamen hair color test in *Tradescantia*	*54–56*
	Chlorophyll-deficiency mutations in corn, barley, and other plants	*57–59*
E. *Drosophila* tests:		
1. Gene mutations and small deletions	Sex-linked recessive lethal test	*60–62*
F. Mammalian tests:		
1. Gene mutations and/or deletions in germ cells	Mouse morphological specific locus test	*31, 32, 63*
	Mouse electrophoretic specific locus test	*64*
	Mouse skeletal mutations	*65*
	Mouse cataract mutations	*66, 67*
2. Gene mutations in somatic cells	Mouse spot test (somatic cell specific locus test)	*63, 68–70*
Tests for chromosomal damage		
A. Mammalian cell culture tests:		
1. Chromosomal aberrations	Human or rodent cell cytogenetics	*71, 72*
2. Sister chromatid exchanges	Human or Chinese hamster cells	*73–75*
B. Vascular plant tests:		
1. Chromosomal aberrations in mitotic cells	Cytogenetic analysis of shoot tips or root tips in *Vicia faba*, onion, barley, or other plants	*76–78*
2. Chromosomal aberrations in meiotic cells	Cytogenetic analysis of microsporocytes	*76*
3. Micronucleus test	Micronuclei derived from treated microsporocytes in *Tradescantia*	*79, 80*

chemicals is decreased. It is therefore inherent in testing that there is a greater likelihood that a positive result is a false positive when the chemicals tested are predominantly noncarcinogens. Although in many circumstances, false negatives are a more important failing of a test than false positives, this relationship points out that specificity is an important aspect of testing and suggests that one should not be unconcerned about false positives. False positives and false negatives both detract from the predictive value of a test; their consequences, however, may differ at different stages in the toxicologic testing of chemicals. With further refinement and validation of tests, testing strategies may be devised to use combinations of tests that compensate for deficiencies of individual tests in either sensitivity or specificity.

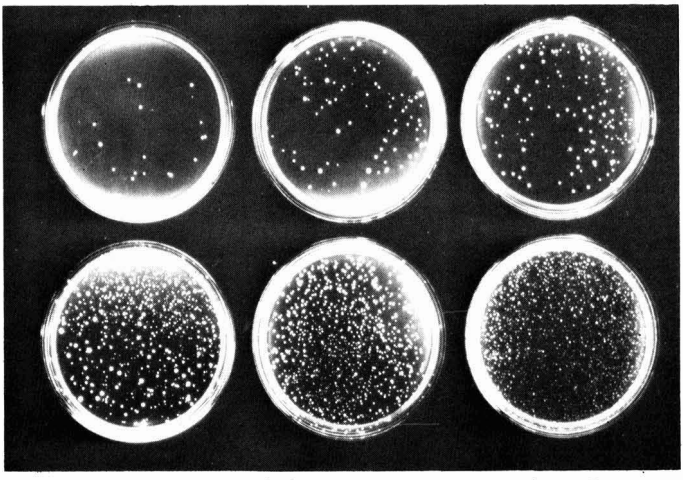
A short-term assay is said to be validated if it performs well in tests of a large number of chemicals in several laboratories and is consistent over time. The compounds should be derived from diverse chemical classes and should include weak as well as potent mutagens and carcinogens, because tests differ in the effectiveness with which they respond to different classes of compounds, and potent mutagens are typically easiest to detect. The most useful short-term test is one that has been extensively validated and combines a high sensitivity with a high specificity. Some tests, such as the *Salmonella*/mammalian microsome test (*37*), meet these criteria reasonably well and consequently are widely used.

Screening for mutagens

Experimental tests have been developed to detect genetic effects of chemicals in bacteria, fungi, mammalian cell cultures, vascular plants, insects, and mammals. The data base on chemical mutagens is expanding rapidly, and the files of the Environmental Mutagen Information Center in Oak Ridge, Tenn., now include more than 40 000 publications concerning genetic effects of at least 13 000 different chemicals.

Table 2 lists major test systems in genetic toxicology. The tests range from short-term tests that can be performed in a few weeks to rather long-term, expensive tests for mutations in mammalian germ cells. Although many tests are listed, relatively few of them are being used extensively in many laboratories. Widely used tests include the *Salmonella*/mammalian microsome test; tests for gene mutations in cultured Chinese hamster or mouse lymphoma cells; the sex-linked recessive lethal test in *Drosophila;* tests for chromosomal aberrations,

Category of test	Examples	References
4. Chromosomal aberrations in haploid cells	Chromatid aberrations in nuclei of treated pollen grains in *Tradescantia*	*79*
C. *Drosophila* tests:		
1. Chromosomal aberrations	Heritable translocation tests	*60–62*
D. Mammalian tests:		
1. Chromosomal aberrations	Cytogenetic analysis of rodent bone marrow, spermatogonia, spermatocytes, or oocytes	*72, 81*
2. Sister chromatid exchanges	Rodent bone marrow, spleen, or spermatogonia	*73–75*
3. Chromosome breakage	Micronucleus tests	*82, 83*
4. Indirect evidence of chromosome damage in germ cells	Mouse or rat dominant lethal test	*63, 84, 85*
5. Heritable chromosomal aberrations in germ cells	Mouse heritable translocation test	*33, 63*
Tests for aneuploidy		
A. Fungal tests:		
1. Aneuploidy in mitotic cells	Monosomy in *Saccharomyces* strain D6	*86, 87*
2. Meiotic nondisjunction	Disomy in *Neurospora* ascospores	*88*
B. *Drosophila* tests:		
1. Chromosome breakage and loss	Sex-chromosome loss test	*60–62, 89*
C. Mammalian tests:		
1. Chromosome breakage and nondisjunction	Sex-chromosome loss test	*63, 90, 91*
Tests for other genetic damage		
A. Bacterial tests:		
1. Repair tests	*rec* assay for differential killing of rec^+ and rec^- strains of *Bacillus subtilis*	*92, 93*
	polA test for differential killing of $polA^+$ and $polA^-$ strains of *E. coli*	*93, 94*
2. Inductests	Induction of lysis in *E. coli* lysogenic for prophage λ	*95, 96*
B. Fungal tests:		
1. Recombinogenicity tests	Induced mitotic crossing over in *Saccharomyces*	*97–99*
	Induced mitotic gene conversion in *Saccharomyces*	*98, 99*
C. Mammalian cell culture tests:		
1. Repair tests	Unscheduled DNA synthesis in human fibroblasts	*100*
	Unscheduled DNA synthesis in rat hepatocytes	*101, 102*
2. Cell transformation assays	Morphological changes indicative of malignant transformation in mammalian cells	*103–106*
D. Mammalian tests:		
1. Sperm abnormality test	Morphological sperm abnormalities in the mouse; indicative of spermatotoxicity and possible genetic damage	*107, 108*



Ames test. *Petri dish at upper left shows spontaneous revertant colonies. From upper left to lower right, bacteria treated with increasing amounts of sodium azide show increases in numbers of mutant colonies/plate which are dose-dependent.*

sister-chromatid exchanges, and unscheduled DNA synthesis in mammalian cell cultures; and cytogenetic analysis in rodents. Some of the other tests, however, can provide data as good as those from the more common assays. It should be emphasized that there is no single best genetic toxicology test, that new test methods are being developed, and that existing tests are being refined. It is therefore necessary to revise testing strategies in accordance with progress in test methodology.

Mutations are commonly detected in microorganisms by selecting for reversions in an auxotrophic strain (that is, a strain with a specific nutritional requirement caused by a mutant gene) or forward mutations that confer resistance to an inhibitory chemical. As indicated in Table 2, however, other means of detecting genetic damage in microorganisms are also used. Microbial tests can be conducted quickly and inexpensively and are therefore suitable for screening large numbers of chemicals. Such tests also offer an extensive data base for comparative purposes.

The most widely used of all mutagenicity tests is the *Salmonella*/mammalian microsome test developed by Bruce Ames and his colleagues (*37*). In the Ames test, mutations are detected in histidine-auxotrophic strains of *Salmonella typhimurium* as bacterial colonies that grow in the absence of histidine. The test includes some strains that revert by base-pair substitutions and others that revert by frameshift mutations. Another test, based on the selection of mutants resistant to the toxicity of 8-azaguanine, detects a diversity of mutagens in a single *Salmonella* strain (*39*).

Some of the methods used in microbial tests, such as detecting mutations that confer resistance to inhibitory chemicals, can also be used in cultured mammalian cells. Mammalian cells, like other animal cells and plant cells, have a *eukaryotic* cellular organization characterized by a membrane-bound nucleus and discrete cell organelles. *Prokaryotic* organisms (bacteria and blue-green algae) differ from eukaryotes in the organization of their genetic material and do not have membrane-bound nuclei and cell organelles. Because of their eukaryotic cellular organization, mammalian cells may respond to mutagenesis more as human cells would in vivo than do bacterial cells. Mammalian cell tests therefore offer an increase in presumed relevance for human health at an increase in expense that is modest relative to that incurred with mammalian in vivo tests.

The most widely used mutagenicity tests in mammalian cell cultures are the detection of resistance to 6-thioguanine and other purine analogues or trifluorothymidine and other pyrimidine analogues (Table 2). Since these tests detect forward mutations at various sites in a gene, mutants can arise by a variety of molecular mechanisms. An exception to the generalization that tests based on drug resistance detect a broad spectrum of genetic events is that resistance to ouabain in mammalian cells results from a specific alteration in a membrane-associated adenosine triphosphatase (ATPase) (*50*); mutations that totally eliminate the ATPase activity are lethal (*1*). Ouabain resistance is therefore less suitable for use in screening than are other mutations to drug resistance.

For use in mutagen screening, test systems in microorganisms or mammalian cell cultures must be modified so as to have metabolic capabilities like those of a mammal. Metabolic activation systems are needed to detect some classes of carcinogens, such as nitrosamines, polynuclear aromatic hydrocarbons, and aromatic amines. Chemicals that are mutagenic and carcinogenic only when metabolized are called *promutagens*; they can be activated in vitro by using homogenates of mammalian tissues in the short-term tests. For example, the promutagens dimethylnitrosamine (*109*) and benzo[*a*]pyrene (*4*) are not mutagenic themselves but can be detected as mutagens in short-term tests if the indicator organisms or cells are simultaneously exposed to the chemical and to extracts of mouse (*109*), rat (*4*), or human (*4*) liver. The rat liver metabolic activation system, frequently called an *S9* (that is, 9000 × g supernatant) mix, is now a standard part of mutagenicity testing (*37*).

Besides gene mutations, short-term tests are used to detect the induction of reparable DNA damage in bacteria or mammalian cells, mitotic recombination in yeast, aneuploidy in yeast, and chromosomal aberrations and sister-chromatid exchanges in mammalian cells (Table 2). Exogenous metabolic activation is required with most of these tests, an exception being an assay for unscheduled DNA synthesis in cultured hepatocytes that have the capacity to activate promutagens (*101*, *102*).

Major disadvantages of short-term tests are that the indicator organisms or cells are not comparable to intact mammals in dosimetry, routes of exposure, and toxicokinetics. Exogenous metabolic activation systems do not mimic metabolism in intact animals perfectly, and differences in repair processes among organisms may cause differences in mutational responses. Short-term tests, possibly excluding tests in *Drosophila*, cannot account for differences between germ cells and somatic cells in sensitivity to mutagenesis; however, *Drosophila* tests do evaluate chemical effects in germ cell stages that are analogous to those in mammals. *Drosophila* tests also permit the detection of a broad range of genetic changes, including gene mutations, chromosome aberrations, and chromosome loss (Table 2).

Tests for gene mutations and chromosomal alterations in mammals, especially mice, are important in genetic toxicology because of their relevance for human health. Unfortunately, most genetic tests in intact mammals (Table 2) are too costly and time consuming for screening large numbers of chemicals. The evaluation of mutagenic hazards therefore requires both short-term tests for screening and mammalian tests for assessing genetic risks posed by important compounds.

Environmental samples

Not all chemicals that pose a mutagenic risk for humans would be identified by screening pure compounds, because complex environmental mixtures may contain mutagenic substances that would not seem to warrant mutagenicity testing in their own right. In addition, chemicals in complex mixtures need not act additively in their mutagenicity; rather, there may be synergisms or antagonisms between mutagens, or interactions between mutagens and nonmutagens. Although nonadditivity is sometimes difficult to demonstrate unequivocally, the mutagenesis literature includes examples of antagonistic (*110*, *111*) and of synergistic or comutagenic (*112*, *113*) interactions involving mutagens.

The possibility of interactions among chemicals suggests that mixtures of chemicals should be tested. Although all compounds of interest cannot possibly be tested in pairwise combinations, it is feasible to test complex environmental samples and, if mutagenicity is detected, to fractionate the samples to identify mutagenic components. Short-term tests are uniquely suited to testing environmental samples. The inexpensiveness of the tests permits large numbers of samples and fractions to be tested, and only small volumes of sample are required. Mutagenic components of the samples can then be studied more thoroughly in other tests, if such tests are warranted.

Mutagenicity studies of environmental samples require a broad range of techniques for the collection of samples, their extraction or concentration, and their fractionation to characterize mutagenic components. Sampling and analytic methods have been the subject of several recent papers and reviews (*114–121*).

Most tests of complex mixtures have used the *Salmonella*/mammalian microsome test (*37*). Complex mixtures that have been studied with this assay include: drinking water (*114*, *118*, *122–125*); swimming-pool water (*126*); industrial emissions or effluents (*127*, *128*); municipal sewage sludge (*52*); welding fumes (*129*); automotive emissions (*130–132*); wood, peat, and oil combustion emissions (*133*); fossil fuels (*114*, *134*); shale oils (*115*, *116*, *135*); synthetic oils and fuels (*114*, *115*); Athabasca tar sands (*110*); photocopy toners (*136*); typewriter ribbon extracts (*137*); coal fly ash (*129*); coal gasification and liquefaction products (*138*); ambient air samples (*117*, *129*, *139–145*); coffee and tea (*146*); cooked meat and fish (*147–149*); smoke from charred meat (*129*, *150*); and tobacco smoke (*129*, *151*, *152*).

Mutagenic environmental samples can be fractionated to characterize mutagenic components. In studies of fuels, for example, shale oils and coal distillates were found to be mutagenic in strain TA98 of the *Salmonella*/mammalian microsome test, while crude petroleum was not (*134*). The mutagenicity of coal liquid distillates in strain TA98, which detects frameshift mutations, was associated with aromatic amines, in that the active fractions were found by gas chromatographic mass spectral analysis to contain aminonaphthalenes, aminoanthracenes, aminophenanthrenes, aminopyrenes, and aminochrysenes (*153*).

An interesting result concerning interactions among chemicals is that a polyaromatic fraction from tar sands was found to suppress the mutagenicity of 2-aminoanthracene in *Salmonella typhimurium* when this known mutagen was mixed into the tar sand fraction (*110*). The possibility of antagonisms among chemicals argues that a negative result in tests of complex mixtures, as was obtained with tar sands (*110*), should not be interpreted simplistically as precluding the presence of mutagens.

In some studies, variations of standard test procedures have been devised for analyzing complex mixtures. For example, a novel modification of the Ames test combines the bacterial test with thin-layer chromatography (TLC) (*137*). Developed TLC plates on which samples had been separated are placed in large petri dishes, and medium is poured over them. After several hours, the bacteria and metabolic activation mixture are poured into the petri dishes. The mutagenic activity of several known mutagens, as well as of extracts of city air and of typewriter ribbon, could be detected as clusters of mutant bacterial colonies above mutagenic compounds in the TLC plates. Although the method may not be suitable for all classes of compounds, it permits large numbers of samples to be tested, and mutagens in the samples can be identified by chemical analysis of extracts from duplicate TLC plates (*137*).

Because of expanding use of diesel engines, diesel exhaust is being heavily studied in mutagenicity tests. Besides the Ames test, diesel exhaust and fractions derived from it are being tested for the induction of mitotic recombination in yeasts, gene mutation in mammalian cells, unscheduled DNA synthesis in mammalian cells, and sex-linked recessive lethal mutations in *Drosophila* (*154*). Diesel emissions have also been tested in mammalian cell transformation (*130*, *154*) and animal carcinogenesis tests (*130*). The short-term assays may prove particularly beneficial in monitoring the effects of variations in fuel composition and the operating characteristics of diesel engines (*130*). The application of inexpensive mutagenicity tests can serve as a useful adjunct to the development of technology for minimizing the toxic properties of emissions.

Air samples from industrial and residential locations have been studied in *Salmonella*, and higher levels of mutagenicity were found to be associated with the industrial sites; however, some mutagenicity was detected in all of the samples (*145*). The composition of the samples included at least 28 polynuclear aromatic hydrocarbons (PAHs) (*145*), a number of which are known to be promutagens that induce frameshift mutations. However, not all of the mutagenic activity in air samples is ascribable to promutagens; and mutagens that do not require metabolic activation have been detected in air samples from Buffalo, N.Y., and Berkeley, Calif., (*143*).

Appropriate sampling procedures are essential for testing complex mixtures, in that the sample should reflect the environmental composition of the mixture (*117*). Artifacts can originate, for example, from reactions between compounds that occur together on filters at high concentrations. It has been reported that frameshift mutagens that do not require metabolic activation are formed on glass fiber filters by exposure of the promutagen benzo[*a*]pyrene, or the nonmutagens perylene or pyrene, to 1 ppm nitrogen dioxide and a trace of nitric acid in air (*141*, *155*). Direct-acting mutagens have also been found to occur in automobile exhaust (*132*), and in both

studies the mutagenicity appears to be associated with nitro derivatives of PAHs (*132*, *155*). Although highly mutagenic nitro derivatives of hydrocarbons may be formed in ambient atmospheres, such reactions may occur preferentially on the surface of filters when large quantities of gas are drawn over particulates for an extended time (*129*, *141*). The possibility of filter artifacts must therefore be considered in interpreting results on air filtrates.

The physical properties of environmental samples must also be considered in testing. For example, the mutagenicity of urban aerosols and of serum extracts of coal fly ash in *Salmonella* is reported to decrease with increasing particle size. Sampling procedures should therefore be designed so that mutagenicity associated with fine particles is not obscured by a high proportion of large particles in a sample (*129*). Sampling methodology, such as that at electrostatic precipitators or baghouse filters, that allows a disproportionate amount of fine, respirable particles to escape can cause erroneous negative results or an underestimation of mutagenicity (*129*). Other factors that can affect the mutagenicity of environmental samples are the temperature of collected particulates, weather conditions at the time of collection, the distribution of particulates by winds, and sunlight (*129*).

As in sampling, artifacts can be introduced through the processing of samples. For example, the duration and temperature of storage may influence the mutagenicity of samples of particulates (*129*). Extraction procedures are also important, since the same environmental sample can yield different results with different means of extraction (*129*). For example, a horse serum extract of coal fly ash was found to be more mutagenic in *Salmonella typhimurium* than a saline extract or a cyclohexane extract (*129*, *156*).

Aqueous environmental samples, such as municipal water, are typically too dilute for mutagenicity testing. Methods used to concentrate aqueous samples or isolate organic compounds from them have recently been reviewed by Jolley (*118*). Concentration techniques include reverse osmosis and lyophilization (*118*, *157*); isolation methods include adsorption to resins and solvent extraction (*118*, *157*, *158*).

Tap water and lake water samples from an agricultural community in Illinois were concentrated 3000× by passing them through columns of XAD-2 resin, and the concentrates were found to be mutagenic in *Salmonella typhimurium* strains TA98 and TA100 (*123*). Moreover, the use of XAD-2 resin to remove organic compounds from aqueous solutions for mutagenicity testing has become standard in testing urine samples for the presence of mutagens (*158*) and seems well-suited to testing municipal water supplies, lakes, streams, and other environmental samples (*157*). The possibility of artifacts generated by test procedures must always be considered in processing aqueous samples. For example, solutions of isoniazid or fresh urine from rats treated with isoniazid were found to be nonmutagenic (*159*); when tested at the same concentrations, however, samples that had been lyophilized or stored at room temperature were found to contain mutagenic substances (*159*).

Tests of complex mixtures can be used both in environmental monitoring and in quality control procedures. For instance, when products may have mutagenic contaminants, short-term tests can be used to screen for their presence. Information on mutagenic contaminants can also be helpful in monitoring the effectiveness of pollution control mechanisms, containment facilities, and industrial processes (*128*). Short-term tests can therefore be used to monitor for changes in environmental conditions associated with changes in industrial processes (*114*, *128*).

In situ monitoring

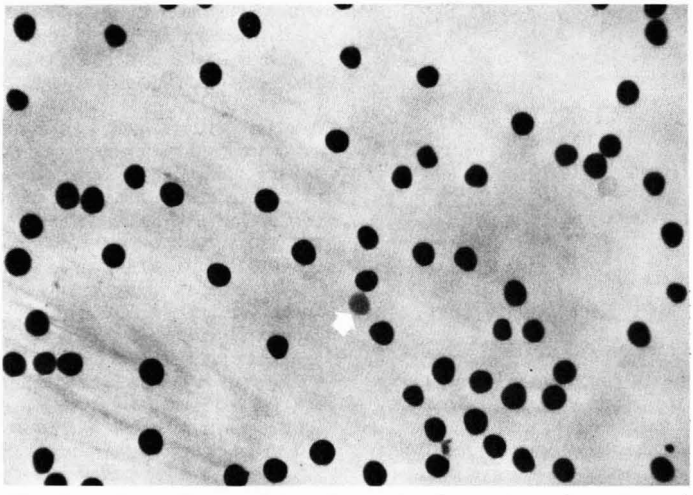
Besides testing environmental samples, in situ monitoring can be used to detect mutagens in the environment. In situ monitoring involves the measurement of mutagenic effects in test organisms that are grown in the environment of interest. The organisms are not given controlled, artificial exposures to test substances, but are compared with organisms grown in an environment that can serve as a negative control for the conditions being tested. Tests in plants seem particularly well suited to serving as in situ monitors.

The *Tradescantia* stamen hair test, which is reputed to be highly sensitive to gaseous and airborne mutagens (*55*, *160*), has been used as an in situ monitor for mutagenic air pollutants. The test detects somatic gene mutations that cause a change in the pigmentation of stamen hair cells from blue to pink. With plants maintained in a mobile laboratory equipped with exposure chambers and control chambers, mutagenic effects were detected in industrial locations, including Baton Rouge, La., Houston, Tex., Elizabeth, N.J., and Charleston, W.Va. (*54*, *55*); the result obtained from a clean-air control site at Grand Canyon, Ariz., was negative (*55*). The greatest response was obtained for industrial sites in New Jersey during periods of high temperature and automobile traffic (*55*, *117*). Tests of air samples from these locations in the *Salmonella*/mammalian microsome test were consistent with the results from the plant in situ monitors (*117*). Seasonal variations, weather conditions, industrial work schedules, traffic, and other factors have been observed to affect the pollutant mixtures and mutagenicity results (*55*, *161*). *Tradescantia* has also been used to monitor mutation frequencies in the vicinity of nuclear power plants in Japan (*162*).

The *waxy locus* test in corn has been used to monitor for mutagens in both air and soil. In this test (*52*, *53*) pollen grains that have the dominant gene *Wx* stain black with iodine, because their starch is composed of both amylose and amylopectin. Unlike these *starchy* pollen grains, pollen grains with the recessive allele *wx* are *waxy*; they contain only amylopectin and *do not stain with iodine.* Mutations at the *waxy* locus are detected by changes in the stainability of pollen grains. Mutagenic effects at the *waxy* locus are reported for plants exposed to air near a lead smelter (*163*) or grown in soils that were treated with municipal sewage sludge (*52*). Mutagenic effects of sewage sludge were also detected in a test for micronuclei, which indicate chromosome breakage, in *Tradescantia* (*52*).

Most work on in situ monitoring for mutagens involves growing indicator organisms in the environment of interest. Natural populations of organisms can also be monitored for evidence of genetic damage. For example, the frequency of chromosome aberrations or sister chromatid exchanges in a study population can be compared with that of control populations in a similar habitat that lacks the pollutant or other environmental factor of interest.

Chromosomal aberrations have been observed in populations of royal fern (*Osmunda regalis*) growing beside a river polluted with effluents from paper recycling industries (*164*, *165*). The study population was reported to have a higher frequency of aberrations than did control populations. Examining natural populations of organisms for evidence of genetic damage is an interesting adjunct to other forms of mutagen monitoring. To draw conclusions from the data, however, it is important that control



Waxy locus. *Corn pollen grain (shown by arrow) underwent forward mutation and cannot synthesize amylose; thus it stains tan instead of the normal black in the presence of iodine.*

populations be defined carefully and that differences in habitats not be overlooked. Relative to well-defined test systems in experimental organisms, there are many variables that can influence results obtained from natural populations.

Monitoring human populations

The ability to detect effects of mutagens in people can contribute to reducing mutagen exposures, because some mutagens may evade detection in experimental organisms. Screening populations that have known or suspected contact with mutagenic substances could also be useful in quantifying exposures, assessing risks, and identifying situations in which protective measures are inadequate. To monitor for effects of mutagens in human populations, it is necessary that the population under study always be compared with an appropriate control population. A variety of factors, such as age, sex, smoking habits, and medical history, must be taken into consideration for the selection of controls. For effective monitoring, methods that can discern relatively small differences between study populations and their matched controls are required.

One approach to monitoring human populations for evidence of mutagenesis in germ cells involves recording effects in the offspring of the study population. In theory, an increased incidence of "sentinel phenotypes," such as certain dominant genetic diseases, can serve as an indicator of an increase in rates of mutation. The sentinel phenotypes approach, however, is not a sensitive indicator of mutagenesis (*166*). Individual genetic diseases are rare; their diagnosis is not always unequivocal; and their etiology is sometimes complex. The approach would require monitoring large populations in which it may be impossible to ascribe an increase in the incidence of the sentinel phenotypes to a specific cause. Detecting electrophoretic protein variants in blood samples of the offspring of a study population (*167*, *168*) would similarly require that large populations be screened and involve long times between exposure and effect.

Although phenotypic and electrophoretic monitoring contribute to the knowledge of human mutation frequencies, they are not readily applicable to monitoring human populations of limited size for evidence of mutagenesis. Other characteristics that have been suggested as indicators of genetic damage include alterations in birth weights, childhood development, the frequency of fetal or neonatal deaths, and the incidence of congenital defects (*20*). These characteristics have the disadvantage, however, that some of their causes are not genetic.

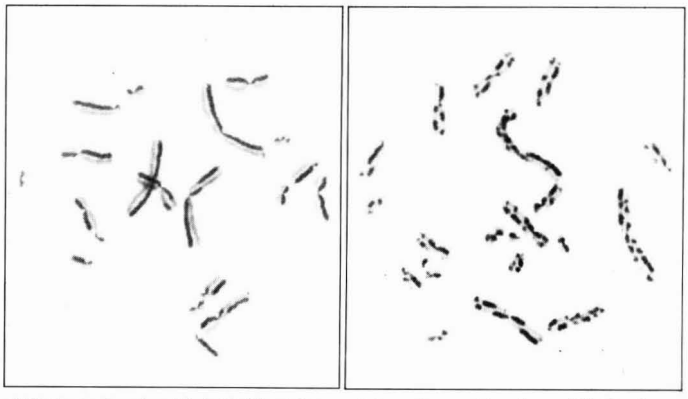
Because of these difficulties in detecting evidence of mutagenesis from human health statistics and monitoring programs, there is no definitive evidence for the induction of heritable alterations in human germ cells by any mutagen. Although imperfect, monitoring for health effects can be useful when combined with other methods because it can add to the weight of evidence for mutational effects in a population. For example, data on frequencies of perinatal mortality and congenital malformations in children of fathers who smoke cigarettes are supported by data on cytogenetic damage in somatic cells of smokers, the presence of mutagens in their urine, and frequencies of morphologically abnormal sperm in suggesting that smoking poses a genetic risk (*169*).

The insensitivity of monitoring for health effects is suggested, however, by the absence of clear evidence of increases in the incidence of congenital malformations, cytogenetic abnormalities, perinatal mortality, or childhood mortality in a study of 71 000 children of survivors of the atomic bombings of Hiroshima and Nagasaki (*170*). A negative result in population monitoring programs may therefore reflect the insensitivity of current methodology, rather than the absence of genetic damage.

Because of the difficulty of detecting mutagenic effects in human germ cells, alternative methods are being developed to detect and measure mutagenic exposures in humans. Most of these methods detect effects in somatic cells rather than in germ cells, making the unit of measurement an individual cell rather than an individual person; relevance for genetic disease is sacrificed in order to permit the detection of effects in small numbers of people.

Cytogenetic studies have occupied a prominent position in monitoring people for exposure to mutagens (*171–175*), particularly in occupational settings (*176–178*). For example, peripheral blood lymphocytes can be monitored for chromosomal aberrations (*171–173*) in workplaces where there may be exposures to mutagens; employees can be tested when they are first employed, and then at regular intervals or after accidents, to monitor for cytogenetic damage (*128*, *179*). The limitations in cytogenetic monitoring are that control individuals vary considerably in frequencies of aberrations; the methods may not be sensitive enough to detect effects of low doses or small increases in aberration frequencies; the interpretation of the tests is somewhat subjective; there are often confounding variables; and aberrations in lymphocytes are not readily interpreted with respect to human health. Nevertheless, cytogenetic tests do provide an indication of exposure to a mutagen.

A promising newer method in cytogenetic monitoring is the detection of sister chromatid exchanges (SCE) (*74*, *175*, *177*, *178*, *180*). Although the



SCE. *Cyclophosphamide (with S9 mix) caused sister chromatid exchange (SCE), shown by the pattern of light and dark chromosomal material in the Chinese hamster cell on right.*

genetic mechanism of SCE formation is not understood, many mutagens induce SCEs. Relative to classical cytogenetic analysis, scoring results in SCE tests is less subjective, more rapid, and less costly. The SCE method has also been shown to be sensitive to low chemical concentrations in experimental organisms (*73*).

Gene mutations can be detected in human somatic cells in vivo, but the techniques for doing so are at early developmental stages. The most advanced method is that developed by Albertini and his colleagues for detecting mutations in the hypoxanthine–guanine phosphoribosyltransferase (HGPRT) gene in peripheral lymphocytes (*181*, *182*). Mutants are detected by their resistance to the toxic purine analogue 6-thioguanine (6-TG). Frequencies of resistant lymphocytes in blood samples from cancer patients treated with multiple therapeutic agents, including some known mutagens (such as nitrosoureas, cyclophosphamide, and X-rays), were found to be higher than frequencies in control individuals (*182*). Although the early results are encouraging, considerable variation in frequencies of 6-TG-resistant lymphocytes in control individuals complicates the system; and, in some cases, patients have been found to have elevated frequencies of variant lymphocytes even before chemotherapy was initiated (*183*). More developmental work is needed to refine the methods and characterize the 6-TG-resistant cells that are detected. Selective influences on variant frequencies and the possible occurrence of phenocopies (that is, nonmutant cells that under certain conditions mimic the characteristics of the mutants) must also be studied further (*181*).

In another method being developed to detect mutations in somatic cells in vivo, human red blood cells that contain mutant hemoglobin are detected by their fluorescence when they are labeled in fixed blood smears with fluorescent antibodies against specific mutant hemoglobins (*184*, *185*). In mixtures of normal cells and cells from people who are heterozygous for mutant hemoglobins, the frequency of cells that bind fluorescent antibody has been shown to correspond to the expected frequency of mutant cells in the mixtures (*184*, *185*). The frequency of red blood cells that contain hemoglobin S or hemoglobin C in normal individuals was determined to be about 10^{-8}–10^{-7} (*184*). Although the detection of hemoglobin mutations with fluorescent antibodies is an interesting prospect, the capacity of the method to detect induced mutations has yet to be assessed.

It is often difficult to know when significant mutagen exposures occur; and even when exposure is certain, it is difficult to quantify the exposure and estimate the risk. Direct measurements of chemical concentrations in blood are impractical when doses are low or when exposures involve unidentified compounds or complex mixtures. Sensitive biological indicators of mutagen exposure would therefore be useful, even if they measure nongenetic effects. For instance, measuring alkylation of amino acids in hemoglobin has been proposed for use as a dosimeter of exposure to alkylating agents in assessing risks (*186*). In theory, the method is applicable to many agents, because most mutagens and carcinogens are electrophiles or are metabolized into electrophiles that form adducts in macromolecules.

Calleman et al. (*186*) tested workers in ethylene oxide sterilization plants for N-3-(2-hydroxyethyl)-histidine in their hemoglobin and found elevated levels associated with ethylene oxide exposure. Ethylene oxide workers have also been reported to have elevated frequencies of SCEs in their lymphocytes (*178*). Measurements of chemical concentrations in the air are not definitive indicators of workplace exposures. Higher levels of alkylated hemoglobin than those expected from measured environmental concentrations may indicate sensitive individuals in the population, high concentrations during periods when atmospheric concentrations were not measured, or unanticipated exposures (*186*).

The discovery by Siebert and Simon (*187*) that the urine of a patient receiving chemotherapy with cyclophosphamide induced mitotic recombination in yeast led to the important realization that microbial tests can be used to detect the presence of mutagens in the urine of mutagen-exposed people. Yamasaki and Ames (*158*) have shown that the urine of cigarette smokers contains mutagens, and they provided a simple means of extracting mutagens from urine for mutagenicity testing. Urine samples are passed through a column of the resin XAD-2; the column is rinsed with water to remove urinary histidine, which interferes with the Ames test; and the adsorbed substances are then eluted from the resin and tested for mutagenicity. Since many toxicants are excreted as conjugates (for example, β-glucuronides), urine extracts can be tested in the presence of enzymes (such as β-glucuronidase) that cleave conjugates (*188*). Urine samples can also be prepared for testing by lyophilization or by solvent extraction (*189*), but these procedures tend to be more complicated and less broadly applicable than resin adsorption.

Besides being found in the urine of cigarette smokers, mutagens have been detected in the urine of patients being treated with cancer chemotherapeutic drugs (*190*); nurses who handle cancer chemotherapeutic drugs (*190*); rubber workers (*191*); and people exposed to the antischistosomal drug niridazole (*192*), the trichomonacide metronidazole (*192*), the industrial chemical epichlorohydrin (*189*), and the wine stabilizer 3-(5-nitro-2-furyl) acrylic acid (*193*). Disadvantages of urine assays are that they detect excreted mutagens and cannot measure cumulative effects of exposure. The possibilities of losing mutagens or introducing artifacts in processing urine samples must also be considered. Nevertheless, testing urine is a simple, inexpensive means of detecting human exposures to mutagens. As such, it can

contribute to the avoidance of mutagen exposures, including the protection of workers from occupational exposures.

The advantage of monitoring somatic cells rather than progeny is shared by sperm cells, in that data can be collected from small numbers of individuals. Measuring effects in sperm has the added attraction of relevance for effects in future generations. Various mutagens cause morphological abnormalities in the sperm of exposed mice (*107*, *108*); and several agents, including X-rays, lead, and cigarette smoke, have been reported to induce morphological sperm abnormalities in humans (*108*, *194*, *195*). Although the mechanism underlying the formation of sperm abnormalities is uncertain, there is at least some evidence that morphological abnormalities in sperm can have a mutational origin (*108*). However, nongenetic factors, such as trauma to the testes, can also affect sperm morphology (*194*). Although the data are not yet extensive enough to assess the merits of the test adequately, it nevertheless has promise as a simple and inexpensive test for effects of chemicals in germ cells.

A test is being developed to detect aneuploidy in human sperm by a cytochemical technique. Human Y chromosomes stained with quinacrine contain a fluorescent region, and a fluorescent spot is detectable in stained spermatozoa (*196*, *197*). It has been proposed that spermatozoa with two fluorescent spots (YFF) represent sperm with two Y chromosomes (*198*). Elevated frequencies of YFF sperm have been observed in men who have had exposures to X-rays, the nematocide 1,2-dibromo-3-chloropropane, or the drugs Adriamycin or metronidazole (*198*). Although the method may prove to be a useful indicator of mutagen-induced aneuploidy in germ cells, stronger evidence that the YFF sperm actually contain two Y chromosomes is needed.

A recent development in mammalian mutagenesis is the use of fluorescent antibodies against a sperm-specific isozyme of lactate dehydrogenase to detect altered gene products in mouse sperm; Ansari et al. (*199*) have reported dose-dependent increases in the frequency of fluorescent sperm in mice exposed to the mutagen procarbazine. It is possible that after more study in experimental animals, a similar system can be developed to detect gene mutations in human sperm (*200*).

Although the current ability to detect effects of mutagens in people is primitive, there has been progress. Most of the methods are still in developmental stages, but they suggest some basis for optimism about growing capabilities to detect mutagen exposures and understand their significance for human health.

Perspectives

The principal concern in environmental mutagenesis is that mutagenic agents can lead to increases in the incidence of cancer and genetic diseases by inducing mutations in human somatic cells and germ cells, respectively. The emphasis in environmental mutagenesis is on the detection of mutagens and prevention of human exposure to them. Detecting mutagens requires sensitive short-term tests to screen large numbers of compounds rapidly and inexpensively; mammalian tests are also required to evaluate mutagenic hazards posed by compounds to which significant human exposures are likely.

In the past two decades, many mutational assays (Table 2) have been developed, and some are now widely used. These assays permit the detection of a variety of mutagens in diverse experimental organisms. It is important that mutagen testing programs have the capability of detecting several types of gene mutations, structural changes in chromosomes, and aneuploidy, because all of these genetic changes have implications for human health.

Currently, test systems for detecting gene mutations and structural changes in chromosomes are more advanced than those for detecting aneuploidy. Although several promising assays for aneuploidy are now under development, continued emphasis on the development of such tests is required. Effective testing for aneuploidy will require assays in lower eukaryotes that are suitable for use in mutagen screening and tests in higher organisms that are similar to humans with respect to gametogenesis. It should be stressed, however, that even for gene mutations and chromosomal aberrations, there is no single assay that meets all needs and that combinations of tests are necessary.

The extensive data base of chemical mutagenesis should be used systematically to define batteries of tests for optimum detection of mutagens; in this respect, means should be explored to use tests in combinations that compensate for deficiencies of individual tests in either sensitivity or specificity. It is important, however, that tests and test batteries do not become rigidly fixed; testing strategies must be revised on a continuing basis to take advantage of advances in test methodology.

Although improvements in short-term tests may be anticipated, it is in testing in intact mammals that some of the greatest needs lie. Genetic tests for detecting mutations in mammalian germ cells are still badly needed; emphasis should be placed on methods that detect defined genetic events, preferably scoring for effects in many genes simultaneously. Detecting mutations directly in sperm can also be a cost-effective approach in mammalian mutagenesis. In any case, refined mammalian tests are essential, in that they will occupy a central position in efforts to quantify mutagenic risks to humans.

One aspect of mutagenicity testing that is receiving growing attention is the study of complex environmental mixtures. It is increasingly evident that genetic effects of chemicals need not be additive and that there can be synergisms and antagonisms among mutagens or interactions among mutagens and nonmutagens. The implications of interactions among chemicals are greatest in interpreting effects of environmental samples. The study of complex mixtures requires a combination of the methodology of environmental chemistry and that of genetic toxicology.

Methods of collecting environmental samples and preparing them for mutagenicity testing must continue to be refined; in this respect, possible artifacts associated with the collection and handling of environmental samples must be identified and better understood. Current work suggests that testing complex mixtures and fractionating them to identify mutagens will be an important adjunct to screening pure compounds. It will be increasingly necessary, however, to carry the testing of complex mixtures beyond the level of identifying the presence of mutagens in environmental samples; specific compounds should be identified, and interactions among components of mixtures should be explored. Besides identifying mutagens, testing complex mixtures can have expanded application in monitoring the effectiveness of mutagen-containment facilities and in quality control of industrial processes and products.

Test systems that are suited to in situ mutagen monitoring can also contribute to the detection of mutagens in environmental mixtures. In situ monitoring has been applied only on a limited scale, however, and more carefully designed studies are required to determine its sensitivity and cost-effectiveness. Assessing the proper role

of in situ mutagen monitoring in environmental toxicology therefore awaits further developmental work.

In the last few years, there have been significant advances in methods to detect effects of mutagens on exposed people. The development of such methods is important because the activity of some mutagens may be undetected in experimental organisms. Data from people can also be useful in identifying situations in which protective measures are inadequate or in assessing risks in cases of known exposure.

The insensitivity and expense of methods that involve screening the progeny of exposed people are major impediments to progress in detecting effects of mutagens in human germ cells. Nevertheless, methods for the direct detection of genetic effects in sperm show some promise. A variety of genetic effects can be detected in human somatic cells in vivo; of these, SCEs and chromosome aberrations can be monitored most effectively. Methods for detecting gene mutations in somatic cells in vivo are also being developed, and the next few years should provide critical information on their utility. Techniques whereby short-term tests are used to monitor for the presence of excreted mutagens in human urine are now sufficiently advanced that expanded application seems warranted; the monitoring of urine can provide convincing evidence of human exposure to mutagenic agents.

The presence of mutagenic chemicals in the environment poses complex problems that will not easily be resolved. Recent progress in mutation research and genetic toxicology testing, however, offers encouragement about a growing capacity to detect mutagens and minimize human exposure to them. Two pressing needs in genetic toxicology are achieving a better understanding of the effects of mutagens in environmental mixtures and learning to quantify the risks that mutagens pose to human health.

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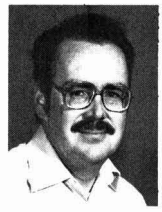

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ES&T PRODUCTS

Compact flatbed recorder
A single-channel recorder has a chart width of 200 mm and uses roll-chart or Z-fold paper. Some of its features are 12 input spans, 16 chart speeds, 0.4-s full-scale response time, overall limit of error of less than ±0.5%, electronic override event marker, and remote chart drive programming. Linear Instruments **101**

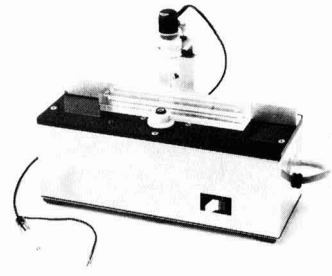
Silicon photodetector
UV-enhanced unit has a UV-grade quartz window and an integral housing with adapters that can be attached directly to Kratos monochromators. The detector has a photosensitive surface area of 33 mm^2 and a flat response profile between 200–1080 nm. Kratos Analytical Instruments **102**

Radioisotope laboratory hood
Stainless steel hood is designed for handling radiochemicals. It is constructed in one piece and the interior is free of joints, cracks, or gaskets. An integral cup sink can be used to dispose of liquids and as a drain during washdown. The hood has fixtures for gas, air, and water and has both 230- and 115-V electrical receptacles. Labconco **103**

Columns for ion chromatography
These columns are capable of separating eight ions in 5 min. They can be used with Wescan ion analyzers or adapted to virtually any existing HPLC system. Wescan Instruments **104**

HPLC valves
Injector consists of two two-position rotary valves turned in tandem by a pneumatic activator that is operated either manually or automatically. This device performs enrichment and injection as well as sample cleanup and other column-switching tasks. The valves operate at pressures up to 7000 psi and have narrow flow passage. Rheodyne **105**

Micro distillation column
Spinning band column includes a digital head, temperature readouts to 0.1 °C, temperature control, and two-position motor speed control. The column performs qualitative and quantitative separations with only a 0.1-mL holdup. It accommodates samples from 5–25 mL. B/R Instrument **106**



Automatic pH-gradient scanner
Scans the pH gradient of an electrofusing gel in approximately 10 min. Tedious slicing and soaking of gel sections before measurement are unnecessary. The scanner may be used in conjunction with most pH meters and chart recorders. Bio-Rad Laboratories **107**

Solid-state storage system
High-speed unit with modular construction stores up to 10 megabytes in a 7-in.-high rack-mounted chassis. It has an internal battery backup and full error detection and correction. Versions of the system that can be attached to various computers as a disc emulating unit are available. Imperial Technology **108**

Lab timers
Three new timers are designed for a variety of laboratory applications. A three-channel alarm timer can program three different activities from 10 h to 1 s. The four-channel alarm timer extends the range to 20 h and has a clock. A multipurpose lab controller has a combination equipment controller, a three-channel alarm timer, a metric converter, a calculator with a six-digit display, and a clock. Markson Science **109**

Low-volume air sampler
Instrument samples particles down to 0.01 μm at calibrated air flows from 15–35 L/min. Equipped with an interchangeable filter head that accommodates filter holders of various sizes. Available in 110 or 220 V ac, this model can operate continuously indoors and outdoors. Staplex **110**

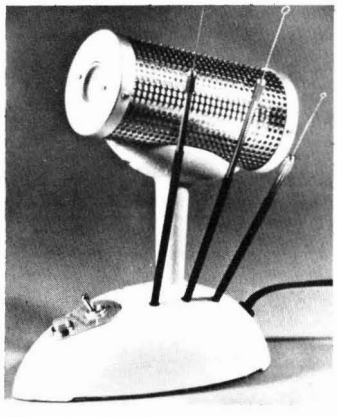
pH/mV/temperature meter
Digital meter provides automatic temperature compensation in the laboratory and in the field. Both line- and battery-operated, the meter has a pH range of 0–14 with a resolution of ±0.005, a temperature range of 5–100 °C, and a recorder output of ±100 mV. Orion Research **115**

Gas blender
Provides controlled dilution and concentration of gases for calibration of gas analysis systems that measure vehicle exhaust. The blender can use either air or nitrogen as a diluent for such pollutants as CO, CO_2, NO, and C_3H_8. The system features 100% mass flow control and 0.5% repeatability. Tylan **116**

Postcolumn reactor
Determines metals such as Fe^{+3}, Fe^{+2}, Ni^{+2}, Cu^{+2}, Pb^{+2}, and Co^{+2}. The detector has a pneumatic pump, mixing tee, and a packed bed reactor in a self-contained unit. It can be installed in a Dionex Series 2000i ion chromatograph. Dionex **117**

Pyranometer
Measures solar radiation with a cosine and azimuth error less than 3% at 10° sun altitude and less than 1% at 30° sun altitude. The sensitivity is 4–6 $\mu V/W/m^2$ over a temperature range of −10–40 °C. The instrument is not affected by tilt or orientation. Kipp & Zonen **118**

Digital air velocity meters
Portable, compact, linear meters also measure air temperature and static pressure and are useful for energy management. Full-scale velocities of 0–200 fpm to 0–200 fps are available. Kurz Instruments **119**



Flameless sterilizer
Sterilizes inoculating loops, needles, and culture tube mouths with infrared heat. The device does not require oxygen and can be used in anaerobic chambers. The temperature is at least 1500 °F at all points in the heating element cavity. Lancer **120**

Acoustic antenna
Designed for use with an acoustic radar and Doppler acoustic sounder, this antenna measures winds in the lower atmosphere with a pencil beam of sound. The antenna dish (which was 1.2 m in diameter in the earlier model) is 1.8 m in diameter and permits data collection to higher altitudes and more data from altitudes where signal strength is low. The antenna is completely mobile because the entire system on its trailer does not exceed normal highway width limits. AeroVironment **121**

Temperature indicators
May be used with most popular thermocouples to provide linear temperature readings on a 0.55-in. planar gas-discharge display. Standard ranges are −150–1100 °C with type I iron-constantan thermocouples and −120–1350 °C with type K chromel–alumel thermocouples. Indicators feature automatic cold-junction compensation and automatic polarity indication. Weston Instruments **123**

Pipetter/dispenser
Adjustable dispenser snaps onto serum vials and most other bottles. Three models dispense volumes from 100 μL to 10 mL. All have barrels and plungers made of glass and a body made of polypropylene. Tri-Continent Scientific **124**

Particle monitoring system
Up to 48 locations in liquid or air may be monitored simultaneously for particle contamination. Airborne particles as small as 0.3 μm and liquid-borne particles as small as 0.5 μm are detected, counted, and recorded. Sensors for determining relative humidity, temperature, conductivity, resistivity, and air flow velocity may be added to the system. Climet Instruments **125**

Magnetometer
Battery powered with rechargeable batteries, this 7-lb device can be used in the field or test lab. Field changes as small as 5 gammas can be detected. The output pulses from a saturable ring core provide the magnetic field strength information. Electro-Mechanics Company **129**

Mass spectrometer system
This routine mass spectrometer can be upgraded at a future time by adding a gas or liquid chromatograph and a data system. For more spectral information and added separation, MS/MS capabilities can be added to any of the above units. Extranuclear Laboratories **130**

ES&T LITERATURE

Lime for wastewater. Case history C-236 tells how a company uses machinery to transport lime for treatment of wastewater; blockages and bridging are eliminated. Vibra Screw **151**

Fluorescence detectors. Brochure describes fluorescence detectors for high-performance liquid chromatography as well as a spectrofluorometer and filter fluorometer, models 970 and 950, respectively. Kratos **152**

Laboratory supplies. 1982–83 laboratory supply handbook features pH testers, electronic balances, safety and emergency equipment, chemicals, and many other items. LaPine Scientific **153**

Radiometer. Brochure describes YSI-Kettering radiometer, which measures radiation in restricted areas for photobiology, photochemistry, botany, and agriculture. Instrument contains a small sensor and is wavelength independent. Yellow Springs Instrument **154**

Dual-media filters. Bulletin CF-52 gives design information on dual-media, deep-bed filters especially useful for removing oil and taking in suspended solids below 1 ppm. Transamerica Delaval **155**

Refuse-fired stoker. Brochure describes ReciproGrate, a reciprocating, refuse-fired stoker with water-tube boiler applications. It has 50–100 ton/d capacities. Detroit Stoker **156**

Centrifugal pumps. Catalog No. 11.3 lists and describes all-plastic, self-priming centrifugal pumps, 5–175 gal/min, for handling corrosive fluids to 250 °F. Vanton Pump & Equipment **157**

Materials containers. Buyers' guide lists polyethylene materials containers such as drums, totes, tanks, and barrels. Plastech **158**

Thermal processing. Brochure describes Bartlett-Snow rotary thermal processing equipment for waste management and many other applications. It can incinerate toxic and hazardous wastes. C-E Raymond **159**

Metal removal from water. Brochure describes FKJA process and FKJ-72 agent, based on formaldehyde, for removal and recovery of heavy metals and destruction of cyanide. No toxic substances remain or evolve. Greco Bros. **160**

pH measurements. Brochure describes 870 Electrochemical Two-Wire Transmitter and 871 Sensors using electronic technology to measure pH, conductivity, and the like. Foxboro Analytical **161**

Total ion analysis. Brochure lists column and detector capabilities for total ion analysis, as well as analysis of amines, surfactants, aliphatic and aromatic sulfonates, and others. Dionex **162**

Materials analysis laboratory. Brochure describes materials analysis laboratory and analytical services available on contract or fee basis. Many analytes plus zeta potential, particle size, and other parameters are available. Micromeritics **163**

Dust control. Brochure describes stockpile dust control system that uses water with specially formulated dust suppression chemical. Johnson-March **164**

Water resources engineering. Brochure describes full range of services concerning surface and groundwater and water quality, including hydraulics, ecosystems, planning, and numerical and physical modeling. Tetra Tech **165**

Dust collection. Announcement describes tube-type after-filter for use where medium dust volumes are created in manufacturing processes, and clean air is required. Aget Manufacturing **166**

***Companies interested in a listing** in this department should send their releases directly to* Environmental Science & Technology, *Attn: Literature, 1155 16th St., N.W., Washington, D.C. 20036*

Bio-mailing and storage. Brochure describes mailers and dry-ice shipping containers for biological samples, as well as refrigerant packs, cryogenic transfer vessels, and other such items. Polyfoam Packers **167**

Gas chromatography. Application sheet describes gas chromatography (GC) injection systems, capillary components, and high-resolution GC systems. Erba Instruments **168**

Chemical resistance. Guide lists chemical resistances of membrane and glass filters, filter holders, and sealing rings. Schleicher & Schuell **169**

Waste management. Newsletters provide information about environmentally acceptable services for regional facilities for hazardous waste treatment and disposal. Rollins Environmental Services **170**

Laboratory instruments. G82 catalog features laboratory instruments, including all-plastic absolute pressure controls and micrometric dispensers. Other instruments also are listed. Gilmont Instruments **171**

Filter selection. Guide lists particle size retention in μm, and filtration speed in mL/s of seven grades of qualitative filter papers, quantitative papers, and other items. Funnels and crucibles also described. Whatman **172**

Meteorological equipment. Catalog lists, describes, and specifies full line of meteorological equipment, and equipment for hydrology, air pollution control, and other such applications. WeatherMeasure **173**

MS capability increase. *Pinnacle* for February 1982 discusses latest mass spectrometry techniques for analyzing compounds once considered intractable because of volatility or stability problems. Extranuclear Laboratories **174**

Fabric filter systems. Brochure tells about advantages of installing an air correction custom fabric filter. Its title is "Custom-Engineered Fabric Filter Systems." UOP **175**

Laboratory services. Brochure lists laboratory services for nine major industries, including environmental. Hauser Laboratories **176**

HPLC equipment. Catalog, "Sourcebook for Successful HPLC," lists columns, cartridges, and other components for high-performance liquid chromatography (HPLC), with recommendations for applications. Waters Associates **177**

Scintillation counting. Bulletin 304A describes reagents and supplies for liquid scintillation counting. Reagents are purified and use-tested. Fisher Scientific **178**

Graphics. Brochure describes DI-3000, a "toolbox" of FORTRAN-callable graphics subroutines. Maps, 3-D displays, and many different forms are possible. Could have environmental applications. Precision Visuals **179**

Fuel gas antifoulant. Brochure describes ZP-903 fuel gas antifoulant, which is nonhazardous. Includes solvents and antioxidants. Zimmite **180**

Chlorine handling. Manual, "Chlorine Safe Handling," explains how to handle chlorine, ship it, load and unload it, and describes emergency procedures for problems that might arise. PPG Industries **181**

Surveying instruments. Catalog lists surveying instruments, such as transits, levels, alidades, and accessories such as tripods, compasses, rods, tapes, files, and safety equipment. Warren-Knight Instrument **182**

Hazardous material safety. Catalog describes more than 70 books concerning chemically and biologically hazardous materials, including safety data, first aid, toxicology, and spill control. More than 874 chemicals are covered. Lab Safety Supply **183**

Static aerator. Bulletin describes static aerator for ponds, lagoons, and basins, both municipal and industrial, for aerating wastewater and aiding sludge and digestion processes. Semblex **184**

Electrodeless measurements. Bulletin 228 describes the theory and principle of operation of electrodeless conductivity systems—usable where conventional electrode systems will not work well, or at all. Beckman Instruments **187**

Fluoride analysis. Bulletin AB-41 describes ion analyzer for analyzing fluoride in drinking water in the 0.1–100-ppm range. Samples with more fluoride can be properly diluted. Analyzer has microprocessor circuitry. Fisher Scientific **188**

Great Lakes water quality. Report to Secretary of State (GAO/CED-82-97) calls for greater U.S. involvement in International Joint Commission activities. U.S. General Accounting Office, Washington, D.C. 20548 (write direct)

Cancer prevention. Brochure, "Safeguards Against Cancer," updates a 1972 leaflet on the subject. Magazine Services, American Cancer Society, 4 West 35th St., New York, N.Y. 10001 (write direct)

Hazardous waste disposal. Flyer sheet announces film, "The Burial Ground," for sale as film or videocassette. Tells how to avoid waste disposal problems. Sponsored by SCA Services, Inc., (Boston, Mass.). Thomas McCann & Associates, 223 Commonwealth Ave., Boston, Mass. 02116 (write direct)

Conservation directory. Announcement tells about forthcoming Conservation Directory. Jay D. Hair, National Wildlife Federation, 1412 16th St., N.W., Washington, D.C. 20036 (write direct)

Texas water. "Water Research: A Sound Investment" points up research needs for the state and is aimed at business leaders. Texas Water Resources Institute, Texas A & M University, College Station, Tex. 77843 (write direct)

"One-stop EPA." Report describes Louisiana's "one-stop environmental protection agency," its staff, and services. La. Environmental Protection, Suite 2100, 733 Third Ave., New York, N.Y. 10017 (write direct)

Renewable resource problems. Interim report sets forth environmental problem potentials with different *renewable* energy sources, by Larry Madsker. Eileen Highes, Office of University Relations, Fordham University, Lincoln Center Campus, New York, N.Y. 10023 (write direct)

POTW performance. Protocol for evaluating publicly owned treatment works (POTW). Project summary EPA-600/S2-82-015. By Hugh Roberts et al., Municipal Environmental Research Laboratory, U.S. EPA, Cincinnati, Ohio 45268 (write direct)

Wastewater problem solving. Industrial Wastewater Problem Solver Chart is available. AFL Industries, Inc., 3661 West Blue Heron Blvd., Riviera Beach, Fla. 33404 (write direct)

ES&T BOOKS

Genotoxic Effects of Airborne Agents. Raymond R. Tice et al., Eds. xiii + 658 pages. Plenum Press, 233 Spring St., New York, N.Y. 10013. 1982. $75, hardcover.

Exposure to carcinogens can occur in a number of ways in the workplace and, to a lesser extent, in the home. This volume explores genotoxic effects of specific airborne agents and details currently accepted in vitro and in vivo test methods, as well as exposure and analytical techniques. Chemicals looked at include benzene, vinyl chloride, radon, and many others.

Patty's Industrial Hygiene and Toxicology, Vol. 2C, 3rd revised ed. George D. and Florence E. Clayton, Eds. xx + 1295 pages. John Wiley & Sons, Inc., 605 Third Avenue, New York, N.Y. 10016. 1982. $100, hardcover.

This book is regarded as a classic reference work in occupational health. This third and final volume covers glycols, inorganic compounds of oxygen, aliphatic nitro compounds, nitrates/nitrites, polymers, alcohols, aldehydes, ketones, organic phosphates, cyanides, nitriles, and carboxylic acids (aliphatic).

Toxicological Effects of Emissions from Diesel Engines. Joellen Lewtas, Ed. xi + 380 pages. Elsevier North-Holland, 52 Vanderbilt Ave., New York, N.Y. 10017. 1982. $65, hardcover.

Diesel cars have become popular because of their efficiency and fuel-miserliness. But some scientists believe their emissions can pose problems. This collection of symposium papers looks at emission characterization, chemical and biological assays, pulmonary toxicology, mutagenesis/carcinogenesis, and risk assessment.

Third Symposium on Biotechnology in Energy Production and Conservation. Charles D. Scott, Ed. viii + 666 pages. John Wiley & Sons, Inc., 605 Third Avenue, New York, N.Y. 10016. 1982. $60, paper.

Biotechnology emphasizes renewable energy sources. The book, growing out of a symposium, covers wood energy, thermal/chemical conversion, other bioconversion, environmental control, and waste utilization. Advanced biotechnology concepts are explored, especially with regard to producing certain needed chemicals.

Systems Safety: Technology and Application. 2nd ed. Sol W. Malasky. 343 pages. Garland STPM Press, 136 Madison Ave., New York, N.Y. 10016. 1982. $37.50, hardcover.

This edition, like the first, looks into systems safety, but adds coverage on ethical considerations, product liability, and recent technological advances. It discusses the role and language of systems safety, interfaces with events, hazard analysis, fault "tree" analysis, and uncertainties in safety measurements. Checklists, plan outlines, and a glossary are also given.

Water Reuse. E. Joe Middlebrooks. xii + 851 pages. Ann Arbor Science Publishers, P.O. Box 1425, Ann Arbor, Mich. 48106. 1982. $56.95, hardcover.

This book looks into several aspects of water reuse, including factors affecting system design; aquaculture/wetlands; municipal and industrial reuse; virus and bacterial monitoring and removal; and health effects and persistent compounds.

Home Gardening Wisdom. Dick & Jan Raymond. vi + 303 pages. Garden Way Publishing, Charlotte, Vt. 05445. 1982. $9.95, paper.

The authors impart much of their gardening know-how, including pest control, intensive yields, best fertilizing approaches, and many other aspects. They aim at imparting the easiest, most productive techniques. Dick Raymond has been the star of a recent television series on the subject.

Three Mile Island Cleanup: Experiences, Waste Disposal and Environmental Impact. Lester J. King, James H. Opelka, Eds. 44 pages. E. L. Florio, American Institute of Chemical Engineers, 345 East 47th Street, New York, N.Y. 10017. 1982. $35 ($17.50 for AIChE members), paper.

One paper in this book examines the incorporation of loaded zeolite into a type of glass as a final waste disposal

form. The book also evaluates various impacts of the TMI cleanup and examines results of the TMI Information and Examination Program. It is Vol. 78, No. 213 in the AIChE Symposium Series.

Hazardous Waste Processing Technology. Yen-hsiung Kiang, Amir A. Metry. xviii + 549 pages. Ann Arbor Science Publishers Inc., P.O. Box 1425, Ann Arbor, Mich. 48106. 1982. $44.95, hardcover.

This book presents in-depth views of technologies such as thermal processing, incineration of many types, chemical treatment, separation, and biological treatment. Proper disposal sites and many other pertinent topics are also discussed.

An Introduction to Biological Control. Robert van den Bosch et al. xv + 247 pages. Plenum Press, 233 Spring St., New York, N.Y. 10013. 1982. $18.95, hardcover.

Chemicals are one way of controlling insect pests; another way could be the use of given pests' natural biological enemies. These enemies consist of predatory insects, for example, or microbial diseases, which are emphasized in this book. Actual control techniques, procedures in introduction of the controls, limitations, and degrees of success are also discussed.

Energy Conservation in the Design and Operation of Wastewater Treatment Facilities (MOP FD-2). James F. Stahl, producer. 130 pages. Water Pollution Control Federation, 2626 Pennsylvania Ave., N.W., Washington, D.C. 20037. 1982. $15 ($11.50 for WPCF members).

This work addresses current practice involving energy considerations for design/operation, energy recovery/reuse, and energy management. It is aimed principally at the designer and at plant personnel.

Northeastern Environmental Science. Periodical, quarterly. Stephen R. Scholle, Ed. Northeastern Environmental Science, P.O. Box 746, Troy, N.Y. 12181. $24/year, companies; $19, individuals and nonprofit organizations.

This peer-reviewed journal addresses natural resource and environmental health issues of northeastern North America. This year's issues emphasize water-borne toxic wastes, energy development, acid precipitation, and pertinent general subject matter.

Reclamation and Revegetation Research. Periodical, quarterly. M. K. Wali, E. M. Watkin, Eds. Elsevier Scientific Publishing Co., P.O. Box 211, 1000 AE Amsterdam, The Netherlands. $76/year.

This journal covers reclamation and revegetation of lands injured because of human activity. It will cover soil science, biology, engineering, geology, agronomy, hydrology, ecology, and legal and planning aspects.

The Market for Operation and Maintenance Services in Municipal and Industrial Water and Wastewater Treatment Plants in the U.S. William T. Lorenz. 349 pages. William T. Lorenz & Co, 31 Fairfield St., Boston, Mass. 02116. 1982. $875, paper, ring-bound.

This market forecast looks into many aspects of water/wastewater treatment markets, including the water laws/regulations, products, and competitors. Examines the municipal and industrial markets in detail, with factors affecting them, as well as the private market.

Handbook of Electrode Technology. 144 pages. Orion Research Inc., 840 Memorial Drive, Cambridge, Mass. 02139. 1982. $10, hardcover.

Electrode technology is one of the linchpins of analysis, including analysis for pollutants. This book defines all aspects of this technology from "Absolute Millivolt Mode" to "Zirconium in Thorium and Uranium Solutions." It also explains standard calibration, titration, incremental methods, reference electrode potential, sample pH, interferences, and many other aspects of the use of electrodes for testing and analytical purposes.

Current Controversy. Periodical, monthly. Scientists' Institute for Public Information, 355 Lexington Ave., New York, N.Y. 10017. $35/year.

Do synthetic fuels have a future? Can low-level radwastes be safely dumped in the ocean? Should gasoline have less lead? These and many other questions are discussed in this periodical, with views from different sides of the given issue.

Flue Gas Desulfurization. John L. Hudson, Gary T. Rochelle, Eds. 432 pages. Distribution Office 43, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. 1982. $41.95 ($50.95 outside U.S. and Canada), hardcover.

This volume provides current research that leads to a *quantitative* understanding of flue gas desulfurization (FGD) process. It reports on five projects supported by the Department of Energy. Rate processes and innovations in throwaway slurry scrubbing are included, as are alternatives to throwaway slurry scrubbing.

Halogenated Hydrocarbons: Solubility–Miscibility with Water A. L. Horvath. 920 pages. Marcel Dekker AG, Elisabethenstrasse 19, Postfach 34, 4010 Basel, Switzerland. 1982. About $150.

Halogenated hydrocarbons can be found on the priority pollutant list. Here is a book that looks at them with relation to water, including intermolecular forces, polar/nonpolar fluids, hydrogen bonding, temperature/pressure dependence, association of molecules, and many other scientific aspects.

Prime Farmland in Georgia. James E. Kundell et al. 49 pages. Publications Program, Institute of Government University of Georgia, Terrell Hall, Athens, Ga. 30602. 1982. $6.50.

Although this book deals mainly with farmland in Georgia, it also points out a general trend of farmland being preempted for other purposes—an issue of increasing concern.

Common Boundary/Common Problems: The Environmental Consequences of Energy Production. Circulation Department, American Bar Association, 1155 East 60th St., Chicago, Ill. 60637. 1982. $6.

This book, which deals with transcontinental pollution stemming from energy production, is the result of a symposium on the subject held late last year. It considers, for example, transboundary water and air pollution, acid rain, pipeline development, and the role of government in preventing such large-scale pollution.

Biodegradation and Detoxification of Environmental Pollutants. A.M. Chakrabarty, Ed. 176 pages. CRC Press, Inc., 2000 Corporate Blvd. (N.W. 24th St.), Boca Raton, Fla. 33431. 1982. $48.50, hardcover.

This book discusses recent advances in the understanding of the biodegradation and detoxification of various pollutants. For example, one topic considered is the use of microbial enzyme systems for breaking down and disposing of pesticides. Other similar processes are covered, as well as the genetics and evolution of these processes. Topics include the mercury

cycle, chlorinated compounds, and the role of plasmids.

Geophysics in the Affairs of Man. Charles C. Bates et al. Pergamon Press Inc., Maxwell House, Fairview Park, Elmsford, N.Y. 10523. 1982. $25, flexicover; $60, hardcover.

Here is a technical and economic history showing how three major aspects of earth science evolved from simple beginnings and came to affect civilization in many diverse and important ways. Topics include relations between government, industry, and academia that led to a try at an underground nuclear test-ban treaty; opening of the Arctic to exploration; interactions with environmentalists, especially during the 1970s; and recent personal achievements of noted geophysicists.

Progress and Privilege. William Tucker. 336 pages. Doubleday & Co., Inc., 245 Park Ave., New York, N.Y. 10167. 1982. $17.95, hardcover.

This work looks at the environmental movement, covering its good points and its flaws. It examines a wide range of issues, including population growth, wilderness preservation, endangered species, and genetic engineering. The author distinguishes between concerns he feels are genuine and those he believes were used as a "smokescreen" for other objectives. He also says that an exaggerated picture of a bleak environmental future has caused people to jump on bandwagons without questioning specific positions and motivations of the environmental organizations involved.

Analysis of Pesticides in Water. Alfred S. Y. Chau et al., Eds. 3 vols., 216, 256, and 264 pages. CRC Press, Inc., 2000 Corporate Blvd. (N.W. 24th St.), Boca Raton, Fla. 33431. 1982. $69.50, $72, $74.50, respectively, hardcover.

This set offers a detailed survey of methodology used in the analysis of pesticides. Vol. 1 considers environmental impacts and basic principles, residue identification, and cyclodienes; Vol. 2 covers organochlorine and organophosphorus pesticides and phenoxyalkyl acid herbicides; and Vol. 3 discusses carbamates and substituted urea and triazine herbicides.

Heterogeneous Atmospheric Chemistry. David R. Schryer, Ed. 280 pages. AGU Publications, 2000 Florida Ave., N.W., Washington, D.C. 20009. 1982. $27.

This volume brings together an exchange of ideas, information, and methodologies from many fields directly and indirectly related to the newly emerging science of heterogeneous atmospheric chemistry.

STP 737 Aquatic Toxicology and Hazard Assessment. D. R. Branson, K. L. Dickson, Eds. 466 pages. ASTM, 1916 Race St., Philadelphia, Pa. 19103. 1982. $43, hardcover.

This volume grows out of the Symposium on Aquatic Toxicology and Hazard Assessment, held by the ASTM E-47 Committee on Biological Effects and Environmental Fate. It covers safety margins, hazard assessment, carcinogenesis in aquatic organisms, monitoring, statistical analysis of toxicity data, and new concepts.

Potential Health Effects in the Human from Exposure to Polychlorinated Biphenyls (PCBs) and Related Impurities. National Electrical Manufacturers Association, 2101 L St., N.W., Washington, D.C. 20037. 1982. $15.

This report proposes that there is no demonstrated connection between PCB exposure and cancer, birth defects, and liver disease; only skin disorders and insignificant changes in enzyme production can be linked to PCBs, according to the scientists who prepared the report. They added that the risk to human health of even high-level occupational exposure "has been shown to be low."

Proceedings of the 75th APCA Annual Meeting. 4-volume set. Air Pollution Control Association, P.O. Box 2861, Pittsburgh, Pa. 15230. 1982. $350 for the set; inquire as to prices for individual session books.

The set comprises the complete proceedings of the meeting, and covers inhalable particulates, crop loss, source monitoring, aerometric measurements, airborne toxic substances, and many other pertinent subjects.

The Clean Water Act: The Second Decade. Morris A. Ward. 54 pages. E. Bruce Harrison Co., 605 14th St., N.W., Washington, D.C. 20005. 1982. $11.95.

This work is a section-by-section analysis of the law, with a review of water resources legislation in the U.S., in language understandable to the layman. The author is editor of *Environmental Forum*.

Hazardous Waste in America: Our Number One Environmental Crisis. Samuel S. Epstein et al. 640 pages. Sierra Club Books, 2034 Fillmore St., San Francisco, Calif. 94115. 1982. $27.50, hardcover.

This book presents thorough coverage of what hazardous waste is and the danger it presents. Also discussed are legislation and regulations, how to hunt and report a dump, ways to curb hazardous waste production, safe disposal technologies, and nontoxic alternatives.

Atmospheric Pollution 1982. Michel M. Benarie, Ed. xii + 404 pages. Elsevier North-Holland Inc., 52 Vanderbilt Ave., New York, N.Y. 10017. 1982. $88.25, hardcover.

The main thrust of this book is the pollution problems of hot and desert regions in various parts of Asia and the U.S. Southwest. North African areas are also considered. NO_x emission controls are also discussed. The book contains Proceedings of the 15th International Colloquium (Paris, May 1982).

Resource Conservation Glossary. 191 pages. Soil Conservation Society of America, 7515 Northeast Ankeny Rd., Ankeny, Iowa 50021. 1982. $7 ($6 for SCSA members), paper.

This is an in-depth compilation and glossary of terms pertinent to conservation of all types of resources.

Prohibitive Policy. Steven Lewis Yaffee. xii + 239 pages. MIT Press, 28 Carleton St., Cambridge, Mass. 02142. 1982. $17.50, hardcover.

Many critics have said that the Endangered Species Act virtually outlaws any negotiation between conflicting social objectives—those of preserving habitats and those of economic projects considered necessary. The author shows that there is, in fact, considerable latitude for negotiation and balance. He also delineates capabilities and limitations of scientific expertise with respect to endangered species preservation.

Environmental Mutagenesis, Carcinogenesis, and Plant Biology. Vol. I. Edward J. Klekowski, Ed. xi + 193 pages. Praeger, 521 Fifth Ave., New York, N.Y. 10175. 1982. $21.50, hardcover.

Warning: Not all mutagens and carcinogens are manufactured. Some, for example, are metabolic products of plants. This volume examines metabolism of chemicals to mutagens by fungi and higher plants; mutagenic and carcinogenic mycotoxins; fungal mutagen assays; and environmental desmutagens and antimutagens. A

comparison of chemical metabolism by plants and by animal liver enzyme systems is also provided.

Metabolic Maps of Pesticides. Hiroyasu Aizawa. xvi + 243 pages. Academic Press, Inc., 111 Fifth Ave., New York, N.Y. 10003. 1982. $35 (add $1.50 for shipping and handling), hardcover.

This book graphically shows the metabolic chemistry of many pesticides in animal and plant systems. Included are acid amides, amidines and guanidines, anilines, nitrobenzenes, pyrethroids, phosphorodithiolates, and about two dozen other chemical classifications.

Total Environmental Control: The Economics of Cross-Media Pollution Transfers. J. Lowe et al. 134 pages. Pergamon Press Ltd., Headlington Hill Hall, Oxford, OX3 0BW, U.K. 1982. $21.50, hardcover.

This book evaluates cross-media pollution in an economic framework, both theoretically and empirically. Featured are chapters dealing with alternative approaches to pollution damage evaluation. It looks at media themselves, various industries, energy problems, and many other pertinent matters.

Soft Energy Notes. Periodical, six issues/year. *Soft Energy Notes*, 1045 Sansome St., San Francisco, Calif. 94111. $25/year ($50 for business/government agencies; $15 for Friends of the Earth members).

This periodical states that Americans have gotten 50 times more new energy from improving efficiency than from expanding energy supply. It adds that the largest expansion has been from renewable resources and that in Japan, for instance, solar collectors are a $500 million/year industry. Other renewable energy news items, national and worldwide, are featured in this periodical.

Ecology of Coastal Waters: A System Approach. K. H. Mann. x + 322 pages. University of California Press, 2223 Fulton St., Berkeley, Calif. 94720. 1982. $18, paperback; $36, hardcover.

This book reviews several types of coastal systems. It discusses grass and mangrove systems, seaweed systems, phytoplankton systems, the role of microorganisms, coral reefs, sediment communities, fish and shellfish, and water movement and productivity. Models and management are also examined.

ES&T MEETINGS

Oct. 20–22 Atlantic City, N.J.
Energy Cost Reduction. Association of Energy Engineers

Fee: $495, regular; $455, AEE members; $199, teams. *Write:* Association of Energy Engineers (AEE), P.O. Box 3727, Santa Monica, Calif. 90403; (213) 450-0500

Oct. 22 Kings Point, Long Island, N.Y.
Water Pollution on Long Island. American Chemical Society and U.S. Merchant Marine Academy

Fee: $15. *Write:* Robert A. Saar, Geraghty & Miller, Inc., 6800 Jericho Turnpike, Syosset, N.Y. 11791; (516) 921-6060

Oct. 25–27 Philadelphia, Pa.
The 7th International Conference on Fluidized Bed Combustion. The U.S. Department of Energy, EPRI, and the Tennessee Valley Authority

Write: Annmarie Pittman, Courtesy Associates, Inc., 1629 K St., N.W., Suite 700, Washington, D.C. 20036; (202) 296-8100

Oct. 25–27 Pittsburgh, Pa.
The 43rd Annual Meeting of the International Water Conference. Engineers' Society of Western Pennsylvania

Fee: $100. *Write:* Mary Jean Edgar, Engineers Society of Western Pennsylvania, William Penn Hotel, 530 William Penn Place, Pittsburgh, Pa. 15222; (412) 261-0710

Oct. 25–28 Burlington, Vt.
Acid Precipitation—The North American Challenge. New Hampshire–Vermont and Ontario Chapters of the Soil Conservation Society of America

Fee: $25. *Write:* New Hampshire–Vermont Chapter, Soil Conservation Society of America, P.O. Box 77, Essex Junction, Vt. 05452

Oct. 25–28 Cincinnati, Ohio
2nd Hazardous Materials Workshops & Exposition. Hazardous Materials Management Association and Ohio Environmental Protection Agency

Write: Hazardous Materials Workshops & Exposition, 1406 Third National Building, Dayton, Ohio 45402

Oct. 26–28 Columbus, Ohio
7th International Symposium on Polynuclear Aromatic Hydrocarbons. Battelle Columbus Laboratories

Fee: $195. *Write:* Dr. Marcus Cooke, Battelle Columbus Laboratories, 505 King Ave., Columbus, Ohio 43201; (614) 424-5024

Oct. 31–Nov. 2 Greenville, N.C.
1st Annual Scientific Meeting of the Society for Environmental Geochemistry and Health (SEGH). East Carolina University and the ECU School of Medicine

Write: First Annual Scientific Meeting, SEGH 1982, Candis Harrington, Meeting Secretary, Department of Surgery, School of Medicine, East Carolina University, Greenville, N.C. 27834; (919) 757-4629

Nov. 7–10 Detroit, Mich.
International Conference on Atmospheric Deposition. Air Pollution Control Association (APCA)

Write: Howard Murray, Wayne County Health Department, Air Pollution Control Division, 1311 East Jefferson, Detroit, Mich. 48207; (313) 224-4650

Nov. 8–9 Arlington, Va.
The Reagan/Gorsuch EPA—Its Impact on Industry. *Inside EPA* weekly report and The Center for Energy and Environmental Management

Fee: $595. *Write:* Center for Energy and Environmental Management (CEEM), P.O. Box 536, Fairfax, Va. 22030; (800) 424-9068 or (202) 250-5900

Nov. 8–9 Arlington, Va.
The 1982 Washington Conference on Alcohol. *Alcohol Week* and the Renewable Fuels Association

Fee: $495. *Write: Alcohol Week*, P.O. Box 7167, Benjamin Franklin Station, Washington, D.C. 20044; (800) 424-9068 or (202) 347-1941

Nov. 9–12 Ocean City, N.J.
4th Annual Northeast Conference on Hazardous Waste. Environmental Hazards Management Institute (EHMI)

Fee: $300. *Write:* Northeast Conference, EHMI, P.O. Box 283, Portsmouth, N.H. 03801; (603) 436-3950

Nov. 10–11 Las Vegas, Nev.
National Symposium on Water Reuse. CH_2M–Hill

Fee: $195. *Write:* Water Reuse Symposium, Attn.: Marilyn Hennessy, CH_2M–Hill, P.O. Box 22508, Denver, Colo. 80222; (800) 525-7964 or (303) 771-0900

Nov. 11–12 Ruston, La.
Symposium on Biological and Chemical Removal of Sulfur and Trace Elements in Coal and Lignite. Louisiana Tech University

Write: Joseph B. Fernandes, Chemical Engineering Dept., P.O. Box 10348 T.S., Louisiana Tech University, Ruston, La. 71272; (318) 257-2777

Nov. 14–17 Arlington, Va.
3rd Annual Meeting of SETAC—Predictability in Environmental Toxicology and Chemistry. The Society of Environmental Toxicology and Chemistry (SETAC)

Write: Richard E. Tucker, SETAC, P.O. Box 352, Rockville, Md. 20850; (301) 468-6704

Nov. 14–18 Los Angeles, Calif.
75th Annual AIChE Meeting—Precipitation Kinetics and Crystallizer Instabilities. Purdue University, School of Civil Engineering

Write: Robert W. Peters, Environmental Engineering, Purdue University, School of Civil Engineering, West Lafayette, Ind. 47907

Nov. 16–18 Gaithersburg, Md.
7th Annual Conference on Materials for Coal Conversion and Utilization. National Bureau of Standards (NBS) and others

Write: Samuel J. Schneider, Room A257, Materials Building, National Bureau of Standards, Washington, D.C. 20234; (301) 921-2845

Nov. 18–19 Washington, D.C.
9th Annual Environment and Safety Briefing Sessions. The Bureau of National Affairs, Inc.

Write: Environment and Safety Briefing Sessions Registrar, BNA Conferences, Suite S-602, 1231 25th St., N.W., Washington, D.C.; (800) 424-9890 or (202) 452-4420

COURSES

Oct. 21–22 Arlington, Va.
Pesticide Regulation Course. Executive Enterprises, Inc.

Fee: $525; $595, team. *Write:* Executive Enterprises, Inc. 33 West 60th St., New York, N.Y. 10023; (212) 489-2680

(continued on p. 584A)

(*continued from p. 583A*)

Oct. 25–29 Houston, Tex.
Basic Principles of Chemical Engineering. The Center for Professional Advancement

Fee: $980. *Write:* The Center for Professional Advancement, P.O. Box 964, East Brunswick, N.J. 08816-0964; (201) 249-1400

Nov. 6 Detroit, Mich.
Atmospheric Deposition: Concepts, Current Research, and Monitoring Techniques. Air Pollution Control Association (APCA)

Fee: $185, APCA members; $210, nonmembers. *Write:* John McGovern, APCA Education Services Dept., P.O. Box 2861, Pittsburgh, Pa. 15230; (412) 621-1090

Nov. 7 Detroit, Mich.
Permitting under the Clean Air Act. Air Pollution Control Association (APCA)

Fee: $185, APCA members; $210, nonmembers. *Write:* John McGovern, APCA Education Services Dept., P.O. Box 2861, Pittsburgh, Pa. 15230; (412) 621-1090

Nov. 8–10 Washington, D.C.
Carcinogenicity/Mutagenicity. The Center for Professional Advancement

Fee: $650. *Write:* The Center for Professional Advancement, Dept. NR, P.O. Box H, East Brunswick, N.J. 08816; (201) 249-1400

Nov. 8–12 Austin, Tex.
Advanced Water Pollution Control: Physical and Chemical Waste Treatment. Continuing Engineering Studies, College of Engineering, the University of Texas at Austin

Fee: $450. *Write:* Continuing Engineering Studies, College of Engineering, Cockrell Hall 2.102, the University of Texas at Austin, Austin, Tex. 79712; (512) 471-3506 or 471-3396

Nov. 9–10 Columbia, Mo.
Environmental Chemodynamics. Department of Chemical Engineering, College of Engineering and Extension Division, University of Missouri—Columbia

Fee: $295. *Write:* Virginia Nettleton, 1020 Engineering Building, UMC, Columbia, Mo. 65211; (314) 882-3469

Nov. 9–11 Denver, Colo.
Wastewater Engineering. Vanderbilt University

Fee: $575. *Write:* Peter G. Hoadley, Director, Continuing Engineering Education, Vanderbilt University, Box 1525, Station B, Nashville, Tenn. 37235; (615) 322-2924

Nov. 15–19 Salt Lake City, Utah
Industrial Hygiene Chemistry (NIODH 590). The Rocky Mountain Center for Occupational and Environmental Health—University of Utah

Fee: $500. *Write:* RMCOEH, K. Blosch, University of Utah, Building 512, Salt Lake City, Utah 84112; (801) 581-5710

INTERNATIONAL

Nov. 7–12 Beijing (Peking)
1st U.S.–China Conference on Energy, Resources, and Environment. The China Society for Energy Research and the Society of Engineering Science

Write: S. W. Yuan, School of Engineering and Applied Science, George Washington University, Washington, D.C. 20052

Dec. 14–17 Singapore
1st International Public Services and Environmental Engineering Exhibition. Industrial and Trade Fairs International Limited

Write: Aideen Barrett, Industrial and Trade Fair International Limited, Radcliffe House, Blenheim Court, Solihull, West Midlands, B91 2BG, U.K.

CALL FOR PAPERS

Nov. 15 deadline
Specialized Conference: Energy Savings in Water Pollution Control. International Association for Water Pollution Research and Control and European Water Pollution Control Association

Conference will be held Sept. 26–28, 1983, in Paris. *Write:* A.G.H.T.M. (Mr. Bres), 9 Rue de Phalsbourg, 75854 Paris Cedex 17, France

Dec. 15 deadline
The 66th Canadian Chemical Conference and Exhibition. The Chemical Institute of Canada

The conference will be held June 5–8, 1983, at the Convention Centre in Calgary, Alberta. *Write:* Arvi Rauk, M.C.I.C., Department of Chemistry, University of Calgary, Calgary, Alberta, T2N 1N4, Canada; (403) 284-6247

Dec. 31 deadline
2nd International Conference on Ecology and Environmental Quality. Israel Ecological Society

Conference to be held May 24–26, 1983, in Jerusalem, Israel. *Write:* H. Shuval, Chairman, Israel Ecological Society, Hebrew University–Hadassah Medical School, P.O. Box 1172, Jerusalem, Israel.

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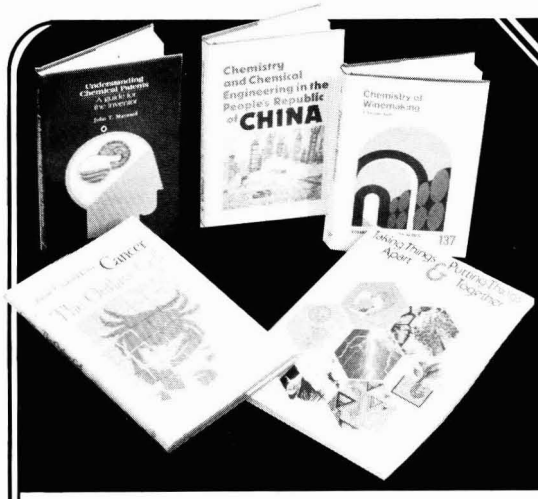

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134	135	136	137	138	139	140	141	142	143	144
145	146	147	148	149	150	151	152	153	154	155
156	157	158	159	160	161	162	163	164	165	166
167	168	169	170	171	172	173	174	175	176	177
178	179	180	181	182	183	184	185	186	187	188
189	190	191	192	193	194	195				

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156	157	158	159	160	161	162	163	164	165	166
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ES&T RESEARCH

Particulate and Gaseous Emissions from Wood-Burning Fireplaces

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General Motors Research Laboratories, Warren, Michigan 48090-9055

■ Particulate and gaseous emissions were measured from three wood-burning fireplaces. An average of 10 g of particles/kg of wood burned was emitted. The particles were spherical with a mass median diameter of about 0.17 μm. Although the material is carbonaceous, the organic carbon/elemental carbon split seems to depend on both the wood type and the size of the log burned. Benzo[*a*]-pyrene emissions as well as Ames tests results on the particulate are reported. Continuous measurements of gases indicated average emissions of 110 g/kg CO, 1.5 g/kg HC, and 0.7 g/kg NO_x. The emission values measured here were used in conjunction with other measurements to estimate the importance of wood burning in wintertime Denver. Based on three estimating techniques, wood burning accounts for 20–30% of the Denver wintertime fine particulate.

Introduction

Wood burning has recently been recognized as an important particle-emission source in certain areas of the northern United States. For instance, as much as half of the respirable particulate in a residential area in Portland, OR, was attributable to wood burning (*1*). Recent wood-burning emission studies have centered on wood-burning stoves due to their rapid increase in recent years and the oxygen-deficit conditions under which they operate (*2, 3*).

Less attention has been paid to fireplaces since their use is not increasing as dramatically as wood stoves. However, fireplace emissions are still an important factor as evidenced by the fact that 58% of new homes built in 1976 had at least one fireplace (*4*). Fireplace use is still much more likely than wood-stove use in urban areas where pollutant levels are highest. In addition, a recent study of indoor air pollution from wood burning has shown higher levels of polycyclic aromatics from fireplaces compared to wood stoves (*5*).

A study of fireplace emissions has been completed by using two residential fireplaces and a freestanding fireplace installed in the laboratory. Measurements were made of gas and particle mass emission rates as well as the size and composition of the particles. On the basis of these findings and ambient measurements, the influence of wood burning on wintertime Denver particulate levels has been estimated.

Sampling Procedures

Over 40 fireplace tests were performed, both at residences and in the laboratory. Residential sampling was conducted at two homes, both of which had brick fireplaces built on an outside wall of the house. An aluminum chimney extension with an 8-cm port was placed on the chimney, and the sample probe was inserted through the port. The two residences had chimney heights from 4.5 to 5 m above ground level.

Laboratory sampling was conducted on a Preway free-standing fireplace installed in the laboratory. The exhaust gases were drawn by natural draft through a 20-cm diameter flue pipe to the roof. The sampling port was located 2 m above the grate, and sampling equipment was positioned on scaffolding erected beside the fireplace. The burning rate was monitored by recording the change in mass of wood during burning. For this purpose, a weighing bucket rain gauge was modified to hold a wood grate rather than a rain bucket. The decrease in wood mass during combustion was recorded continuously.

Emissions from five softwoods and nine hardwoods were measured. In addition, two synthetic logs were tested, each consisting of a cellulose base held together with wax. A test consisted of burning a preweighed charge of wood that was split into pieces approximately 45 cm in length and 100 g each. Since it is impossible to simulate the vast variety of burning conditions used by homeowners, this standard condition was used to facilitate a fast, complete burn and to allow a comparison between wood types. For comparison, a few tests were also run with quarter or half logs. In these tests, the wood burned incompletely and was reweighed after a test.

Particles were collected by using standard EPA method 5 sampling procedures except that sampling was done from the center of the chimney rather than traversing the chimney. The temperature was measured at the sampling point. The sampling rate was adjusted every 3 min to maintain isokinetic sampling throughout the test. Three fractions of particles were collected, the front catch, the filter catch, and the condensable catch. The front catch consists of material that collects in the nozzle, probe, and cyclone. The cyclone collects particles greater than 10 μm in diameter. Beyond the cyclone is a Type A glass-fiber filter where the filterable material collects. The probe, cyclone, and filter are all held at 120 °C. Finally, the filtered gas stream passes through two water-filled impingers where the condensable material collects.

Particulate samples were also collected from diluted stack gas onto Nuclepore or Fluoropore filters. The exhaust was diluted three-to-one with filtered room air, thus allowing enough cooling for organics to condense. These samples were used for metal and SEM analysis.

Four gases, carbon monoxide, carbon dioxide, total hydrocarbons, and nitrogen oxides, were measured continuously during several laboratory tests. The monitoring instruments used were a Beckman-315A infrared analyzer for CO and CO_2, a Beckman-108A hydrocarbon analyzer,

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and a Teco Model-10A chemiluminescent analyzer for nitrogen oxides.

Analytical Procedures

Mass. Particulate was collected on Whatman A glass-fiber filters. These were weighed before and after collection after equilibrating for 24 h at constant temperature and humidity. The front catch (nozzle, probe, and cyclone) was rinsed with deionized water and acetone into a preweighed beaker, taken to dryness over low heat, and reweighed. The impinger water and rinsings, which made up the condensable catch, were treated similarly.

Particle Size and Morphology. A Sierra Series-220 stainless steel in-stack cascade impactor was used to obtain a size distribution of the particulate. Particles were collected on six stages on glass-fiber filter substrates that covered the range from less than 0.5 μm to more than 12 μm. The cascade impactor was allowed to reach stack temperatures before sampling began. The sampling rate was held constant during a test.

A TSI Model-3030 electrical aerosol analyzer (EAA) was used to obtain the particle size below 0.5 μm. Diluted exhaust was drawn through the EAA to obtain the size distribution from 0.01 to 1 μm. Since the particle loading was continually changing, the step 3 voltage was measured between each step voltage and used for normalization.

Carbon. All filters were analyzed for organic and elemental carbon by using a modification of the method of Cadle and Groblicki (*6*). The original method consisted of heating a 1-cm^2 section of filter to 650 °C in helium. Organics were volatilized and catalytically oxidized to CO_2. During the second stage of analysis, air entered the system, and the elemental carbon was oxidized to CO_2. The CO_2 levels from the two stages were related to the organic and elemental carbon concentrations, respectively. It was possible that some of the organic carbon charred in the first stage of analysis. Charred material was then detected as elemental carbon in the second stage. It was found that charring is a large problem for natural products such as wood. For this reason the method was modified in the following manner: One sample was run by using the original method. A second sample of each filter was heated in a tube furnace to 350 °C in air, which was hot enough to remove organics but was not hot enough to cause charring. After the organics were removed, the sample was then analyzed for elemental carbon by the original method. The difference between the total carbon determined by the first method and the elemental carbon determined by the second method represented the organic carbon. For illustration of the extent of the charring problem, the apparent elemental carbon content of the hardwood emissions decreased on the average from 41% to 5% after charring was eliminated by the modified procedure.

Percent Extractable and Benzo[*a*]pyrene. The extractable percentage and benzo[*a*]pyrene (BaP) concentrations were determined by the method of Swarin and Williams (*7*). A portion of the glass-fiber filter was extracted in benzene–ethanol and taken to dryness to determine the extractable fraction. The extract was then reextracted in hexane–methylene chloride, dried, and dissolved in acetonitrile. An aliquot was injected into a liquid chromatograph with a Zorbax ODS column, and the BaP was detected by fluorescence techniques. Since BaP may not be collected efficiently by a heated filter, extracts from impinger collections were also analyzed. No effort was made to determine the total collection efficiency for BaP using EPA method 5 collection techniques.

Ames Testing. A sample of the material extracted from the filter was taken to dryness and dissolved in dimethyl sulfoxide and sent to Litton Bionetics for Ames testing. Five doses of the sample (usually 10, 25, 50, 100, and 200 μg of extracted material) were added to the test system consisting of a *Salmonella typhimurium* strain in a growth medium. One set of these plates represented a nonactivated system and a second set was activated with S9 homogenate prepared from adult male rat liver. The plates were incubated for 2 days, and the number of revertant colonies were counted. A negative control consisting of the solvent alone and a positive control consisting of a compound known to revert the strain were run with all tests.

Potassium. Particulate was collected from a diluted stack gas stream onto Nuclepore or Fluoropore filters. After an acid digestion, potassium was measured by atomic absorption.

Table I. Particulate Emissions from Wood-Burning Fireplaces (g/kg)

wood type	test location	no. of tests	emissions av	emissions range
softwoods				
Ponderosa Pine	residential	3	4.9	3.7-5.5
Pinyon Pine	residential	1	5.0	
Eastern Spruce	laboratory	3	13	10-15
Jack Pine	laboratory	4	10	6-14
Cedar	laboratory	1	13	
hardwoods				
Willow	residential	2	17	15-18
Americal Elm	residential	1	1.5	
White Ash	residential	3	7	2-15
Sugar Maple	residential	1	17	
Hickory	residential	2	2.9	2.1-3.7
Soft Maple	laboratory	2	9.3	9.0-9.6
Birch	laboratory	2	12	10-15
Hard Maple	laboratory	2	11	10-11
White Ash	laboratory	2	12	9-14
Red Oak	laboratory	7	8.8	6.6-12
synthetic logs				
type I	residential	1	5.9	
type I	laboratory	1	19	
type II	laboratory	1	20	

Results

Test Characteristics. The tests lasted from 15 to 206 min with the synthetic logs and halved logs taking the longer times. The median test time was 42 min. The average gas velocity during a test varied from 62 to 1330 fpm with a median velocity of 560 fpm. The average temperature at the sampling point during a test varied from 39 to 155 °C with a median of 88 °C. The maximum temperature recorded was 308 °C.

Particle Emissions. The particle emissions from 39 tests using either split wood or whole synthetic logs are shown in Table I. Total particle emissions varied from 2 to 18 g/kg with averages of 9 ± 4 g/kg from softwoods (12 tests), 10 ± 5 g/kg from hardwoods (24 tests), and 15 ± 8 g/kg from synthetic logs (3 tests).

The average fractionation of the particulate between the front catch (nozzle, probe, and cyclone), filter catch, and impinger catch is shown in Table II. The soft- and hardwoods are similar, with half of the material collected in the impingers and the other half divided between the front catch and filter catch. The synthetic logs show large variations between brands and even between tests with the same logs. However, in general, over half of the particulate emissions from the synthetic logs is collected on the filter.

The log size seems to have the greatest effect on particulate emissions. Most of the tests were run with split wood (pieces of wood about 100 g each) to facilitate a fast, complete burn. However, a few tests were run with halved

Table II. Fractionation of Particulate Collected

	no. of tests	front catch, %	filter catch, %	impinger catch, %
softwoods	11	32 ± 11	27 ± 13	41 ± 18
hardwoods	23	21 ± 12	26 ± 15	53 ± 19
synthetic woods	3	12 ± 5	59 ± 13	29 ± 16

Table III. Effect of Log Size on Particulate Emissions (g/kg)

wood	front	filter	impinger	total
Pinyon Pine (split)	1.4	1.9	1.7	5.0
Pinyon Pine (halved)	0.7	2.6	4.7	8.0
Soft Maple (split)	2.1	1.5	5.7	9.3
Soft Maple (quartered)	2.6	3.9	17	24
Red Oak (split)	2.7	2.9	3.9	9.5
Red Oak (halved)	3.3	3.6	22	29

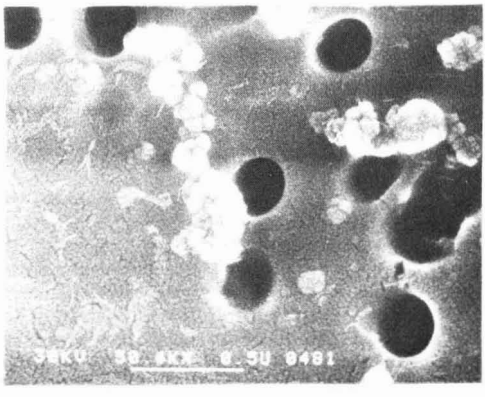

Figure 1. Scanning electron micrograph of wood-smoke particles on a Nuclepore filter. Line indicates length of 0.5 μm.

or quartered logs where each log weighed about a kilogram. This led to decreased burn rate, temperature, and flow rate. Since the logs burned only partially, they were reweighed after a test to obtain the mass emission rate. The results are shown in Table III. Total particle emissions are higher when large logs are used. This is due almost entirely to the impinger collection, which is the organic material. This may be due to insufficient oxygen or temperature for complete burning, leading to higher organic emissions.

Morphology. A representative scanning electron micrograph of the particulate from a red oak test is shown in Figure 1. The particles, which are on a 0.4-μm pore Nuclepore filter, consist of clusters of spheres. The particle size ranges from about 0.05 μm for a sphere to about 1 μm for a large cluster of spheres. The material looks similar to diesel exhaust particles (*8*).

Size Fractionation. Five cascade-impactor tests were made. Sampling lasted the entire time that flames were present and varied from 19 to 42 min for the five tests. In all cases, the majority of the material mass (83–90%) was on the backup filter. There were no obvious differences between softwoods, hardwoods, and synthetic logs. Since most of the particles were too small to be fractionated with the cascade impactor, the electrical aerosol analyzer was also used to obtain a size distribution below 1 μm. The resulting distribution is shown in Figure 2. The mass median diameter was approximately 0.17 μm.

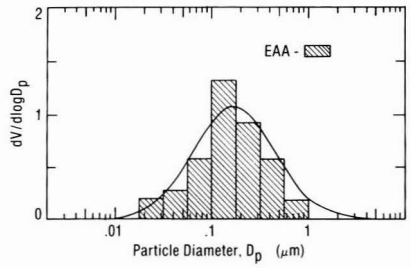

Figure 2. Size distribution of wood-smoke particles obtained with an electrical aerosol analyzer.

Table IV. Carbon Content of the Particulate

wood	no. of tests	organic carbon, %	elemental carbon, %	remainder, %
softwoods	7	38 ± 6	33 ± 13	29 ± 15
hardwoods	14	46 ± 7	8 ± 7	46 ± 7
synthetic	3	49 ± 2	15 ± 15	36 ± 4

Carbon Content. The carbon content of the emissions was measured in 21 tests. The front catch (probe and cyclone material) was assumed to be the same composition as the filter catch. The filter catch was analyzed by the carbon method described earlier. The impinger material was assumed to be entirely organic material. On average, it was 45% carbon, with the remainder consisting of organically bound oxygen and hydrogen.

Based on these three fractions, the carbon analyses of the total particulate from several tests are shown in Table IV. The softwood emitted much more elemental carbon than the hardwood, which emitted primarily organic material. The synthetic log emissions were extremely variable. The two tests with one brand showed high organics and low elemental carbon, but another brand of log showed just the reverse.

Although the particulate in all cases is primarily carbonaceous, there are distinct differences between emissions from different woods. This is illustrated by using the method of Cadle and Groblicki (*6*) in which the filtered sample is slowly heated in air and the evolution of CO_2 is monitored. Thermograms from four types of wood are shown in Figure 3.

The top thermogram is from the burning of red oak. The filtered particulate was distinctly brown rather than black, which is suggestive of a low elemental-carbon content. Most of the carbon evolves at low temperatures (less than 500 °C), indicating organic carbon being burned off. The second thermogram is from a less dense hardwood (birch). In this case, the filter was black and a second peak representing elemental carbon is seen at a higher temperature. The softwood, pine (thermogram c), had a larger high-temperature peak, corresponding to the higher elemental-carbon content. The final thermogram is from a synthetic log filter, which has a peak coming off at extremely high temperatures. The peak most likely indicates elemental carbon, but possibly in a more highly ordered structure.

Benzo[*a*]pyrene. Several filters and two impinger samples were analyzed for benzo[*a*]pyrene (BaP), which is a suspected carcinogen. The results are shown in Table V. Obviously, the results cover a very wide range. Tests 1 and 3 were made on the same type of wood, and the emission rates were quite different. Two aliquots of impinger water extracts were also analyzed. One sample had

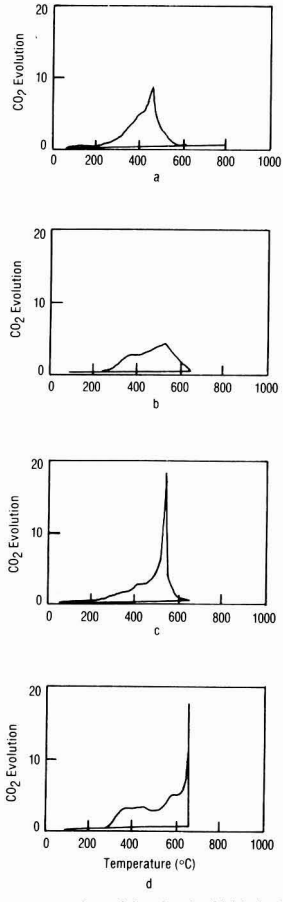

Figure 3. Thermograms from (a) red oak, (b) birch, (c) pine, and (d) synthetic log.

Table V. Benzo[*a*]pyrene Content of Filterable Fireplace Emissions

wood	ppm[a]	μg of BaP/kg of wood
Ponderosa Pine	24	50
Willow	105	700
Willow	141	1900
White Ash	3	5
White Ash	7	17
Sugar Maple	11	45
Hickory	120	130
synthetic log	18	58
synthetic log	40	400
average		370
median		58
coal, power plant[b]		2
coal, residential[b]		25000
auto, noncatalyst[c]		16
auto, catalyst[c]		0.4

[a] μg of BaP/g of filterable particulate. [b] Reference 9. [c] Reference 10.

no detectable BaP, and the second sample (white ash) had a BaP content that corresponded to an emission rate of 0.08 μg/kg, an insignificant amount compared to the filter

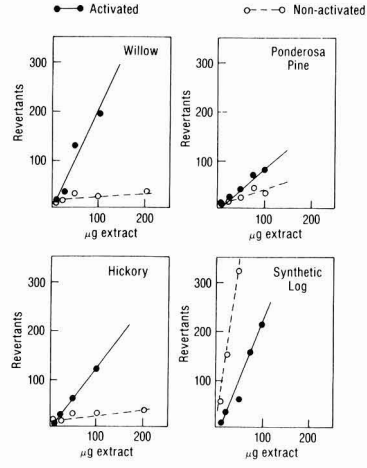

Figure 4. Results of Ames testing on four types of fireplace particulate extract.

catch levels. This suggests that the BaP is almost totally associated with the particulate emissions. For comparison, BaP emissions per kilogram of fuel are listed in Table V for other fuels. The only BaP levels that are higher appear to be those from less efficient combustion processes such as residential coal burning. In contrast, more efficient coal-burning in power plants produces much lower fuel specific BaP levels. Automobiles also emit some BaP, but most of this is destroyed by the catalytic converter.

Ames Tests. Since BaP levels in fireplace emissions are sometimes quite high, there also exists the possibility of mutagenic activity. Five extracted particulate samples were sent to a commercial laboratory for Ames testing. Graphs showing the revertants as a function of dosage for the sample extracts are shown in Figure 4 for both the nonactivated and activated samples. The control was subtracted from each sample. The slope of the graph in revertants/μg is a measure of the mutagenicity of the extracts. The slopes are shown in Table VI adjusted to the total amount of filtered material rather than just the extracted quantity. This makes a large difference especially for the synthetic wood, which showed high mutagenic activity but only 10% of the filtered particulate was extractable.

The three natural wood samples give similar results, with the nonactivated samples showing only minimal activity. At the highest dosage, the activity was approximately doubled over the control value. However, when activated with rat liver enzyme, all of these samples showed significant activity. The single impinger sample, which was extracted in dimethyl sulfoxide, showed very low overall activity but higher activity in the nonactivated test. The one synthetic log sample was interesting because it behaved differently from the natural woods. In contrast to the natural woods, the extract from the synthetic log burn showed lower mutagen activity when it was activated.

The natural wood emissions can be considered to be indirect-acting mutagens because activation was necessary to obtain a response. Chemicals such as benzo[*a*]pyrene and tobacco tar compounds are also indirect mutagens. There appears to be some correlation between BaP concentration and the activated dose response. However, it is unlikely that BaP itself is responsible for the activity since the detection threshold for BaP in an Ames test (200 ng/plate) is much higher than the doses used here (*11*).

Table VI. Results of Ames Tests

wood	extracted, %	nonactivated revertants, μg	activated revertants, μg	BaP, μg/g
Ponderosa Pine	46	0.14	0.38	24
Willow	74	0.067	1.5	105
Hickory	87	0.10	1.1	120
Hickory (impinger)	100	0.16	0.056	
synthetic log	10	0.67	0.24	40

Table VII. Gaseous Emissions from Fireplaces (g/kg)

wood	CO	HC	NO_x
softwoods			
Eastern Spruce	58	1.1	0.8
Jack Pine	160	1.1	0.2
hardwoods			
Soft Maple	120	2.7	0.8
Red Oak	90	1.6	0.8
Birch (dry)	71	1.0	
Birch (green)	180	1.4	0.7
synthetic logs			
Sterno	200	5.1	0.9
Northland II	120	9.7	1.0

The synthetic log emissions and possibly the impinger catch from natural logs are direct-acting mutagens in that activation is not necessary for a response. This is the type of behavior exhibited by nitro compounds and by extracts of vehicle exhaust particulates (*11*).

Potassium. The K/Fe ratio has been used to trace the contribution of wood smoke to ambient particle loadings (*12*, *13*), based on the fact that wood emissions have a much higher K/Fe ratio than other combustion-source emissions. However, there is only one known measurement of these concentrations in wood smoke. Based on two tests of fireplaces burning softwoods, Watson measured concentrations of 5.3 mg/g K and 23 μg/g Fe in the particulate (*14*).

We collected diluted wood smoke to analyze for K and Fe. Unfortunately, the iron concentration was so low compared to background that no reliable measurement could be made. However, as will be shown later, only the K concentration from woodsmoke is needed if the Fe level is as low as Watson's data indicated. The K concentration from three softwood samples was 4.1, 5.1, and 9.0 mg/g, and the concentration from three hardwood samples was 7.7, 10, and 13 mg/g. Although there is a large range of K concentrations within a wood type, the K levels from softwoods appear to be lower than from hardwoods.

Gases. Continuous gas measurements were made during eight tests, and the results are shown in Table VII. Average emissions for natural woods were 110 g/kg CO, 1.5 g/kg HC, and 0.7 g/kg NO_x. These values are similar to fireplace emissions estimates in AP-42 of 60 g/kg CO, 2.5 g/kg HC, and 0.5 g/kg NO_x (*15*). More recently, average values of 22 g/kg CO and 1.9 g/kg NO_x were measured by DeAngelis et al. (*3*). One explanation of the variability between studies is that the burning rate can greatly affect the emission of gases. For instance, the high burning rate employed in the latter study may have led to lower CO emissions and high NO_x emissions. Another problem is that the other studies based their results on grab samples rather than continuous measurements. Since gas concentrations vary by an order of magnitude during a test, it is important to make continuous measurements and integrate concentrations over the entire test time.

There are few obvious differences between the emissions for various wood types, although the synthetic logs appear to have higher hydrocarbon emissions. The green-birch burn led to higher CO and hydrocarbon emissions than the dried birch, probably due to the lower temperature of the burn.

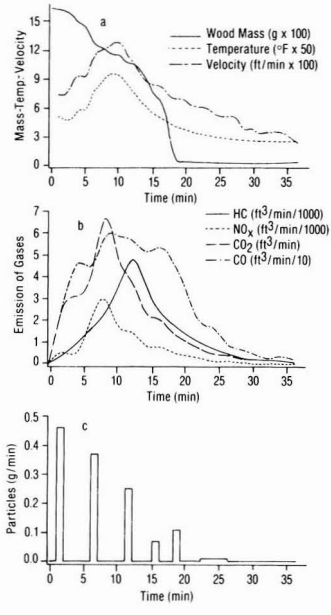

Figure 5. Continuous measurements during a birch burn of (a) burning parameters, (b) gas emissions, and (c) particle emissions.

Continuous measurements of wood-mass change, stack temperature, flow rate, and gas and particle emissions were made during several tests. The characteristic features of a natural wood burn are shown in Figure 5. The wood-mass change is only approximate since wood that fell off the grate was not measured. This occurred primarily at the end of a burn. The upper plot shows the decrease in wood mass during the burn and the temperature and velocity as measured 2 m above the grate. The velocity and the temperature track quite well. The center plot shows the continuous measurement of CO_2, CO, HC, and NO_x. The CO_2 and NO_x emissions peak at the same time as the temperature. Hydrocarbon emissions peak somewhat later. The CO emissions are much more erratic. The particle emissions, as shown in the lower curve, start high and decrease rapidly with time. This has also been shown by Butcher and Sorenson (*2*). It is interesting to note that gas and particle emissions continue after the flames have gone out. As much as 20–30% of the hydrocarbons and CO are emitted during this smolder stage. This is an important consideration when measuring emission rates of gases.

Discussion

The emission results measured here will be used to estimate the importance of wood burning in wintertime

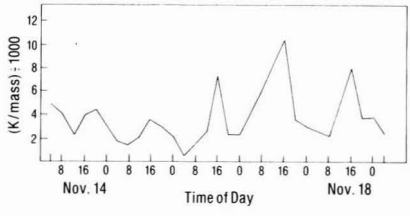

Figure 6. Daily variation in K/mass ratio in Denver ambient particulate.

Denver. Denver has a wintertime haze problem commonly referred to as the "Denver brown cloud". The cause of the visibility problem has been associated with fine particulate in the atmosphere. Two independent studies identified wood burning as responsible for part of the problem (*12, 13*). Based on ambient measurements made in Denver during the winter of 1978 by Countess et al. (*16*) and Wolff et al. (*12*) and the fireplace emission numbers measured here, it is possible to estimate the contribution of fine-particle wood smoke to the urban particulate problem. This will be done by using three different methods: (1) a mass emission estimate, (2) the K/Fe ratio method, and (3) the ^{14}C method.

Mass Emission Estimate. The importance of wood burning can be estimated by multiplying the mass of wood burned in Denver by the emission rate. The quantity of wood burned can be determined crudely, based on population. According to the latest housing census, there are 545 000 detached homes in the Denver Metropolitan Area. One report estimated that one-third of the houses in the country have fireplaces and that fireplace owners burn three-quarters of a cord of wood in a winter season (*17*). The fireplace season is assumed to be 150 days long. Therefore, the quantity of wood burned in Denver would be 1.0×10^6 kg/day. This compares favorably with an estimate of 1.2×10^6 kg/day burned in fireplaces in the Denver area based on a telephone survey (*18*).

Two common types of firewood used in Denver are ponderosa pine and pinyon pine. Samples of these two woods were shipped from Denver, and their emissions were measured. The total mass emissions (including impinger catch) ranged from 3.7 to 8.4 g/kg, averaging 6.0 g/kg. On the basis of two cascade-impactor measurements of softwood emissions, about 86% of the particles were in the fine-particle fraction of less than 2.5 μm. This leads to fine-particle emissions from firewood of 5200 kg/day. Based on a source characterization in Denver, it can be estimated that fine-particle emissions from all sources are 17 000 kg/day (*12*). Therefore, fireplace emissions comprise 30% of the total emissions.

K/Fe Ratio. The ratio of K/Fe in the ambient particulate has been used as a tracer for firewood emissions (*12, 13*). Most sources have K/Fe ratios of 0.35 or less. Remote Colorado aerosol has a K/Fe of 0.38 (*12*). However, the K/Fe ratio from wood smoke is between 15 and 230 (*14*). Therefore, the ambient particulate K/Fe ratio will increase if wood smoke is a major source of air pollution. The two Denver studies have measured a diurnal variation in the ambient K/Fe ratio that peaks in the evening hours when fireplaces are most used. On the basis of ambient data collected by Wolff (*19*) in Denver in 1978, the ratio of K/mass has been plotted for 5 days in Figure 6. (There were too many missing Fe values to plot K/Fe.) There is clearly an increase in the K/mass ratio during each evening.

The wood-burning contribution can be determined based on the K concentration in wood smoke and average Denver wintertime fine-particle concentrations by using the following formula:

$$K_D = K_w X + (K/Fe)Fe_D$$

where K_D = average K concentration in Denver = 0.10 $\mu g/m^3$ (*16*), K_w = K concentration in wood burning particulate, X = particle concentration due to wood burning in $\mu g/m^3$, K/Fe = background ratio = 0.38 (*12*), Fe_D = average Fe concentration in Denver = 0.11 $\mu g/m^3$ (*16*). The assumption is made that there is no wood-burning contribution to the Fe concentration. Since wood-particulate emissions contain about 23 ppm Fe compared to 3300 ppm in ambient particulate, this is a reasonable assumption (*14*). All of the concentrations used are for the fine-particle portion only. The K concentration from softwoods tested averaged 6.1 mg/g. From insertion of these values in the formula, the particle concentration due to wood burning (X) can be calculated to be 9.5 $\mu g/m^3$. The average fine-particle mass is 33.7 $\mu g/m^3$, so 28% of the wintertime Denver fine particulate is due to wood burning.

^{14}C Measurements. A final method for determining the importance of wood burning is based on ^{14}C measurements. Recently living material such as wood has a higher $^{14}C/^{12}C$ ratio than fossil fuels. By measuring the ^{14}C content of ambient particulate, it is possible to determine the fraction of "contemporary carbon" present. Since plant-derived material is insignificant in the winter and refuse burning is not permitted in Denver, the sole source of contemporary carbon is considered to be wood burning. The particulate carbon mass in Denver consisted of 33% contemporary carbon (*12*). Since 39% of the ambient fine particulate in Denver was carbon (*16*), 13% of the particulate was due to wood smoke carbon (39% × 0.33). The Denver wood particulate was analyzed for carbon content and was found to average 64% carbon. Therefore, the contribution of wood burning to fine-particulate mass in Denver is 20% based on the ^{14}C technique.

Summary. The results of the three approaches were quite similar, considering the number of assumptions incorporated in each estimate. The fraction of fine particulate due to wood burning is 30% based on the amount of wood burned, 28% based on the K/Fe ratio, and 20% based on ^{14}C measurements. Therefore, it appears clear that wood burning has a significant effect on ambient wintertime particulate concentrations in Denver. Although these results cannot be generalized, wood burning may be an important source of atmosphere particulate in many locations.

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Vapor Pressure Correlations for Low-Volatility Environmental Chemicals

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■ Four equations are proposed and tested that relate vapor pressures at ambient temperatures for low-volatility solid and liquid chemicals of environmental interest to their boiling and melting points. The equations may be used to estimate vapor pressure from boiling point, check the reasonableness of experimental data, or correlate these data. The preferred equation, which is a version of the Rankine equation, gives a mean error in vapor pressure of a factor of 1.25 for 72 selected hydrocarbons and halogenated hydrocarbons. It is suggested that versions of the equation may be developed for other classes of compounds.

Introduction

The tendency for an environmental contaminant or pesticide to partition into the atmosphere is determined largely by its vapor pressure. It is thus recognized that for assessing the likely environmental behavior of new and existing chemicals a knowledge of their vapor pressures is essential.

The vapor pressure P (Pa) can be regarded as a measurement of the maximum achievable amount or solubility of the substance in the vapor of air phase, the corresponding concentration being obtained from the gas law as P/RT (mol/m^3) where R is the gas constant (8.314 J/mol K) and T is absolute temperature (K). It is not always recognized that high molecular weight hydrophobic substances such as DDT or PCBs, which have very low vapor pressures and hence low atmospheric concentrations, may still partition appreciably into the atmosphere as they also have low aqueous solubilities. The ratio of the concentration in the atmosphere to that in the water (i.e., the air–water partition coefficient) may thus be large despite the low vapor pressure. This partition coefficient can be expressed as a dimensionless Henry's law constant H/RT where H is defined as the ratio of partial pressure P to aqueous concentration (mol/m^3). Compounds of high H tend to partition predominantly into the atmosphere, and the rate at which they evaporate from water is usually controlled by the water-phase mass-transport resistance. For substances of low H, partitioning is predominantly into the water, and the evaporation rate tends to be controlled by the resistance in the air phase, where the concentration is lower.

It is noteworthy that many of the data published in the literature for vapor pressures are erroneous, especially for very low vapor pressure substances (Spencer et al. (*1*)). Little difficulty is encountered experimentally in measuring vapor pressures exceeding 1 kPa, since an isoteniscope can be used. For lower vapor pressures, the preferred approach is to flow a stream of gas through a vessel containing the volatile solid or liquid solute coated on packing, such that the gas stream is saturated. The exit gas is then analyzed for solute concentration. Such methods have been described by Spencer et al. (*1*), Sinke (*2*), and Macknick and Prausnitz (*3*), and although straightforward, they require meticulous experimental technique. For some substances of environmental interest the only vapor pressure information that may be available is the boiling point, and it is useful to devise methods of using these data to estimate vapor pressures approximately at lower temperatures. In this paper we thus examine the physical–chemical factors that influence vapor pressure, suggest correlations for fitting vapor pressure data, for determining vapor pressure from boiling point in the absence of experimental vapor-pressure data, and for checking the reasonableness of experimental vapor pressure data. Our focus here is thus on low vapor pressure solids or liquids well below their boiling point. For more volatile compounds, direct vapor pressure measurement is easy and there is little merit in prediction.

Thermodynamic Basis

A comprehensive discussion of the theory underlying liquid vapor pressure is provided by Reid et al. (*4*), and only the salient points are reviewed here. Typical vapor pressure characteristics of a substance are illustrated in Figure 1a. The range of environmental temperatures may lie anywhere on this diagram for a given substance, relative to the phase transition points. The solid and liquid vapor pressure lines are highly nonlinear, and no method is currently available for calculating from theory the mag-

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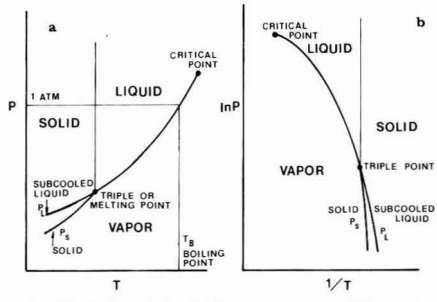

Figure 1. Illustrative plots of (a) vapor pressure (P) vs. absolute temperature (T) and (b) ln vapor pressure vs. reciprocal absolute temperature ($1/T$).

nitude of vapor pressure or its dependence on temperature. The second law of thermodynamics provides a constraint on the vapor pressure–temperature curve in the form of the differential Clapeyron and Clapeyron–Clausius equations, below, which give the slope of the curves as a function of the enthalpy of vaporization ΔH^v and the volume change on vaporization ΔV. Here we ignore compressibility effects since the pressure is low and the gas law can be applied by ignoring the relatively small liquid molar volume. The resulting equation in rearranged form suggests that $d(\ln P)/d(1/T)$ should be fairly constant if ΔH^v is fairly constant. Figure 1b shows this plot, which is close to linear over small temperature ranges.

$$dP/dT = \Delta H^v/T\Delta V = \Delta H^v P/RT^2 \quad (1)$$

$$d(\ln P)/d(1/T) = -\Delta H^v/R \quad (2)$$

Integration of the equation with the assumption of constant ΔH^v leads to eq 3 and 4, which are successfully used to correlate vapor pressure data over narrow temperature ranges.

$$\ln (P_1/P_2) = (\Delta H^v/R)(1/T_2 - 1/T_1) \quad (3)$$

$$\ln P = A - B/T \qquad \text{where } B = \Delta H^v/R \quad (4)$$

The fit of the equation can be considerably improved by introducing a third parameter in the form of the Antoine equation, which is widely used to correlate experimental vapor pressure data. Values of C are typically −20 to −50 K, and rules have been suggested to correlate C.

$$\ln P = A - B/(T + C) \quad (5)$$

The principal region of predictive interest for environmental chemicals is the low-pressure region well below the boiling point in which the two problems are estimation of the absolute value of ΔH and estimation of its temperature dependence, the $\ln P$ vs. $1/T$ plot being invariably curved, as shown in Figure 1b. The assumption that ΔH^v is constant implies that this line is straight and results in an overestimation of vapor pressure at low temperatures. ΔH^v tends to increase at low temperatures, thus the vapor pressure decreases more rapidly as shown. It is thus necessary to devise methods to predict ΔH^v and its temperature dependence.

Prediction of H^v_B. Trouton's rule states that the entropy of vaporization at the normal boiling point (subscript B) H^v_B/T_B is 20.67 cal/mol K or 86.4 J/mol K. Kistiakowsky (*5*) improved on this by relating the entropy of vaporization to boiling point, i.e.

$$\Delta H^v_B/T_B = 36.6 + R \ln T_B \quad (6)$$

Greater accuracy can be obtained by correlating classes of compounds separately, for example, by Fishtine (*6*, *7*). In this work we use only the Trouton and Kistiakowsky Rules.

Temperature Dependence of ΔH^v. The enthalpy of vaporization is zero at the critical point T_C but rises rapidly at temperatures approaching the normal boiling point (which is often approximately $0.66T_B$), and then it rises more slowly at lower temperatures. The most successful correlating equation is that of Watson (*8*)

$$\Delta H_1/\Delta H_2 = [(1 - T_1/T_C)/(1 - T_2/T_C)]^{0.38} \quad (7)$$

in which the subscripts 1 and 2 refer to different temperatures, one of which may be the boiling point. Since most high molecular weight compounds have critical temperatures in the 700–900 K range, environmental conditions fall in the region where T/T_C is 0.30–0.45. The temperature range of interest here is thus from T/T_C of 0.30 to 0.66.

The usual approach for developing vapor pressure correlations at higher temperatures is to substitute the Watson equation and the Haggenmacher compressibility equation into the Clapeyron–Clausius equation and integrate. Direct analytical integration is unfortunately impossible, and the alternative is to devise an empirical correlation based on numerical integration or to integrate a series expansion. Notable in this regard are the equations developed by Miller (*9*) and Thek and Stiel (*10*). The Watson equation requires a knowledge of the critical temperature T_C, and for substances of low volatility reliable estimates may not be available. Methods are available to estimate T_C by additive structural contributions, for example, that of Lyderson, but in principle it seems unwise to rely on a T_C estimate if it can be avoided.

Vapor Pressure Equations

1. Trouton Constant ΔH^v (TCH). If Trouton's rule is adopted and ΔH^v is assumed to be constant and equal to ΔH^v_B, the Clapeyron–Clausius equation can be integrated directly to give

$$\ln (P_1/P_2) = -(\Delta H^v_B/R)(1/T_1 - 1/T_2) \quad (8)$$

If T_2 is the boiling point T_B, P_2 becomes 1 atm, replacing $\Delta H^v_B/R$ by $86.4T_B/8.314$ or $10.6T_B$, and substituting yields

$$\ln (P_1/P_2) = -10.6T_B(1/T_1 - 1/T_2)$$

or

$$\ln P_1 = -10.6(T_B/T_1 - 1) \qquad \text{(eq TCH)} \quad (9)$$

2. Kistiakowsky Constant ΔH^v (KCH). In this case $\Delta H^v_B/R$ is replaced by $T_B(36.6 + R \ln T_B)$ giving

$$\ln (P_1/P_2) = -T_B(4.40 + \ln T_B)(1/T_1 - 1/T_2)$$

or

$$\ln P_1 = -(4.40 + \ln T_B)(T_B/T_1 - 1) \quad (10)$$

These equations are variants of eq 4, in which, for example, in the TCH equation, A is 10.6 and B is $10.6T_B$. The TCH equation can be used to estimate vapor pressure from boiling point (although overestimation is likely), or it can be used to fit boiling point and experimental vapor pressure data in a one-parameter equation, i.e., fitting a constant instead of 10.6. If the constant deviates greatly from 10.6, i.e., by 10%, it is likely that one measurement is in error or the molecule has exceptional properties.

3. Trouton Linear ΔH (TLH). Adopting Trouton's rule and allowing ΔH to vary linearly with temperature in the range below the boiling point introduce another parameter, which must improve the data fit. A suitable ΔH equation with one constant K is

$$\Delta H = \Delta H_B(1 + K(1 - T/T_B)) \quad (11)$$

which has the correct property that ΔH is ΔH_B when T is T_B. The Watson equation can be used to estimate the likely magnitude of K. A compound of T_C = 800 K will have a T_B of 528 K, environmental temperature T_1 being 290 K. Substitution in the Watson equation gives a $\Delta H_1/\Delta H_B$ ratio of 1.27, thus K should have a value of approximately 0.6.

Substituting into the Clapeyron–Clausius equation yields

$$\ln P_1/P_2 = \int_{T_2}^{T_1} \Delta H_B(1 + K(1 - T/T_B))\, dT/RT^2$$
$$= -\Delta H_B(1 + K)(1/T_1 - 1/T_2)/R - \Delta H_B K \ln (T_1/T_2)/RT_B \quad (12)$$

and substituting $10.6T_B$ for $\Delta H_B/R$ gives

$$\ln (P_1/P_2) = -10.6T_B(1 + K)(1/T_1 - 1/T_2) - 10.6K \ln (T_1/T_2)$$

or

$$\ln P_1 = -10.6\{(1 + K)(T_B/T_1 - 1) - K \ln(T_B/T_1)\} \quad \text{(eq TLH)} \quad (13)$$

The vapor pressure calculated by eq TLH will always be lower than that of eq TCH for a positive value of K.

4. Kistiakowsky Linear ΔH (KLH). From the previous derivation, the quantity 10.6 in the TLH equation can be replaced by 4.40 + ln T_B to yield the KLH equation.

The TLH equation is a form of the Rankine or Kirchoff equation:

$$\ln P = A - B/T + C \ln T \quad (14)$$

If data are available for the boiling point and vapor pressures at lower temperatures, the TLH of KLH equations can be used to correlate the data by regarding 10.6 and K as adjustable parameters. The advantage of the TLH or TKH equations is that they can be used to predict vapor pressures from boiling point by using a reasonable value for K or they can be used to check the reasonableness of data by determining K.

Solid Vapor Pressures. If the compound is solid, its vapor pressure P_S will be lower than that of the subcooled liquid P_L by the factor of the fugacity ratio P_S/P_L. This has been previously shown to be expressible by

$$\ln (P_S/P_L) = -6.8(T_M/T - 1) \quad (15)$$

where T_M is the melting point (Yalkowsky (*11*), Mackay et al. (*12*), and Mackay and Shiu (*13*)).

The constant 6.8 is an average empirical value and may be substantially in error for certain compounds.

For solids, this (negative) group is added to the liquid vapor pressure equation as follows, as illustrated for the TCH equation:

$$\ln (P_S/P_B) = \ln (P_S/P_L) - \ln (P_L/P_B)$$
$$= -6.8(T_M/T - 1) - 10.6(T_B/T - 1) \quad (16)$$

For other equations the appropriate second term is substituted.

In summary, four equations have been stated, all of which enable liquid vapor pressures to be predicted at low (environmental) temperatures from the boiling point. The first pair (TCH and KCH) contain one parameter (e.g., 10.6), the second pair (TLH and KLH) two parameters (e.g., 10.6 and K). The parameter K is not freely adjustable, and it is expected that it will have similar values, at least for a class of structurally similar compounds.

Data Analysis

Vapor pressure, boiling point, and melting point data were gathered in Table I for 72 compounds of environmental interest, all of which boil above 100 °C, the principal sources being various compilations of toxic substance properties (ref 14–18). The compounds selected were hydrophobic (low aqueous solubility) organic compounds such as hydrocarbons and halogenated hydrocarbons. Compounds containing polar groups were excluded for two reasons. These more soluble compounds tend to partition negligibly into the atmosphere (i.e., H is low) thus a knowledge of P is less useful. They also tend to have higher and more variable ΔH values. The vapor pressure data were then compared to the TCH and KCH equation predictions as shown. Comparison was also made with the TLH and KLH equations, and a "best" value of K was found to be 0.7626 for the TLH equation and 0.803 for the KLH equation. The procedure by which these K values are obtained should avoid giving excessive weight to higher vapor pressures, and thus direct least-squares fitting is undesirable. This problem was solved by regression of the logarithm of the vapor pressures, and thus the quantity minimized was effectively the ratio between experimental and correlated values rather than the difference.

Inspection of the data showed that the TCH and KCH equations tend to predict high vapor pressures by a mean factor of 2.64 and 2.66, respectively. The mean absolute values of the logarithm of the ratio of the calculated and literature values for these two equations were 0.342 and 0.356, corresponding to factors of 2.20 and 2.27. It is thus concluded that, as expected, these equations overpredict the vapor pressures by a factor of 2–3 because of the assumed constancy of ΔH.

The TLH and KLH equations give mean errors in the absolute logarithm term of 0.0960 and 0.0957, respectively corresponding to factors of 1.247 and 1.246. These equations are thus superior to the TCH and KCH equations and are recommended for use in calculating vapor pressures from boiling point. It is surprising that the KLH equation is not significantly more accurate than the TLH equation, but this may be due to masking by the errors in the data. In principle the KLH equation is judged to be the best of the four.

It is believed that the TLH and KLH equations should yield predicted vapor pressures with an average error of only a factor of 1.25, but errors of over a factor of 2.0 are expected with a frequency of 10% for compounds similar in characteristics to those used to develop the correlation. Since the equation is most likely to be used for solid compounds of high boiling point for which no vapor pressure data are available, it is likely that the errors will generally be larger, but it is impossible to estimate their likely magnitude.

Figure 2 illustrates the KLH correlation in two forms. The A set of curves are calculated solid and liquid vapor pressures of a substance of boiling point 500 K. The effect of melting point is apparent. Also shown is the linear TCH equation, which overestimates vapor pressure due to the assumption of constant enthalpy of vaporization. The B curves give the calculated vapor pressure at 25 °C of substances with the indicated boiling point. Again the effect of melting point is apparent, the solid vapor pressures being displaced downward by the fugacity ratio by an equal factor or interval on the logarithmic scale.

Table II illustrates the caution that must be exercised in using the correlation by applying it to other compounds.

Table I. Vapor Pressure Data at 25 °C for 72 Compounds and Correlated Values[a]

chemical	melting point, K	boiling point, K	exptl, atm	KLH, atm
octane	216.40	398.66	0.186×10^{-1}	0.203×10^{-1}
3-methylheptane	152.50	388.00	0.257×10^{-1}	0.319×10^{-1}
2,3,4-trimethylpentane	163.80	386.50	0.355×10^{-1}	0.339×10^{-1}
nonane	222.00	423.80	0.564×10^{-2}	0.675×10^{-2}
2,2,5-trimethylhexane	167.20	397.10	0.218×10^{-1}	0.217×10^{-1}
4-methyloctane	159.80	415.40	0.891×10^{-2}	0.979×10^{-2}
decane	243.30	447.10	0.173×10^{-2}	0.235×10^{-2}
undecane	247.41	468.90	0.515×10^{-3}	0.851×10^{-3}
dodecane	263.40	489.30	0.155×10^{-3}	0.321×10^{-3}
hexadecane	291.17	560.00	0.905×10^{-5}	0.942×10^{-5}
1-octene	171.30	394.30	0.229×10^{-1}	0.244×10^{-1}
methylcyclohexane	146.40	373.90	0.610×10^{-1}	0.573×10^{-1}
ethylcyclopentane	134.56	376.40	0.526×10^{-1}	0.517×10^{-1}
ethylcyclohexane	161.68	402.90	0.169×10^{-1}	0.169×10^{-1}
cis-1,2-dimethylcyclohexane	222.90	402.70	0.190×10^{-1}	0.170×10^{-1}
trans-1,4-dimethylcyclohexane	236.00	392.40	0.298×10^{-1}	0.265×10^{-1}
1,1,3-trimethylcyclopentane	258.80	377.90	0.523×10^{-1}	0.486×10^{-1}
propylcyclopentane	155.70	376.00	0.162×10^{-1}	0.525×10^{-1}
toluene	178.00	383.60	0.370×10^{-1}	0.383×10^{-1}
ethylbenzene	178.00	409.20	0.130×10^{-1}	0.128×10^{-1}
p-xylene	286.20	411.00	0.115×10^{-1}	0.119×10^{-1}
m-xylene	225.10	412.00	0.109×10^{-1}	0.114×10^{-1}
o-xylene	247.80	417.40	0.860×10^{-2}	0.896×10^{-2}
1,2,4-trimethylbenzene	229.20	442.35	0.267×10^{-2}	0.292×10^{-2}
1,2,3-trimethylbenzene	247.60	449.10	0.199×10^{-2}	0.214×10^{-2}
1,3,5-trimethylbenzene	228.30	437.70	0.318×10^{-2}	0.361×10^{-2}
cumene	176.40	437.70	0.605×10^{-2}	0.361×10^{-2}
propylbenzene	171.40	432.20	0.451×10^{-2}	0.463×10^{-2}
1-ethyl-2-methylbenzene	192.20	438.20	0.326×10^{-2}	0.353×10^{-2}
1-ethyl-4-methylbenzene	210.60	435.00	0.388×10^{-2}	0.408×10^{-2}
n-butylbenzene	185.00	456.00	0.135×10^{-2}	0.156×10^{-2}
isobutylbenzene	221.50	445.80	0.271×10^{-2}	0.249×10^{-2}
sec-butylbenzene	197.50	446.00	0.238×10^{-2}	0.247×10^{-2}
tert-butylbenzene	215.20	442.00	0.282×10^{-2}	0.297×10^{-2}
1,2,4,5-tetramethylbenzene	193.80	469.80	0.650×10^{-3}	0.815×10^{-3}
1-isopropyl-4-methylbenzene	205.10	450.10	0.200×10^{-2}	0.205×10^{-2}
n-pentylbenzene	198.00	478.40	0.431×10^{-3}	0.542×10^{-3}
naphthalene (S)	353.20	491.00	0.108×10^{-3}	0.840×10^{-4}
1-methylnaphthalene	251.00	517.64	0.921×10^{-4}	0.802×10^{-4}
2-methylnaphthalene* (S)	307.60	514.10	0.715×10^{-4}	0.768×10^{-4}
1-ethylnaphthalene*	259.20	531.70	0.248×10^{-4}	0.398×10^{-4}
2-ethylnaphthalene* (295.9 K)	256.60	530.90	0.336×10^{-4}	0.414×10^{-4}
biphenyl (S)	344.00	528.90	0.130×10^{-4}	0.160×10^{-4}
acenaphthene* (S)	369.20	550.50	0.588×10^{-5}	0.302×10^{-5}
fluorene* (S)	389.00	568.00	0.874×10^{-6}	0.782×10^{-6}
1,1,2-trichloroethane	236.50	386.80	0.399×10^{-1}	0.335×10^{-1}
1,1,1,2-tetrachloroethane	202.80	403.50	0.183×10^{-1}	0.164×10^{-1}
1,1,2,2-tetrachloroethane	237.00	419.20	0.856×10^{-2}	0.828×10^{-2}
1,1,2,2,2-pentachloroethane	244.00	435.00	0.592×10^{-2}	0.408×10^{-2}
tetrachloroethene	254.00	394.00	0.245×10^{-1}	0.247×10^{-1}
trichloropropane	258.30	429.90	0.408×10^{-2}	0.514×10^{-2}
1,2-dibromomethane	238.30	440.30	0.267×10^{-2}	0.321×10^{-2}
bromoform	264.70	422.50	0.710×10^{-2}	0.715×10^{-2}
chlorobenzene	227.40	405.00	0.156×10^{-1}	0.154×10^{-1}
o-dichlorobenzene	256.00	453.50	0.193×10^{-2}	0.175×10^{-2}
m-dichlorobenzene	248.30	446.00	0.303×10^{-2}	0.247×10^{-2}
p-dichlorobenzene* (S)	326.10	447.00	0.888×10^{-3}	0.124×10^{-2}
1,2,3-trichlorobenzene* (S)	326.00	491.00	0.276×10^{-3}	0.156×10^{-3}
1,2,4-trichlorobenzene	289.95	486.50	0.598×10^{-3}	0.368×10^{-3}
1,3,5-trichlorobenzene* (S)	336.00	481.00	0.760×10^{-3}	0.201×10^{-3}
1,2,3,4-tetrachlorobenzene* (S)	320.50	527.00	0.514×10^{-4}	0.301×10^{-4}
1,2,3,5-tetrachlorobenzene* (S)	327.50	519.00	0.967×10^{-4}	0.383×10^{-4}
1,2,4,5-tetrachlorobenzene* (S)	413.00	516.00	0.711×10^{-5}	0.631×10^{-5}
α-chlorotoluene	234.00	452.30	0.171×10^{-2}	0.185×10^{-2}
α,α,α-trifluorotoluene	243.89	375.06	0.491×10^{-1}	0.546×10^{-1}
bromobenzene	242.18	429.00	0.545×10^{-2}	0.535×10^{-2}
m-dibromobenzene* (308 K)	266.00	491.00	0.563×10^{-3}	0.296×10^{-3}
p-dibromobenzene (S)	360.33	492.00	0.212×10^{-3}	0.680×10^{-4}
2-bromoethylbenzene*	205.50	491.00	0.322×10^{-3}	0.296×10^{-3}
iodobenzene	241.79	461.30	0.130×10^{-2}	0.122×10^{-2}
1,4-bromochlorobenzene (S)	341.00	469.00	0.340×10^{-3}	0.317×10^{-3}
trichlorohydrin	258.30	429.85	0.408×10^{-2}	0.515×10^{-2}

[a] (S) refers to solids. Asterisked values are extrapolated.

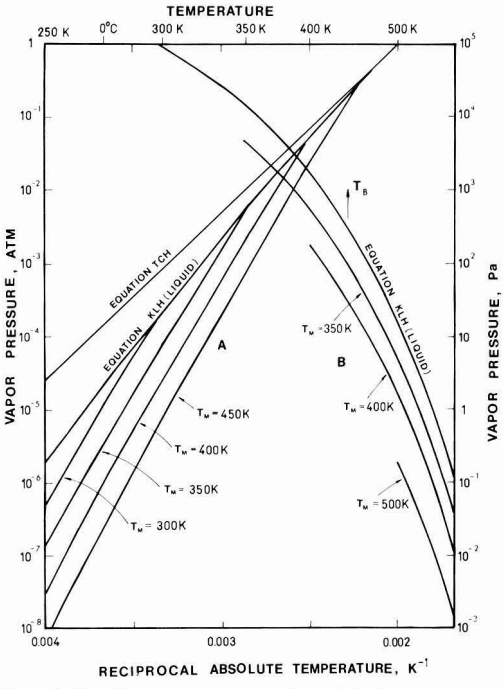

Figure 2. Plot of vapor pressure vs. reciprocal absolute temperature for (A) the TCH and KLH equations applied to a substance of boiling point 500 K and (B) the vapor pressure at 298 K (25 °C) of substances with the indicated boiling point.

Table II. Application of the KLH Equations to Selected Oxygen, Nitrogen, and Sulfur Compounds Illustrating Its Poor Predictive Accuracy (Ref 18 and 19)

compound	T_M, K	T_B, K	T, °C	KLH vapor pressures, atm exptl	KLH vapor pressures, atm calcd
phenol	314	455	20	2.6×10^{-4}	7.1×10^{-4}
o-cresol	304	464	25	3.2×10^{-4}	9.4×10^{-4}
p-cresol	308	475	25	1.5×10^{-4}	5.1×10^{-4}
1-pentanol	194	411	20	3.7×10^{-3}	8.8×10^{-3}
1-octanol	256	468	54	1.3×10^{-3}	5.7×10^{-3}
nitrobenzene	279	484	20	2.0×10^{-4}	2.8×10^{-4}
diphenyl sulfide	233	569	96	3.7×10^{-3}	1.2×10^{-3}
benzo[*b*]thiophene	304	493	20	2.6×10^{-4}	1.4×10^{-4}
dibenzothiophene	373	605	20	2.6×10^{-6}	8.2×10^{-8}
quinoline	257	511	25	1.2×10^{-5}	1.1×10^{-4}

The potential for misuse is obvious, it being necessary to develop different correlations for oxygen-, nitrogen-, phosphorus-, and sulfur-containing substances.

An implication of this work is that in gathering property data for new chemicals, a measurement of boiling point is always justified even when the boiling point greatly exceeds any conceivable environmental temperatures. When no vapor pressure data are available, a "default" value can be estimated from the boiling point by using the KLH equation.

Conclusions

Four equations have been proposed, all of which can be considered as versions of existing equations and can be used to (i) predict environmental vapor pressures from boiling points, (ii) check the reasonableness of experimental vapor pressure and boiling point data, or (iii) correlate vapor pressure and boiling point data in a single equation.

The equations apply to solid and liquid substances, an extra term being required for solids.

The equations are subject to the qualification that they apply only to hydrocarbons and halogenated hydrocarbons that boil above 100 °C.

The preferred equation is the KLH version, which can be stated as

$$\ln P = -(4.4 + \ln T_B) \times \{1.803(T_B/T - 1) - 0.803 \ln (T_B/T)\} - 6.8(T_M/T - 1)$$

where P is the vapor pressure (atm) at environmental temperature T (K) and T_B and T_M are the boiling and melting point temperatures (K). The third term including the melting point is ignored for liquids, i.e., when the melting point is lower than the environmental temperature.

It is suggested that versions of this equation be developed for other classes of compounds of environmental interests, notably organophosphorus, -nitrogen, -sulfur, and -oxygen compounds.

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Non-Methane Hydrocarbons in the Atmosphere of Sydney, Australia

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■ The results of a sampling program for atmospheric hydrocarbons in Sydney, a city of 3.2 million people with large emissions of hydrocarbons and a significant photochemical smog problem, are presented. The methods developed for the sampling and analysis of atmospheric hydrocarbons are described, and their accuracy and precision are demonstrated. The detailed C_2–C_{10} composition of Sydney's air is reported, and a comparison is made with other cities. The composition of Sydney's air is, in general, similar to that in cities in the United States. The diurnal behavior of hydrocarbon concentrations is demonstrated to be dominated by the early-morning increase in traffic density and by meteorology.

Introduction

The role of non-methane hydrocarbons in the formation of photochemical smog has been known since the early 1950s (*1*). Although the quantitative relationship between the atmospheric concentrations of hydrocarbons and oxides of nitrogen and those of the photochemical oxidants they produce is still imperfectly understood, it is widely agreed that the most effective way to reduce the occurrence of smog is some form of hydrocarbon control. This strategy appears to apply not only to American cities (*2*) but also to London (*3*) and Sydney (*4, 5*).

Control measures are frequently based on measurements of the ambient concentrations of total non-methane hydrocarbons [NMHC]. However, the differences in photochemical reactivity that exist between different hydrocarbons make it desirable to supplement this information with knowledge of the concentrations of the individual hydrocarbon species present. The latter data can also be used as inputs to models of the urban atmosphere (*3, 6*).

Another reason for obtaining a body of data of this kind is for use in determining the relative importance of the various emission sources by the source reconciliation method (*7*). In the course of such an investigation, currently in progress, atmospheric concentrations of about 50 hydrocarbon species were determined systematically in the city of Sydney over a period of 10 months. The results are summarized and discussed in this paper.

During the early part of the work much experimentation was required to develop rapid, convenient, and precise procedures for the sampling and analysis of the atmospheric hydrocarbons. The procedures finally adopted and the accuracy obtained are also reported.

Early methods (*8–12*) for the analysis of individual atmospheric hydrocarbons usually involved freezing out the hydrocarbons from a volume of air (typically 0.1–1.0 L) onto a precolumn packed with a chromatographic support at liquid oxygen or nitrogen temperature, the analysis often being limited to C_2–C_6 hydrocarbons.

The great number of isomeric possibilities among the less volatile hydrocarbons, including the aromatics, has necessitated the use of chromatographic columns of reasonably high resolution, the main analytical variation being in the means of preconcentrating the sample. Charcoal (*13*) and graphitized carbon black (*14*) have been used as absorbents, as have thermally stable hydrophobic sorbents with large specific surface areas, such as Tenax (*15–18*). With these materials, however, we were not able to achieve the precision required for our purposes (*19*) nor was it possible to determine important C_2–C_4 hydrocarbons such as acetylene by these procedures. In the present study, the samples were concentrated by a freeze-out technique common to the entire range of C_2–C_{10} hydrocarbons, which is a modification of that first proposed by Westberg et al. (*20*).

The sampling of atmospheric hydrocarbons has usually been performed in plastic bags fabricated from materials such as Tedlar (*10*) or in stainless steel tanks (*21*). However, Tedlar bags tend to contaminate the air samples with acetaldehyde and acetone (*22*), and both techniques require the use of Teflon-lined diaphragm pumps or metal bellows pumps to fill and evacuate the sampling containers. We have used glass containers that can be filled without the sampled air coming into contact with the pump. They can also be purged to remove any hydrocarbons adsorbed on the glass surface, and unlike plastic bags, the glass is not a source of any organic material.

The method ultimately developed enables the full range of C_2–C_{10} hydrocarbons (at concentrations of 0.1–50 ppbv) to be determined.

Experimental Section

Geography of Sydney and Location of Sampling Sites. The city of Sydney is on the east coast of Australia (latitude 34° S) and has a population of approximately 3.2 million. The city is surrounded by high ground to the north, south, and west, with the highest density of population and industrial development in the eastern half of the basin.

The vehicle population of the Sydney region is in excess of 1 million. At the time of this study there were two fully operational oil refineries, one situated at Silverwater (capacity 65 000–87 000 barrels/day) and the other at Kurnell (capacity 145 000–155 000 barrels/day). In addition there are a number of petrochemical plants in Sydney, and significant amounts of hydrocarbon and related solvents are manufactured and used.

Sampling sites were chosen on the basis of considerations of meteorology (*23*) and source location. Under the conditions of drainage flow characteristic of the region, two of the sites (Goat Island and Rozelle Hospital (GI and RH)) were 10 km downwind of a refinery–petrochemical complex, while the third (Eastern Suburbs Hospital (ESH)) was 5 km downwind of the central business district.

Samples were taken in the mornings only, for the following reasons: (i) morning emissions have been shown to be responsible for oxidant formation later in the day (*4*), (ii) the lower concentrations in the afternoon that result from increases in the mixing depth of the atmosphere and other factors are less suitable for use in the source reconciliation program, for which (iii) changes in the composition of the atmospheric hydrocarbons that develop as the result of differences in reactivity must be avoided.

Sampling. Samples were collected from the atmosphere at a height of 4 m from the ground and conveyed by Teflon tubing (6.4 mm o.d.) to 400-mL glass pipettes equipped with Teflon taps at both ends. The air was sucked si-

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multaneously through four pipettes in parallel, initially at a total flow of 2 L/min for 5 min. This sampling rate and time were found to be sufficient to displace the volume of the four pipettes and replace it with sample. The sampling rate was then reduced to 200 mL/min for 10 min, and at the end of this period the sample present in the pipettes was isolated by closing the Teflon taps. Sets of eight pipettes were mounted in wooden boxes that were kept closed to the light during storage of the sample. In general, at any sampling site, six duplicate samples were collected at hourly intervals from 6 a.m. until 12 noon. Sampling was terminated earlier on days when the windspeeds were high and concentrations consequently low.

Analysis. Four pipettes were used for duplicate analyses of the C_2–C_6 and C_4–C_{10} hydrocarbon fractions. Identical trapping systems were used for concentrating both hydrocarbon fractions. Each pipette was connected to a flow of helium (90 mL/min) purified of any hydrocarbons by passage through a 100 mm × 19 mm o.d. stainless steel trap packed with 80–100 mesh Chromosorb 105 (Johns-Manville, U.S.) immersed in liquid nitrogen. The pipette was purged for 20 min, and the sample was trapped at liquid nitrogen temperature on a precolumn (150 mm × 3 mm o.d. stainless steel) filled with glass beads (ASTM Grade 80, 0.177-mm diameter) and connected to a gas chromatographic sampling valve. Helium was used as purge gas to avoid condensation of oxygen or nitrogen in the precolumn. Methane was also eluted from the precolumn under the conditions used. Condensation of water in the precolumn was not a problem, and the flow rate remained constant during the concentration procedure. After the concentration step the sample valve was switched so that helium carrier gas flowed through the precolumn, the liquid nitrogen was replaced with hot water, and the sample eluted onto the analytical column.

A Durapak column (octane/Porasil C, 6.1 m × 1.5 mm o.d. stainless steel) was used to separate the C_2–C_6 fraction. It was maintained at −50 °C for 4 min to ensure a plug injection of material frozen on the front of the column. The oven was then programmed at 16 °C/min to 60 °C, at which temperature it was held for 30 min. The total analysis time was about 1 h.

For the C_4–C_{10} fraction the column was an SE-30 glass capillary ($N_{eff} \approx 50\,000$, 50–100 m × 0.5 mm i.d.). It was maintained at −80 °C for 10 min for injection, during which time the C_2 hydrocarbons were eluted but hydrocarbons from C_3 upwards were "frozen on" the front of the column. The column oven was then quickly heated to −20 °C, and after a 1-min stabilization period, a temperature program at 2 °C/min to 110 °C was begun. The C_3 hydrocarbons were eluted almost immediately, and the separation of C_4–C_{10} hydrocarbons followed. The total analysis time was about 1.5 h.

Peak identifications were achieved in two ways. For the C_4–C_{10} fraction a combined gas chromatography/mass spectrometry (GC/MS) system was used (*24*). This was fitted with a glass support coated capillary column (75 m × 0.5 mm i.d.) coated with SE-30 phase and coupled directly to an Atlas CH4 mass spectrometer. The mass spectrometer was a single-focusing instrument that was fitted with a double ion source so that while the mass spectra were being recorded at 70 eV, an ion current chromatograph was being produced at 20 eV. The mass spectrometer was coupled to a PDP-15 computer via a high-speed interface, and the raw data were stored on magnetic tape. Computer programs processed the data, which were subsequently printed as tables of m/e values vs. relative abundance, with background spectra subtracted. For routine analysis relative retention times based on the GC/MS work were used. For the C_2–C_6 fraction, analyzed on the Durapak column, peaks were identified by the injection of pure compounds.

Table I. Comparison of Observed and Expected Hydrocarbon Concentrations in Smog Chamber Experiments

hydrocarbon	concn in mixture	av concn in smog chambers, ppbv (±1 sd)	concn expected	obsd/expected
	(a) C_2-C_4 Gas Mixture			
ethane	0.60[a]	8.2 ± 0.6	7.9[c]	1.04
ethylene	4.28[a]	56.1 ± 2.4	56.5[c]	0.99
acetylene	3.97[a]	51.0 ± 1.6	52.2[c]	0.98
propylene	1.40[a]	18.0 ± 0.7	18.5[c]	0.97
butane	0.76[a]	9.8 ± 0.7	10.0[c]	0.98
isobutene	0.28[a]	3.8 ± 0.2	3.7[c]	1.03
	(b) Solvent Mixture			
toluene	21.3[b]	63.2 ± 1.1	66.7[d]	0.95
octane	0.7[b]	1.8 ± 0.3	1.8[d]	1.00
ethylbenzene	2.4[b]	6.9 ± 0.4	6.5[d]	1.06
o-xylene	3.2[b]	9.2 ± 0.4	8.7[d]	1.06
m,p-xylenes	8.3[b]	21.7 ± 1.3	22.5[d]	0.96
nonane	2.4[b]	5.1 ± 0.2	5.4[d]	0.94
decane	2.6[b]	5.9 ± 0.8	5.3[d]	1.11

[a] % v/v. [b] % w/w. [c] Based on an injection of 27 mL of mixture and a chamber volume of 20.44 m^3. [d] Based on an injection of 28 μL of mixture, a density of 0.861 g/mL, and a temperature of 25 °C.

The concentrations of the hydrocarbons were determined by means of a Spectra-Physics SP-4000 chromatographic integration system. The chromatographs were calibrated with National Bureau of Standards hydrocarbon standards (4.05 ± 0.04 ppm methane, 0.991 ± 0.010 ppm propane in air, and 9.42 ± 0.09 ppm propane in air) by using both direct injection of 0.5 mL and cryogenic preconcentration. Calibrations for other hydrocarbons were obtained from published response factors (*25*).

Accuracy and Precision. The accuracy of the technique was checked by experiments whereby known hydrocarbon concentrations similar to those observed in the urban atmosphere were injected into the CSIRO smog chambers. These comprise two 20-m^3 cubical Teflon boxes, both of which may be housed in the dark or exposed to sunlight (*26*). The present experiments were conducted in the dark. Samples were collected and analyzed in the usual way. The air in the chambers was supplied by a clean air plant that produced hydrocarbon concentrations of less than 0.1 ppbv of an individual species. In five experiments a volume of a C_2–C_4 gaseous hydrocarbon mixture was injected into the chambers. The concentrations of the hydrocarbons in the mixture were certified by the supplier (Commonwealth Industrial Gases) and checked in this laboratory by the direct injection of 0.5 cm^3 of the mixture into the gas chromatograph by using a gas sampling valve. The certified values of the concentrations of the six hydrocarbons and our determinations agreed to within ±5% in all cases. In each experiment 27 mL of this mixture was added to the chambers. Table Ia shows the observed and expected concentrations. The values agree to within ±4% for concentrations in the range 3.8–56.1 ppbv.

Similarly, in a further five experiments, a volume of a mixture of the solvents used in Sydney was injected. The composition of the solvent mixtures was determined by direct injection to the gas chromatograph. In each experiment 28 μL of the mixture was added to the chambers. Table Ib shows the observed and expected concentrations

Table II. Atmospheric Hydrocarbon Analysis: Precision of Method

hydrocarbon	method	no. of duplicates	av concn, ppbv	range, ppbv	rel std dev, %
ethane	C_2–C_6	71	9.4	0.8–42.4	9.1
ethylene	C_2–C_6	68	15.3	0.9–57.4	9.8
acetylene	C_2–C_6	66	12.1	0.8–39.6	8.7
propane	C_2–C_6	67	7.2	0.3–44.9	10.3
propylene	C_2–C_6	73	9.3	0.5–57.2	7.5
butane	C_2–C_6	72	9.5	0.8–52.0	7.5
isobutane	C_2–C_6	72	5.8	0.5–30.5	7.0
pentane	both	117	6.6	0.5–23.5	6.5
isopentane	both	135	11.2	1.0–46.9	7.0
hexane	both	109	2.8	0.2–13.4	8.1
2-methylpentane	both	127	3.3	0.3–12.2	9.3
3-methylpentane	both	114	2.1	0.2–6.9	8.2
benzene	C_4–C_{10}	71	3.3	0.3–11.3	8.8
2-methylhexane	C_4–C_{10}	62	1.7	0.1–7.0	8.8
toluene	C_4–C_{10}	66	11.4	1.0–36.8	8.7
octane	C_4–C_{10}	61	0.5	0.1–2.1	11.7
ethylbenzene	C_4–C_{10}	62	1.8	0.2–8.6	9.4
m,p-xylenes	C_4–C_{10}	64	5.0	0.6–23.3	9.8
o-xylene	C_4–C_{10}	64	2.0	0.3–11.0	8.9
nonane	C_4–C_{10}	56	0.4	0.1–1.6	11.3
1,2,4-trimethylbenzene	C_4–C_{10}	55	1.7	0.2–7.6	14.2
m,p-ethyltoluenes	C_4–C_{10}	56	1.4	0.2–6.7	12.0
decane	C_4–C_{10}	54	0.7	0.1–3.3	10.2

for some representative C_7–C_{10} species. With one exception the values agree to within ±6% for concentrations in the range 1.8–66.7 ppbv. The exception was decane, which in some cases was not resolved from an adjacent peak.

The accuracy observed in these two sets of experiments is excellent considering the cumulative uncertainties in the chamber volumes, in the volumes added to the chambers, and in the composition of the mixtures. It may be assumed that equivalent accuracies would be observed for C_5–C_6 hydrocarbons.

The samples in these experiments were analyzed at periods ranging from 1 to 8 days after they had been collected from the chambers. The variation in storage period had no detectable effect on the concentrations observed; the standard deviations obtained are within those observed for duplicate reproducibility (see below). This suggests that the glass containers are a reliable alternative to stainless steel containers in terms of their storage capabilities.

The precision of the technique was examined by an analysis of the reproducibility of duplicates in the atmospheric analyses. A preliminary consideration of the data showed that the reproducibility was largely independent of concentration in the range 0.1–50 ppbv. In these circumstances a pooled standard deviation, S, can be calculated for each hydrocarbon by performing a log-transformation on the data; S is then given by

$$S^2 = \frac{1}{2N}\sum_{j=1}^{N}\left(\ln\left(\frac{x_{1j}}{x_{2j}}\right)\right)^2$$

where x_{1j} and x_{2j} are the duplicate values and N is the number of duplicates. Confidence limits for some observation x are given by $xe^{\pm S}$.

The data for 23 hydrocarbons were examined; of these 7 were determined by the C_2–C_6 method, 11 by the C_4–C_{10} method, and 5 by both methods. At least 50 duplicate pairs were examined for each compound. Since $e^{\pm S}$ is approximately equal to $1 \pm S$ for small S, then S represents the relative standard deviation. Table II presents the details of this analysis. The relative standard deviations, derived as above, lie in the range 6.5–14.2% and for most compounds are less then 10%. The rather high relative standard deviations for C_9 aromatics and decane may be due to the lack of resolution in this region of the chromatogram. 1,2,4-Trimethylbenzene, in particular, was often not fully resolved from an adjacent peak. It is perhaps worth emphasizing that the figures presented in Table II pertain to a method applied to a large number of samples in a concentration range of 0.1 to about 50 ppbv collected at various times and places. The errors show what can be expected with the sampling and storage time differences experienced in the circumstances and the chromatographic reproducibility and integrator responses experienced over a wide range of concentrations.

The concentrations of the C_5–C_6 hydrocarbons could be determined by both methods. The overlap between the two methods for these species was good and of the same order as the reproducibility between duplicates.

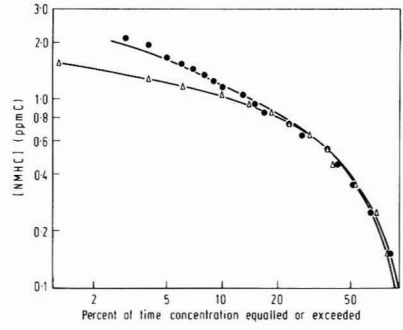

Figure 1. Frequency distribution of non-methane hydrogen concentrations [NMHC] in the Sydney atmosphere: (●) this work (140 samples, September 1979 to June 1980); (△) data of Post (ref 5, 836 samples, 1975–1977).

Results and Discussion

Non-Methane Hydrocarbon Concentrations in Sydney. Before proceeding to the concentrations of individual hydrocarbons, the major aim of this study, it is appropriate to consider briefly the values for [NMHC] which can be derived from the present data. In particular, it is useful to compare the data with the more extensive data for [NMHC] in Sydney obtained by Post (*5*). Post's data were obtained at 47 sampling sites on 836 occasions with a continuous hydrocarbon analyzer that did not discriminate between different hydrocarbons. Our data for [NMHC] were obtained by summing the concentrations of individual species.

Figure 1 shows frequency distributions of [NMHC] derived from the two sets of data. The general similarity between the two distributions is noteworthy. It provides evidence that the present data are broadly representative of atmospheric conditions in Sydney. Whether the small difference in absolute concentrations is to be attributed to different conditions prevailing in the different sampling periods or at the different sampling sites or to a systematic discrepancy between the measuring techniques is not clear. The lack of agreement at the high-concentration end of the frequency distribution is probably due to two factors: first, in the present study there were relatively few samples

Table III. Average Hydrocarbon Concentrations and Composition in Sydney's Air

hydrocarbon[a]	av concn,[b] ppbv	mol %	wt %
ethane	7.5	6.2	2.9
ethylene	12.5	10.4	4.5
acetylene	10.1	8.4	3.4
propane	5.9	4.9	3.3
propylene	7.4	6.1	4.0
methylacetylene	0.5	0.4	0.2
butane	7.5	6.2	5.6
isobutane	4.7	3.9	3.5
1-butene	1.0	0.8	0.7
isobutene	1.4	1.2	1.0
trans-2-butene	1.1	0.9	0.8
cis-2-butene	1.0	0.8	0.7
pentane	5.0	4.1	4.6
isopentane	9.0	7.5	8.3
1-pentene	0.4	0.3	0.3
trans-2-pentene	0.6	0.5	0.5
cis-2-pentene	0.7	0.6	0.7
2-methyl-1-butene	0.5	0.4	0.5
2-methyl-2-butene	1.3	1.0	1.1
cyclopentane	0.8	0.6	0.7
hexane	2.1	1.7	2.3
2-methylpentane	2.6	2.2	2.9
3-methylpentane	1.6	1.4	1.8
2,2-dimethylbutane	0.5	0.4	0.6
2,3-dimethylbutane	0.9	0.7	1.0
methylcyclopentane	1.2	1.0	1.2
cyclohexane	0.9	0.7	1.0
benzene	2.6	2.2	2.6
heptane	0.7	0.5	0.8
2-methylhexane	1.2	1.0	1.5
3-methylhexane	0.8	0.7	1.0
2,4-dimethylpentane	0.7	0.6	0.9
methylcyclohexane	0.6	0.5	0.8
1,3-dimethylcyclopentanes	0.2	0.2	0.3
toluene	8.9	7.4	10.5
octane	0.4	0.3	0.5
2,2,4-trimethylpentane	1.2	1.0	1.8
other C_8 alkanes	2.0	1.6	2.9
ethylbenzene	1.3	1.1	1.7
m,p-xylenes	3.9	3.3	5.3
o-xylene	1.5	1.2	2.0
nonane	0.4	0.3	0.6
propylbenzene	0.4	0.3	0.6
1,2,4-trimethylbenzene	1.3	1.1	2.0
1,3,5-trimethylbenzene	0.5	0.4	0.7
m,p-ethyltoluenes	1.1	0.9	1.7
o-ethyltoluene	0.4	0.3	0.6
decane	0.5	0.4	1.0

[a] [NMHC] = 0.55 ppmC. [b] Based on 140 samples at Eastern Suburbs Hospital (ESH), Goat Island (GI) and Rozelle Hospital (RH), September 1979 to June 1980.

with high concentrations; second, Post's data were restricted to the summer months whereas the present work includes measurements made in May and June. The concentrations are likely to be higher in these months because of lower inverstion heights consequent on the more stable meteorology.

Composition of Atmospheric Hydrocarbons in Sydney. The average atmospheric concentrations of the 48 hydrocarbons regularly measured in Sydney's air during the present work are given in Table III. The averages are based on 140 samples collected on 30 days at Goat Island, Rozelle Hospital, and Eastern Suburbs Hospital. These components comprise at least 90% by weight of the total non-methane hydrocarbons; hence although over 200 hydrocarbons and other organic species are likely to be found

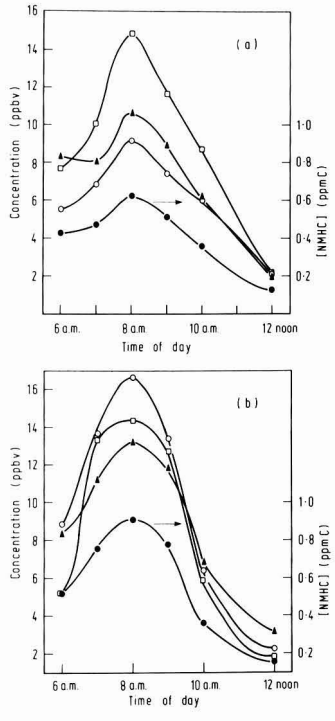

Figure 2. Diurnal variation of average individual hydrocarbon concentrations and NMHC at (a) Eastern Suburbs Hospital, (b) Goat Island and Rozelle Hospital (combined): (□) acetylene; (○) isopentane; (▲) toluene; (●) NMHC.

in Sydney's air (*27*), the number of compounds that contribute significantly to the total [NMHC] is much smaller. On a weight basis the most prevalent species are toluene, isopentane, butane, *m,p*-xylenes, pentane, and ethylene; on a volume basis, they are ethylene, acetylene, isopentane, toluene, butane, and ethane. Overall the results show the hydrocarbon composition of Sydney's air to be 53% w/w (of the NMHC) alkanes, 15% olefins, 28% aromatics, and 3.5% acetylene. The cycloolefins cyclohexene and methylcyclopentene were detected by GC/MS and found to be minor constituents (<1% w/w) of Sydney's atmosphere. They were not measured routinely in the present work. Examination of diurnal behavior was based on a number of key compounds: acetylene, for which vehicle exhaust is the dominant source (*28*); isopentane, which comes from both exhaust and evaporative emissions (*7*); toluene, which comes from exhaust, evaporative and solvent emissions (*7*). In Figure 2 the average concentrations of these compounds (and [NMHC]) are plotted as a function of time of day for the two sampling locations (Goat Island and Rozelle Hospital being close enough together to be considered as one site). Concentrations rise to a maximum at 8 a.m. and fall to a minimum at 12 noon. Similar behavior was observed for all the individual hydrocarbons measured and for NHMC at both sites. This suggests that the dominant effect in the early morning is the increase in traffic density even for compounds that originate, in part, from sources other than vehicle exhaust. The increase in traffic density will increase both exhaust and vehicle evaporative emissions during the early morning. As expected, the relative increase in the concentration of toluene, which has a significant nonvehicular source, is less than that for acetylene which is derived only from exhaust. In the latter part of

Table IV. Atmospheric Hydrocarbon Composition of Various Cities

hydrocarbon class	[NMHC], % (ppmC basis)						
	Sydney	Houston[a]	Philadelphia[a]	Baltimore[a]	Newark[a]	Boston[a]	Washington[a]
alkanes	50.4	64	67	58	61	66	59
alkenes	14.8	11	6[b]	10	11	8	6[b]
aromatics	29.5	23	25	29	26	23	31
acetylene	3.6	1.5	1.3	2.3	1.6	2.1	2.5

[a] Reference 29. [b] Does not include ethylene.

the morning the dominant effect is meteorology in the form of decreased atmospheric stability due to surface heating and increased windspeed, resulting in an increasing mixing height.

Comparison with Other Cities. A quantitative comparison was made between the atmospheric hydrocarbon compositions of Sydney and those of six cities of comparable size in the U.S. (*11*, *29*, *30*). More extensive comparisons are precluded by the lack of suitable data for other cities (see however below). The hydrocarbons toluene, isopentane, and butane were prominent at every location. On a weight basis the top six compounds included these three at every location. Other prominent species are ethane, ethylene (not reported for the cities studied by Sexton and Westberg (*29*) because of sampling problems), propane, isobutane, pentane and *m,p*-xylenes. Inspection of the referenced data will show that the overall composition of the atmosphere (as shown in Table IV) is remarkably consistent from one city to another. The contribution to the total [NMHC] by the various hydrocarbon types is 50–67% (percentage of NMHC, ppmC basis) aliphatics, 8–15% olefins, 23–31% aromatics, and 1.3–3.6% acetylene for all locations.

Data available for other cities, notably Delft (*30*, *31*), Zurich (*13*), Paris (*14*), the Cologne–Bonn area (*32*), six large cities in the USSR (*18*), and Houston (*33*) are insufficiently complete to allow them to be compared quantitatively with the present results. Nevertheless, qualitatively, it is clear that our data show marked similarities with those for Northern Hemisphere cities. Toluene, *m,p*-xylenes, isopentane, and butane make significant contributions to the weight of NMHC in the atmosphere of these cities as they do in Sydney.

The models that are currently used to make control predictions for photochemical smog (*3*, *6*) require hydrocarbon composition data of this complexity. The data obtained in the present work and in the other studies show a consistent pattern in terms of composition. It is possible therefore to make a reasonable estimate of the composition of the air in cities for which no sampling data exists. Such variation as does exist is probably due to differences in the gasoline and solvent compositions in the different cities and in the magnitude of industrial emissions.

Conclusions

Rapid and precise techniques for the sampling and analysis of atmospheric hydrocarbons have been developed. With these techniques, the hydrocarbon composition of Sydney's atmosphere has been determined on about 150 occasions at sites representative of vehicular and industrial emissions. The diurnal behavior of the concentrations of individual hydrocarbons is dominated by the early morning increase in traffic density and by meteorology.

The composition of Sydney's air is consistent with that found in cities in Europe and the United States.

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Calibration Procedure for PAN Based on Its Thermal Decomposition in the Presence of Nitric Oxide

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■ A calibration procedure for peroxyacetyl nitrate (PAN) is presented. The procedure is based on the thermal decomposition of PAN in the presence of NO. Experimental and computer modeling results are shown to demonstrate the stoichiometry beween PAN and NO. Benzaldehyde is added to the PAN–NO reaction mixture to control the chemistry and eliminate interference from system contaminations. PAN calibration is based on the measurement of NO by a standard NO chemiluminescent analyzer. The PAN calibration can thus be traced to National Bureau of Standards (NBS) NO standards.

Introduction

Peroxyacetyl nitrate (PAN) is an important product of photochemical smog. It has been shown to be a strong eye irritant (*1*) and a phytotoxicant (*2*). Peroxyacetyl nitrate is not a chemically stable compound and undergoes thermal decomposition. Because of this chemical instability PAN has received interest as an important source of NO_2 in sustaining photochemical smog (*3*). Despite the importance of PAN information to our understanding of ozone–precursor relationships, the ambient air data base for this compound is sparse. The reason for the limited information is the need for a sophisticated instrumental procedure for making ambient air PAN measurements. The general procedure consists of a gas chromatograph (GC) equipped with an electron capture detector (ECD). Another difficulty is the performance of accurate calibration procedures, especially at field site locations.

Past calibration procedures for PAN involved the use of sophisticated infrared (IR) techniques (*4*, *5*). Due to the delicate nature of the IR system, calibrations of the PAN GC equipment are generally performed at a central laboratory facility before taken to field sampling sites. Occasionally, field calibration for PAN was performed by preparing a PAN standard in a 2-mil Tedlar bag (*6*). The prepared standard was calibrated by IR procedures, then transported to the field site for PAN GC–ECD calibration. The PAN standard stored well in the conditioned bag in controlled laboratory conditions. However, PAN loss increased significantly when subjected to severe increases in ambient temperature. Consequently, precautions had been taken to avoid drastic environmental changes between the time the PAN sample was calibrated and taken to the site for utilization.

A colorimetric procedure was reported for PAN determination and is particularly suitable for calibration of field PAN GC systems (*5*, *7*). The procedure involves the collection of PAN in a 1% potassium hydroxide solution. Peroxyacetyl nitrate undergoes hydrolysis to produce a quantitative yield of nitrite ions that are then analyzed by the Saltzman absorbing reagent. This procedure is more portable than the IR approach but requires a skilled technician, expert in wet chemistry and UV spectrophotometry. High PAN concentrations also should be used for improved color development, i.e., concentrations 1–2 orders of magnitude above typical ambient levels of PAN.

An alternate approach is suggested here that makes use of the thermal dissociation of PAN in the presence of NO. In this procedure, PAN calibration is based on a quantitative reaction with NO. The thermal dissociation of PAN has been reported by several investigators (*3*, *8*, *9*). In these studies, PAN was shown to be an unstable molecule in equilibrium with acetylperoxy radicals and NO_2:

$$\mathrm{PAN} \rightleftarrows \mathrm{CH_3C(O)O_2\cdot} + \mathrm{NO_2} \qquad (1)$$

Ordinarily in the absence of sunlight and reactive compounds, PAN can remain in equilibrium for some time, since the only apparent important removal reaction is the chain termination recombination of two acetylperoxy radicals. However, in the presence of NO the equilibrium is destroyed by the acetylperoxy radical reacting preferentially with NO to produce NO_2. The acetoxy radical produced by this reaction undergoes decomposition and in the presence of O_2 further oxidizes NO molecules to NO_2. In an air system, the reaction scheme is given by reactions 2–7.

$$\mathrm{CH_3(O)O_2\cdot} + \mathrm{NO} \rightarrow \mathrm{CH_3C(O)O\cdot} + \mathrm{NO_2} \qquad (2)$$

$$\mathrm{CH_3C(O)O\cdot} \xrightarrow{\mathrm{O_2}} \mathrm{CH_3O_2\cdot} + \mathrm{CO_2} \qquad (3)$$

$$\mathrm{CH_3O_2\cdot} + \mathrm{NO} \rightarrow \mathrm{CH_3O\cdot} + \mathrm{NO_2} \qquad (4)$$

$$\mathrm{CH_3O\cdot} + \mathrm{O_2} \rightarrow \mathrm{HO_2\cdot} + \mathrm{HCHO} \qquad (5)$$

$$\mathrm{HO_2\cdot} + \mathrm{NO} \rightarrow \mathrm{OH\cdot} + \mathrm{NO_2} \qquad (6)$$

$$\mathrm{OH\cdot} + \mathrm{NO} \rightarrow \mathrm{HONO} \qquad (7)$$

The reaction scheme shows that four molecules of NO are consumed for every molecule of PAN decomposed. Such a stoichiometry, if consistent, would serve as a suitable basis to calibrate prepared samples of PAN and ultimately a PAN GC–ECD system. This calibration can be accomplished with an ordinary NO chemiluminescent instrument found in most field laboratories. The NO instrument could be used to measure NO lost by its reaction with a prepared uncalibrated sample of PAN. The original concentration of PAN can be calculated to be one-quarter the amount of NO reacted.

This paper presents the experimental and modeling data concerning the stoichiometry of the NO and PAN reaction and suggests the application of this procedure for PAN calibration.

Experimental Section

Peroxyacetyl nitrate and NO measurements in these studies were performed with standard GC–ECD and chemiluminescent techniques. The PAN GC procedure consists of a 90 cm × 3.2 mm o.d. glass column packed with 10% Carbowax 600 on 60–80 mesh Gas Chrom Z. A 1-Ci tritiated scandium constant-current electron capture detector (Analog Technology Corp., Pasadena, CA) was used in these experiments. Methane–Argon (P-5 mixture, Linde Division, Union Carbide, Somerset, NJ) was used as the carrier gas and detector sensitizing gas. The column flow rate was maintained at 70 cm^3/min. Both column and detector were operated at room temperature, 23–25 °C. Occasionally, the detector was heated overnight at 160 °C to recondition detector surfaces and improve sensitivity. Recalibrations of the system were performed after each treatment. Calibrations of the GC system were performed by the analyses of air-diluted mixtures of a PAN standard. Measured aliquots of the PAN standard were injected into metered volumes of zero-grade air. Sample injections of 5 cm^3 were made onto the GC system with an automated valve. The PAN standard was prepared from the photodissociation of chlorine in the presence of acetaldehyde and NO_2 (*10*). The prepared standards were calibrated with IR techniques (*4*, *5*). The PAN standards used in this study ranged from 15 to 35 ppm.

The NO measurements were made with a chemiluminescent analyzer (Model 8440, Monitor Labs, San Diego, CA). Calibration of the system was performed by the dynamic dilution (Model 101, ThermoElectron Corp., Hopkinton, MA) of a certified 53.9 ppm NO in N_2 standard (AIRCO Industrial Gases, Murray Hill, NJ).

The PAN–NO reaction studies were performed in 50–100-L 2-mil Tedlar (poly(vinyl fluoride) (PVF), E. I. du Pont de Nemours and Co., Wilmington, DE) bags. A measured aliquot of a PAN standard was injected into a metered volume of zero-grade air. A period of 10–30 min was allowed to acclimate the bag surface to PAN. After this time, an aliquot of the 53.9 ppm NO in N_2 standard was injected into the bag to commence the reaction. A period of 3–5 min for mixing was permitted before the first sample was taken. Consequently, the first experimental point is actually 3–5 min of reaction time. In the initial studies, samples for PAN and NO were taken within 1 or 2 min of each other. In later runs, the reaction system was modified to permit simultaneous sampling of NO and PAN.

For the free radical scavenging experiments, diethylhydroxylamine (DEHA) or benzaldehyde was added to the reaction mixture. In these instances, liquid injections of the compounds were made in the reaction bags 10 min prior to the addition of either PAN or NO. The presence of benzaldehyde in the reaction mixture can be disruptive to the GC analysis of PAN. Benzaldehyde is a conjugated electrophore (*11*) that will capture electrons and thus respond in the ECD. Its retention time on the GC column under our conditions is approximately 120 min. In a typical PAN–NO reaction study, samples were taken every 20 min. Since normally more than 75% of the PAN reacted in 120 min, at least five analyses of PAN could be made before the benzaldehyde from the first sample eluted from the GC column. However, an additional 2–3-h waiting period was required to elute all the benzaldehyde from the other subsequent samples. An alternate approach was later used in these studies. A GC column back-flush valve was installed to remove benzaldehyde from the column before the injection of proceeding samples. The procedure consisted of a 5-min front-flush period followed by a 14-min back-flush time.

Results and Discussion

The approach presented here is based on the stoichiometric reaction of PAN with NO. The stoichiometry is expected to be four molecules of NO reacted per molecule of PAN based upon the eight-step reaction mechanism (reactions 1–7). This mechanism, however, is oversimplified and overlooks other important reactions that can also occur. For example, the products, NO_2 and HCHO, can compete with NO for OH (reaction 7). Rate constants for NO_2 and HCHO with OH are approximately 2 times greater than the NO + OH reaction (*12*). The reaction of HCHO with OH can act, in effect, as a chemical amplifier. Such a mechanism involves reaction 8 followed by reac-

$$\mathrm{HCHO} + \mathrm{OH}\cdot \xrightarrow{O_2} \mathrm{HO_2}\cdot + \mathrm{CO_2} \qquad (8)$$

tions 6 and 7. This mechanism results in the reaction of two NO molecules instead of just the one converted by reaction 7. The reaction of NO_2 with OH is chain terminating, resulting in the production of HNO_3 as shown in reaction 9. Consequently, the simple stoichiometry of

$$\mathrm{NO_2} + \mathrm{OH}\cdot \rightarrow \mathrm{HNO_3} \qquad (9)$$

four NO molecules reacting with one of PAN is not quite correct, and the initial concentration conditions for PAN and NO are an important consideration when conducting these studies.

To determine the stoichiometry more accurately, we used the CHEMK computer photochemical model (*13*) of the U.S. Environmental Protection Agency. The model's reaction mechanism includes all known important reactions involving the compounds and radical species expected from the PAN and NO reaction. The model also offered the opportunity to investigate the effects of concentration conditions on the NO and PAN stoichiometry. Peroxyacetyl nitrate concentrations in the model simulation runs ranged from 10 to 100 ppb. Nitric oxide concentration was 200 ppb for each run. Initial concentration ratios for NO to PAN ranged from 20:1 to 2:1. All photolytic reactions of the model were removed. Temperature conditions were constant at 25 °C.

The results for five computer model simulation runs at initial NO–PAN concentration ratios ranging from 20:1 to 2:1 are given in Table I. In each simulation, the stoichiometry given as Δ[NO]:Δ[PAN] was lower than the expected value of 4. For the two simulation runs in which the initial NO concentration is in large excess to PAN, i.e., 20:1 and 10:1, the determined Δ[NO]:Δ[PAN] ratio was within 5% of the expected stoichiometry and is certainly within the error limits of the reaction rate constants included in the model. The fact that the determined Δ[NO]:Δ[PAN] for all these simulation ratios was less than

Table I. Stoichiometric Ratios Δ[NO]:Δ[PAN] from Modeling Simulations of PAN and NO Mixtures in the Dark[a]

[PAN], ppm	initial [NO]:[PAN]	av Δ[NO]:Δ[PAN]
0.010	20:1	3.89
0.020	10:1	3.80
0.040	5:1	3.67
0.080	2.5:1	3.56
0.100	2:1	3.54

[a] NO concentration for all runs was 0.200 ppm.

Table II. Experimental Results for the Reaction of NO with PAN in 60-75-L 2-mil Tedlar PVF Bags at 22-24 °C[a]

run	initial [PAN], ppb	initial [NO], ppb	Δ[NO]:Δ[PAN]
1	9.5	355	6.7
2	18.1	162	6.2
3	8.3	180	5.8
4	18.1	185	6.1
5	20.9	190	6.5
6	20.3	180	5.5
7	19.2	270	4.7
8	21.9	265	5.0
9	22.1	255	5.1
10	17.3	231	4.3
11	19.3	222	3.5
12	15.8	268	4.2
13	22.0	250	3.9
14	21.2	282	3.8
15	24.4	345	3.5
16	21.3	260	4.1
			av 4.9 ± 1.1

[a] Run times ranged from 120 to 160 min.

4 suggests that the reaction of HCHO with OH may not be as important as earlier suggested. Stoichiometric ratios greater than 4 would be expected if reaction 8 contributed more significantly to the oxidation of NO. The observation of decreased stoichiometric ratios when initial [NO]:[PAN] ratios are lowered indicates that NO_2 is competing with NO for OH (reaction 9).

The model simulation suggests that the NO–PAN reaction is reasonably uniform, resulting in consistent stoichiometry through the reaction period. The model runs also indicates that initial [NO]:[PAN] conditions are important. Excess NO should be used to obtain stoichiometric ratios near the theoretical value of 4.

Having theoretically shown that NO can be used to quantitatively titrate PAN, laboratory tests of the NO–PAN mixtures were performed. The results for 16 experimental runs are given in Table II. In keeping with modeling observations, the [NO]:[PAN] conditions for all 16 runs was selected near 10:1 or greater to ensure excess NO and minimize OH reaction with NO_2. Two of the runs had initial [NO]:[PAN] conditions exceeding 20:1.

The results in Table II indicate that the experimental stoichiometric ratios (Δ[NO]:Δ[PAN]) are not as consistent as those predicted by the model. These values were obtained by applying a linear regression equation to the observed data pairs. The slope determined from this mathematical treatment was Δ[NO]:Δ[PAN]. Experimental stoichiometric ratios ranged from 3.5 to 6.7 with the average ratio determined to be 4.9 ± 1.1. The precision of the average stoichiometric ratio is a rather poor ±22%. Just 7 of the 16 experimental ratios were within 10% of the 3.9 model estimate, and four of these ratios were

Table III. Stoichiometric Ratios Δ[NO]:Δ[PAN] from Modeling Simulations of a 0.020 ppm PAN + 0.200 ppm NO Mixture for Various Concentrations of Added Acetaldehyde

C_2H_4O, ppm	av Δ[NO]:Δ[PAN]	C_2H_4O, ppm	av Δ[NO]:Δ[PAN]
0.000	3.80	0.050	5.26
0.010	4.09	0.100	6.59

greater than 4.0. These large experimental stoichiometric ratios suggest that other reactions not considered in the model were occurring. Also the contribution of these reactions was inconsistent, resulting in a rather wide range of experimental ratios. These reactions probably involved some type of contamination that was further consuming the NO.

The mechanism is similar to that outlined earlier for HCHO reaction with OH and would include the reactions given in eq 10–13. The organic contaminate (VOC) pro-

$$VOC + OH\cdot \rightarrow RO_2\cdot + H_2O \quad (10)$$

$$RO_2\cdot + NO \rightarrow RO\cdot + NO_2 \quad (11)$$

$$RO\cdot + O_2 \rightarrow HO_2\cdot + VOC^* \quad (12)$$

$$HO_2\cdot + NO \rightarrow OH\cdot + NO_2 \quad (13)$$

duces RO_2 and HO_2 radicals, which oxidize additional molecules of NO to NO_2. The extent of this interference depends upon the chemical nature of the organic contaminate. The oxidized product of VOC (VOC*) could continue to produce RO_2 and HO_2 radicals.

The source of contamination is unclear. Bag surface outgassing contamination is a likely explanation (*14, 15*). However, some unreacted acetaldehyde was also probably injected into the reaction chamber during the initial injection of PAN. As mentioned earlier, the PAN used in these experiments was prepared by the photodissociation of chlorine in the presence of acetaldehyde and NO_2. The procedure's efficiency for preparing PAN is dependent upon irradiation time and the original stoichiometric relationship of acetaldehyde, chlorine, and NO_2. In our prepared standard, we estimated that 60–65% of the acetaldehyde was converted to PAN. Consequently, unreacted acetaldehyde also was injected into the reaction chamber. However, similar injections of the PAN standard were used for most of the 16 experimental runs. Acetaldehyde impurities, therefore, should have been constant, yet the observed Δ[NO]:Δ[PAN] ratios were not. We were unable to determine the exact cause of the inconsistent Δ[NO]:Δ[PAN] ratio observed in these experiments. Perhaps both acetaldehyde and bag outgassing contamination were responsible for these inconsistent ratios.

Since we were unable to explain the experimental results, the CHEMK model was used again to test the effect organic contribution had on the Δ[NO]:Δ[PAN] ratio. Acetaldehyde was used as a surrogate for the organic contamination, since the pertinent reactions were already in the model. Three computer simulations were performed consisting of an identical mixture of PAN and NO at different initial concentrations of acetaldehyde. The results, given in Table III, show that the addition of just 10 ppb acetaldehyde resulted in a 7% increase in Δ[NO]:Δ[PAN]. Increasing the acetaldehyde concentration an order of magnitude resulted in a 75% increase in the stoichiometric ratio. Comparison of the results in Table III with the experimental Δ[NO]:Δ[PAN] ratios in Table II indicates that the contamination levels in experimental

runs 1–6 were equivalent in reactivity to 50–100 ppb acetaldehyde. The results suggest that chamber contamination levels must be controlled to obtain a usable Δ[NO]:Δ[PAN] ratio for future calibration activities. For experimental runs 7–16 in Table II, precautions were taken to minimize contamination by reflushing the reaction chamber several times with clean air before usage to minimize surface contamination. This action resulted in a lower Δ[NO]:Δ[PAN] ratio of 4.2 and an improved standard deviation, ±0.57. The 4.2 value for the stoichiometric ratio is within 10% of the model estimate of 3.9. The precision of this experimental value is a much improved 13.6% and is certainly comparable to other field calibration procedures for PAN.

In retrospect, acetaldehyde may have been a poor selection as a surrogate for the organic contamination compounds, because acetaldehyde will regenerate PAN when it reacts with OH in the presence of NO_2. Consequently, the 75% increase in the Δ[NO]:Δ[PAN] ratio for 100 ppb acetaldehyde is probably a conservative estimate for a similar quantity of contamination.

Efforts to improve the precision of the experimentally determined Δ[NO]:Δ[PAN] ratio beyond ±13.6% would involve one or two approaches. First, the outgassing contamination from the reaction chamber surface should be minimized to an even greater extent. These attempts, however, have proven to be futile in the past (*14*, *15*). Frequent reflushing with clean air, mild heat treatment, and exposure of the surface to sunlight irradiation have reduced the contamination but have not eliminated it. The other approach would control the chemistry of the PAN and NO reaction mechanism, in particular the reactions involving OH. Heicklen et al. (*16*, *17*) have proposed the use of free radical scavengers to inhibit the production of photochemical smog. These scavengers preferentially react with OH to diminish its reaction with hydrocarbons, producing RO_2 and HO_2 radicals that ultimately oxidize NO to NO_2.

Based on past experience we decided that our chances for improving the techniques would be greater if we used the radical scavenger approach rather than to reduce contamination. One such additive compound was diethylhydroxylamine (DEHA). Diethylhydroxylamine was expected to remove OH, preventing a significant contribution from reaction 7 and resulting in an expected stoichiometric ratio of 3. In laboratory tests, however, inconsistent stoichiometric ratios were observed. In three such tests Δ[NO]:Δ[PAN] ranged from 2.4 to 3.3, representing essentially a deterioration of the precision range observed in the experimental runs without DEHA. An unexplained NO response was observed from gas-phase mixtures of DEHA in air. In further tests, DEHA apparently was reacting with PAN, most likely the peroxyacetyl radical. Diethylhydroxylamine added to PAN–air mixtures increased PAN loss rates from 2–3%/h by about an order of magnitude higher. Because the chemistry of DEHA is not well understood (*18*), further laboratory tests using DEHA to control OH chemistry were discontinued.

Another reported free radical scavenger is benzaldehyde (*19*). Benzaldehyde is an aromatic aldehyde that reacts with OH in much the same way as the aliphatic aldehydes. In the presence of NO_2, a PAN-type compound, peroxybenzoyl nitrate (PBzN) is formed. Peroxybenzoyl nitrate, like PAN, undergoes thermal decomposition and oxidizes NO to NO_2. Unlike its aliphatic counterpart, the aromatic radical is stabilized by the aromtic ring and does not break apart to generate RO_2 and HO_2 radicals in the presence of O_2. Thus, no chemical amplification effect exists for

Table IV. Stoichiometric Ratios Δ[NO]:Δ[PAN] from Computer Simulations of PAN and NO Mixtures in the Dark in the Presence of 2.00 ppm Benzaldehyde[a]

[PAN], ppm	initial [NO]:[PAN]	av Δ[NO]:Δ[PAN]
0.010	20:1	4.88
0.020	10:1	4.78
0.040	5:1	4.52
0.080	2.5:1	4.19
0.100	2:1	4.13

[a] NO concentration for all runs was 0.200 ppm.

oxizing NO to NO_2. The general mechanism for the addition of benzaldehyde is given in reactions 14–20. The

$$C_6H_5\text{–}CHO + OH\cdot \rightarrow C_6H_5C(O)\cdot \quad (14)$$

$$C_6H_5C(O)\cdot + NO_2 \xrightarrow{O_2} C_6H_5C(O)O_2NO_2 \quad (15)$$

$$C_6H_5C(O)O_2NO_2 \rightarrow C_6H_5C(O)O_2\cdot + NO_2 \quad (16)$$

$$C_6H_5C(O)O_2\cdot + NO \rightarrow C_6H_5C(O)O\cdot + NO_2 \quad (17)$$

$$C_6H_5C(O)O\cdot \xrightarrow{O_2} C_6H_5O_2\cdot + CO_2 \quad (18)$$

$$C_6H_5O_2\cdot + NO \rightarrow C_6H_5O\cdot + NO_2 \quad (19)$$

$$C_6H_5O\cdot + NO_2 \rightarrow \text{stable product} \quad (20)$$

mechanism does not generate OH but does oxidize two molecules of NO. If excess benzaldehyde is added to the PAN–NO system, reaction 7 is expected to be strongly depressed. However, the two additional NO molecules oxidized results in a theoretical stoichiometric ratio, Δ[NO]:Δ[PAN], of 5. The pertinent reactions pertaining to the general mechanism outlined by eq 10–16 were added to the CHEMK model to determine a more accurate assessment of the stoichiometric ratio. The results for five model simulations are given in Table IV. Similar initial [NO]:[PAN] ratios used previously (Table I) were used for these runs. Benzaldehyde concentration was selected to be 2.00 ppm.

The results in Table IV show, as in the previous computer simulation without benzaldehyde (Table I), that the stoichiometric ratio, Δ[NO]:Δ[PAN], was somewhat lower for all simulation runs than the theoretical ratios of 5. However, at the higher initial [NO]:[PAN] ratios 20:1 and 10:1, the determined stoichiometric ratios were within a few percent of this theoretical value. As in the case with the previous computer simulation without benzaldehyde (Table I), a decrease in the inital [NO]:[PAN] ratio resulted in a significant decrease of the stoichiometric ratio. For the computer simulation with benzaldehyde (Table IV), an order of magnitude decrease in the initial [NO]:[PAN] ratio from 20:1 to 2:1 resulted in a 15% decrease in the determined stoichiometric ratio. These observations again point out the importance of using excess NO in any future experimental run.

To test the effect of contamination on the stoichiometric Δ[NO]:Δ[PAN] ratio, we ran computer simulations of the PAN, NO, and benzaldehyde mixture at different concentration levels of acetaldehyde. The run conditions and concentrations were similar to those reported earlier without benzaldehyde (Table III). The results, presented in Table V, readily show the OH controlling effect of benzaldehyde by reactions 10–16. The addition of even 100 ppb acetaldehyde only resulted in a 3.6% increase in Δ[NO]:Δ[PAN].

Laboratory experiments were then conducted with mixtures of PAN, NO, and excess benzaldehyde. Five

Table V. Stoichiometric Ratios Δ[NO]:Δ[PAN] from Modeling Simulations of a 0.020 ppm PAN + 0.200 ppm NO + 2.00 ppm Benzaldehyde Mixture for Various Concentrations of Added Acetaldehyde in the Dark

C_2H_4O, ppm	av Δ[NO]: Δ[PAN]	C_2H_4O, ppm	av Δ[NO]: Δ[PAN]
0.000	4.78	0.050	4.86
0.010	4.80	0.100	4.95

Table VI. Experimental Results for the Reaction of NO with PAN in a 75-L 2-mil Tedlar PVF Bag at 24-25 °C[a]

run	initial [PAN], ppb	initial [NO], ppb	initial [benzaldehyde], ppb	Δ[NO]: Δ[PAN]
1	48.8	342	5.00	4.7
2	50.1	348	5.00	4.7
3	50.9	340	1.25	4.4
4	28.1	298	1.25	4.7
5	25.7	301	10.00	4.8
				av 4.7 ± 0.2

[a] Run times ranged from 120 to 160 min.

experimental runs were conducted at three different benzaldehyde concentrations, 1.25, 5.0, and 10.0 ppm. Initial concentrations for PAN and NO ranged from 25 to 50 and 300 to 350 ppb, respectively. The results, given in Table VI, demonstrate that the experimental values of Δ[NO]:Δ[PAN] are quite consistent, ranging from 4.4 to 4.8. The average ratio of 4.7 is quite comparable to the 4.8–4.9 ratio predicted by the computer simulations. The standard deviation value of 0.2 indicates an excellent precision of ±4.2%. The three different benzaldehyde concentrations used apparently had little effect on the observed Δ[NO]:Δ[PAN] ratio. The 1.25-ppm concentration was sufficient to control the fate of OH and suggests that perhaps even lower concentration levels could be used. This concentration could be determined by the model. Three of the five experimental tests were run at initial [NO]:[PAN] ratios of 7, which was somewhat less than the intended 10:1 to 20:1 ratio. This lower ratio did not appear to affect Δ[NO]:Δ[PAN]; however, greater excess NO is recommended.

The improved precision offered by the addition of benzaldehyde to the PAN–NO mixture renders this procedure as the more preferable approach for calibration. The one experimental drawback, mentioned earlier, is the interference of benzaldehyde on the GC–ECD system. However, the back-flush valve arrangement worked well for these experiments and eliminated this problem.

Experimental runs of PAN and NO were conducted to demonstrate the effect that benzaldehyde had on the control of the OH chemistry. In these experiments, new Tedlar reaction chambers were prepared. New bags are known to have higher level of outgassing contamination (*14, 15*). Also, the use of new bags eliminated the possibility of a benzaldehyde memory effect. The bags were filled with room air and stored at 80 °F for 48 h. After that time, aliquots of PAN were injected, and the chambers were conditioned for 6 min or until PAN storage stabilized. At that time, an aliquot of the 53.9 ppm NO in N_2 (certified) standard (AIRCO) was injected into the chambers and measurement of NO and PAN commenced. Peroxyacetyl nitrate and NO losses were sampled for 40 min, resulting in three data pairs. At that point, benzaldehyde was injected to obtain a chamber concentration of 2.00 ppm. Six data pairs for NO and PAN were taken over the next 2 h. The results of two such runs are given in Table

Table VII. Experimental Results for PAN-NO Mixtures in Which 2.00 ppm Benzaldehyde Is Injected after 40-Min Reaction

run	initial [PAN], ppb	initial [NO], ppb	Δ[NO]: Δ[PAN] (0-40 min)	Δ[NO]: Δ[PAN] (40-160 min)
1	22.1	480	7.4	4.8
2	50.1	330	6.0	4.5

VII. The observed stoichiometric ratio Δ[NO]:Δ[PAN] without benzaldehyde exceeded a value of 6 in both experiments, suggesting involvement of contamination in the PAN–NO chemistry. The stoichiometric ratios of 4.5 and 4.8 observed after the addition of benzaldehyde are within the precision limits of the experimentally determined factor, 4.7 ± 0.2.

The experimental runs for these studies were conducted at room temperature (22–24 °C). These temperature conditions were used to control the thermal dissociation of PAN and permit accurate measurements of PAN and NO for reaction periods greater than 120 min. A total of seven data pairs for PAN and NO can be made in this time period. PAN loss at 22–24 °C and 120 min is approximately 85%. Since the sensitivity of the PAN GC–ECD system is about 0.2 ppb, accurate measurements can be made beyond the 120-min reaction time, providing the initial PAN concentration exceeds 8–10 ppb. When room temperature is increased to 30 °C, time to 85% PAN loss would decrease to 41 min. Fewer data pairs of PAN and NO measurements could be accurately made unless the initial PAN concentration is significantly increased. This change in temperature, however, does not affect the Δ[NO]:Δ[PAN] ratio.

Conclusions

The reaction of NO with PAN is a suitable alternate procedure for the calibration of PAN. The procedure recommended here involves the stoichiometric reaction of PAN with NO in the presence of benzaldehyde. The stoichiometric factor, Δ[NO]:Δ[PAN], determined in this work was 4.7 ± 0.2 for PAN–NO mixtures in the presence of excess benzaldehyde. The presence of benzaldehyde serves to control the OH radical chemistry resulting from the PAN and NO reaction mechanism and produces a more precise PAN calibration. In the absence of benzaldehyde, the stoichiometric factor determined was 4.2 ± 0.5. However, we do not recommend using this procedure unless approximate values of PAN are sufficient.

The NO component in these calibrations is traceable to a certified NBS standard and is intrinsically a very accurate approach. The determination of the PAN GC calibration factor is given by

$$\text{PAN GC factor (ppb/mm)} = \frac{\Delta[\text{NO}]\ \text{(ppb)}}{(4.2 \pm 0.5)(\Delta[\text{PAN}]\ \text{(mm)})}$$

for the PAN–NO system or by

$$\text{PAN GC factor (ppb/mm)} = \frac{\Delta[\text{NO}]\ \text{(ppb)}}{(4.7 \pm 0.2)(\Delta[\text{PAN}]\ \text{(mm)})}$$

when benzaldehyde is added to the system to control the OH chemistry. In both equations, Δ[NO] is the loss of NO measured with an NO chemiluminescent analyzer. The Δ[PAN] term is the measured loss of the PAN GC peak in mm (peak heights) over the same reaction period.

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Trace-Metal Adsorption Characteristics of Estuarine Particulate Matter: Evaluation of Contributions of Fe/Mn Oxide and Organic Surface Coatings

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■ Metal solubilization resulting from specific chemical extractions has frequently been employed to define the solid-phase association of trace metals in naturally occurring particulates. Adsorption of Cd and Pb onto the residual surface phase after extraction yields supporting evidence with respect to the influences of extracted components on metal-binding properties. Trace metal binding to surficial sediments in the South San Francisco Bay estuary was examined with the aid of chemical extractant and adsorption techniques. System-composition-dependent adsorption of Cd and Pb onto estuarine sediments behaved in a manner analogous to adsorption onto single-phase hydrous oxide surfaces. Extraction results show Cd, Cu, and Pb to associate with operationally defined organic and/or metal (Fe, Mn) oxide surface coatings. Changes in the Cd and Pb adsorption behavior after specific extractions were consistent with the hypothesis that Fe/Mn hydrous oxides and organic coatings substantially control the sorptive behavior of estuarine particulate matter.

Introduction

Substantial information is currently available demonstrating that many toxic trace metals (e.g., Cd, Pb, Cu) are strongly associated with particulate phases in aquatic environments (*1–4*). These particle-bound metals can be solubilized to varying degrees with specific chemical extractant procedures (*5*, *6*). This information has been utilized to operationally define the metal of interest as being relatively accessible to solution reaction and/or associated with particulate components having different chemical characteristics. It follows that the binding characteristics of particulate surfaces could be important in regulating changes in solid–solution partitioning in response to environmental chemical changes such as variations in solution ionic strength, pH, and ligand and metal concentrations. This is especially important given the accumulating evidence as to the strong correlation between metal speciation (particularly the aquo metal ion activity) and the toxic impact of the metal on exposed biota (*7*, *8*). A fundamental understanding of the fate of trace metals in natural systems requires description of the alterations in metal distribution between particulates and bulk solution which result from variations in chemical conditions occurring, for example, during dredging or estuarine mixing. This understanding hinges to a great extent upon elucidation of the nature of naturally occurring particulate surfaces vis-à-vis adsorption/desorption reactions.

Particulates present in rivers, estuaries, and oceans are comprised of a diverse mixture of component "phases" ranging from clays to metal oxides to organic detritus (*9–11*). A mixture of such materials would be expected to have a wide range of surface chemical properties and, by inference, a wide range of trace-metal adsorption characteristics. This complex situation might be simplified if most particulate surfaces were coated with a limited array of materials, thereby occluding the underlying bulk material matrix and decreasing the degree of surface chemical heterogeneity. Substantial evidence exists suggesting that natural organic compounds (e.g., humics) and the hydrous oxides of iron and manganese are important surface phases in environments ranging from seawater to soils (*12–16*).

Hydrous metal oxide and organic coatings, together with the underlying bulk material matrix, may be combined conceptually to create a model particulate phase with a given metal adsorption behavior. Overall adsorption characteristics of a natural material for a particular trace metal would be expected to vary as the relative proportioning of surface sites among the component metal adsorbing phases changes. This conceptual approach suggests that information concerning the metal adsorption behavior of a single adsorbent phase system might be used to understand the behavior of more complex natural materials. Adsorption studies of single component systems

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have been accomplished for a range of model solids, and the observed experimental behavior has been shown to be consistent with fundamentally based conceptual models (*21*). Pertinent studies have investigated the adsorption/complexation characteristics of humic and hydrous oxide coating materials and have defined their intensity and capacity factors for binding with a number of trace metals. Specifically, natural organic isolates such as humic and fulvic acid compounds have been characterized as to their complexation of Cu, Cd, Pb, and other metals (*17–19*). The adsorption of Cd, Cu, Pb, Zn onto amorphous $Fe_2O_3 \cdot H_2O$ and other hydrous oxides has been studied over a wide range of adsorbate-to-metal concentrations as a function of variable pH (*20, 21*). These studies suggest general characteristics likely to be observed in multicomponent natural solid systems. The results for cation adsorption by hydrous oxides (*20, 22*) can be summarized as follows:

(i) Fractional trace-metal adsorption as a function of pH typically increases sharply over a narrow range of 1 to 2 pH units (the "pH adsorption edge").

(ii) The fraction of metal adsorbed increases with increasing solid concentration at fixed total metal concentration and constant pH. This behavior is directly analogous to the titration of a metal cation with a dissolved complexing ligand (*22*).

(iii) At fixed solids concentration and very low adsorption site occupancies (e.g., less than 1%), fractional metal adsorption increases as the total metal concentration decreases at constant pH. This behavior is attributed to variations in site–metal binding energies due to differences in the nature of surface sites present (*20, 22*).

(iv) For the same adsorbent and pH the fraction of metal adsorbed varies with differing metal cations (at equivalent total metal–adsorbent concentration ratios). This is attributed to differences in the site-binding energies for different trace metals (*22*).

Characteristics comparable to those described above have also been observed in the binding reactions of trace metals with fulvic acid ligands: (i) variations in binding energies are observed as a function of site occupancy (*17*) and (ii) different metal cations have different binding intensities (*23*).

Chemical extractions are often employed to evaluate the solid component association of metals, and extractant-determined metal–component associations have been used to assess metal bioavailability in natural systems (*5, 6, 24, 25*). Luoma and Bryan (*26*) have recently reported statistical studies that indicate significant correlations between the extractable amount of particular trace metals and the amount present of operationally defined estuarine sediment components. Their results suggest that metals are competitively divided among available substrates with Zn and Pb being primarily associated with hydrous Fe oxides while Cu and Ag were partitioned between hydrous Fe oxides and humic compounds.

In all cases extraction methods are utilized to operationally define a chemically attackable portion of the particulate matrix. It must be recognized, however, that extraction procedures suffer from a lack of chemical specificity (*27, 28*). In the study described here, trace-metal adsorption has been employed as an analytical tool to aid in the evaluation of changes in particulate surface properties. Examinations of metal adsorption behavior before and after successive differing extractions of estuarine particulates have been used to provide supporting information with respect to the importance of metal binding by extracted components. In addition, the adsorptive behavior of unaltered estuarine sediments has been qualitatively compared to that observed in well-characterized hydrous oxide systems.

Table I. Sequential Extraction Protocol[a]

	extraction conditions	presumed phase affected
1.	1.0 M $MgCl_2$, pH 7.0	exchangeable metals
2.	1.0 M NaOAc, pH 5.0	carbonates
3.	0.04 M $NH_2OH \cdot HCl$, 25% (v/v) HOAc at 96 °C	Fe–Mn oxyhydroxides
4.	0.02 M HNO_3, 30% H_2O_2 at 85 °C	organics

[a] After Tessier et al. (*29*).

Experimental Section

Sediment samples A and B were obtained on June 9 and August 8, 1980, respectively, at low tide from the oxidized surface layer of exposed mudflats in the South San Francisco Bay estuary. Sediments were stored at approximately pH 8 and 4 °C in the Stanford Laboratories as continuously stirred slurries in 0.6 M $NaClO_4$ (sediment A) or 0.6 M $NaNO_3$ (sediment B). The intent of the sample storage procedure was to minimize sediment alteration by maintenance of conditions of pH, ionic strength, and redox potential approximating those in the estuarine environment and to discourage biologically induced modifications. The use of inert, noncomplexing electrolytes ($NaClO_4$ or $NaNO_3$) permitted trace-metal adsorption to be studied in the absence of competitive ligand effects. No attempt was made to exclude atmospheric CO_2 from the sediment slurries to reduce the likelihood of carbonate mineral dissolution. Also, small residual amounts of chloride and sulfate may have remained (ca. $\simeq 10^{-6}$ and 10^{-7} M, respectively) at the final dilute sediment concentrations used in the adsorption experiments. These ligand concentrations are not expected to interfere with the experimental results.

Slurry solids concentration (w/w) and adsorptive properties remained constant during the time required to perform the extraction and adsorption experiments as monitored by replicate adsorption experiments. BET surface areas, measured by N_2 adsorption onto 105 °C dried sediment, were 21.6 and 16.2 m^2/g for sediments A and B, respectively. Sediments were analyzed for total carbon and inorganic carbon (organic carbon by difference) by using a Leco Model WR 12 carbon determinator. Total carbon was measured by furnace combustion to CO_2 and IR analysis. Inorganic carbon was measured by CO_2 release during heated digestion with concentrated H_3PO_4.

Sequential extraction of sediment B was accomplished by using the protocol of Tessier et al. (*29*). This procedure estimates exchangeable, carbonate, Fe–Mn oxide, and organic fractions of bound trace metals and is summarized in Table I. Sediment extracts were stored in acid-cleaned polyethylene bottles at 4 °C and analyzed for Ca, Cd, Cu, Fe, Mn, and Pb by flame or flameless (heated graphite atomizer) atomic absorption spectrophotometry.

Adsorption experiments were performed in 500-mL jacketed reactors at 25 °C. Slurries of sediments were diluted to desired concentrations with 0.6 M $NaClO_4$ or 0.6 M $NaNO_3$ and spiked with known amounts of either Cd or Pb plus trace amounts of the radioisotopes ^{109}Cd or ^{210}Pb. The pH of the dilute sediment/trace-metal suspensions was adjusted with microliter quantities of HNO_3 or NaOH, and 15-mL aliquots were removed at regular pH intervals. Sample aliquots were equilibrated for 4 or 24 h in glass centrifuge tubes on rotary tumblers. After equilibration, solids were removed from solution by cen-

trifugation, a supernate aliquot was removed, and the equilibrium pH was measured on the remaining stirred slurry. Residual supernate metal levels were determined by crystal-scintillation counting for ^{109}Cd and liquid-scintillation counting for ^{210}Pb. Uncentrifuged slurry aliquots were counted as reference for total activities. All glassware was cleaned in 10% w/v HNO_3 prior to each experiment. Chemicals used for adsorption and extraction experiments were analytical reagent grade.

Results and Discussion

Although numerous trace-metal adsorption studies have been performed on well-characterized solid surfaces (*20–22*), relatively few investigations have been conducted to similarly characterize the adsorptive behavior of naturally occurring solid surfaces. The initial studies of metal adsorption onto relatively unaltered estuarine particulate surfaces were undertaken to evaluate adsorption kinetics, reversibility, experimental precision, and the effect of adsorbate/adsorbent concentration ratio on adsorption equilibria.

Kinetic studies are a common prerequisite to "equilibrium" adsorption experiments. Monitoring of adsorptive uptake as a function of time permits identification of a suitable equilibration time necessary to obtain results that are "time invariant". Studies of reversibility compare forward (adsorption) and backward (desorption) reaction rates. Some measureable backward extent of reaction is a minimum requirement for the assumption that the adsorption process may be described by a reversible reaction with an associated equilibrium constant.

Kinetic experiments on sediment B showed Cd adsorption at pH ~5.5 to occur in two stages—a rapid initial uptake of metal that was complete within 30 to 60 min, followed by a very slow release of metal over the next 96 h. Subsequent experiments indicated that the long-term kinetic behavior may be pH dependent with both long-term increases and decreases in adsorption having been observed (unpublished data). Investigations of the sediment-adsorption kinetics are being continued. In the absence of more detailed information, it is assumed that solid/solution partitioning after a 4-h time period reflects a pseudoequilibrium value representative of the surface chemistry of the estuarine particulate matter. Selection of 4- or 24-h equilibration periods also facilitates comparison of the sediment-system results with those previously obtained on hydrous oxides (*20–22*).

Reversibility of the adsorption reaction was examined by separate experiments for Pb and Cd onto sediment B. Reaction systems were equilibrated for 24 h at the appropriate pH for approximately 90% metal adsorption as determined from prior experiments, the pH was then lowered to that appropriate for 20% adsorption, aliquots were removed with time, and the fractional metal adsorption was determined. The results (Figure 1a) indicate slow release of adsorbed Cd within a time frame of 96 h. Adsorbed Pb was substantially nonlabile over the 264-h duration of the experiment (Figure 1b). Data for four replicate adsorption experiments for Cd on sediment B are shown in Figure 2. The precision of adsorption experiments was excellent; for example, the relative errors for the pH value at which 20% and 70% metal adsorption occurred were ±0.5% and ±0.9%, respectively.

Adsorption curves for Cd and Pb onto marsh sediments at variable solids concentrations are shown in Figure 3, parts a and b; data for similar type experiments (*20, 22*) of Cd adsorption onto amorphous ferric oxyhydroxide (am $Fe_2O_3 \cdot H_2O$) are also shown (see Figure 3c). The characteristics of the adsorption edges for the sediment system

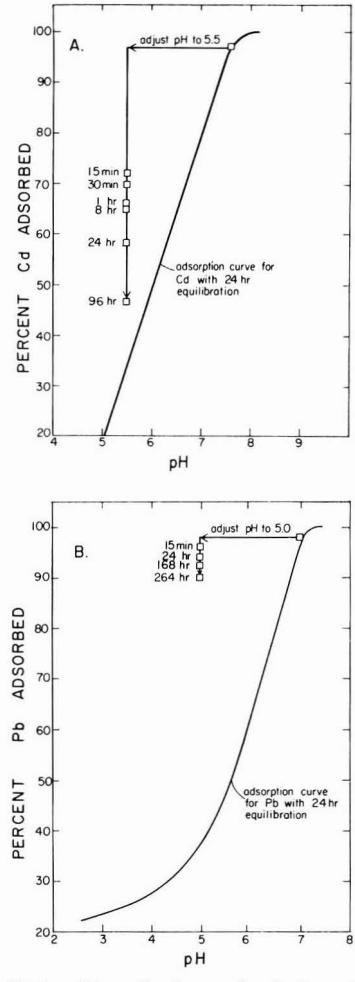

Figure 1. Kinetics of desorption from unaltered salt marsh sediment B: (A) cadmium; (B) lead.

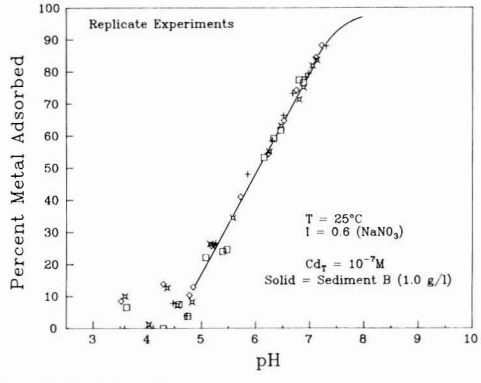

Figure 2. Cadmium adsorption onto unaltered estuarine salt marsh sediment B (replicate adsorption experiments).

appear qualitatively similar to those for the am $Fe_2O_3 \cdot H_2O$ system in spite of the diverse nature of the sediment particles. Adsorption occurred over a narrow range of 1–2 pH units (the "adsorption edge"). The position of the

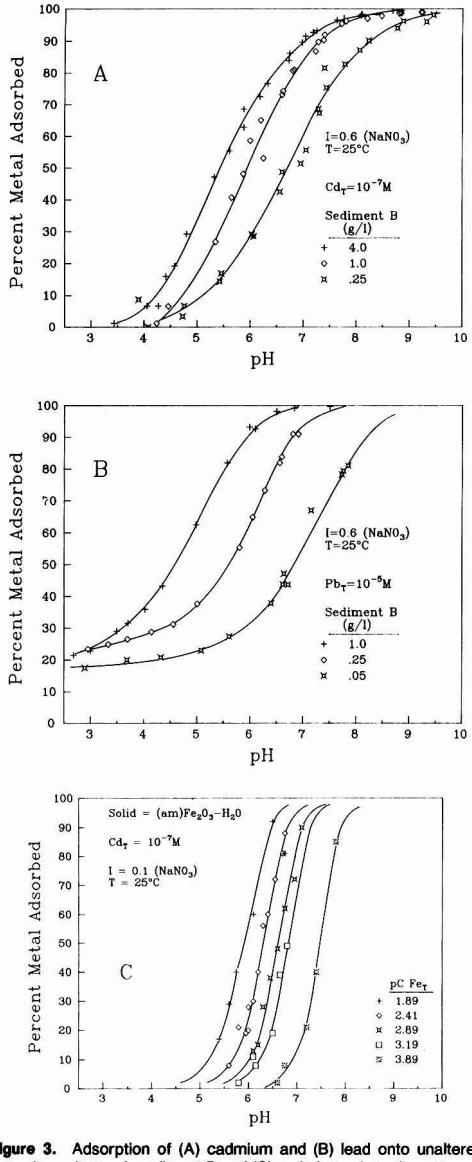

Figure 3. Adsorption of (A) cadmium and (B) lead onto unaltered estuarine salt marsh sediment B and (C) cadmium adsorption onto am $Fe_2O_3 \cdot H_2O$ [after Benjamin and Leckie (*20*)] at variable solids concentrations.

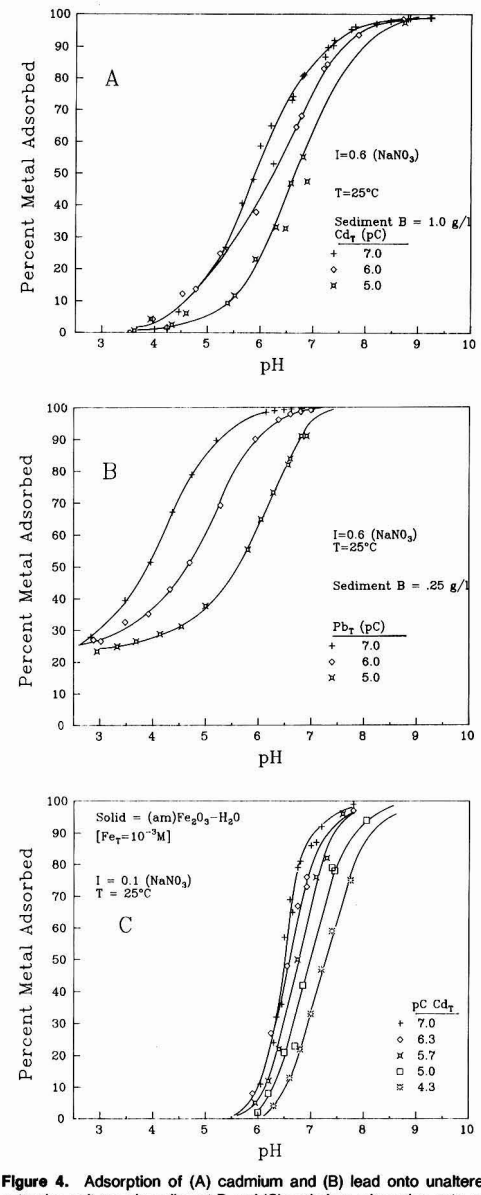

Figure 4. Adsorption of (A) cadmium and (B) lead onto unaltered estuarine salt marsh sediment B and (C) cadmium adsorption onto am $Fe_2O_3 \cdot H_2O$ [after Benjamin and Leckie (*20*)] at variable metal concentration.

pH–adsorption edge for Cd and Pb was a function of both adsorbate and adsorbent concentrations. As noted previously, the observed shift of adsorption edges for Cd and Pb to lower pH with increasing solids concentrations results from a reaction comparable to the titration of a metal with a dissolved ligand. Comparison of parts a and c of Figure 3 reveals that the slope of the adsorption edge for Cd on the estuarine sediment was less than that for Cd on am $Fe_2O_3 \cdot H_2O$. The differences in slope reflect differences in metal-binding intensities, site densities, and reaction stoichiometries between the sediment and am $Fe_2O_3 \cdot H_2O$. Differences in ionic strength between the sediment and hydrous oxide experiments shown are not expected to impair their comparison; the results of Swallow (*30*) indicate Pb adsorption onto hydrous ferric oxide in $NaClO_4$ electrolyte to be unaffected by ionic strengths ranging from 0.005 to 0.5 M.

Adsorption curves for Cd and Pb onto marsh sediments at variable metal concentrations are shown together with comparable curves for Cd adsorption onto am $Fe_2O_3 \cdot H_2O$ in Figure 4. At fixed solid concentration and fixed pH the percent metal adsorbed was observed to increase with decreasing total metal. This behavior is currently thought to result from the existence of a range of binding intensities between the metal and solid surface sites (*20*). This assessment assumes the total concentration of surface sites

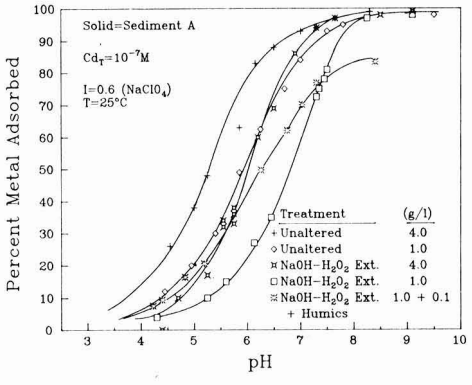

Figure 5. Cadmium adsorption onto unaltered and NaOH/H_2O_2-stripped estuarine salt marsh sediment A: effect of solids concentration and humic acid extract addition.

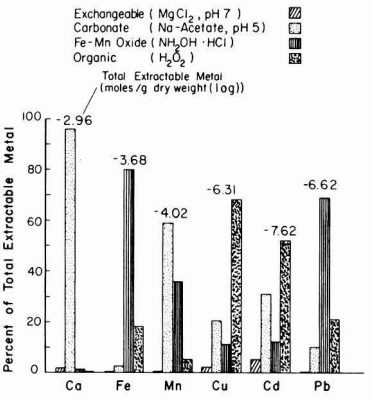

Figure 6. Extractable Ca, Fe, Mn, Cu, Cd, and Pb in estuarine salt marsh sediment B.

was much greater than total metal concentrations in the sediment adsorption experiments. One source of variability in metal-binding intensity in the sediment particulates is the likely presence of different component functional groups on the solid surface. Our subsequent investigations on the estuarine sediments therefore focused on evaluation of the contribution of chemically defined surface components to the adsorption of trace metals.

Preliminary experiments that examined the contribution of organic coatings to Cd adsorption onto sediment A are shown in Figure 5. After exhaustive repeated extraction of humic materials from the sediment in 0.1 N NaOH and oxidation of the sediment with ca. 3% H_2O_2 at room temperature resulting in a decrease in sediment organic carbon content from 2.0% to 0.16%, the Cd adsorption capacity (or intensity) was decreased by a magnitude approximating that observed with a 4-fold decrease in unaltered sediment concentration. Thus, stripping of organics from the sediment surface had an effect comparable to reducing the number of surface sites present by approximately a factor of 4 or of changing the average binding constant by a similar amount. Attribution of the observed change in adsorption behavior to removal of an organic surface phase was qualitatively confirmed by examining the adsorption in a mixed adsorbent system containing NaOH–H_2O_2-stripped sediment plus added sediment-derived humic substances. The latter were present on a weight basis rougly comparable to that measured in the as-collected sediment. The system was equilibrated without metal for approximately 20 h at pH $\simeq$6 to allow partitioning of the humics between sediment surface and solution. The composite system adsorption edge observed approximates that of the unaltered sediment A. One possible reason for the residual difference observed is competition of humics remaining in the solution phase for the cation. This effect would likely be greater at higher pH as the solubility of humics increases with ionization, thereby bringing additional humics previously surface associated at lower pH into solution. This trend is observed. The experimental results do not allow determination as to whether the enhanced adsorption in the presence of humics results from Cd adsorption to a humic-coated surface, adsorption of Cd–humic solution complexes, or both.

It is recognized that during the NaOH–H_2O_2 extraction many chemical alterations of the sediment surface other than the simple removal of organics may have occurred. The above results therefore do not confirm but only suggest that organic coatings were important determinants for the adsorptive behavior of the unmodified particulate material. These experimental data are, however, consistent with those of Davis and Leckie (*31*), who demonstrated that the presence of adsorbing organic ligands can result in an increased intensity of Cu binding to oxide surfaces. Similarly, Harvey (*32*) has shown that adsorbed bacterial exopolymer can increase the Pb-binding intensity of α-alumina and organically stripped sediment particulates.

It should be noted that adsorption experiments for Cd and Pb onto estuarine sediments in a 0.6 M $NaNO_3$ or $NaClO_4$ medium are studied here to investigate the adsorption process per se and are not directly applicable as a predictive tool. The presence of dissolved complexing ligands (both inorganic and organic) would be expected to influence the extent of adsorption of metals in the marine environment. In particular, the complexation of Cd by chloride and sulfate has been shown to decrease adsorption onto oxide surfaces (*33*).

A more detailed characterization of trace-metal surface-phase association and particulate adsorptive behavior was performed on sediment B. The results of metal solubilization during sequential extraction of the sediment using the procedures of Tessier et al. (*29*) (Table I) are summarized in Figure 6. Of principal interest is the finding that substantial fractions of total extractable Cd and Cu (50% and 65%, respectively) were found to be associated with operationally defined organic phases while approximately 70% of total extractable Pb was removed during the extraction of Fe/Mn oxides. These data suggest that Fe–Mn oxide and organic coatings may indeed be of importance in the binding of Cd, Cu, and Pb to the estuarine particulate surfaces. The data also indicate that Fe–Mn oxide coatings may play a relatively greater role in the binding of Pb while adsorption of Cd and Cu may be controlled to a greater extent by organic coatings.

It is also noteworthy that a substantial portion of extractable Mn was found to be removed by NaOAc extraction at pH 5. Thus, it appears that the specificity of the carbonate extraction step in the sequential procedure may be less than desirable or that a portion of extractable Mn was present in association with carbonates. The carbonate carbon content of unaltered sediment B was approximately 5% by weight. Essentially all of the extractable Ca was removed in the carbonate extraction step, while approximately 80% of exchangeable Fe was removed in the extraction step for Fe–Mn oxides.

Results of adsorption experiments for Cd and Pb onto the sequentially modified sediment B are shown in Figures

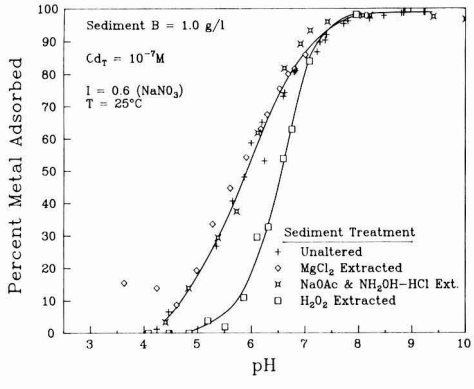

Figure 7. Cadmium adsorption onto sequentially extracted estuarine salt marsh sediment B.

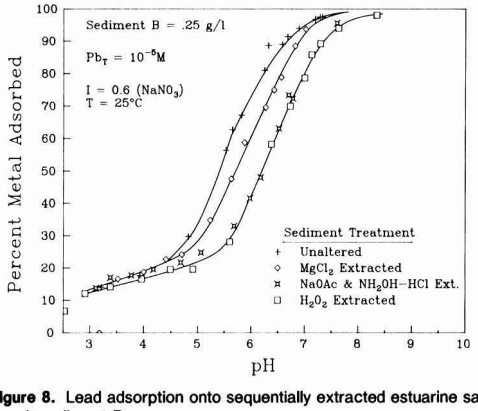

Figure 8. Lead adsorption onto sequentially extracted estuarine salt marsh sediment B.

7 and 8. The adsorption experiments performed serve, in effect, as surface-chemical probes, with a shift of the adsorption edge to lower fractional metal adsorption at a given pH being indicative of a decrease in surface-site density or a decreased intensity of interaction of metal with the particulate surface (at constant solids concentration). The experimental results show that the adsorption edge for Cd shifted dramatically to lower fractional adsorption across the pH range after the organic extraction step, while the edge for Pb shifted to lower fractional adsorption after extraction of carbonate plus Fe–Mn components.

Although the chemical extractions performed probably alter particulate surfaces by processes other than removal of the extracted phase, it is noteworthy that the sediment Cd-adsorption characteristics were unaffected by any chemical extraction other than that for organic materials. Similarly, extraction of organics did not alter the adsorption characteristics of the sediment for Pb. The observed shifts in the sediment adsorption characteristics have several possible explanations. It is conceivable that alterations in adsorption-site density or binding intensity occurred that obscured extractant effects or resulted in shifts of the adsorption edge not attributable to phase removal. In order to explain the results in this manner, it is still necessary to invoke different binding sites for Cd and Pb; otherwise, an adsorption-edge shift for one metal would also be reflected in the adsorption behavior of the other. Results by Benjamin and Leckie (*22*) indicate Cd and Pb (to a large extent) occupy different sites on am $Fe_2O_3 \cdot H_2O$ surfaces. Although the total effect of the extractants on the surface chemistry of the sediments is not known, it is known that the extractants solubilized components of the particulate matrix and that the process of solubilization was to some extent selective (see Figure 6). We have therefore tentatively assigned the observed shifts in sediment adsorption behavior to the removal of selected surface components responsible for binding of Cd and Pb. In support of this assumption we note that the observed shifts in Pb and Cd adsorption curves are consistent with operationally defined phase association of these metals as determined by the analysis of the sequential sediment extracts. The results obtained are also consistent with those of Luoma and Bryan (*26*), who showed strong correlations of extractable Fe with Pb in estuarine sediments and of Cd with extractable organics and Fe. The results were interpreted as indicating that competition (partitioning) for metals occurred between sediment substrates with the partitioning of Pb (and possibly Cd) controlled by hydrous Fe oxides, while Cu was partitioned between both humics and hydrous Fe oxide components (*26*).

Conclusions

The adsorption behavior of extracted sediments provides supporting evidence indicating that the chemical extractants used attack (at least in part) different surface phases on the particulate materials. Operationally defined Fe–Mn oxyhydroxide and organic phases appear important in the binding of Pb and Cd, respectively, in South San Francisco Bay estuarine sediments. The results obtained are speculative in that chemical extractants are known to lack chemical specificity. In addition, extractants may alter the surface-chemical characteristics of sediments by processes other than those that result from removal of extracted components. Despite these flaws, the use of chemical extractants remains as one of the few tools available for the examination of trace-metal chemical associations with natural particulate materials. Chemical extraction techniques have, in fact, proven useful in establishing bioavailability of sediment-bound metals (*6*) and in indicating particulate component competition for bound metals in estuarine sediments (*26*). The results of this study suggest that the role of sediment components may be evaluated from the perspective of competitive adsorption phenomena and that sediment adsorption characteristics and extractant-determined component–metal associations yield consistent information on the binding of metals. In addition, the similarities in adsorption behavior of the salt marsh particulate surfaces and hydrous oxides suggest that the conceptual and computational models that have been developed to describe metal adsorption onto oxide surfaces (*21*, *34–36*) may eventually prove useful in the description of natural systems.

Acknowledgments

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Chlorinated Hydrocarbons and Radionuclide Chronologies in Sediments of the Hudson River and Estuary, New York

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■ The Hudson River received discharges of at least several hundred tons of PCBs from two General Electric capacitor manufacturing facilities in the upper part of the drainage basin over the period between ca. 1950 and 1976. Measurements of PCB compositions and amounts in sediment cores throughout the tidal Hudson (~250 km) indicate that maximum concentrations occurred in the early 1970s, probably due to removal of a dam just downstream of the release area in 1973. Significant decreases in surface sediment PCB concentrations have occurred since about 1973, well before monitored releases of PCBs from the manufacturing facilities ceased in 1976, probably primarily as the result of dilution and burial of the most highly contaminated sediments released upon removal of the dam with soils from the drainage basin. Declines in the concentrations of chlorinated hydrocarbon pesticides and fallout radionuclides since the mid-1960s and reactor-released radionuclides over the period 1971–1975 have also been established from sediment core measurements.

Introduction

The most effective general policy for reducing impacts of toxic chemicals on aqueous systems is to limit or eliminate discharges at their source. However, in some cases the degree of contamination with persistent toxic chemicals is sufficient to warrant consideration of remedial activities such as dredging and containment of the most highly contaminated sediments to reduce exposure of human populations through pathways such as consumption of fish. One such case is the Hudson River, which received substantial discharges of at least several hundred tons of polychlorinated biphenyls (PCBs) over the period of ca. 1950–1976 (*1*). The composition of PCBs in Hudson sediments and their spread throughout the entire axis of the tidal Hudson has been reported elsewhere (*2*, *3*). We discuss here the time history of PCB concentrations in Hudson sediments, which can be deduced from measurements of core samples. Temporal variations of chlorinated hydrocarbon pesticide residues in the same samples are also examined. A number of similar investigations have employed natural and man-made radionuclides to provide a time frame for studying the accumulation of anthropogenic pollutants associated with recent sediments in natural water systems. Hom et al. (*4*) used radiometric dating to study PCB and DDE accumulation in the Santa Barbara Basin; Robbins and Edgington (*5*) described the accumulation of fallout radionuclides in Lake Michigan

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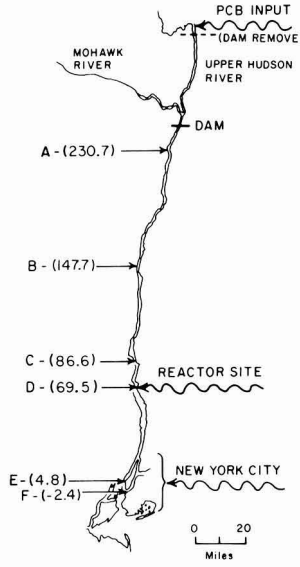

Figure 1. Map of the Hudson River and Estuary with core locations denoted in parentheses by kilometer point (kmp). Tidal currents extend upstream to a dam just downstream of the confluence of the Mohawk and Upper Hudson Rivers.

sediments; Goldberg et al. (*6–8*) reconstructed trace metal chronologies for Narragansett Bay, Chesapeake Bay, and the Savannah River Estuary sediments utilizing natural and fallout radionuclides as time indicators; Wakeham et al. (*9*) referenced data on natural radionuclides in a study of polycyclic aromatic hydrocarbons in recent lake sediments; Cutshall et al. (*10*) interpreted kepone profiles in James River sediment cores based on fallout radionuclide measurements. We have been analyzing fallout and reactor-derived radionuclides in Hudson River sediments for the past decade in conjunction with studies of the accumulation of recent, fine-grained sediments (*11, 12*) and associated trace metals (*13*) and trace organics (*3*). In the present study, geochronology of the core profiles has been determined primarily from analyses of fallout and reactor nuclides for which the history of inputs is well documented.

Experimental Section

Sediment samples from the Hudson were collected with a gravity corer, with a piston corer, or by hand coring at sites ranging from near the upstream end of the fresh-water reach of tidal waters to New York harbor, which has ambient salinities of about two-thirds of that of the open ocean (Figure 1). Sections of the cores were analyzed for ^{137}Cs, ^{134}Cs, and ^{60}Co by nondestructive γ-ray spectrometry using a lithium-drifted germanium detector and a multichannel analyzer. Portions of the samples were analyzed for fallout $^{239,240}Pu$ by α spectrometry. PCB and chlorinated hydrocarbon pesticide measurements were made by electron-capture gas chromatography. Standards were obtained from the EPA at Research Triangle Park, NC, and run at least daily. Pesticide peak assignments were made with use of retention times on two glass columns, a 6 ft × 2 mm i.d. column packed with 1.5% OV-17/1.95% QF-1 on 80–100 mesh Chromosorb W HP and a similar column packed with 4% SE-30/6% OV-210 also on 80–100 mesh Chromosorb W HP. The latter column was employed routinely for sample quantification. Additional confirmation of peak assignments was obtained by treating selected extracts with concentrated H_2SO_4 (*14*), which removed some interfering peaks and quantitatively destroyed dieldrin, and by alkali treatment (*15*) of selected extracts, which produced dehydrochlorination products from chlordane, DDD, and DDT. As an indication of the precision of the reported analyses, two separate portions of 14 of the sediment samples were analyzed. The average coefficient of variation was 6.5% for PCBs, 5.2% for *pp'*-DDD, 13% for dieldrin, and 7.4% for α- and γ-chlordane. All concentrations of chlorinated hydrocarbons and activities of radionuclides are reported on a per dry weight of sediment basis. More detailed descriptions of our analytical procedures have been reported elsewhere (*2, 3, 11, 12, 16*).

Results and Discussion

Radionuclides and Time Stratigraphy in Hudson Sediments. As a result of their affinity for a wide range of chemical substances including radionuclides, PCBs, and chlorinated hydrocarbon pesticides, the fine-grained sediments of estuarine systems contain a recoverable chronology of many ubiquitous environmental pollutants. The estuarine geochemistry of the substances discussed is strongly influenced by partitioning between water and particle phases. In all cases, the preference for particle phases is great enough to leave an identifiable signal in the sediments and to prevent significant postdepositional redistribution via solution processes (*3, 16*). Accumulation patterns and transport rates of fine-grained sediments in large estuaries are quite complicated in space and time, especially in systems that have been significantly perturbed by dredging activities. Most of the total surface area of the tidal Hudson at present experiences relatively little net sediment accumulation (<a few mm/year). Protected environments such as coves and areas that have been artificially deepened by dredging such as New York harbor can have net accumulation rates of sediment of a few to several tens of cm/year. We have found these rapid deposition sites to be valuable sampling locations for reconstructing the history of contaminant delivery and transport in the Hudson. In general, sites with sediment accumulation rates of 1 cm/year or greater appear to have experienced relatively little vertical redistribution of stratigraphic markers as the result of biological activity or other mechanical mixing processes (*17*).

The primary indicators of sediment accumulation rates upon which we have relied are fallout (^{137}Cs and $^{239,240}Pu$) and reactor (^{137}Cs, ^{134}Cs, and ^{60}Co) radionuclides. The history of fallout nuclide delivery to the Hudson drainage basin is based largely on measurements of ^{90}Sr in precipitation collected at a station in New York City over the last 3 decades by the Health and Safety Laboratory/Environmental Measurements Laboratory of the AEC/ERDA/DOE. Deposition of ^{137}Cs and $^{239,240}Pu$ per unit surface area for the same time period can be estimated (Figure 2), by assuming ratios of $^{137}Cs/^{90}Sr$ and $^{239,240}Pu/^{90}Sr$ of 1.5 and 0.017, respectively (*18–20*). Measurable fallout from weapons testing began in 1954 and reached a maximum in 1963. Reactor releases (Figure 2) are based largely on published reports from Consolidated Edison Co. (*21*). Upstream of about kilometer point 90, the primary time indicator is the peak activity level of ^{137}Cs and $^{239,240}Pu$ associated with maximum fallout in 1963. Downstream of this location, the proportion of reactor ^{137}Cs increases to a maximum near the reactor site at Indian Point (kilometer point (kmp) 69.2) where the ^{137}Cs activity in sediments is strongly correlated with activity levels of the reactor-derived nuclides ^{134}Cs and ^{60}Co. The year of

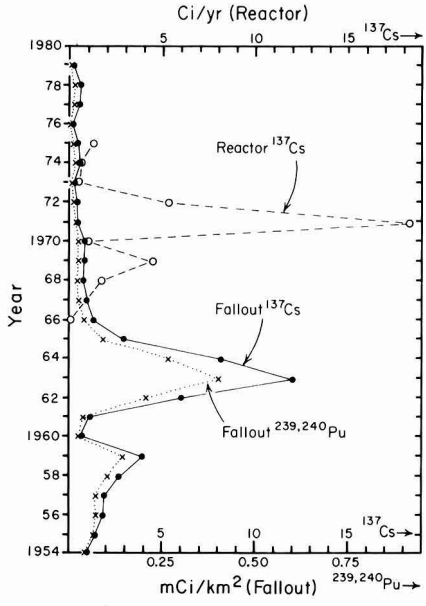

Figure 2. Time history of fallout radionuclides delivered at New York and reactor releases from the Indian Point facility, decay corrected to 1980.

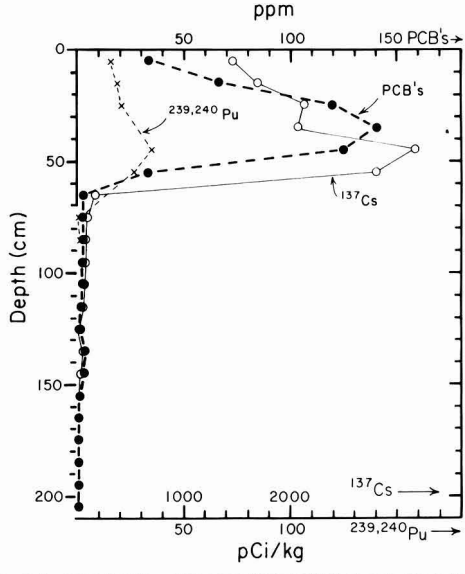

Figure 3. Fallout radionuclides and PCBs (1242) at core site A (kmp 230.7) sampled in July, 1977, following dredging of the site in August–October, 1972.

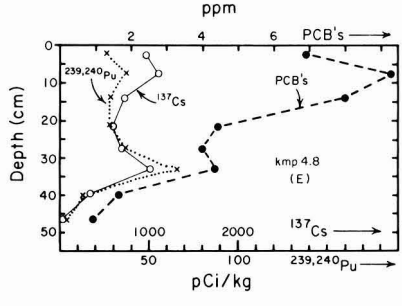

Figure 4. Fallout and reactor radionuclides and PCBs (1242) at core site E (kmp 4.8) sampled in September, 1975.

maximum release of ^{137}Cs, ^{134}Cs, and ^{60}Co from Indian Point was 1971. $^{239,240}Pu$ measured in the sediments appears to have been derived predominantly from fallout and is not associated with the releases of reactor fission and activation products (*22*, *23*).

Activities of fallout and reactor nuclides in cores collected between 1975 and 1977 from six sites along the axis of the Hudson (Figure 1) are listed in Tables I–III. Reported activities have been corrected to the date of collection. Control number (CN) designations unambiguously identify a particular core and are reported in all publications from this laboratory. The core sites have been designated A–F and are located in Figure 1 by their kilometer points, which correspond to the number of kilometers upstream of the southern tip of Manhattan measured along the axis of the channel. Piston cores were taken at two sites (A and F), site C was cored by hand through the ice in winter, and the other cores were taken with a gravity corer. Sites A (Table I), D (Table II), and F (Table III) were from locations that had been previously dredged and thus served as deposition basins for new sediment subsequent to dredging. Site A at kmp 230.7 near the upstream end of tidal water was an embayment used for large cargo vessels and was most recently dredged extensively from August to October of 1972, prior to collection of our piston core in July 1977. We interpret the low and relatively constant activity of ^{137}Cs between 70 and 190 cm as indicative of slumping during and/or shortly after dredging. The radionuclide activities above 60 cm are consistent with upper portions of other cores from this area of the Hudson, suggesting the top 60 cm of this core should be representative of sediments accumulating in this area for the period from late 1972 to 1977, which yields an average rate of about 10 cm/year (Figure 3). The sediment throughout this core is predominantly fine-grained mud mixed with small amounts of fine sand. Site B, approximately midway in the tidal fresh water reach of the Hudson, adjacent to the navigation channel, has a maximum in ^{137}Cs and $^{239,240}Pu$ activities between 20 and 28 cm depth (Table I), which we associate with the year of maximum fallout (1963), suggesting an average sedimentation rate of 1.5–2 cm/year. Site C (Table II), a cove at kmp 86.6, contains fallout nuclides to a depth of 24–25 cm with a maximum at 13–14 cm, both of which suggest a mean deposition rate of about 1 cm/year. The reactor nuclide peak at 3–4 cm suggests a somewhat slower rate of sediment accumulation, about 0.6 cm/year. Site D, in a small cove adjacent to the reactor site, has a very strong peak in reactor nuclides at 8–12 cm (Table II), which we believe contains the sediments accumulated during the year of maximum releases (1971), indicating sedimentation of about 2 cm/year. Cores at sites B, C, and D were composed of fine-grained mud over their entire lengths. Two cores (E and F) were collected from New York harbor. Both have a reactor nuclide maximum that we associate with the 1971 releases, while one of the cores (E) also appears to have a peak in fallout nuclides (Table III, Figure 4). The core from site E was comprised of fine-grained black mud over its entire length while the piston core at F had similar sediment throughout the top 120 cm, which includes the 1971 reactor peak. Below this level, variations in radionuclide and chlorinated hydrocarbon content of this core are strongly influenced by changing sediment characteristics, including sand layers

Table I. Sediment Activities of Fallout Radionuclides and Concentrations of PCBs from the Tidal Hudson River (1977)[a]

depth, cm	^{137}Cs, pCi/kg	^{239,240}Pu, pCi/kg	Aroclor, ppm 1242	Aroclor, ppm 1254
		Core Site A (kmp 230.7, 7/13/77, CN 1298)		
0-10	1452 ± 50	15.8 ± 0.9	33.3 ± 4.0	1.81 ± 0.33
10-20	1685 ± 47	18.3 ± 0.8	66.4 ± 11.5	2.93 ± 0.34
20-30	2120 ± 61	20.4 ± 1.4	119 ± 19	5.04 ± 1.21
30-40	2060 ± 62		(140 ± 39)[b]	5.92 ± 0.21
40-50	3165 ± 76	34.9 ± 1.8	125 ± 27	5.39 ± 1.17
50-60	2796 ± 79	33.0 ± 2.3	(32.9 ± 4.3)[d]	3.47 ± 0.60
(60-70)[c]	159 ± 27		2.56 ± 0.47	0.96 ± 0.10
70-80	89 ± 16	0.8 ± 0.1	2.50 ± 0.47	1.08 ± 0.09
80-90	84 ± 25	1.8 ± 0.3	2.24 ± 0.57	<0.46
90-100	68 ± 20		2.00 ± 0.43	<0.37
100-110	65 ± 16		2.76 ± 0.64	<0.26
110-120	54 ± 16		1.57 ± 0.34	<0.26
120-130	7 ± 16		1.44 ± 0.36	<0.21
130-140	45 ± 12		3.23 ± 0.70	<0.24
140-150	37 ± 12		2.25 ± 0.52	<0.20
150-160	14 ± 13		0.88 ± 0.29	<0.19
160-170	8 ± 11		0.38 ± 0.09	<0.08
170-180			0.35 ± 0.07	<0.05
180-190	6 ± 10		0.27 ± 0.11	<0.07
190-200			0.21 ± 0.03	<0.05
200-210	−9 ± 10		0.24 ± 0.07	<0.02
		Core Site B (kmp 147.7, 7/14/77, CN 1329)		
0-2	730 ± 31	7.4 ± 0.4	5.25 ± 0.61	0.56 ± 0.06
2-4	995 ± 67		11.3 ± 0.9	1.01 ± 0.18
4-8	1800 ± 38	16.2 ± 0.5	(28.8 ± 4.8)[b]	2.39 ± 0.80
8-12	1900 ± 52		(11.1 ± 1.1)[d]	1.86 ± 0.17
12-16	1620 ± 33	19.3 ± 0.6	9.07 ± 0.97	1.60 ± 0.12
16-20	1660 ± 36		9.24 ± 0.99	1.54 ± 0.11
20-24	2050 ± 42	27.4 ± 1.0	8.38 ± 0.80	1.86 ± 0.16
24-28	(2380 ± 55)[e]		10.13 ± 0.99	2.70 ± 0.27
28-32	900 ± 27	19.3 ± 0.8	4.09 ± 0.42	1.52 ± 0.14
32-36	(51 ± 9)[f]		0.28 ± 0.07	0.34 ± 0.07
36-40	9 ± 10	ND	0.06 ± 0.013	~0.03
40-44			0.08 ± 0.014	~0.01
44-48			0.06 ± 0.009	~0.01
48-52			0.04 ± 0.007	~0.01
52-54			0.03 ± 0.003	~0.01

[a] Activities and concentrations are reported on a dry weight basis. Cs and Pu numbers are reported with statistical counting errors (±1σ). The ± values on the PCB numbers are the average deviation of the peaks used in quantification from the mean value. [b] We interpret the maximum concentration in PCBs to have resulted from removal of a dam just downstream of the release area in 1973. [c] Low and relatively constant amounts of fallout nuclides and PCBs at this depth and below are believed to have been produced by slumping and redistribution of sediment during or shortly after extensive dredging of this site between August and October of 1972. [d] All samples above this depth have significant proportions of Aroclor 1016, although the concentrations are reported as Aroclor 1242. Aroclor 1016 was first used at the industrial facilities on the upper Hudson in 1971. [e] We interpret the maximum in fallout nuclides to be associated with the year of highest fallout from nuclear weapons testing (1963). [f] We interpret the first appearance of fallout nuclides in this core to be associated with the year of beginning of measurable fallout from nuclear weapons testing (1954).

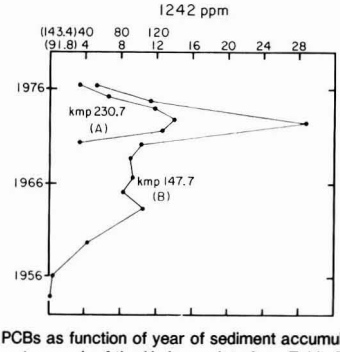

Figure 5. PCBs as function of year of sediment accumulation in the tidal fresh-water reach of the Hudson: data from Table I were used to estimate age as a function of depth.

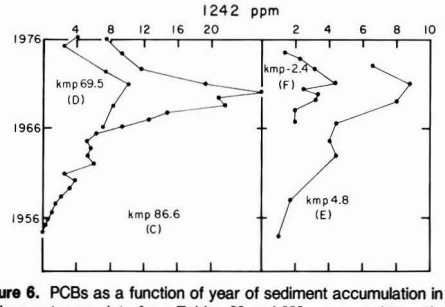

Figure 6. PCBs as a function of year of sediment accumulation in the Hudson estuary: data from Tables II and III were used to estimate age as a function of depth.

and regions of laminated sediment (*12*, *16*). Mean sedimentation rates for these two locations appear to be about 2–3 cm/year for site E and ~15 cm/year for site F. Thus all six of the sites appear to have relatively rapid average sediment accumulation rates, ranging from about 1 to about 15 cm/year.

PCBs and Time Stratigraphy in Hudson Sediments. Each of the six coring sites has reasonably clear

Table II. Sediment Activities of Fallout and Reactor Radionuclides and Concentrations of PCBs from Coves in the Low-Salinity Reach of the Hudson Estuary (1977)

depth, cm	^{137}Cs, pCi/kg	^{134}Cs, pCi/kg	^{60}Co, pCi/kg	^{239,240}Pu, pCi/kg	Aroclor, ppm 1242	Aroclor, ppm 1254
			Core Site C (kmp 86.6, 1/77, CN 1240)			
0-1	1530 ± 38	28 ± 13	73 ± 10	27.9 ± 1.4	7.48 ± 0.52	0.97 ± 0.22
1-2	1610 ± 44	47 ± 16	55 ± 13	28.6 ± 1.7	9.28 ± 0.65	1.15 ± 0.35
2-3	2000 ± 48	(75 ± 16)[b]	98 ± 13	30.9 ± 1.4	11.6 ± 0.5	1.42 ± 0.42
3-4	(2400 ± 56)[b]	(75 ± 16)[b]	(145 ± 13)[b]	34.7 ± 1.9	19.3 ± 0.9	2.35 ± 0.54
4-5	2240 ± 55	30 ± 16	110 ± 14	35.4 ± 1.9	(26.0 ± 1.4)[a]	3.06 ± 0.82
5-6	2060 ± 56	−7 ± 13	89 ± 15	41.4 ± 2.7	20.8 ± 1.7	2.32 ± 0.60
6-7	2010 ± 48	5 ± 10	67 ± 12		21.6 ± 1.6	2.38 ± 0.61
7-8	2180 ± 54	12 ± 11	83 ± 12	47.5 ± 2.2	14.7 ± 1.3	1.77 ± 0.33
8-9	2130 ± 54	−7 ± 11	95 ± 13	53.4 ± 1.9	12.6 ± 0.9	1.64 ± 0.29
9-10	1970 ± 49	−7 ± 10	100 ± 12	49.6 ± 2.3	9.36 ± 0.87	1.49 ± 0.20
10-11	2120 ± 50	1 ± 10	70 ± 11	54.9 ± 2.3	6.31 ± 0.41	1.17 ± 0.11
11-12	2130 ± 59	−14 ± 13	41 ± 15	68.3 ± 2.6	5.17 ± 0.31	1.44 ± 0.13
12-13	2170 ± 57	−13 ± 12	67 ± 14	73.8 ± 2.0	5.57 ± 0.43	1.26 ± 0.09
13-14	2140 ± 68	−10 ± 16	47 ± 19	(76.6 ± 5.3)[c]	5.30 ± 0.33	1.39 ± 0.13
14-15	1990 ± 48	−18 ± 10	36 ± 11	55.6 ± 1.9	5.70 ± 0.60	1.60 ± 0.03
15-16	1680 ± 55	4 ± 16	43 ± 18	53.1 ± 2.1	2.60 ± 0.20	0.78 ± 0.06
16-17	1440 ± 38	2 ± 9	17 ± 10	48.6 ± 1.9	3.90 ± 0.30	1.21 ± 0.10
17-18	1160 ± 42	−10 ± 14	16 ± 15	39.8 ± 2.1	3.30 ± 0.23	1.10 ± 0.16
18-19	770 ± 29	−8 ± 11	−4 ± 14	25.9 ± 0.8	2.17 ± 0.18	0.92 ± 0.09
19-20	580 ± 29	−11 ± 9	−8 ± 10	20.4 ± 0.9	1.58 ± 0.15	0.90 ± 0.08
20-21	380 ± 21	−5 ± 11	24 ± 13	12.5 ± 0.6	1.20 ± 0.09	0.73 ± 0.08
21-22	200 ± 18	1 ± 11	13 ± 13	6.3 ± 0.4	0.72 ± 0.04	0.47 ± 0.06
22-23	105 ± 15	8 ± 10	26 ± 11	3.2 ± 0.3	0.51 ± 0.02	0.34 ± 0.06
23-24	22 ± 12	8 ± 9	−14 ± 11	0.8 ± 0.1	0.22 ± 0.03	0.23 ± 0.07
24-25	(19 ± 11)[d]	−6 ± 9	8 ± 9	(0.5 ± 0.1)[d]	0.33 ± 0.03	0.19 ± 0.04
25-26	−9 ± 13	−5 ± 10	−6 ± 10	0.2 ± 0.1	0.25 ± 0.07	0.09 ± 0.02
			Core Site D (kmp 69.5, 7/17/77, CN 1264)			
0-2	1090 ± 51	82 ± 25	96 ± 21	5.7 ± 0.5	3.95 ± 0.62	0.57 ± 0.04
2-4	1130 ± 54	54 ± 25	95 ± 21	8.2 ± 1.0	2.29 ± 0.37	0.34 ± 0.03
4-8	1730 ± 66	120 ± 28	195 ± 27	10.2 ± 0.6	7.41 ± 0.51	0.87 ± 0.09
8-12	(4140 ± 93)[b]	(395 ± 29)[b]	(420 ± 20)[b]	10.0 ± 1.2	(10.06 ± 0.60)[a]	1.29 ± 0.19
12-16	3220 ± 70	255 ± 22	280 ± 17	9.8 ± 0.3	8.30 ± 0.53	1.07 ± 0.19
16-20	2200 ± 46	160 ± 12	175 ± 9	10.9 ± 0.9	7.23 ± 0.25	0.90 ± 0.13
20-24	1590 ± 43	78 ± 14	115 ± 14	11.0 ± 0.2	6.72 ± 0.27	0.88 ± 0.15
24-28	1280 ± 38	52 ± 15	190 ± 16	9.2 ± 0.4	7.34 ± 0.37	0.90 ± 0.12
28-32	970 ± 32	32 ± 13	99 ± 14	7.6 ± 0.4	4.90 ± 0.35	0.71 ± 0.06
32-36	860 ± 41	15 ± 16	100 ± 19	8.4 ± 0.4	3.70 ± 0.39	0.52 ± 0.03
36-40	1020 ± 35	7 ± 13	145 ± 16	9.8 ± 0.7	4.28 ± 0.39	0.53 ± 0.04
40-44	845 ± 35	19 ± 9	130 ± 12	6.8 ± 0.4	3.57 ± 0.28	0.40 ± 0.04
44-48	520 ± 35	4 ± 18	47 ± 19	5.3 ± 0.3	2.10 ± 0.34	0.31 ± 0.04
48-52	410 ± 19	8 ± 9	47 ± 11	4.2 ± 0.2	1.61 ± 0.14	0.25 ± 0.01
52-56	255 ± 21	11 ± 13	17 ± 16	1.7 ± 0.2	0.65 ± 0.09	0.11 ± 0.01
56-60	(11 ± 10)[e]	−9 ± 9	3 ± 9		<0.03	<0.02
60-64	−5 ± 10	14 ± 8	−5 ± 9		<0.03	<0.02

[a] We interpret the maximum concentration in PCBs to have resulted from removal of a dam just downstream of the release area in 1973. [b] Maximum activities in reactor nuclides (^{134}Cs, ^{60}Co, and part of the ^{137}Cs) are attributed to releases made in the year of maximum releases at the reactor site (1971). [c] We interpret the maximum in fallout nuclides to be associated with the year of highest fallout from nuclear weapons testing (1963). [d] We interpret the first appearance of fallout nuclides in this core to be associated with the beginning of measurable fallout from nuclear weapons testing (1954). [e] The first appearance of anthropogenic radionuclides in this core can most probably be associated with the last dredging episode at this site, which apparently occurred in the late 1960s.

indication of subsurface maximum concentrations of PCBs that decline to values significantly lower at the sediment surface. When these data are normalized to a common age profile, the maxima all fall within 1–3 years of the same estimated age. In addition, the magnitude of the PCB concentration maxima decreases regularly downstream by about a factor of 50 (Figures 5 and 6). To the first approximation the PCB maxima in the four cores from the saline water reach of the Hudson (C–F) correlate with the maxima in reactor nuclides in the same samples, which are believed to result from releases in 1971. Our best time control on the peak in PCB concentrations is for core site A, which we know from communications with the Corps of Engineers to have been dredged in August–October 1972. The only post-1972 "event" that appears to provide a reasonable explanation for the strong maximum in PCBs associated with relatively slowly decreasing ^{137}Cs activities was removal of a dam at Fort Edward, NY, during the summer of 1973 (*24*) (Figure 1). This dam had provided the first impoundment of water downstream of the PCB discharges from the two industrial facilities which began operations in 1947 and 1952. Our interpretation of the sediment data is that the maximum in PCB concentrations resulted from removal of the dam in 1973 and the high fresh-water runoff the following spring. The existence of the PCB maximum throughout the system indicates that upstream inputs are the major source of PCBs to Hudson sediments even in New York harbor where substantial sewage inputs exist. This finding is consistent with our earlier estimate that sewage supplies on the order of 25% of the PCBs in harbor sediments (*3*).

Data for PCBs provided here (Tables I–III) are reported in terms of quantities of two commercial mixtures, Aroclor 1242 and Aroclor 1254, the first of which was used almost

Table III. Sediment Activities of Fallout and Reactor Radionuclides and Concentrations of PCBs from New York Harbor (1975)

depth, cm	^{137}Cs, pCi/kg	^{134}Cs, pCi/kg	^{60}Co, pCi/kg	^{239,240}Pu, pCi/kg	Aroclor, ppm 1242	Aroclor, ppm 1254
			Core Site E (kmp 4.8, 9/15/75, CN 1380)			
0-5	965 ± 32	110 ± 31	84 ± 17	23.9 ± 2.8	6.90 ± 0.53	1.95 ± 0.20
5-10	(1100 ± 27)[b]	71 ± 17	(155 ± 11)[b]	36.0 ± 1.5	(9.27 ± 0.37)[a]	2.63 ± 0.33
10-18	720 ± 24	−1 ± 8	76 ± 15	27.9 ± 1.1	7.99 ± 0.65	2.63 ± 0.34
18-25	595 ± 20	−1 ± 8	61 ± 15	27.8 ± 0.7	4.43 ± 0.44	1.85 ± 0.19
25-30	690 ± 22	−5 ± 7	38 ± 14	35.1 ± 2.0	4.00 ± 0.71	2.19 ± 0.26
30-36	(1010 ± 27)[c]	16 ± 7	17 ± 13	(65.6 ± 2.7)[c]	4.36 ± 0.79	2.31 ± 0.28
36-43	340 ± 13	−1 ± 6	6 ± 9	13.9 ± 0.9	1.65 ± 0.38	1.23 ± 0.21
43-50	37 ± 11	−6 ± 8	−11 ± 12	5.4 ± 0.6	~1	0.80 ± 0.20
			Core Site F (kmp −2.4, 10/18/75, CN 1048)			
0-10	260 ± 21	14 ± 15	12 ± 13	19.2 ± 0.9	1.63 ± 0.05	0.61 ± 0.08
10-20	455 ± 30	40 ± 21	25 ± 17	33.0 ± 1.5	2.30 ± 0.13	0.95 ± 0.11
20-30	345 ± 23	3 ± 14	10 ± 14	25.0 ± 1.8		
30-40	420 ± 34	12 ± 19	13 ± 20	29.3 ± 1.6	3.15 ± 0.32	1.25 ± 0.08
40-50	350 ± 26	60 ± 18	115 ± 18	24.4 ± 2.0		
50-60	620 ± 32	64 ± 18	89 ± 17	33.3 ± 2.4		
60-70	(1090 ± 44)[b]	(105 ± 23)[b]	(120 ± 19)[b]	40.9 ± 1.4	(4.73 ± 0.09)[a]	1.43 ± 0.09
70-80	(950 ± 36)[b]	(140 ± 22)[b]	(95 ± 15)[b]	38.5 ± 2.0	2.68 ± 0.18	0.99 ± 0.04
80-90	(1080 ± 42)[b]	(150 ± 23)[b]	(105 ± 15)[b]	28.9 ± 1.9	3.57 ± 0.15	1.22 ± 0.07
90-100	815 ± 42	115 ± 24	57 ± 20	43.9 ± 3.6		
100-110	635 ± 33	54 ± 18	58 ± 17	51.3 ± 2.3	3.29 ± 0.39	1.67 ± 0.12
110-120	495 ± 30	64 ± 19	9 ± 14	42.8 ± 3.0		
120-130	290 ± 18	36 ± 12	8 ± 11	26.2 ± 2.2	1.84 ± 0.06	0.76 ± 0.06
130-140	340 ± 25	44 ± 15	20 ± 14	32.0 ± 1.3	2.44 ± 0.10	0.91 ± 0.06
140-150	350 ± 18	−1 ± 9	24 ± 10	35.7 ± 1.5	2.07 ± 0.05	1.04 ± 0.10
150-160	365 ± 28	−4 ± 12	20 ± 17	32.5 ± 1.8	2.54 ± 0.15	1.10 ± 0.11
160-170	350 ± 30	−16 ± 12	21 ± 17	29.9 ± 1.9	2.40 ± 0.09	1.15 ± 0.14
170-180	395 ± 21	10 ± 11	24 ± 12	50.3 ± 2.3	3.75 ± 0.13	1.52 ± 0.18
180-190	350 ± 20	−6 ± 8	15 ± 11	42.3 ± 2.5		
190-200	200 ± 22	−7 ± 11	18 ± 14	18.0 ± 1.0	0.69 ± 0.04	0.38 ± 0.03
200-210	470 ± 25	12 ± 15	18 ± 12	37.4 ± 2.0	1.58 ± 0.15	0.98 ± 0.10
210-220	425 ± 27	−10 ± 11	26 ± 14	48.2 ± 1.4		
220-230	390 ± 22	12 ± 15	9 ± 12	53.9 ± 2.5		
230-240	335 ± 18	13 ± 12	28 ± 10	38.5 ± 1.6		
240-250	500 ± 27	−1 ± 12	28 ± 14	59.2 ± 1.8	2.03 ± 0.23	1.31 ± 0.20
250-260	46 ± 11	−5 ± 8	6 ± 9	4.2 ± 0.4		

[a] We interpret the maximum concentration in PCBs to have resulted from removal of a dam just downstream of the release area in 1973. [b] Maximum activities in reactor nuclides (^{134}Cs, ^{60}Co, and part of the ^{137}Cs) are attributed to releases made in the year of maximum releases at the reactor site (1971). [c] We interpret the maximum in fallout nuclides to be associated with the year of highest fallout from nuclear weapons testing (1963).

exclusively at the two upstream industrial sites until 1971. At that time, purchases became almost exclusively Aroclor 1016, which is very similar in composition to 1242. The only significant difference between them is that 1016 has greatly reduced abundances of biphenyls with five or more chlorine atoms per molecule. Such compounds comprise less than 10% of 1242 (*25*). Concentrations of 1242 (1016) components were computed by averaging the values for three individual peaks on a packed-column chromatogram that correspond to PCBs with three and four chlorine atoms per molecule. At sites A and B, the upper core sections contain relatively high proportions of 1016, which are reported as 1242, and the maximum concentrations of PCBs clearly have a substantial 1016 component (*3*). Since conversion of purchases from 1242 to 1016 took place in 1971, this finding is consistent with our correlation of the maximum concentration of PCBs with sediment mobilization events in 1973. Concentrations of 1254 components were computed by averaging the values for three individual peaks that correspond to PCBs with five and six chlorine atoms per molecule. In most Hudson sediment samples we believe these latter compounds were derived originally from discharges of 1242, and have a greater relative abundance in sediments than in pure 1242 because of the greater mobility in the environment of the lower chlorinated PCBs (higher solubilities and vapor pressures) (*2, 3*). The proportion of PCB components reported as 1254 provides a first-order indication of the degree of modification that has taken place in the original 1242 mixture. An additional perturbation of the composition of sediment-associated PCBs occurs in New York harbor as a result of sewage and possibly industrial discharges (*2, 3*), but no evidence was found for significant degradation of PCB components in sediment columns on a time scale of decades (*2*). The chromatograms of the PCB fraction of the sediment extracts also contained minor peaks corresponding to hepta- and octachlorobiphenyls, which are components of higher chlorinated PCB mixtures such a Aroclor 1260; however, the major features of all PCB chromatograms are well represented by the values of 1242 and 1254 reported in Tables I–III.

Pesticides and Time Stratigraphy in Hudson Sediments. Chlorinated hydrocarbon pesticides found in Hudson sediments include DDT and its derivatives DDD and DDE, chlordane and its derivative oxychlordane, and dieldrin a pesticide in its own right and a breakdown product of the more commonly used pesticide aldrin. Our findings were not at all surprising since these chemicals are among the most ubiquitous and persistent contaminants of the environment and have been found consistently in samples of human adipose tissue (*26*), indicating widespread environmental distribution. DDT-related compounds including *pp'*-DDT, *pp'*-DDE, *pp'*-DDD, and *op'*-DDD were found in all cores sampled. The best of

Table IV. *pp'*-DDD Concentrations in Samples from Core Sites B and C[a]

depth, cm	*pp'*-DDD, ppb	depth, cm	*pp'*-DDD, ppb
Core Site B (kmp 147.7, 7/14/77, CN 1329)			
0-2	14	28-32	23
2-4	19	(32-36)[c]	14
4-8	27	36-40	<2
8-12	26	40-44	(<0.3)[d]
12-16	24	44-48	(<0.3)[d]
16-20	28	48-52	<1
20-24	32	52-54	<1
(24-28)[b]	27 (25)		
Core Site C (kmp 86.6, 1/77, CN 1240)			
0-1	26	(13-14)[b]	74
1-2	30	14-15	72
2-3	39	15-16	66
(3-4)[e]	44	16-17	94
4-5	48	17-18	98
5-6	43	18-19	86
6-7	50	19-20	93
7-8	46	20-21	85
8-9	60	21-22	72 (59)
9-10	57	22-23	55
10-11	70 (66)	23-24	25
11-12	70	(24-25)[c]	23
12-13	82 (80)	25-26	11

[a] Values in parentheses are the results of analysis of a separate portion of sediment from the same core section. [b] Samples from this depth interval have a maximum in fallout nuclides which we associate with the year of highest fallout from nuclear weapons testing (1963). See Tables I and II. [c] Samples from this depth interval are associated with the first appearance of fallout nuclides from nuclear weapons testing (1954). See Tables I and II. [d] These extracts were acid treated, which removed interfering peaks from the chromatograms, resulting in a significant lowering of our value for the maximum possible amount of *pp'*-DDD present. [e] Samples from this depth interval have a maximum in reactor nuclides which we associate with the year of maximum releases at the reactor site (1971). See Tables I and II.

these for constructing a chronology is *pp'*-DDD, which occurs in recent Hudson sediments at levels of a few tens to a few hundred ppb and appears to be stable in anoxic sediment columns on the time scale of decades (Tables IV and V). Studies of the persistence of DDD in flooded soils (*27*) support this latter contention. The usefulness of *pp'*-DDT is hindered by its labile nature (*28*) and poorly understood geochemistry in anoxic sediments. In most samples, levels of *pp'*-DDT were generally less than about 15% of the *pp'*-DDD levels, indicating efficient conversion to derivatives; however, some samples (most notably, site F, 140–180 cm) contained much higher levels of *pp'*-DDT (up to >300 ppb, confirmed by conversion to *pp'*-DDE (*15*)), which approached and sometimes exceeded those of *pp'*-DDD in the same sample. *pp'*-DDE is difficult to quantify in our samples because it is found in the PCB fraction and masked on our chromatograms by the extremely high levels of PCB compounds. *op'*-DDD was found in all of our samples at levels ranging between about 10% and 25% of the total (*pp'* + *op'*)DDD. This is consistent with reported formulations of technical DDT which contains "ca. 80% *pp'* and 20% op'" isomers (*29*) and suggests that both isomers behave similarly in the environment. Cores from upstream of New York harbor (B and C, Table V) have maximum values of *pp'*-DDD contamination that correspond approximately with the period between the late 1950s and late 1960s. By the mid-1970s, levels have dropped to between 25% and 50% of their maximum values. Although no comprehensive records of

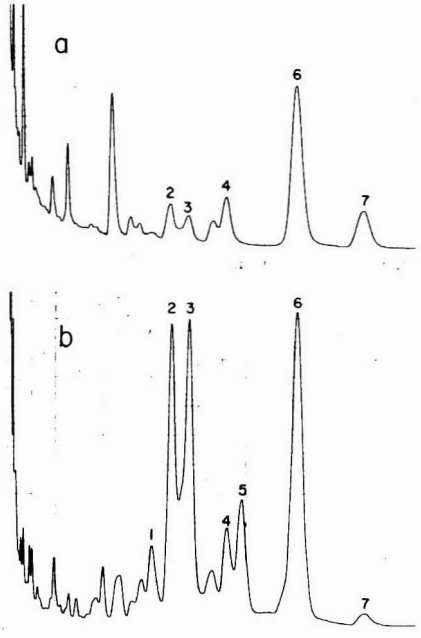

Figure 7. (a) Chromatogram of the pesticide fraction of the extract of the 20–24-cm section of the core from site B (kmp 147.7). (b) Chromatogram of the pesticide fraction of the extract of the 25–30-cm section of the core from site E (kmp 4.8). Peak assignments are (1) oxychlordane, (2) γ-chlordane, (3) α-chlordane, (4) *op'*-DDD, (5) dieldrin, (6) *pp'*-DDD, and (7) *pp'*-DDT.

DDT use in the Hudson drainage basin are available, this pattern is consistent with estimates of overall U.S. consumption of DDT, which averaged about 60 million pounds yearly between 1950 and 1960 and decreased approximately linearly to less than 20 million pounds in 1972 when the EPA suspended virtually all domestic uses of DDT (*30*). Chlordane and dieldrin, which are major contaminants of harbor sediments, were not easily detected in these upstream samples. All samples contained <8 ppb chlordane and <2 ppb dieldrin. Acid (H_2SO_4) treatment of selected extracts (*14*), which removed some of the interfering peaks as well as any dieldrin present, often yielded chromatograms with discrete minor peaks corresponding to the chlordane isomers. Maximum levels of α- and γ-chlordane observed by using this technique were <5 ppb. A chromatogram of the pesticide fraction (acid treated) of an extract of sediment from the core at Site B is shown in Figure 7a.

In contrast, New York harbor cores E and F contain relatively high concentrations of both chlordane and dieldrin (Table V, Figure 7b), indicating a dominant urban source for these pesticides. Harbor samples also exhibited a peak corresponding to oxychlordane, a persistent chlordane derivative. Individual samples had oxychlordane contents that ranged from about 8% to 15% of their total α-chlordane + γ-chlordane concentrations. In addition, *pp'*-DDD levels are also generally greater than in the upstream cores. Figure 8 is a plot of *pp'*-DDD, γ-chlordane, and dieldrin levels in the core from site E as a function of time. All of these pesticides show subsurface maximum concentrations that occur well below the maximum PCB concentrations. These maxima appear to be approximately contemporaneous with fallout nuclide maxima in the early to mid-1960s.

Table V. Pesticide Concentrations in Samples from New York Harbor Core Sites E and F[a]

depth, cm	γ-chlordane, ppb	α-chlordane,[b] ppb	dieldrin, ppb	*pp'*-DDD, ppb
	Core Site E (kmp 4.8, 9/15/75, CN 1380)			
0-5	34 (36)	30 (30)	14 (19)	113 (123)
(5-10)[c]	39 (44)	41 (34)	<3 (<3)	120 (119)
10-18	77 (85)	87 (96)	53 (67)	177 (204)
18-25	80 (78)	85 (84)	49 (56)	179 (193)
25-30	77 (82)	83 (87)	41 (56)	222 (250)
(30-56)[d]	91 (90)	106 (107)	63 (72)	274 (290)
36-43	57 (53)	54 (40)	19 (18)	176 (183)
43-50	41 (48)	40 (33)	~7 (<10)	186 (202)
	Core Site F (kmp -2.4, 10/18/75, CN 1048)			
0-10	76	89	37	65
10-20	89	103	49	89
(30-40)[e]	94	108	57	101
(60-70)[c]	113	127	58	113
(70-80)[c]	70	80	33	101
(80-90)[c,e]	95 (104)	105 (124)	56 (63)	106 (107)
120-130	58	63	39	84
130-140	80	93	47	116
140-150	72	77	46	131
(150-160)[e]	84 (96)	94 (104)	54 (66)	117 (110)
170-180	116	126	73	197
190-200	38	43	26	60
220-230	77	82	50	165
240-250	100	103	71	460

[a] Values in parentheses are the results of analysis of a separate portion of sediment from the same core section. [b] The peak quantified as α-chlordane also contains a small contribution from trans-nonachlor, a minor chlordane component not resolved under the chromatographic conditions employed. [c] Samples from this depth interval have a maximum in reactor nuclides which we associate with the year of maximum releases at the reactor site (1971). See Table III. [d] Samples from this depth interval have a maximum in fallout nuclides which we associate with the year of highest fallout from nuclear weapons testing (1963). See Table III. [e] Earlier reported values (2) for *pp'*-DDD and γ- and α-chlordane in these samples were somewhat lower (an average of 17%) due to minor recovery problems in our procedure, which have been corrected.

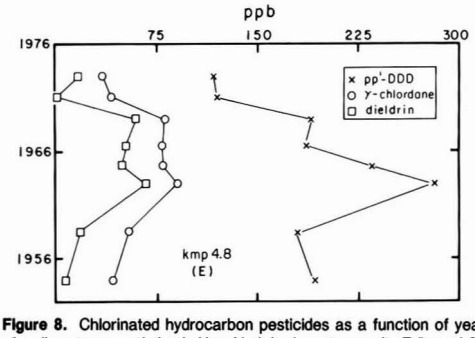

Figure 8. Chlorinated hydrocarbon pesticides as a function of year of sediment accumulation in New York harbor at core site E (kmp 4.8): data from Table III were used to estimate age as a function of depth. Pesticide values plotted are the average of the two values given in Table V.

Rates of Decline of Persistent Contaminants in Hudson Sediments. All of the contaminants discussed here could be classified as persistent in terms of their behavior in the environment. The radionuclides discussed have known half-lives, pesticides can be transformed chemically to related compounds, and PCBs undergo significant evolution in composition primarily because of differences in physical properties (i.e., distribution coefficients between water and particles, and vapor pressure) among its component compounds. However, the dominant process responsible for the recent decreases in the concentrations of these materials in sediments appears to be mobilization of soils from the drainage basin as suspended particles, which leads to dilution and burial of more highly contaminated sediments already present in the tidal Hudson. The rate of decline in contaminant level is not identical for each of these persistent components nor is it always consistent from one core to the other. There are, however, some clear general patterns that do provide an indication of the time scale of reduction of contaminant levels that has occurred over the past 1–2 decades.

One simple way to compare the rates of decline for the persistent contaminants is to compute the halftime for decrease from maximum sediment concentrations to the levels present at the time of core collection (Table V). The PCB (1242) concentrations since the maximum values in the early 1970s have generally decreased with a half-time of about 2 years. This is similar to the observed decrease rates for reactor nuclide (^{60}Co and ^{134}Cs) activities. Fallout ^{137}Cs and ^{239,240}Pu activity levels in Hudson sediments since the early 1960s have declined more slowly, with an average half-time of about 6 years (3.5–8.9 years).

As a first-order model, after a point-source pulse of input directly to the river, the surface concentration of a persistent contaminant in the sediments of the Hudson at a particular site of fairly rapid sediment accumulation (1–10 cm/year) appears to decrease with a half-time of about 2 years. This case applies to both reactor nuclide inputs in 1971 and PCB inputs related to the dam removal in 1973. For contaminants delivered primarily as a single pulse over the entire drainage basin such as fallout radionuclides, the half-time for decrease after maximum loading appears to be about 6 years. The slower calculated response in such cases is due to the fact that the contaminant is not delivered directly to the river but enters the system over a longer period of time determined by sediment mobilization and transport processes in the drainage basin.

Recent trends of PCB contamination in Hudson sediments are dominated by the effect of the dam removal in the upper drainage basin ($t_{1/2} \sim 2$ years). Over the next few years, the delivery of PCBs to the lower Hudson can be expected to evolve to a more "natural" situation controlled by the transport of contaminated sediment from the upper Hudson during periods of high flow caused by storms or spring runoff. Since similar processes have been

Table VI. Decline of PCB and DDD Concentration and Radionuclide Activities in Sediments of the Hudson River Estuary (1963-1977)

core site	contaminant	C_1	C_2	Δt, years	$t_{1/2}$,[a] years
A	Aroclor 1242 (1016)	140 ppm	33 ppm	4	1.9
B	Aroclor 1242 (1016)	29 ppm	5 ppm	4	1.6
C	Aroclor 1242	26 ppm	7 ppm	4	2.1
D	Aroclor 1242	10 ppm	4 ppm	5[b]	3.8
E	Aroclor 1242	9.3 ppm	6.9 ppm	2	4.6[c]
F	Aroclor 1242	4.7 ppm	1.6 ppm	2	1.3
B	*pp'*-DDD	27 ppb	14 ppb	4	4.2
C	*pp'*-DDD	48 ppb	26 ppb	4	4.5
A	^{239,240}Pu	35 pCi/kg	16 pCi/kg	4	3.5
B	^{239,240}Pu	27 pCi/kg	7 pCi/kg	12	6.2
C	^{239,240}Pu	77 pCi/kg	28 pCi/kg	13	8.9
E	^{239,240}Pu	66 pCi/kg	24 pCi/kg	12	8.2
A	^{137}Cs	3200 pCi/kg	1500 pCi/kg	4	3.7
B	^{137}Cs	2400 pCi/kg	730 pCi/kg	12	7.0
D	^{60}Co	420 pCi/kg	96 pCi/kg	5[b]	2.3
D	^{134}Cs	395 pCi/kg	82 pCi/kg	5[b]	2.2
F	^{60}Co	~110 pCi/kg	12 ± 13 pCi/kg	4	0-1.9[d]
F	^{134}Cs	~140 pCi/kg	14 ± 15 pCi/kg	4	0-1.8[d]

[a] Half-time for decrease in concentration over the period of years specified was computed from $C_2 = C_1 e^{-\lambda \Delta t}$, where $t_{1/2} = (\ln 2)/\lambda$. [b] Because the maximum PCB concentration (1973) and maximum ^{134}Cs and ^{60}Co activities (1971) occur at the same level in this core (D) (Table II), we have assigned a date of 1972 to this sample for the purpose of this calculation. [c] A large uncertainty is associated with this result because of poor stratigraphic resolution due to the fact that C_1 and C_2 are from adjacent samples (0-5 and 5-10 cm). For this same reason, ^{60}Co and ^{134}Cs results are not tabulated for this core (E). [d] $t_{1/2}$ values for these samples are based on a 1σ range of C_2. This was done because in these cases the uncertainty in C_2 was large relative to the measured value.

responsible for transport of fallout radionuclides to the Hudson from the drainage basin, we believe that under such conditions PCB concentrations in Hudson sediments would decrease at a significantly slower rate, approaching the 6-year half-life observed for fallout radionuclide concentrations. This prediction assumes no further major sediment mobilization events in the upper Hudson, where a considerable reservoir of very highly contaminated sediments remains impounded behind a series of small dams. It also does not consider the potentially ameliorating effect of the proposed dredging and removal of some of the most highly contaminated sediments from this area of the river (*31*).

The simple analysis presented here accounts for the gross features of Hudson river sediment profiles of PCBs and radionuclides. It should be emphasized that the application of a simple exponential equation to describe the decrease in contaminant levels observed in our sediment cores does not imply that we feel the processes operating are first order. Indeed, similar conclusions about the rates of decrease would be obtained from a linear model. Our sole purpose was to use the simplest method possible to make comparisons between cores that is consistent with the gross features of the available data. Furthermore, we feel that any attempt to use more intricate models to explain the data in greater detail will be severely hampered by the well-documented complexity of the system with respect to sediment transport and deposition (*11*, *12*, *16*), and we doubt that the presently available data could be used to constrain any model of more than one or perhaps two adjustable parameters. Other factors influencing the observed distributions including the geochemistry of the individual substances and variations in sediment characteristics have been discussed elsewhere (*2*, *3*, *16*).

The situation with respect to the observed decrease in pesticide concentrations is complicated by the fact that the primary input is not constrained to a short period of time relative to the period of observation. For cores significantly upstream of New York harbor, it can be argued that sediment *pp'*-DDD levels reflect the pattern of use of DDT in the drainage basin. Subsequent to the nationwide DDT ban in 1972, the situation becomes more analogous to that of fallout radionuclides since 1963. While there are no significant additional inputs either directly to the river or to the drainage basin, the previously contaminated soils of the drainage basin contribute significant contamination to river sediments. By analogy to fallout radionuclides, we would expect post-1972 *pp'*-DDD residues in cores from these areas to decrease with half-times ranging from about 3.5 to 8.9 years (Table VI). Calculated half-times of decrease in *pp'*-DDD at core sites B and C between 1973 (the maximum PCB concentration) and the time of coring are both approximately 4 years (Table VI).

Pesticides in harbor sediments are probably derived from agricultural products brought into the New York City area and from local applications of chlordane, dieldrin, and aldrin for termite and garden pest control. Additionally, for *pp'*-DDD, there is significant downstream transport from the drainage basin. Pesticides enter the river with New York City area sewage which is discharged into the lower Hudson estuary and surrounding waters. A sample of sludge from the city's sewage-treatment plant on Ward's Island contained all of the pesticide residues that were found in harbor sediments. An additional possible source of pesticides applied locally is urban and suburban runoff. This source is potentially most important for chlordane, which has been used extensively by commercial pest control operators and by homeowners for lawn and garden application (*32*). In any case, the recent decline in pesticide levels observed in harbor sediments is almost certainly related to the growing awareness of the persistence and toxicity of organochlorine pesticides and the resulting EPA restrictions on domestic use of these compounds. As mentioned previously, most uses of DDT were suspended in 1972, while the use of dieldrin and its environmental precursor aldrin was severely restricted in 1974 and the registration of chlordane was suspended in 1975. In addition, the upgrading of sewage treatment over the past 2 decades, which tends to remove a greater fraction of sediment-associated contaminants (*33*), could also have

played a significant role in the observed decrease. It is reasonable to conclude from the decrease in sediment pesticide levels in New York harbor sediments since the mid 1960s that our national environmental management policies with respect to chlorinated hydrocarbons have had a significant positive impact on the state of our urban estuaries.

The general features of the profiles in Figure 8 correspond fairly well to estimates of national sales of the pesticides and their precursors. The compounds under discussion were developed as pesticides between 1939 (DDT) and 1950 (dieldrin). Domestic consumption of DDT was greatest from about 1950 through the early 1960s and dropped by about two-thirds between 1959 and 1971. Dieldrin and aldrin use peaked in the mid-1960s and decreased by about 50% between 1966 and 1974 (*30*). Data on chlordane use are not as readily available. The only estimates we have found cover the period from 1971 through 1974 and show an increase of about a factor of 2 in domestic sales over that span of time (*32*). This feature is certainly not evident in the core from site E (Figure 8) but could possibly be detected in future cores with more detailed recent chronologies. Our data also indicate that the delivery of chlordane to sediments of the lower Hudson estuary was greater in the mid 1960s than at any time in the 1970s, an observation that can only be explained when more complete information related to that sources of this pesticide becomes available.

Conclusions

The history of contamination of persistent pollutants in natural water systems can be reconstructed by studying areas of fairly rapid sediment accumulation and combining information gained from sediment radionuclide measurements with determinations of sediment concentrations of particular pollutants (*4*, *6–10*). As demonstrated for the Hudson River and estuary, this approach is particularly well suited to the study of PCBs and chlorinated hydrocarbon pesticides and can provide basic information concerning the response time of the natural system and the geochemical behavior of persistent contaminants in natural waters. Such information is important both for the assessment of past environmental management policies and the planning of future ones. Our observations in natural water systems often describe the overall effects of many complex processes. Greater understanding of the system and the dominant processes can be gained by further observation aimed at the exploitation of geochemically significant events such as radioactive fallout, nuclear reactor operations, sewage discharges, and major physical alterations of the system such as dam removal.

A final point not emphasized in the main body of the paper concerns the use of chlorinated hydrocarbon pesticides as geochemical tracers of fine-particle transport and accumulation. Traditionally in the Hudson we have used radionuclides and PCBs for this purpose. In other natural water systems which might not receive reactor effluent or have enormously elevated levels of PCB contamination, DDD and chlordane residues are potentially useful particle tracers that could be used in conjunction with fallout radionuclides. They are stable in anoxic sediment columns, amenable to quantitative analysis at low (ppb) levels, can be confirmed in extracts by relatively simple techniques, and have been previously reported in sediments (*34*), agricultural soils (*35*), and urban soils (36).

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Decomposition of Ozone in Water: Rate of Initiation by Hydroxide Ions and Hydrogen Peroxide

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■ The initiation of ozone decomposition in "pure water" is first order in O_3 and OH^- concentration and k_{O_3,OH^-} becomes 70 ± 7 M^{-1} s^{-1} when a sequence of reactions is assumed by which three molecules of O_3 are eliminated per primary event. The difference between this value and higher values reported in the earlier literature may be explained by interferences by radical chain reactions which have not been totally inhibited in those studies. H_2O_2 also reacts with O_3 when present as an anion, HO_2^-. k_{O_3,HO_2^-} is $(2.8 \pm 0.5) \times 10^6$ M^{-1} s^{-1} when it is assumed that two molecules of O_3 are eliminated per primary event. Therefore, whenever $[H_2O_2] > 10^{-7}$ M (pH <12), HO_2^- has a greater effect than OH^- on the decomposition rate of O_3 in water. The high reactivity of HO_2^- explains that H_2O_2 is observed as a significant intermediate in the ozonated water only if the pH is low, e.g., <6.

Introduction

Ozone is used in many drinking water plants for the oxidation of organic micropollutants and manganese and for disinfection. Since mixing processes and many of the desired direct chemical reactions of O_3 with dissolved solutes M are often rather slow (*1*), ozonation processes are typically designed for process times lasting in the order of 10 min. A significant fraction of the O_3 dosed to the water can be lost during this time. Often this loss is kinetically controlled by the decomposition of O_3 rather than by ozonation of dissolved substances (see Figure 1). A characterization of the parameters that regulate this decomposition has been of great interest ever since O_3 has been used for water treatment.

Most of the studies on the decomposition of O_3 in water are largely based on phenomenological descriptions of overall kinetics found for "pure water". However, these systems are kinetically complex because a primary decomposition of O_3 produces free radicals (*2-4*) which may either become scavenged by bicarbonate and organic solutes or which may react with further O_3 to yield more free radicals (*3*, *5*), thus accelerating the decomposition of O_3 (see Figure 1). The kinetics of such chain reactions depend on many parameters that have not been separated and identified so far: a comparison of the rate data reported in the literature is therefore rather difficult, and the results from different authors seem contradictory. The proposed rate equations even differ in the reaction order to be considered for the concentrations of O_3 or OH^-. Discussions including lists for comparisons and literature references have been presented by Stumm (*6*), Peleg (*7*), Roth et al. (*8*), and Gurol (*9*).

The purpose of our studies was therefore to separate, identify, and quantify the successive individual reactions that control the overall rate of O_3 decomposition in drinking water and other aqueous solutions. The results will allow better predictions of how the rates will be influenced by changes in water composition (*10*).

In this first paper of a series we will describe the kinetics by which the decomposition of O_3 in water is initiated by water itself (H_2O, OH^-, H_3O^+) under conditions where secondary radical-type chain reactions are excluded by OH· radical scavengers. Such situations resemble those encountered when natural waters are ozonated, in which HCO_3^- and organic solutes inhibit the radical-type chain reactions efficiently (*5*). In addition, H_2O_2 is often an important intermediate product from the ozonolysis of aqueous solutions (see Figure 1). This H_2O_2 formation results either directly from O_3 decomposition (see reaction 4') or from hydrolysis of organic ozonation products (*3*, *11-14*). During this study it was observed that this intermediate can also influence the kinetics of O_3 decomposition. This product (H_2O_2/HO_2^-) behaves like water (H_2O/OH^-) in that it only reacts with O_3 when ionized, and its reaction kinetics could be investigated by similar techniques. The results will also provide general information on the fate of H_2O_2 produced by ozonation.

In contrast, the subsequent chain reactions in which OH· and HO_2· ($\cdot O_2^-$) act as chain carriers have been measured by rather different methods using electron pulse irradiation with kinetic spectroscopy. These systems will therefore be described in separate papers.

Since the submission of this paper, Forni et al. (*15*) have published their work on the kinetics of OH^--initiated ozone decomposition and the subsequent OH· radical formation. Their work, however, was not directly aimed at the study of drinking water processes and therefore somewhat different concepts and much higher pH regions were applied for the measurements.

Experimental Part

Chemicals. Water, deionized by ion exchangers, was distilled and then preozonized by adding 3 mg/L O_3, which was allowed to decompose before the water was used. Aqueous ozone stock solution was prepared as described

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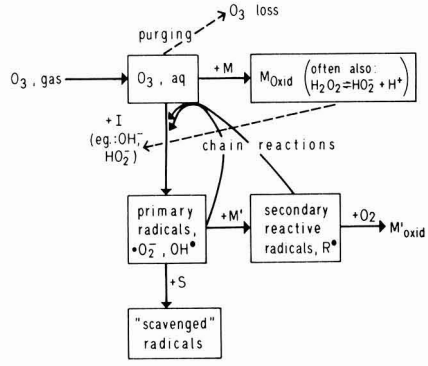

Figure 1. Scheme of reactions of aqueous ozone. M, solutes that consume ozone and become oxidized to M_{oxid} (and H_2O_2); I, solutes that initiate the decomposition of ozone to primary radicals; S, free radical scavenger; M', solutes that react with OH· and form secondary radicals R· and become finally oxidized to M'_{oxid}.

previously (*3*). Phosphate buffer solutions were prepared from phosphoric acid and sodium hydroxide (both suprapure grade). The solutions were preozonized with 3 mg/L O_3. Sodium bicarbonate was analytical grade. Its solutions were preozonized. Nitrous acid and sodium hydroxide standard solutions were Merck Titrisol type reagents (0.1 N). H_2O_2 solutions were prepared from Na_2O_2 (*16*) or from commercial perhydrol solutions that were free from stabilizers. Both reagents gave the same results. The H_2O_2 concentrations were determined by the method of Eisenberg (*17*). For methylmercury preparation see ref 18.

Instrumentation. pH measurements were performed with a glass electrode. The calibration was based on Merck Buffer Titrisols for pH 7 and 10. The instrumental pH scale was calibrated for the determination of OH^- concentrations by solutions of defined OH^- concentration (standard sodium hydroxides and nitrous acid solutions) at pH 10–11 (Gran titration method) (*19*). The ionic strength for these calibrations was adjusted by $NaNO_3$ to correspond to that used for the experiments on the kinetics of the OH^- reactions (I = 0.15 M).

UV absorption measurements were performed on a Beckman DK-2A or Uvikon 810 instrument in thermostated and closed cells.

Methods. Procedure for Kinetic Measurements. All experiments were performed at 20 ± 1 °C. Thermostating was required for measurements lasting more than a short time. Samples from the concentrated aqueous stock solution of O_3 were pipetted to the prepared mixtures of reactants. The flasks were closed and immediately stirred or shaken for 5 s. For kinetic measurements performed to test the effect of carbonate at pH 9 and for all series with H_2O_2, the depletion of O_3 vs. time was directly followed in a 5-cm UV cell at 258 nm. In all other cases the ozonation was performed in a 1-L round bottom flask from which series of 10-mL aliquots were withdrawn at specified time intervals. The residual concentration of O_3 in these samples was determined immediately by direct UV measurements in 1-cm cells (for series at pH 8) or by the indigo method (for all other series) (*20, 21*).

Procedure for Measurements of OH· Radical Yields. The yields of OH· radicals were determined from the stoichiometric factor by which methylmercury was mineralized (*18*). This mineralization is not disturbed by other ozonation reactions. For experimental details see ref 22.

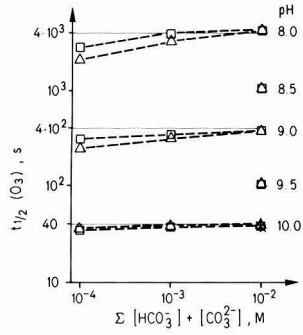

Figure 2. Successive half-lives of ozone vs. concentration of carbonate for different pH values. $[O_3]_0$ = 50 μM: 1st $t_{1/2}$ △; 2nd $t_{1/2}$ □. $[O_3]_0$ = 3 μM X; $[O_3]_0$ = 0.3 μM +; $[PO_4]_{tot}$ = 50 mM.

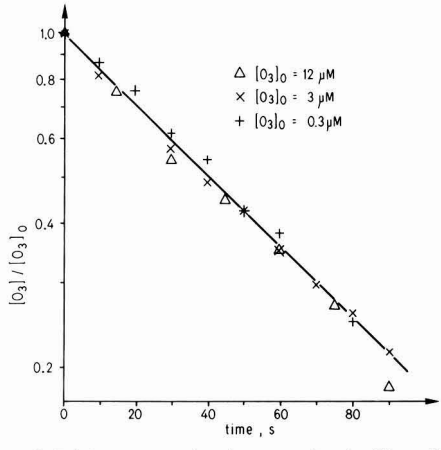

Figure 3. Relative concentration of ozone vs. time for different $[O_3]_0$ at high scavenger concentration: $[HCO_3^-]$ + $[CO_3^{2-}]$ = 10 mM; $[PO_4]_{tot}$ = 50 mM; pH 10.0.

Results and Discussion

Decomposition Initiated by OH^- Ions. Dependence on pH and Scavenger and Ozone Concentration. The concentration of the O_3 added could easily be followed as a function of time in the batch-type reactors when the pH was in the range 8–10. At pH values below 8, measurements were still possible, but the rates of elimination of O_3 became very small and could be disturbed by other reactions such as wall effects. At pH values above 10 the decomposition of O_3 became so fast that it could not be followed accurately by the experimental techniques applied here.

From the plots of O_3 concentration vs. time, half-lives for the concentration of O_3 have been determined for succeeding time intervals. As shown in Figure 2, these half-lives depended mainly on pH. At constant pH they increased when carbonate was added to scavenge OH· radicals (*5*). At low carbonate concentrations they also varied with initial O_3 concentration and time. However, when sufficient carbonate was added, the half-lives approached a plateau value for each pH, and they became independent of the O_3 concentration. Similar results were obtained when methylmercury was used as a scavenger for OH· radicals (*18*).

Semi-log plots of O_3 concentrations vs. time yield straight lines for those experiments performed at high

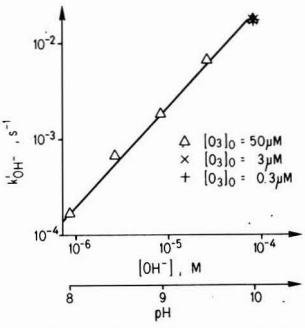

Figure 4. Measured pseudo-first-order rate constant for the decomposition of ozone vs. hydroxide ion concentration. A pH scale is given for comparison. $[HCO_3^-] + [CO_3^{2-}] = 10$ mM; $[PO_4]_{tot} = 50$ mM.

scavenger concentration as demonstrated in Figure 3 for a series of measurements at pH 10. The slopes of these lines do not vary with O_3 concentration in the range 0.3–50 μM. Therefore, the results presented in Figures 2 and 3 for high concentrations of radical scavengers can be described by a pseudo-first-order rate law:

$$-(d[O_3]/dt)_{pH} = k'_{OH^-}[O_3]^{1.0} \quad (1)$$

where $k'_{OH^-} = \ln 2/t_{1/2}$. As shown in Figure 4 the pseudo-first-order rate constants k'_{OH^-} increase by a factor of 10 per increased pH unit. For later convenience the pH scale in Figure 4 has also been converted to a scale of increasing OH^- concentration by the calibration procedure described in the Experimental Part. The slope of log k'_{OH^-} vs. log $[OH^-]$ becomes 0.99 ± 0.05 (error range for $p = 0.95$) when the regression is based on seven series of measurements performed at five different pH values. Thus, the measured rate of decomposition of O_3 can be described by

$$-d[O_3]/dt = k_{O_3,OH^-}{}^{measd}[O_3]^{1.0}[OH^-]^{1.0} \quad (2)$$

for which the second-order rate-constant becomes

$$k_{O_3,OH^-}{}^{measd} = k'_{OH^-}/[OH^-]^{1.0} = (210 \pm 20)\ M^{-1}\ s^{-1} \quad (3)$$

where $[OH^-]$ is the analytical OH^- concentration. When based on the experimental pH scale, the values become somewhat different because $[OH^-]$ is not exactly $10^{-14} \times 10^{pH}$ M (*19*). Transformed to the pH scale, the numerical values become

$$k_{O_3,pH}{}^{measd} = k'_{OH^-}10^{14-pH} = (175 \pm 10) \times 10^{14-pH}\ M^{-1}\ s^{-1} \quad (3')$$

Ranges of errors are based on the precision of the measurements and on $p = 0.95$; the accuracy of the data is, however, limited by the accuracy of pH or $[OH^-]$ measurements, for which we assume a range of error of 0.05 units or 10%.

Discussion. On the basis of these results we assume that the pH-dependent decomposition of O_3 is due to a reaction that is kinetically controlled by the OH^- concentration. The phenomenon cannot be due to a pH-dependent change of O_3 molecules (such as formation of HO_3^+ or O_3OH^-) because all other known O_3 reactions are strictly pH independent except in those cases where the degree of dissociation of the other reactant changes with pH (*21*). Also the fact that OH^--initiated decomposition of O_3 is of first order, both in O_3 and in OH^- concentration, is consistent with our experience with reactions of O_3 with other solutes (*21*).

The kinetic rate laws now found for aqueous solutions that contain OH· radical scavengers are different from those reported in the literature for "pure water". Even the orders of reaction are different. This result is not surprising since in most earlier studies the rate of the decomposition in "pure water" was accelerated by undefined chain reactions subsequent to OH^- attack.

The rate constant $k_{O_3,OH^-}{}^{measd}$ is small when compared with the rate constants quoted for other reactions of O_3. This measured value is still different from the rate constant of the primary OH^- attack on O_3 molecules because it must be assumed that more than one O_3 molecule is destroyed per primary initiation step. To get an estimation of the overall stoichiometry of the $O_3 + OH^-$ reaction (when all OH· radicals are scavenged before reacting with O_3) the following reaction sequences can be considered:

Hypothesis I ((*2*) extended for dissociation of HO_2· and electron-transfer mechanism)

$$O_3 + OH^- \xrightarrow{k_{O_3OH^-}{}^{prim}} \cdot O_2^- + HO_2\cdot \quad (4)$$

where

$$HO_2\cdot \rightleftharpoons H^+ + \cdot O_2^- \qquad pK_a = 4.8 \quad (5)$$

$$O_3 + \cdot O_2^- \xrightarrow{k_6} \cdot O_3^- + O_2 \quad (6)$$

$$\cdot O_3^- + H_2O \xrightarrow{k_7} OH\cdot + OH^- + O_2 \quad (7)$$

Hypothesis II (this study and ref 11)

$$O_3 + OH^- \xrightarrow{k_{O_3OH^-}{}^{prim}} HO_2^- + O_2 \quad (4')$$

where

$$H_2O_2 \rightleftharpoons HO_2^- + H^+ \qquad pK_a = 11.6 \quad (8)$$

$$O_3 + HO_2^- \xrightarrow{k_{O_3HO_2^-}{}^{prim}} OH\cdot + \cdot O_2^- + O_2 \quad (9)$$

followed by reactions 6 and 7.

Hypothesis III (*23*)

$$O_3 + OH^- \xrightarrow{k_{O_3OH^-}{}^{prim}} \cdot O_3^- + \cdot OH \quad (4'')$$

followed by reaction 7.

The occurrence of $\cdot O_2^-$ as an intermediate (hypotheses I and II) is supported by qualitative chemical detections based on the reduction of tetranitromethane (*22*). The transient existence of O_3^- has now been positively proved by kinetic spectroscopy (*15*) as well as by pulse radiolysis studies on ozonated water (kinetic spectroscopy) (*24*).

Hypothesis III was proposed for observations made at extreme conditions of very high pH values (pH ~14). For our system the stoichiometric yield of OH· radical formation was found to be 0.55 ± 0.08 (*3*). This value is significantly less than 2.0 predicted by hypothesis III, but it is close to 0.67 as predicted by hypotheses I and II. We therefore can reject hypothesis III for our case.

Because the observed overall reaction has been found to be first order in O_3 concentration, the sequences of reactions formulated by hypotheses I and II must both be assumed to be rate limited only by the initiation step (reaction 4 or 4'). This is expected: the subsequent reaction of $\cdot O_2^-$ with O_3 is fast and dominant whenever the concentration of O_3 is dominant compared with that of other solutes reactive toward $\cdot O_2^-$. It yields O_3^- (*15*, *24*) (the rate constant for the reaction of $\cdot O_2^-$ with O_3, k_6, is about $10^9\ M^{-1}\ s^{-1}$ (*15*, *24*, *25*)). This is relatively high when compared with other rate constants of $\cdot O_2^-$ (*26*)). Likewise, $\cdot O_3^-$ and H_2O_2 can only exist as a short-lived intermediates in the pH ranges here considered (see ref 24 and later paragraphs).

All sequences of reactions proposed by hypotheses I–III can be followed by OH· radicals interacting with further

O_3 as formulated by reaction 10. However, scavengers such as carbonate, phosphate, or other solutes compete with reaction 10.

$$OH\cdot \xrightarrow{+O_3} HO_2\cdot + O_2 \qquad (10)$$
$$k_{10} = 3.0 \times 10^9\ M^{-1}\ s^{-1}\ (27)$$

$$OH\cdot \xrightarrow{+CO_3^{2-}} OH^- + \cdot CO_3^- \qquad (11)$$
$$k_{11} = 4.2 \times 10^8\ M^{-1}\ s^{-1}\ (28)$$

$$OH\cdot \xrightarrow{+HCO_3^-} OH^- + HCO_3\cdot \qquad (12)$$
$$k_{12} = 1.5 \times 10^7\ M^{-1}\ s^{-1}\ (28)$$

$$OH\cdot \xrightarrow{+HPO_4^{2-}} OH^- + \cdot HPO_4^- \qquad (13)$$
$$k_{13} = 5 \times 10^6\ M^{-1}\ s^{-1}\ (29)$$

In contrast to OH·, $HO_2\cdot$ ($\cdot O_2^-$) is not scavenged and leads to further decomposition of O_3 (see eq 6).

On the basis of previous work (*5*) we assume that the products formed from bicarbonate and carbonate ions do not interact significantly with further O_3, and we assume that reaction 6 is not inhibited by carbonate (reactions between carbonate ions and $HO_2\cdot$ ($\cdot O_2^-$) have also not been observed in pulse radiolysis studies). Therefore, for each pH and each O_3 concentration an appropriate carbonate concentration could be achieved that was sufficient to inhibit the subsequent chain reactions effectively.

In both hypothesis I and II it is assumed that three molecules of O_3 are decomposed per initiating step provided that $\cdot O_2^-$, $HO_2\cdot$, $\cdot O_3^-$, and H_2O_2 are not scavenged by other reactions. Herewith the rate constant of the primary reaction of OH^- with O_3 becomes

$$k_{O_3,OH^-}{}^{prim} = {}^1/_3 k_{O_3,OH^-}{}^{measd} = 70 \pm 7\ M^{-1}\ s^{-1} \qquad (14)$$

This value is in good agreement with the value recently deduced by Forni et al. (*15*) for reactions at pH >10.

Other Possible Primary Reactions in Pure Water. (i). A priori we cannot exclude that the decomposition of aqueous O_3 could also be initiated by other species present in pure water such as by H_3O^+. However, the decomposition of O_3 is not accelerated even at very low pH values. At pH 2 $t_{1/2}$ is larger than 200 000 s. Therefore $k_{O_3,H_3O^+}{}^{measd}$ must be smaller than $4 \times 10^{-4}\ M^{-1}\ s^{-1}$.

(ii). Aqueous O_3 could also decompose in the aqueous matrix by a spontaneous reaction that is not catalyzed by ions. The rate law of this reaction could be formulated by

$$-d[O_3]/dt = k_n[O_3] \qquad (15)$$

On the basis the stability of O_3 at low pH values, we can estimate that the first-order reaction rate constant for such a reaction, k_n, is smaller than $5 \times 10^{-6}\ s^{-1}$. Thus, initiation of O_3 decomposition reactions that are not controlled by OH^-, such as proposed by Alder and Hill (*30*), cannot be of importance.

Decomposition Initiated by H_2O_2 (HO_2^- Ions). Measurements on the rate of the decomposition of O_3 in the presence of radical scavengers were performed on a series of samples that contained different concentrations of H_2O_2. For these measurements methylmercury hydroxide was used as a free radical scavenger instead of carbonate (*18*) (carbonate would be inefficient in the low pH region applied, where it is protonated to form H_2CO_3). H_2O_2 was added in an excess when compared with that of the initial concentration of O_3. All plots of the log of the concentration of residual O_3 vs. time were linear. Thus, pseudo-first-order rate constants for the elimination of O_3

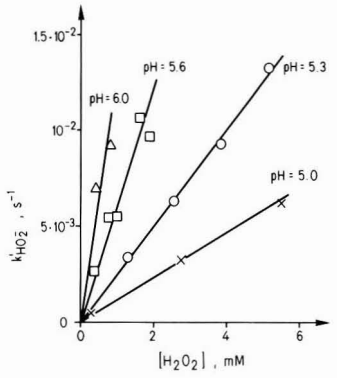

Figure 5. Measured pseudo-first-order rate constants of decomposition of ozone vs. hydrogen peroxide concentration for different pH values: [methylmercury] = 1.5 mM; $[PO_4]_{tot}$ = 50 mM.

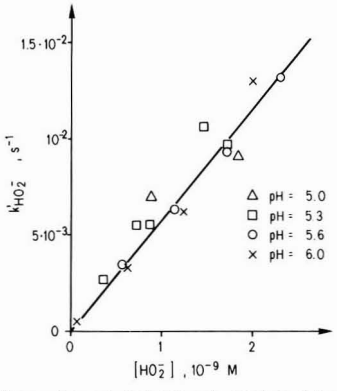

Figure 6. Measured pseudo-first-order rate constant of decomposition of ozone vs. hydrogen peroxide ion concentration: [methylmercury] = 1.5 mM; $[PO_4]_{tot}$ = 50 mM.

could again be deduced from the slope of these lines. At pH 2, H_2O_2 reacts only very slowly with O_3 (*4*). However, at pH values above 5, a strong acceleration of the decomposition of O_3 by H_2O_2 was observed. The effect increased linearly with the concentration of H_2O_2 (see Figure 5). Therefore the reaction rate can be formulated by

$$-(d[O_3]/dt)_{pH} = k_{O_3,H_2O_2}{}^{measd}[O_3]^1[H_2O_2]_{tot}{}^1 \qquad (16)$$

This rate increases by 1 order of magnitude per pH unit. This observation suggests that H_2O_2 also reacts with O_3 only when present in its ionized form:

$$O_3 + H_2O_2 \xrightarrow{very\ slow} \text{see ref 4}$$
$$-H^+ \Big\| +H^+$$
$$O_3 + HO_2^- \xrightarrow{fast} \text{decomposition of } O_3$$

The rate of decomposition of O_3 is plotted in Figure 6 vs. the concentration of HO_2^-. The concentration of HO_2^- was calculated from the total concentration of H_2O_2 and the degree of dissociation, α, calculated for $pK_{H_2O_2} = 11.6$ and the pH applied, where

$$\alpha = [HO_2^-]/([H_2O_2] + [HO_2^-]) = [HO_2^-]/[H_2O_2]_{tot} \qquad (17)$$

or for pH << $pK_{H_2O_2}$

$$\log \alpha = pH - pK_{H_2O_2} \qquad (18)$$

Table I. Rate Constants for the H_2O-O_3 and the Aqueous H_2O_2-O_3 Systems

H_2O	$k_n = <5 \times 10^{-6}\ s^{-1}$	$k_{O_3,H_3O^+} = <4 \times 10^{-4}\ M^{-1}\ s^{-1}$	$k_{O_3,OH^-}^{measd} = 210 \pm 20\ M^{-1}\ s^{-1}$	$k'_{OH^-} = 175 \times 10^{pH-14}\ s^{-1}$ [a]
H_2O_2	$k_{O_3,H_2O_2} = <10^{-2}\ M^{-1}\ s^{-1}$ [c]		$k_{O_3,HO_2^-}^{measd} = (5.5 \pm 1.0) \times 10^6\ M^{-1}\ s^{-1}$	$k'_{HO_2^-} = 5.5 \times 10^6 [H_2O_2]_{tot} 10^{pH-pK}\ s^{-1}$ [b]

[a] For ionic strength $I = 0.15$ M. [b] For ionic strength $I = 0.05$ M. [c] Reference 4.

Rate constants measured at different pH values in the presence of different relative amounts of nondissociated H_2O_2 fit in the same line. This means that the rate can be formulated as a reaction that is first order in the concentration of HO_2^-, and the reaction rate constant can be defined by

$$-d[O_3]/dt = k'_{HO_2^-}[O_3] = k_{O_3,HO_2^-}^{measd}[O_3][HO_2^-] \quad (19)$$

From the data in Figure 6 $k_{O_3,HO_2^-}^{measd}$ becomes $(5.5 \pm 1.0) \times 10^6\ M^{-1}\ s^{-1}$ (range of error based on precision of measurements of series, and $p = 0.95$; this range is larger than the uncertainty of pH and $pK_{H_2O_2}$ values used for calculations). This rate constant is high when compared with that of OH^- or with other reactive anions (*1*, *21*). Therefore, even very small concentrations of HO_2^- become kinetically effective for initiating the decomposition of O_3 (see below).

The stoichiometric yield factor for the production of OH· radicals in this decomposition was measured by the mineralization of methylmercury. The results showed that the formation of inorganic mercury was not significantly different (within ±30%) when the decomposition of O_3 was initiated by HO_2^- instead of OH^- ions. This means that the stoichiometric yield of OH· radical formation does not significantly vary with the type of initiation (reaction 4, 4′, or 9). We therefore can still accept the sequence of reactions proposed by Taube (*4*) where reaction 9 is followed by reactions 6 and 7.

Also, in this system the intermediate species $\cdot O_2^-$ will predominantly react with O_3 (vide supra), and subsequent chain reactions are again expected to be inhibited by OH· radical scavengers. Therefore, we assume that the rate of decomposition of O_3 is twice that of the primary initiation (reaction 9):

$$k_{O_3,HO_2^-}^{prim} = \tfrac{1}{2} k_{O_3,HO_2^-}^{measd} = (2.8 \pm 0.5) \times 10^6\ M^{-1}\ s^{-1} \quad (20)$$

Rate of Decomposition of Hydrogen Peroxide in Ozonation Processes. The interaction of HO_2^- with O_3 will lead to a consumption of HO_2^-, which is rapidly supplied from the dissolved H_2O_2. On the basis of the sequence of reactions 9, 6, and 7, we can therefore formulate the rate of consumption of H_2O_2 by O_3 by

$$-d[H_2O_2]_{tot}/dt = k_{O_3,HO_2^-}^{prim}\alpha[H_2O_2]_{tot}[O_3] \quad (21)$$

and if the concentration of O_3 is kept constant, the lifetime of H_2O_2 in a semi-batch-type reactor becomes

$$t_{1/2} = (\ln 2)/(k_{O_3,HO_2^-}^{prim}\alpha[O_3]) \quad (22)$$

Figure 7 shows that the half-life of H_2O_2 becomes short for high pH values even in presence of radical scavengers. This is the reason why H_2O_2, even when formed as a kinetically important intermediate, will only accumulate during the ozonation process if low pH values (pH <6) are maintained. This is in good agreement with reported observations on H_2O_2 formation in ozonized solutions (*3*, *11*, *12*).

Efficiency of HO_2^- Relative to That of OH^- in Initiating Decomposition of Ozone. The roles of HO_2^- and

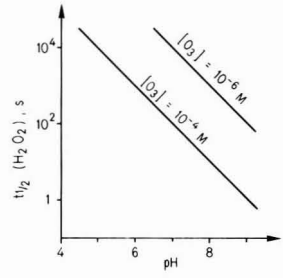

Figure 7. Calculated half-lives of hydrogen peroxide in the presence of constant ozone concentrations at different pH values (all OH· radicals scavenged, see eq 22).

OH^- increase proportionally with their concentrations. The effect of HO_2^- on the rate of decomposition of O_3 becomes larger than that of OH^- if

$$k_{O_3,OH^-}^{measd}[OH^-] < k_{O_3,HO_2^-}^{measd}\alpha[H_2O_2]_{tot} \quad (23)$$

Below pH 11, $[HO_2^-]$ and $[OH^-]$ vary the same way with pH (see eq 18). We can therefore compute a critical H_2O_2 concentration, for which the kinetic effect of HO_2^- (or of $[H_2O_2]_{tot}$) at all pH values below about 11 becomes larger than that of OH^-:

$$[H_2O_2]_{crit} = k_{O_3,OH^-}^{measd}[OH^-]/(k_{O_3,HO_2^-}^{measd}\alpha) > 10^{-7}\ M \quad (24)$$

This critical H_2O_2 concentration is low and independent of the pH at pH values significantly below $pK_{H_2O_2} = 11.6$.

Conclusion

In pure water, the decomposition of O_3 is initiated only by its reaction with OH^- (see Table I). The apparent rate constant for this reaction is $k_{O_3,OH^-}^{measd} = 210 \pm 20\ M^{-1}\ s^{-1}$ and the apparent pseudo-first-order rate constant for the decomposition of O_3 by OH^- becomes $k'_{OH^-} = 175 \times 10^{pH-14}\ s^{-1}$. This value is low when compared with the rate of decomposition of O_3 reported for "pure water". The discrepancy is due to secondary chain reactions of nondefined chain lengths which probably controlled the kinetics reported in earlier studies for solutions containing insufficient concentrations of OH· radical scavengers.

H_2O_2 reacts with O_3 only when present as the anion, HO_2^- (see Table I). The rate constant $k_{O_3,HO_2^-}^{measd} = (5.5 \pm 1.0) \times 10^6\ M^{-1}\ s^{-1}$ is high when compared to that for OH^- (see Table I). In aqueous solutions where the concentration of H_2O_2 becomes larger than 10^{-7} M, the decomposition of O_3 is initiated by HO_2^- faster than by OH^- (this relation holds up to pH <11.6).

At high pH values H_2O_2 will not accumulate even when it is produced as an intermediate ozonolytic product because already in the neutral pH region, where a small degree of dissociation of H_2O_2 becomes apparent, the decomposition of H_2O_2 by reaction of O_3 with HO_2^- proceeds fast (see Figure 7). The decomposition of H_2O_2 increases by a factor of 10 per pH unit increase.

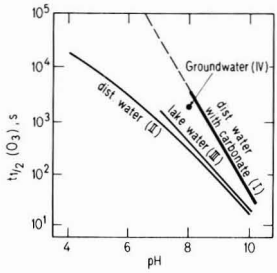

Figure 8. Half-lives ($t_{1/2}$) of ozone in different waters: I, all OH· radicals scavenged (this work); II, distilled water, $[PO_4]_{tot}$ = 50 mM; III, water of the lake of Zürich (*30*); IV, groundwater, infiltrated from Rhine (Basle, Waterwork Hard) (*31*).

Reactions of OH^- and HO_2^- with O_3 can initiate radical chain reactions. The kinetic chain length of such reactions depends on the relative rate by which the radicals formed react with O_3 compared with with other solutes present in the solution. Therefore such chain reactions can be more important in "pure water" than in real drinking waters or in some types of waste waters where bicarbonate and organic impurities may significantly scavenge OH· radicals. In Figure 8, the half-lives of O_3 measured in different types of natural waters are compared with those measured in our model solutions. This comparison also demonstrates that our conclusions are applicable to measurements on real waters.

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Flux of Aliphatic and Polycyclic Aromatic Hydrocarbons to Central Puget Sound from Seattle (Westpoint) Primary Sewage Effluent

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■ Concentrations and mass emission rates are reported for hydrocarbons in a 20-month evaluation of primary municipal waste water discharging to marine waters of Puget Sound from Seattle, WA. On the average, METRO (Westpoint) discharges 475 metric tons/year of aliphatic hydrocarbons and approximately 1 metric ton/year of 3–7 ring polynuclear aromatic hydrocarbons (PAH), corresponding to discharges of 2.6 and 0.005 g/(capita day), respectively. Effluent PAH containing ≥4 rings apparently derive principally from storm-water contributions. A comparison of METRO's yearly average discharge of different hydrocarbon components with observed hydrocarbon fluxes in adjacent Puget Sound surface sediments suggests negligible accumulations of the resolvable alkanes (derived from the effluent), partial accumulations of an unresolved complex mixture and phenanthrene, and substantial accumulations of the ≥4-ring PAH. The discharge accounts for a major portion of the sedimentary aliphatic fossil hydrocarbon flux and is one of several important PAH contributors.

Introduction

Municipal waste-water discharges have been increasingly recognized over the last decade as major sources of petroleum hydrocarbons in coastal marine environments (*1–10*). However, relatively few estimates of the actual hydrocarbon flux in these discharges have been made for either secondary (*2, 6, 7*) or primary (*9*) effluents, so the general applicability of these fluxes is uncertain. Also, questions are still unanswered as to compositional changes undergone by effluent hydrocarbons once in the marine ecosystem and the importance of various components within this discharge to actual hydrocarbon accumulations in recent sediments.

The inland marine waters of Puget Sound in northwestern Washington (Figure 1) have not experienced a major oil spill. Thus, documentation of increased accumulation of fossil hydrocarbons within recently deposited Puget Sound sediments (*11–15*) reflects increased discharges from primarily terrestrial sources. Studies of both aromatic (*11*) and aliphatic (*12–14*) hydrocarbons as well as azaarenes (*15*) and sulfur heterocyclic compounds (*16*) indicate contributions to the sediments of both natural and anthropogenic origin. Given the evidence of increased fossil hydrocarbon concentrations near urban centers of the Sound and hydrocarbon loadings in municipal waste waters elsewhere (*2, 6, 7, 9*), it seems reasonable that combined sewage and storm-water effluent may be a major hydrocarbon source for Puget Sound. A comparison of the typically low organic loadings in rivers vs. municipal waste waters also suggests that hydrocarbon fluxes from relatively small waste-water volumes can be significant.

In the present study, data are presented for a 20-month evaluation of both aliphatic and polynuclear aromatic hydrocarbons in combined sewer/storm-water discharges from a large primary treatment plant serving Seattle, WA. An analysis of the relationship of individual hydrocarbon fluxes to rainfall and street-dust accumulation clarifies the importance of storm-water runoff to hydrocarbon loadings in combined municipal waste-water systems.

In addition to total hydrocarbon flux and in an extension of municipal waste-water studies elsewhere (*2, 6, 7, 9*), data are given here for emission rates of specific hydrocarbon suites and their individual components, along with an estimated potential flux of each assemblage to Puget Sound sediments. These potential fluxes are then compared to corresponding observed accumulation rates within ^{210}Pb dated Puget Sound cores discussed previously (*13, 14*).

Thus, new information concerning the importance of urban waste waters and their ultimate sources to the accumulation of fossil hydrocarbons in coastal marine sediments is given through a correlation analysis of each hydrocarbon class, fluxes of these compounds into the marine environment, and implied alterations in composition occurring during transport and deposition.

Study Site

The Municipality of Metropolitan Seattle (METRO) sewage-treatment facility at Westpoint is the largest of 31 primary and secondary plants discharging (directly) into central Puget Sound (Figure 1), handling about 60% of the total flow (*17*). Even when secondary treatment discharge from METRO (Renton) upstream on the Duwamish River in Seattle (Figure 1) is considered, the Westpoint plant still accounts for over 50% of the total regional waste-water discharge.

METRO (Westpoint) has received an average 380 million L/day (100 million gallons/day) of combined municipal, industrial, and storm-water waste effluents since its opening in 1966 and has a design capacity of 1230 MLD. Industrial users discharge into the METRO system at 120 sites, accounting for about 5% of the total flow, but make up a much higher percentage of the sludge (METRO, personal communication).

Before consolidation of Seattle's sewage system in the 1960s to form METRO, 80% of the area's combined sewer and storm-water runoff discharged untreated into the receiving waters of Puget Sound or into fresh-water systems flowing into the Sound (*18*). During overflow periods, some untreated wastes are still discharged, mainly to Elliott Bay (Figure 1). Primary treatment of the chlorinated influent consists of solids removal by sedimentation and skimming plus anaerobic digestion and clarification before direct discharge into Puget Sound. Characteristics of the outfall, which discharges effluent at an average water depth of 70 m, and basin circulation, are described elsewhere (*19–21*).

Experimental Section

A total of 19 effluent samples were collected in refrigerated, solvent-rinsed, glass bottles by METRO personnel from December, 1977, to Auguest, 1979, at roughly 1-month intervals (1 month was missed). Each 4-L sample was a flow-proportionate composites of at least 5 days (including 1 weekend) of mechanical interval sampling. $HgCl_2$ (0.2 g) was added as a preservative prior to filling.

Following collection, all effluent samples were stored at 2 °C. An aliquot, typically 1 L, was filtered by using precombusted and extracted 0.45 μm Gelman type AE glass fiber filters in an all-glass filtration unit and frozen until extraction. The filtrates of 12 of the 19 filtered

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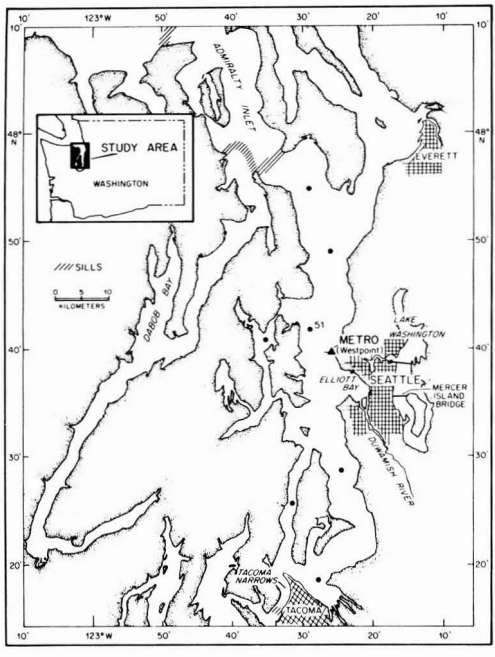

Figure 1. Central Puget Sound in northwestern Washington adjacent to the city of Seattle and the location of the METRO (Westpoint) primary sewage treatment facility. The basin includes the area south of the sill indicated at Admiralty Inlet to the sill at Tacoma Narrows. Closed circles indicate stations discussed previously (*12*, *13*) for which ^{210}Pb profiles were determined for either the same core used in hydrocarbon analyses or a duplicate core from the same multiple core hydrocast. ^{210}Pb-derived accumulation rates (mg/(cm^2 year)) observed at each station assume a dry sediment density of 2.5 g/cm^3 (*39*).

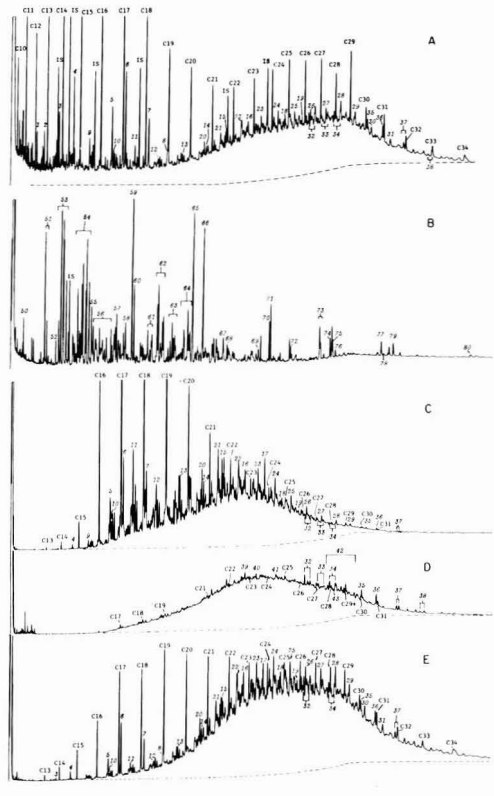

Figure 2. Gas chromatograms of (A) aliphatic and (B) polynuclear aromatic hydrocarbons in METRO (Westpoint) primary sewage effluent collected in September, 1978, (C) aliphatic hydrocarbons in METRO storm-water runoff (January, 1978), (D) analysis of the sample in Figure 2C after storage without preservatives at 2 °C for 3 years, and (E) aliphatic hydrocarbons in Mercer Island Bridge storm runoff (January, 1978; Figure 1). Internal Standards (IS) in order of elution are as follows: 3-methyl C_{13}; hexamethylbenzene (injection standard); 3-methyl $C_{15,17,21,23}$ (anteisoalkanes are recovery standards). Other peak identifications given in Table II. GC conditions: SP2100 glass capillary; splitless isooctane injection at 75 °C; initial hold 0.75 min, then 15 °C/min ramp to 130 °C followed by temperature programming from 130 to 275 °C at 4 °C/min; H_2 carrier gas at 12 PSI. Dotted lines indicate column bleed.

samples were collected in solvent-rinsed flasks and maintained at 2 °C until analysis.

Particulate weights for each sewage effluent sample were determined by using 0.4-μm Nuclepore filters. Organic C and N values were quantitated for duplicate freeze-dried samples with a Carlo Erba CHN analyzer (*22*). Average reproducibility of four triplicates was ±0.3% and ±1.1% for OC and N, respectively (all precisions reported are ±1 relative (%) standard deviation from the mean).

Sample Workup. Filters and filtrates were spiked with five anteisoalkane recovery standards (Figure 2) prior to extraction in order to correct for differential losses of aliphatic hydrocarbons during workup (*13*). Recovery of polynuclear aromatic hydrocarbons (PAH; three rings and up) was frequently checked but not corrected, with a 2-methylanthracene standard (*22*).

Modifications of the analytical procedure reported previously (*13*) include a 24-h Soxhlet extraction (>98% efficiency) for wet filters and replacement of alumina/silica gel chromatography by fully activated silica gel (EM high purity, 70–230 mesh). Procedural steps are discussed extensively by Prahl (*22*).

Filtrate samples were extracted by using simple liquid–liquid partitioning in separatory funnels with pentane followed by CH_2Cl_2 as solvents and were then treated identically to filtered samples. The ratios of the total amounts of extractable organics, aliphatics, and *n*-alkanes recovered in [filters plus filtrates] relative to [unfiltered, CH_2Cl_2 extracted] were 0.8 ± 12%, 1.2 ± 22% and 1.1 ± 14%, respectively (n = 3). Thus, the combined filter plus filtrate results appear to be representative of the total extract. All results have been adjusted for recovery-corrected blank contributions, which typically amounted to less than 5% of sample components.

Gas Chromatography and Mass Spectroscopy. A Hewlett-Packard (HP) 5880 gas chromatograph equipped with 30 m × 0.25 mm SP2100 glass (aliphatics) or SE-54 fused silica (PAH) capillary columns (J&W Scientific) was used for GC analyses. Peak areas quantitated with a GC internal standard by the HP microprocessor vs. a daily series of standard calibration runs were subsequently checked for validity. GC conditions are given in Figure 2. Average total reproducibility for individual compounds were as follows: *n*-alkanes [*n*-C_{14} to *n*-C_{35}], ±19%; PAH [filters only; phenanthrene to benzo[*ghi*]perylene], ±11%.

Selected fractions of filter and filtrate samples were subjected to additional analysis by electron impact GC/MS (HP 5992 or 5993; 30 m × 0.25 mm SE-54 fused silica columns). All compound identifications are made on the basis of GC/MS analyses. When authentic standards were available, identifications were confirmed on the basis of GC/MS analyses of samples and standards plus GC re-

Table I

A. Summary of Effluent Data for Seattle (Westpoint) Primary Treatment Plant

sampling date		no. of dys from last rain >0.5 in.	av flow, million L/day	av[a] suspended solids, mg/L	total part., mg/L	oil and grease,[a] mg/L	% OC	C/N ratio, w/w	total extr orgs, mg/L		total grav HC,[c] mg/L		total grav aliph,[d] mg/L	
									part.	diss	part.	diss	part.	diss
12/15-12/19/77	1.57	0	708	79	80	30.6	27.1	7.20	6.2	nd[f]	nd	nd	1.3	0.44
1/4-1/8/78	1.99	19	746	66	110	20.8	26.9	7.57	9.3	2.5	2.5	0.97	1.8	0.58
2/20-2/28	0.77	5	503	65	123	37.3	29.9	8.06	12.0	2.4	3.4	nd	3.1	0.34
3/23-3/27	0.78	11	541	58	116	30.5	28.7	7.48	8.8	2.9	2.4	0.57	2.2	0.46
4/27-5/1	0.69	10	503	71	105	31.4	31.5	7.56	11.2	6.1	1.6	0.30	0.98	0.23
5/31-6/4	0.00	44	284	76	148	34.1	32.0	7.55	9.1	3.8	3.3	0.28	2.9	0.20
6/29-7/3	t[g]	73	329	99	178	35.7	34.5	8.31	18.0	nd	6.9	nd	3.8	nd
7/27-7/31	0.13	10	337	127	173	39.7	32.9	7.32	20.9	nd	4.2	nd	3.6	nd
9/1-9/5	1.27	36	530	102	150	36.3	33.1	8.03	16.6	nd	3.0	nd	2.7	nd
10/21-10/25	0.88	27	344	140	116	42.8	34.3	7.48	16.4	nd	2.6	nd	2.5	nd
11/9-11/13	0.47	5	386	60	131	26.3	30.0	7.17	12.2	nd	1.8	nd	1.7	nd
11/31-12/4	0.84	0	538	76	102	26.9	29.6	7.08	10.0	nd	2.6	nd	2.5	nd
12/28-1/1/79	0.04	23	360	35	113	18.3	33.7	7.77	11.0	nd	1.4	nd	1.3	nd
3/1-3/5	1.11	16	625	40	83	16.1	27.3	7.37	7.7	3.6	1.4	0.43	1.3	0.33
3/30-4/3	0.14	25	416	55	97	22.6	30.0	6.30	5.3	4.0	2.0	1.2	1.9	0.59
4/26-4/30	t	52	416	51	114	19.6	30.9	5.83	8.5	5.2	1.9	0.29	1.8	0.18
5/31-6/4	0.00	87	348	68	147	28.2	30.5	6.54	13.0	5.7	2.7	0.37	2.6	0.21
7/5-7/9	t	3	379	85	217	16.0	33.9	7.91	25.0	1.3	4.9	0.26	4.7	0.21
8/3-8/7	0.00	32	341	165	195	35.2	34.4	7.83	24.0	7.2	nd	nd	4.6	0.53
av Oct-Mar, $n = 9$	0.94	12	528	69	108	27.7	29.7	7.46	10.0	3.9	2.3	0.66	2.0	0.43
av Apr-Sep, $n = 10$	0.23	37	388	90	152	29.9	32.3	7.32	15.0	4.8	3.4	0.45	3.0	0.31
ratio	4.1[b]	0.3[b]	1.4[b]	0.8	0.7[b]	0.9	0.9[b]	1.0	0.7	0.8	0.7	1.5	0.7	1.4

B. Selected Concentrations (μg/g OC in Particulate)[h]

sampling date	total isopr	Σ_{14}^{20} n-alk	Σ_{21}^{35} n-alk	UCM	Phen	total MePhen	total Me_2-Phen	total high mol wt PAH[e]	Fluor	B[a]-anth	Chry	B[e]py
12/15-12/19/77	482	1231	656	26 700	nd	nd	nd	nd	nd	nd	nd	nd
1/4-1/8/78	866	2649	1545	55 400	41.2	59.1	39.6	95	26.9	7.6	12.7	5.5
2/20-2/28	872	2607	1554	57 300	2.5	23.4	37.6	34	12.3	1.5	3.1	1.5
3/23-3/27	694	1883	795	50 900	14.3	41.0	44.0	52	18.7	2.4	5.3	1.6
4/27-5/1	268	820	733	14 800	25.6	41.8	nd	27	7.5	1.2	2.7	3.8
5/31-6/4	495	1749	1144	39 100	14.0	20.9	nd	11	2.7	1.6	4.1	nd
6/29-7/3	538	1698	933	37 500	23.4	nd	nd	nd	nd	nd	nd	nd
7/27-7/31	540	1690	917	41 400	39.8	37.1	34.2	25	7.8	1.4	3.4	1.0
9/1-9/5	505	1515	740	31 400	26.8	34.0	23.7	69	19.3	3.5	9.3	3.2
10/21-10/25	608	1779	1141	41 400	20.9	34.1	33.3	39	12.9	1.6	6.1	1.5
11/9-11/13	494	1528	832	28 900	11.4	24.1	29.0	24	7.8	1.0	3.8	0.7
11/31-12/4	1410	3676	1321	79 400	22.7	44.9	57.3	45	12.1	1.7	6.4	2.1
12/28-1/1/79	609	1785	852	29 700	17.9	34.3	36.0	24	6.5	0.9	3.1	0.9
3/1-3/5	503	1486	726	35 300	16.1	51.8	40.8	37	9.1	3.1	5.7	1.6
3/30-4/3	499	1144	840	45 500	9.8	26.7	32.4	24	6.8	1.9	3.2	1.1
4/26-4/30	360	1069	626	28 300	9.3	19.5	25.9	17	5.2	1.2	2.2	1.2
5/31-6/4	336	1220	965	56 900	16.8	29.8	40.4	23	7.2	1.6	2.9	2.2
7/5-7/9	494	1481	869	45 300	9.1	22.1	30.9	21	4.3	1.9	3.6	1.3
8/3-8/7	578	1575	869	47 500	20.8	39.2	58.7	24	8.8	1.7	2.5	2.2
av Oct-Mar	726	2069	1047	45 000	18.4	39.1	39.7	44	13.3	2.5	5.8	1.9
av Apr-Sep	461	1396	864	38 800	19.5	30.1	35.2	27	7.7	1.2	3.8	2.0
ratio	1.6[b]	1.5[b]	1.2	1.2	0.9	1.3	1.2	1.6	1.7	2.1	1.5	1.0

[a] Data collected by METRO (Barry Uchida, personal communication). [b] Indicates parameters for which the October-March mean differs significantly (99% confidence level) from the mean value for April-September. [c] Total gravimetric hydrocarbons as the sum of aliphatic and "aromatic" fractions. [d] Total gravimetric aliphatic hydrocarbons as the weight of the pentane eluent from column chromatography. [e] Suite of nine high molecular weight PAH defined in text. [f] Not determined. [g] Trace. [h] UCM, unresolved complex mixture; Phen, phenanthrene; MePhen, methylphenanthrene; Me_2Phen, dimethylphenanthrene; PAH, polyaromatic hydrocarbons; Fluor, fluoranthene; B[a]anth, benz[a]anthracene; Chry, chrysene, B[e]py, benz[e]pyrene.

tention times relative to standards.

Results and Discussion

Table IA summarizes many of the characteristic parameters for each collection period. Selected data for individual compounds and hydrocarbon suites analyzed in particulate samples are given in Table IB. Suspended solids and oil and grease values (Freon extracted), collected

Table II. Selected Compounds Tentatively Identified in Seattle METRO (Westpoint) Municipal Primary Waste-Water Effluent and Storm Waters

Normal Alkanes[a] C_{12}–C_{34} (numbers denote carbon numbers; see Figure 2)			
		Isoprenoid Alkanes	
1	2,6-dimethylundecane	5	2,6,10-trimethylpentadecane
2	2,6,10-trimethylundecane	6	pristane[a]
3	2,6,10-trimethyldodecane	7	phytane[a]
4	2,6,10-trimethyltridecane	8	2,6,10,14-trimethylheptadecane
		n-Alkylcyclohexanes	
9	nonylcyclohexane	15	pentadecylcyclohexane[a]
10	decylcyclohexane	16	hexadecylcyclohexane[a]
11	undecylcyclohexane	17	heptadecylcyclohexane[a]
12	dodecylcyclohexane	18	octadecylcyclohexane
13	tridecylcyclohexane	19	nonadecylcyclohexane[a]
14	tetradecylcyclohexane		
		Unidentified Branched Alkanes	
20–31 homologous series of C_{21}–C_{32} branched alkanes (significant mass spectral fragments include loss of methyl and ethyl)			
		Steroid Hydrocarbons	
32	13β,17α-diacholestane (20*R*,*S*)	42	mixture of C_{27}–C_{29} regular steranes
33	13β,17α-methyldiacholestane (20*R*,*S*)	43	5α,14α-cholestane (*R*) (reference[a])
34	13β,17α-ethyldiacholestane (20*R*,*S*)		
		Triterpenoid Hydrocarbons	
35	17αH,21H-30-norhopane	37	17αH,21βH-30-norhopane
36	17αH,21H-hopane	38	17αH,21βH-hopane
		Diterpenoid Hydrocarbons (Figure 2D)	
39	C_{23} extended tricyclic diterpane	41	C_{25} extended tricyclic diterpane
40	C_{24} extended tricyclic diterpane		
		Aromatic and Polynuclear Aromatic Hydrocarbons	
50	naphthalene	66	pyrene[a]
51	methylnaphthalenes	67	1,2-benzofluorene[a]
52	biphenyl[a]	68	retene[a]
53	C_2 naphthalenes	69	benzo[*e*]phenanthrene
54	C_3 naphthalenes	70	benz[*a*]anthracene[a]
55	fluorene[a]	71	chrysene[a]
56	C_4 naphthalenes	72	mol wt 242 (unknown PAH)
57	mol wt 180 (unknown bicyclic)	73	benzofluoranthenes[a]
58	dibenzothiophene[a]	74	benzo[*e*]pyrene[a]
59	phenanthrene[a]	75	benzo[*a*]pyrene[a]
60	anthracene[a]	76	perylene[a]
61	methyldibenzothiophenes	77	indeno[*cd*]pyrene
62	methylphenanthrenes[a]	78	dibenzo[*a*,*h*]perylene[a]
63	C_2 dibenzothiophenes	79	benzo[*ghi*]perylene[a]
64	C_2 phenanthrenes	79	anthanthrene[a]
65	fluoranthene[a]	80	coronene[a]

[a] Indicates compounds for which confirmations have been made by comparison of GC retention data and GC/MS analysis of samples and authentic standards.

by METRO using standard methods (*23*), are given in Table IA for comparison. Daily METRO data were not available for each time period sampled; thus, averages of two routine measurements that at least bracket the sampling period are reported.

Only slight linear correlations of particulate weights of the filtered effluents were found with the effluent suspended solids content ($r^2 = 0.33$) and influent suspended solids content ($r^2 = 0.49$) over time. In addition to sampling variability, the generally higher particulate weights vs. METRO's effluent suspended solids data probably reflect both a high efficiency for retention of fine-grain material by Nuclepore filters and some tendency for adsorption of dissolved components.

Variations in oil and grease effluent concentrations do not correlate well with changes in any of the study parameters. The ratio of oil and grease to total extractable organics (filter plus filtrate, $n = 11$) and to the bulk particulate organic carbon ($n = 19$) averages 1.8 ± 37% and 0.75 ± 34%, respectively. Coordinated sampling might decrease the observed variations; however, from the limited data at hand, it appears that changes in METRO effluent oil and grease values may not be reliable predictors of specific nonpolar classes such as hydrocarbons. Eganhouse and Kaplan (*9*) find better agreement, at least between total extractable organics and oil and grease, in southern California municipal waste waters.

Aliphatic Hydrocarbons: Distribution and Sources. The compositions of aliphatic hydrocarbons are quite similar in both particulate and filtrate ("dissolved") samples. In all chromatograms (e.g., Figure 2A), low molecular weight *n*-alkanes ($<C_{22}$) dominate over the remaining *n*-alkanes. Besides a suite of isoprenoid alkanes (primarily C_{15}–C_{21}), few other resolved peaks are notable. C_9–C_{19} *n*-alkylcyclohexanes are found as well as a series of unidentified C_{21}–C_{32} branched alkanes. A suite of rearranged (and some regular) C_{27}–C_{29} steranes is present in the region from *n*-C_{26} to *n*-C_{31}, although this component is well distinguished only by GC/MS. A somewhat more pronounced suite of C_{29} to at least C_{31} pentacyclic triterpanes can be seen above *n*-C_{30} in Figure 2. In addition, a slightly bimodal unresolved complex mixture (UCM, *24*, *25*) is prevalent in all samples. This compositional pattern is typical of aliphatic hydrocarbon distributions reported in primary sewage effluents elsewhere (*26*, *10*), and its components are characteristic of the molecular scrambling

evident in many fossil hydrocarbon assemblages (*27–31*). Microbial activity may contribute some low molecular weight alkanes, but the ratio of *n*-alkanes to the suite of isoprenoid alkanes, largely of fossil origin (*32, 33*), suggests a fossil rather than microbial origin for much of the *n*-alkanes.

Carbon preference indices (CPI) over the *n*-alkane ranges C_{14}–C_{20} and C_{20}–C_{34} are relatively constant year-round for both particulate (mean 1.22 and 1.26, respectively) and dissolved aliphatic hydrocarbons (mean 1.13 and 1.10, respectively). The values, near unity, reflect the nearly equal content of odd and even carbon chain lengths typically found in fossil hydrocarbon suites. Greater CPI_{20-34} variability in particulate samples is undoubtedly due to changing input of primarily n-$C_{23,25,27,29,31}$ from plant debris during the year.

Except for precipitation, total particulate concentrations, and percent organic carbon (% OC), few of the effluent parameters (Table I) show statistically significant variation over time. One exception is the low molecular weight particulate normal and isoprenoid alkanes, which have significantly higher average concentrations (μg/g OC) during the colder, rainy months of October–March than April–September (Table IB).

In terms of flux (g/day discharged), however, the corresponding October–March vs. April–September ratios for total isoprenoids (1.4), C_{14}–C_{20} *n*-alkanes (1.3), and C_{21}–C_{35} *n*-alkanes (1.1) are low relative to the OC normalized ratios in Table IB. Because of random variability in the flux of each compound suite, their average fluxes in the two time periods cannot be distinguished. Thus, the observed trend normalized to OC reflects a substantial seasonal variation in the bulk OC flux rather than a major change in the input rate of low molecular weight alkanes.

Contributions during the winter from the increased use of home heating oil may somewhat augment the hydrocarbon flux. More importantly, a year-round flow of primarily low molecular weight alkanes such as a no. 2 fuel oil may be responsible for the nearly constant alkane input observed. In the summer, organics derived from increased primary productivity would add to bulk OC contributions, yielding the measured variations in concentrations.

Samples of urban storm-water runoff (from a METRO storm drain) and automobile bridge runoff (Mercer Island bridge, Figure 1) were collected during a January 1978 storm for comparison to an extensive 15-month sampling series reported by Wakeham (*34*) and to approximate storm-water influx to METRO. Unfiltered samples were analyzed within hours of collection. GC traces of the two aliphatic hydrocarbon fractions shown in Figure 2C,E are similar to those in Wakeham's study, although improved GC columns permit a more detailed examination of the individual compounds. The unextracted remainder of each sample was then stored *without* preservatives at 2 °C. Unlike preserved samples, subsequent analysis of the unpreserved storm-water sample 3 years after collection showed that extensive degradation had occurred (Figure 2D, to be discussed).

Freshly collected runoff samples contain a low ratio of both isoprenoid to normal alkanes and $\leq C_{16}$ *n*-alkanes to $>C_{16}$ alkanes relative to any of the METRO sewage effluent samples (e.g., Figure 2A). In addition, the high ratio of UCM to resolved components in both the storm-water and bridge runoff samples is diminished in METRO effluent. Although the composition of storm-water samples can vary substantially during a storm event (*35*), this again may indicate an additional input of mainly low molecular weight isoprenoid and normal alkanes (CPI $\sim$ 1) to METRO and suggests that a source such as dumping or seepage of undegraded fuel oils may be a major factor. METRO (D. Hildebrand, personal communication) has confirmed that high levels of relatively clean oil have been observed in the downtown sewage corridor and that regular dumping of fuel oils over the last several years is strongly suspected to have occurred.

PAH: Distribution and Sources. Aromatic compounds ranging from naphthalene to coronene (Figure 2B) can be detected in the particulate material of METRO sewage effluent. PAH such as retene and perylene, derived in part from diagenetic processes, were generally in low abundance or undetected in the sewage samples. PAH in filtrate samples are sometimes measurable, but in low concentrations relative to filtered samples, particularly at higher molecular weight. Thus, with the exception of phenanthrene, filtrate PAH were not routinely quantitated.

The PAH composition is more variable over time than that of aliphatic hydrocarbons. Many particulate samples are dominated by phenanthrene and a series of isomeric methyl- and dimethylphenanthrenes. 1,1′-Biphenyl-3-ol is tentatively identified as a major component in filtrate samples. Substantial amounts of alkylated naphthalenes are present in both particulates and filtrates, although the analytical procedure is not specifically designed for efficient recovery of low molecular weight aromatics. Dibenzothiophene and its alkylated derivatives, described in more detail by Bates and Carpenter (*16*), have also been tentatively identified as common particulate components.

Phenanthrene/anthracene ratios vary substantially in METRO samples, down to a minimum of 3. In some cases, anthracene was quite low in abundance or not detected. Overall, changes in phenanthrene concentrations are not well correlated with those of anthracene or higher molecular weight PAH (Table I). This lack of correlation with $\geq$4-ring PAH may be due in part to differential evaporative losses of phenanthrene during the procedural workup. However, it is likely that phenanthrene derives from at least two sources, one of which may contain relatively small amounts of anthracene and higher molecular weight PAH.

Concentrations of $\geq$4-ring PAH are substantially intercorrelated over time. A major source of the entire PAH suite is most likely street runoff, which incorporates atmospheric dust, road-wear particles, and automotive oils and greases, all of which contribute PAH derived from pyrolysis and combustion processes. Wakeham et al. (*36*) have shown a strong correspondance between the composition of PAH accumulating in surface sediments of several lakes, including Lake Washington, and those present in street dust. In particular, the component derived from asphalt (and concrete) particles contains an assemblage of PAH that differs little from observed sedimentary distributions (*36*).

Variations of Hydrocarbon Input as a Function of Precipitation. In order to gauge the importance of street runoff to the input of both aliphatic and aromatic hydrocarbons to METRO, I examined two additional parameters. First, cumulative precipitation was compiled for the day before collection of each effluent sample began to the day before the final collection day of each period.

A second factor determined was the number of days before each collection period that daily rainfall was less than 0.5 in. times cumulative precipitation during each collection period. This factor was considered to reflect street dust accumulations and subsequent contributions to storm runoff. Both terms were than correlated to each compound studied, including normalizations to bulk or-

Table III. Seattle METRO (Westpoint) Sewage Effluent

r^2 Linear Coefficients of Determination[a]

parameter	precip	no. of days since last precip >0.5 in. times precip	high mol wt PAH, g/day flux	diss TAH, g/day flux	part. TAH, g/day flux
high mol wt, PAH, μg/g of OC	0.84[b]	0.71[b]	0.90[b]		
high mol wt, PAH g/day	0.69[b]	0.72[b]		0.49	0.36
diss Phen, g/day	0.33	(−)0.04	0.12	0.39	(−)0.00
part. Phen, g/day	0.20	0.31	0.54[b]	0.19	0.30
diss TAH, g/day	0.74[b]	0.59[b]	0.49		0.03
part. TAH, g/day	0.06	0.08	0.36		
% OC	(−)0.40[b]	(−)0.02	(−)0.08	(−)0.62[b]	0.00
OC, g/day	0.04	0.01	0.40	0.00	0.67[b]

Particulate Aliphatic Hydrocarbon Intracorrelations

parameter, g/day	part. TAH, g/day	part. UCM, g/day	part. total isoprenoids, g/day
part. UCM	0.82[b]		
part. isoprenoids	0.58[b]	0.71[b]	
part. *n*-alkanes	0.75[b]	0.77[b]	0.80[b]

"Dissolved" Aliphatic Hydrocarbon Intracorrelations

parameter, g/day	diss TAH, g/day	diss UCM, g/day	diss total isoprenoids, g/day
diss UCM	0.50[c]		
diss isoprenoids	0.88[b]	0.61[b]	
diss *n*-alkanes	0.79[b]	0.71[b]	0.97[b]

[a] (−) indicates negative correlations; TAH, total aliphatic hydrocarbons; high mol wt PAH: suite of nine PAH defined in text; Phen, phenanthrene. [b] Significant at 99.9% confidence level. [c] Significant at 99.8% confidence level.

ganic carbon, effluent flow, and flux of compounds discharged.

A suite of nine "high molecular weight" PAH was defined as the sum of fluoranthene, pyrene, benz[*a*]anthracene, chrysene, benzofluoranthenes, benzo[*e*]pyrene, benz[*a*]pyrene, indeno[*c,d*]pyrene, and benzo[*ghi*]perylene, which were the major high molecular PAH most consistently observed and quantitated. Results shown in Table III indicate that variations in the concentration (μg/g OC) of these high molecular weight PAH are strongly dependent upon rainfall during each collection period. An inverse relationship between rainfall and % OC tends to accentuate this correlation between rainfall and PAH concentrations normalized to organic carbon, however. Nevertheless, the mass discharge of PAH (μg/day) is substantially correlated to rainfall (Table III).

In addition, and unlike % OC, both the concentration and flux of high molecular weight PAH are well correlated to the indicator of "street-dust accumulation". A similar accumulation factor from number of days that daily rainfall was <0.25 in. yielded somewhat lower correlations, as would be expected if these accumulation factors reflect the dependence of street-dust runoff on rain-storm severity. The phenanthrene flux is poorly correlated with all rainfall indicators, again suggesting an alternate major source.

The concentration of dissolved *n*-alkanes in the effluent (C_{14}–C_{20}) varies from about 0.3 to over 3 ppb and averages 1.4 ppb ± 57%. These values are similar to reported solubilities of about 2 ppb for corresponding *n*-alkanes in fresh water (*37*). In contrast, dissolved phenanthrene concentrations are 6–7 orders of magnitude below reported fresh-water solubilities of about 1 ppm (*38*). The total flux of dissolved aliphatic hydrocarbons appears to be strongly correlated with cumulative precipitation (and total effluent volume) during the sampling period (Table III). One possibility is that the waste waters are near saturation with respect to these alkanes and so their flux may be limited by solubility in the runoff to the sewage collection system. More work is necessary to sort out additional influences such as surface oil slicks, however.

Although the composition of particulate aliphatic hydrocarbons is similar to that of their dissolved counterparts, there is no correlation whatsoever with either precipitation term (Table III). This low correlation with precipitation further suggests that a major source of aliphatic hydrocarbons (or possibly oil-coated particulates) may be the year-round introduction of essentially uncombusted fuel oils. It should be noted, however, that the UCM, isoprenoid, and normal alkanes are all well correlated (Table III) in both dissolved and particulate phases and have linear regression intercepts near zero. By itself, this relationship tends to suggest that one source contributes the bulk of all these materials in the effluent instead of one chronic source that supplies primarily low molecular weight alkanes and another that is episodic and supplies both resolvable alkanes and a major UCM.

From all available information, however, it seems most probable that mixtures of undegraded and degraded fuel oils, the latter derived from a combination of the chronic disposal of waste oils and episodic street runoff, are major sources of aliphatic hydrocarbons to METRO. Although phenanthrene and its alkyl derivatives may also share similar sources, none of the phenanthrenes are significantly correlated with any component of the aliphatic hydrocarbons.

Mass Emission Rates of METRO Primary Effluent. Average mass emission rates (metric tons/year) are summarized in Table IV for a range of METRO sewage effluent parameters. Rates are calculated by multiplying the mass of each component per liter of effluent discharged during each period (g/L) by the corresponding average daily flow (million L/day), converting to a yearly basis (365 days/year), and then averaging over the 9 "winter" and 10 "summer" periods. Suspended solids and oil and grease data collected by METRO and discussed previously are included for comparison. Data are also presented in Table IV for average daily discharge per capita, with the assumption of a service population of about 500 000 people (METRO, personal communication).

Table IV. Seattle METRO (Westpoint) Sewage Effluent Mass Emission Rates and Average Potential Sedimentary Fluxes

parameter	metric tons/year range	metric tons/year av[f]	g/(capita day)	flux to the sediments, μg/(cm² year) av METRO potential[a]	flux to the sediments, μg/(cm² year) obsd flux, station 51[b]	flux to the sediments, μg/(cm² year) ratio of MET/51	flux to the sediments, μg/(cm² year) av flux,[c] central PS	flux to the sediments, μg/(cm² year) range central PS
suspended solids[e]	4300-21350	10720 (±27)	58.8					
total particulate	14600-29900	20750 (±23)	114.0	7950	240 000	0.03	466 000	110 000-1 200 000
oil and grease[e]	2080-6020	4130 (±24)	22.6					
particulate OC	4400-10150	6450 (±25)	35.3	2870	5292	0.5	10 100	260-29 000
particulate N	640-1290	870 (±20)	4.8	300	530	0.6	nd	nd
total extr organics								
part.	800-3390	2000 (±35)	11.0	1060	572	1.8	645	32-1410
"diss"	180-1790	760 (±57)	4.1					
total "hydrocarbon"								
part.	210-830	422 (±42)	2.42					
"diss"	36-260	127 (±68)	0.70					
total aliphatic HC								
part.	180-650	400 (±38)	2.17	380	71.0	2.6	70.0	4-200
"diss"	22-160	74 (±63)	0.41					
total UCM								
part.	150-470	270 (±44)	1.49	125	50.0	2.5	50.0	2-180
"diss"	12-150	51 (±76)	0.28					
total C_{14}-C_{20} alkanes								
part.	5.0-21.8	11.2 (±46)	0.062	6.5	0.35	18.5	0.57	0.02-2.6
"diss"	0.62-4.80	5.7 (±72)	0.032					
total C_{21}-C_{35} alkanes								
part.	3.4-12.5	6.2 (±40)	0.034	3.3	1.29	2.6	1.81	0.10-6.5
"diss"	0.32-1.9	2.5 (±60)	0.014					
total isoprenoid alkanes								
part.	1.64-8.36	4.23 (±47)	0.023	1.9	0.32[d]	6.0	0.35[d]	0.01-1.3[d]
"diss"	0.21-1.78	0.74 (±73)	0.004 1					
17α H,21β H-hopane								
part.	0.08-0.40	0.18 (±52)	0.001 0	0.081	0.12	0.68	0.13	0.006-0.43
"diss"	0.014-0.066	0.031 (±61)	0.000 2					
phenanthrene								
part.	0.02-0.33	0.13 (±67)	0.000 7	0.067	0.033	2.0	0.030	0.0003-0.12
"diss"	0.00-0.15	0.045 (±56)	0.000 2					
additional PAH (part.)								
methylphenanthrenes	0.10-0.48	0.22 (±44)	0.001 2	0.085	0.037	2.3	0.070	0.001-0.41
dimethylphenanthrenes	0.14-0.49	0.25 (±38)	0.001 4	0.096	0.031	3.1	0.062	0.002-0.36
fluoranthene	0.013-0.22	0.068 (±80)	0.000 4	0.026	0.046	0.57	0.055	0.002-0.23
benz[*a*]anthracene	0.006-0.045	0.014 (±75)	0.000 08	0.0054	0.019	0.28	0.024	0.001-0.10
chrysene	0.012-0.10	0.032 (±79)	0.000 2	0.012	0.030	0.40	0.032	0.002-0.12
benzo[*e*]pyrene	0.004-0.034	0.013 (±68)	0.000 07	0.0050	0.023	0.22	0.028	0.001-0.11
indeno[*c,d*]pyrene	0.001-0.034	0.009 (±103)	0.000 05	0.0034	0.023	0.15	0.026	0.001-0.09

[a] Assumes total accumulation area of 2.6×10^{12} cm² muds and sandy muds (Roberts, UW-SeaGrant, unpublished data). [b] Station 51 organic carbon and aliphatic hydrocarbon data are averages of 0-2 cm from duplicate cores collected 1 year apart; PAH data are based on triplicate cores. [c] Fluxes are normalized for the differing accumulation rates determined at each of the seven stations (Figure 1) before averaging. Aliphatic data are calculated from Barrick et al. (*12*); PAH data are calculated from Barrick and Prahl (in preparation). [d] A large marine component of pristane in 0-2 cm of Puget Sound cores (*12*) has been subtracted out. [e] Based on data supplied by METRO (personal communication). [f] The number in parentheses is the percent standard deviation.

Table V. Estimated Hydrocarbon Inputs to Central Puget Sound

	discharge vol, L/year	metric tons/year[a] TAH	Fluor	Chry	B[e]py	Inpy
municipal waste waters[b]	2.5×10^{11}	850	0.120	0.057	0.023	0.016
storm drain/combined sewer overflow[c]	6×10^{9}	3-46				
direct atmospheric dust fall (dry)[d]		50	0.030	0.070	0.070	0.058
direct rainfall[e]	9×10^{11}	16				
rivers (Puyallup, Duwamish, and Lake Washington Ship Canal)[f]	6.4×10^{12}	6-320				

[a] TAH, total gravimetric aliphatic hydrocarbons; Fluor, fluoranthene; Chry, chrysene; B[e]py, benzo[e]pyrene; Inpy, indeno[c,d]pyrene. [b] Extrapolated from METRO (Westpoint) data by using a regional volume estimate (*17, 43*) and excluding METRO (Rentron) secondary treatment discharge of 0.5×10^{11} L/year. [c] Discharge volume is regional estimate (*43*). TAH emission is estimated from 28 storm drain collections by Wakeham (*44*) for Lake Washington. Using an average value of 12.1 mg/L TAH in 16 bridge runoff samples (*44*) yields 75 metric tons/year. [d] TAH emission extrapolated from Lake Washington (90 km^2) data (*44*). PAH emission is based on Seattle air concentrations reported by Prahl (*22*) by assuming a PAH depositional velocity of 0.4 cm/s and a total catch basin of 776 km^2 (Central Puget Sound). The PAH discharges are considered to be *upper estimates*. [e] Volume discharge estimated by Collias and Lincoln (*45*). TAH emission extrapolated from seasonally adjusted Lake Washington data (*44*). [f] Volume is average of May and September discharges (*45*). TAH emission is based on the range of concentrations for 32 total extracts of Cedar River (12 μg/L mean) and Sammamish River (21 μg/L mean) waters flowing to Lake Washington and reported by Wakeham (*44*). These values are similar to the range of ten preliminary samplings of particulate material collected near the mouths of six Puget Sound rivers and the Lake Washington Ship Canal (4-64 μg/L; nine of ten samples are ≤28 μg/L).

"Total hydrocarbon" emission rates presented in Table IV are the sum of the total aliphatic plus "aromatic" gravimetric weights. Much of the "aromatic" weight, however, is not attributable to compounds that elute on the GC and as such overestimates the quantitated PAH. Also, the sum of the UCM plus resolved peaks account for only two-thirds of the total aliphatic hydrocarbons. This difference likely represents a nonvolatile component in both METRO PAH and aliphatic extracts. The total of these two gravimetric fractions comprise roughly 22% of the particulate and 17% of the dissolved extractable organics, comparable to recent estimates for municipal waste waters in southern California (*9*).

Per capita estimates for total hydrocarbon discharges are quite comparable in waste waters from Seattle (3.1 g/(capita day), Providence, RI (2.1 g/(capita day), secondary effluent, *7*), and the range for southern California (3.3–6.0 g/(capita day), mostly primary effluents, *9*). The average 2.6 g/(capita day) discharge of total aliphatic hydrocarbons from METRO is nearly identical with the 2.5 g/(capita day) average for southern California sites (*9*). Compositional similarities noted for the (primary) southern California effluents (*10*) generally hold for METRO's primary effluent, suggesting similar sources in both regions.

Terrestrial Hydrocarbon Sources to Central Puget Sound. Major possible terrestrial sources of natural and anthropogenic hydrocarbons to Puget Sound include municipal combined sewage and storm-water effluents, additional contributions from uncontrolled urban runoff and combined sewer overflows, direct atmospheric transport, and nonurban runoff largely from rivers. Discrete discharges from ship traffic, miscellaneous industrial effluents not incorporated in municipal waste waters, and spoils dumping also contribute to some degree. The greatest volume of these extraneous industrial effluents comes from pulp mills, which are not recognized as significant fossil aliphatic or aromatic hydrocarbon sources.

A summary of hydrocarbon estimates for major sources is given in Table V. The UCM may constitute 60–95% of the total "aliphatic" hydrocarbon (TAH) weight given in Table V, depending on the source. Based on these estimated TAH emissions, municipal waste waters likely constitute a major, if not principal, source of anthropogenic "aliphatic" hydrocarbons to central Puget Sound. The average estimated discharge from municipal waste waters constitutes two-thirds of the total TAH discharge in Table V, with use of upper estimates for the other sources. Eganhouse and Kaplan have also noted a substantial hydrocarbon discharge in southern California municipal waste waters, double that in surface runoff (*9*).

PAH inputs to the Sound are less well defined. A comparison of municipal waste waters and atmospheric dust compositions shows that the two sources differ extensively in their relative contributions of small and large ring PAH (Table V). Implications of this variable composition will be discussed later. Uncontrolled storm water and combined sewer overflow discharges likely contain equivalent or perhaps greater concentrations of PAH than municipal waste waters, but the total volume of these discharges is relatively small.

PAH levels are now being determined in riverborne particulate material entering Puget Sound and will be discussed in a subsequent paper. Small and highly variable amounts of 3–7-ring PAH have been detected in preliminary samples. The composition of the PAH suite in these samples is intermediate to that represented by municipal waste waters and dust fall in Table V. The initial indication is that river PAH input is secondary or at most comparable to that derived from municipal waste waters. From available information, municipal waste waters are likely an important source of PAH to central Puget Sound.

Contribution of METRO Effluent to Central Puget Sound Sediments. Previous work indicated that significantly higher average aliphatic hydrocarbon concentrations (μg/g OC) are observed in surface sediments of central Puget Sound (Figure 1) than in corresponding sediments of any other Puget Sound region studied (*13, 14*). The approximate 10-fold increase in hydrocarbon levels in these ^{210}Pb-dated cores over the last 100 years is proportional to the rate of urbanization on the surrounding shoreline. Also, highest aliphatic hydrocarbon concentrations at midchannel sites are found adjacent to metropolitan areas.

Thus, it follows that urban-derived material that is deposited accumulates principally within the central basin sediments rather than being distributed extensively over the entire Puget Sound region. With this consideration and as a first-order approximation, the METRO mass emission rates have been expressed as an "average" potential sedimentary flux by dividing each rate by an assumed total depositional area of 2.6×10^{11} cm^2 (Table IV).

This depositional area constitutes roughly one-third of the total central Puget Sound area but consists of all of the muds and sandy muds and, thus, is probably a rea-

sonable estimate for the accumulation area for organic material. Because mixing in the Sound is not completely homogeneous, it is possible that the actual depositional area for METRO effluent has been overstated and, therefore, the resulting "average" sedimentary flux is likely a conservative estimate of the true potential.

The actual pattern of deposition within the defined region is less certain. Sediment accumulation rates (mg/(cm^{-2} year)) calculated from excess ^{210}Pb activity vs. total sediment accumulation profiles below any surface mixed layer (*39*) vary substantially in Puget Sound. For 32 cores collected at 25 stations in the greater Puget Sound region and including all cores used for hydrocarbon analyses (Figure 1 and ref 13), mass accumulation rates range from 72 to 1200 mg/(cm^2 year) and average 360 ± 270 mg/(cm^2 year) (M. Peterson, personal communication). These cores include duplicate and comparative analyses using both hydrostatically damped multiple cores and box cores.

Ratios of the estimated potential METRO flux to the sediments vs. observed fluxes for different compound classes at midchannel station 51 nearest the diffuser (accumulation rate 240 mg/(cm^2 year)) are given in Table IV. This average calculated flux exceeds the observed flux of many compound classes by a factor of 2–18, both at station 51 and in comparison to the average for seven central Puget Sound stations. Whether surface sediment mixing causes observed hydrocarbon accumulation rates to be over- or underestimated is not certain (*22*).

An apparent preferential loss of marine-derived organic matter above or near the sea–sediment interface has been previously discussed (*12, 13*). In addition, in spite of sediment mixing considerations, ^{210}Pb flux variations observed, and the assumptions implicit in METRO's potential flux, Table IV results suggest that substantial degradation of some hydrocarbon components in the effluent also occurs during transport and deposition.

Moreover, a comparison of the ratios (Table IV) suggests that relative remineralization efficiencies of effluent components within the water column or at the sea–sediment interface follow the order C_{14}–C_{20} *n*-alkanes > C_{15}–C_{20} isoprenoid alkanes > C_{21}–C_{35} *n*-alkanes ~ UCM > phenanthrene > higher molecular weight PAH (and 17α,21β-C_{30} hopane). This sequence is consistent with the relative intrinsic stabilities of the various components.

In general, a substantial loss of labile organic carbon components, including oxygenated compounds, in METRO discharges occurs in the Sound in addition to dilution of the remaining material with an influx of organic carbon from other terrestrial sources. The presence of naturally derived compounds in Puget Sound sediments, primarily of terrestrial origin and not present in METRO discharge, argues for contribution from additional sources besides municipal waste waters (*11–16*). In consideration of all the degradative processes discussed plus dilution of METRO-derived organic carbon, the seemingly high ratio of the potential METRO-derived bulk organic carbon flux to the observed sedimentary flux (Table IV) is not surprising.

In a previous paper, it was concluded that a degraded unresolved complex mixture in association with a suite of diasteranes and 17α*H*,21β*H*-hopanes were the dominant components of sedimentary aliphatic hydrocarbons derived from urban sources and surviving transport through the water column (*14*). The remaining compounds, including the entire suite of normal and isoprenoid alkanes, apparently derive primarily from natural terrestrial sources whose inputs have been relatively constant over time.

The unpreserved storm-water in Figure 2D, composed of a UCM largely devoid of alkanes plus a dominant suite of diasteranes and hopanes, is similar to the proposed anthropogenic component in Puget Sound sediments. The degradation depicted in Figure 2, thus, suggests that weathering processes including substantial microbial degradation may account for the bulk of the compositional differences between source materials such as streat runoff contributed by municipal waste waters and observed sedimentary distributions.

Rapid sedimentation of organic wastes via incorporation into zooplankton fecal pellets has been discussed by Prahl and Carpenter (*11*). In particular, these authors found that (≥4 ring) PAH were generally preserved during transport through the water column to the sediments of Dabob Bay (Figure 1), a finding recently supported in studies elsewhere by Gschwend and Hites (*40*). If PAH are transported as indicated in these field studies, results in Table IV for fluoranthene to indeno[*c*,*d*]pyrene suggest that METRO effluent, and municipal waste waters in general, could account for a significant portion of these compounds in central Puget Sound sediments.

The ratio of METRO's average potential flux to the observed sedimentary flux declines over the range of 4 to 6 ring PAH (Table IV). The opposite trend is observed when the PAH assemblage derived from atmospheric dust fall is compared to the sedimentary assemblage. As noted by Wakeham et al. (*36*), however, this apparent depletion of lower molecular weight PAH in dust fall samples could be somewhat influenced by sampling procedures.

Thus, the observed sedimentary assemblage could result from a mixture of PAH suites derived from several sources, including atmospheric dust fall and municipal waste waters, whose compositions may vary considerably. In addition, differential loss of PAH derived from fuel oils vs. "combustion"-derived PAH (*41*) in the METRO effluent could yield an assemblage compositionally similar to that observed in Puget Sound sediments. METRO fuel oil derived PAH likely include a small fraction of the ≥4-ring PAH. A more detailed study of PAH distribution in these sediments is in progress.

With historical and compositional evidence taken into account, data in Tables IV and V suggest that municipal waste waters contribute substantially to anthropogenic "aliphatic" hydrocarbon and, to a lesser but still important extent, to PAH accumulations in Puget Sound sediments.

This conclusion is supported by a consideration of the alternative hypothesis that there is a negligible sedimentary contribution from municipal waste waters. If other anthropogenic fossil sources are of similar magnitude to municipal waste waters, then one is forced to call upon as yet unrecognized degradative processes that would act in extreme preference upon anthropogenic hydrocarbons in municipal waste waters as compared to similar hydrocarbon suites within alternate sources, including surface runoff and aeolian transport.

Degradative processes may more reasonably be assumed roughly equivalent for similarly derived anthropogenic fossil suites in the various sources. In this case, alternate sources must be massive (especially with respect to "aliphatic" hydrocarbons) relative to the combined sewer/storm-water discharges to account for the known anthropogenic accumulations in midchannel sediments of Puget Sound. No other known source or combination of sources appears large enough to justify this conclusion (Table V).

No major changes were observed in the sedimentary aliphatic hydrocarbon chronology of midchannel sediments

corresponding to the opening of METRO (Westpoint) in 1966 and the diversion of sanitary sewage from Lake Washington (*13*). However, as stated previously in the discussion of the study site, most of the current municipal waste-water discharge from METRO, including virtually all of the storm-water component, previously flowed to the Sound as untreated wastes. Although treatment has undoubtedly reduced the total load to some extent, the bulk of this discharge is now also directly into the main waters of the Sound rather than being confined to shallow embayments such as Elliott Bay (Figure 1). It is unlikely that fossil hydrocarbon assemblages are compositionally altered during primary treatment (*26*).

Conclusions

PAH in Seattle's METRO (Westpoint) effluent derive from at least two major sources. The flux of the bulk of the PAH in the range from fluoranthene to coronene is highly correlated both to precipitation during each collection period and to a representation of street-dust accumulation in the city. Phenanthrene and its alkylated derivatives may derive in part from street runoff but also appear to have at least one additional major source such as undegraded fuel oils.

The particulate aliphatic hydrocarbon composition, plus a lack of correlation with precipitation, suggests that the introduction of undegraded fuel oils may also be a major source of aliphatics to the discharge, in addition to the input of degraded hydrocarbons from sources such as the disposal of waste crankcase oils and road-wear particles contributed by storm waters. The ratio of particulate to dissolved aliphatic hydrocarbons is approximately 4:1.

A comparison of calculated vs. observed sedimentary hydrocarbon fluxes indicates that almost all compounds thought to derive from undegraded fuel oils in the effluent are recycled in the water column or at the sea–sediment interface. Components accumulating in the sediments likely include a fossil assemblage containing at least a portion of the unresolved complex mixture plus much of the diasteranes, triterpanes, and ≥4-ring PAH. Street runoff is the most probable source for the bulk of this material.

With assumption of similar concentrations and composition of hydrocarbons in the region's primary municipal waste waters and given that METRO (Westpoint) contributes at least 50% of total primary plus secondary discharge, the total flux of aliphatic and aromatic hydrocarbons to central Puget Sound exceeds 1100 metric tons/year. This value is at the upper range of a previous estimate of 100–1000 metric tons/year discharge of hydrocarbons via municipal and industrial waste waters to Puget Sound (*42*).

This discharge is sufficient to account for the bulk of fossil aliphatic hydrocarbons of anthropogenic origin currently accumulating in central Puget Sound sediments. Municipal waste waters likely provide a smaller percentage of the sedimentary PAH, however. The relative importance of METRO-derived PAH to sedimentary accumulations declines with increasing ring size.

Seattle's hydrocarbon discharge is only about 5% of that recently reported for southern California municipal waste water receiving largely primary treatment, including Los Angeles and San Diego (*9*, *10*). On a per capita basis, however, the Seattle average of 3.1 g/(capita day) total hydrocarbon and 2.6 g/(capita day) total aliphatic hydrocarbon discharge is comparable to corresponding values for these southern California waste waters and to total hydrocarbon per capita discharge from a Rhode Island secondary treatment facility (*7*).

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Concentration and Speciation of Dissolved Sugars in River Water

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■ Gas chromatographic analyses of the alditol acetate derivatives of selected pentoses and hexoses were used to determine dissolved (<0.45 μm) sugars in the Williamson River, Oregon. Total dissolved sugar concentrations varied from 0.0 to 7.7 μmol/L, with pentoses constituting about 50% of identified sugars. The lower concentrations were found in spring waters while the higher values were associated with highly colored samples from Klamath Marsh and downstream sampling sites on the Williamson River. The dissolved sugars accounted for an average 2.0% of total organic carbon in this river system. A fractionation scheme, utilizing XAD-7 resin to adsorb humic substances, was developed to determine the distribution of each sugar among monosaccharide (MS), polysaccharide (PS), and humic-bound saccharide (HS) fractions. Monosaccharides averaged 2.6% of dissolved sugars. The PS/HS ratio, which was much higher in lake and marsh samples than in stream samples, may be indicative of the relative contributions of autochthonous and allochthonous sources of dissolved sugars in the Williamson River system.

Introduction

Carbohydrates constitute a large fraction of the photosynthetically assimilated carbon in the Earth's biosphere. In the course of the biogeochemical carbon cycle, most of this carbon is returned to the atmosphere as carbon dioxide. A small amount of organic carbon, primarily in the form of humic substances, temporarily escapes the ultimate fate of oxidation to CO_2 and accumulates in soils, sediments, and natural waters. The extent to which carbohydrates contribute structurally to humic substances has not yet been adequately investigated. It is also unclear at the present time whether the dissolved sugars that are observed in natural waters are present as monosaccharides (MS), polysaccharides (PS), or as humic-bound saccharides (HS).

The fact that humic substances contain significant amounts of alcoholic hydroxyl functional groups has been previously demonstrated by classical wet-chemical analytical methods (*1*). More recently, both ^1H and ^{13}C NMR spectroscopic studies on natural humic substances (*2-5*) and on ^{13}C-enriched methylated derivatives of humic substances (*6*) have established that much of the carbon in many humic substances is aliphatic and that many of the aliphatic carbons are singly bonded to oxygen. Such results imply that sugars or closely related structural moieties are a significant structural component of humic substances. Thus far, however, these expectations have not been confirmed by quantitative analyses of sugars either in soil humic substances or in natural waters (*7-10*). Only very low concentrations of sugars have generally been observed.

Analytical data for sugar concentrations in soils, sediments, and natural waters are most often obtained colorimetrically and reported as total sugar concentration (e.g., in glucose equivalents). Because only monosaccharides react in the color-producing reactions, it is theoretically possible to separately quantify monosaccharides and acid-hydrolyzable saccharides by these methods (*11-14*). At present, very little information is available to indicate whether the acid-hydrolyzable fraction of carbohydrates in natural waters is predominantly PS or HS. In those studies that have addressed this question, only total sugar concentrations have been reported (*9*, *10*).

To ultimately describe the role of carbohydrates in the biogeochemical carbon cycle, and particularly their structural contribution to humic substances, we need much more information regarding individual sugar concentrations and their distributions between MS, PS, and HS. Increased efforts are being made to quantify individual sugars in natural waters, by using highly specific enzymatic assays (*15*) that are directly applied to unfractionated samples and, more commonly, paper, liquid, or gas chromatographic methods that separate and then quantify individual sugars (*16-18*). At a somewhat less specific level, a fluorimetric method has been developed to distinguish between pentoses and hexoses (*19*). The relative merits of colorimetric, enzymatic, and chromatographic methods

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for analysis of carbohydrates in natural waters were recently discussed (*20*).

This study was undertaken to assess the spatial variations in concentration and speciation of dissolved sugars in a river system of highly variable aquatic humus content. Gas chromatography of alditol acetate derivatives (*21*) was selected as the method of analysis, despite its limitations with respect to ketoses, which are incorrectly determined as epimeric aldoses. An empirical fractionation scheme that utilizes XAD-7 resin was used to isolate humic substances and the corresponding HS from MS and PS (*22, 23*). This fractionation scheme was recently used to separate humic-bound amino acids from free amino acids and proteins (*24*).

Experimental Section

Analysis of Standard Sugar Solutions. Standard solutions containing equimolar concentrations of arabinose, xylose, mannose, galactose, and glucose were prepared from commercially available reagent chemicals that were dried overnight at 25 °C and 0.1 torr before use. All standard solutions were preserved with 0.003 M NaN_3 and refrigerated at 5 °C.

The conversion of sugars to their respective alditol acetates was accomplished by using a modified version of a previously described method (*25*). After destruction of excess acetic anhydride with water and evaporation to dryness, the alditol acetates were dissolved in 200 μL of chloroform containing 50 nmol of inositol acetate as an internal standard. Gas chromatographic analyses were conducted with a Hewlett-Packard 5750B gas chromatograph with a flame ionization detector and a Hewlett-Packard 3380A integrator. A 6 ft (1.8 m) glass column (2 mm i.d.) packed with 3% SP-2330 on 100/120 Supelcoport (Supelco Co.) was used in all analyses. The optimum instrument conditions were as follows: column temperature program, 188 °C for 4 min, 2 °C/min for 11 min, 210 °C for 5 min; injection block, 220 °C; detector, 270 °C; N_2, H_2, and air flow rates: 30, 32, and 47 mL/min, respectively.

Standard solutions containing 0–100 nmol each of the alditol acetates of arabinose, xylose, mannose, galactose, and glucose and 50 nmol of inositol acetate in 200 μL of $CHCl_3$ were analyzed gas chromatographically. A linear regression analysis of the results, plotted as area of alditol acetate/area of inositol acetate vs. nmol of alditol acetate, yielded a correlation coefficient of ≥0.998 for each alditol acetate. The average detection limit for the alditol acetates used in this study corresponded to an original concentration of 0.01 μM in an aqueous sample.

Analysis of River Water Samples. River water samples were collected in linear polyethylene bottles at selected sites in the drainage basin of the Williamson River, OR (Figure 1), in January, February, March, and May, 1979. The samples were preserved with 0.003 M NaN_3, refrigerated at 5 °C, and analyzed within 1 week after sample collection. All analyses were conducted on 100-mL aliquots that were filtered through 0.45-μm membrane filters prior to analysis. In most instances, duplicate analyses were obtained.

We have considered dissolved sugars in a natural water sample to exist as monosaccharides (MS), polysaccharides (PS), and humic-bound saccharides (HS). The left side of the analytical scheme given in Figure 2 was used to determine the total concentration (TS = MS + PS + HS) of each sugar in a water sample. Since only MS are converted into alditol acetates by the previously described derivatization procedure, it was necessary to hydrolyze the sample in 3 M HCl at 100 °C for 1 h to convert PS and HS into MS. Some acid hydrolyzate solutions contained

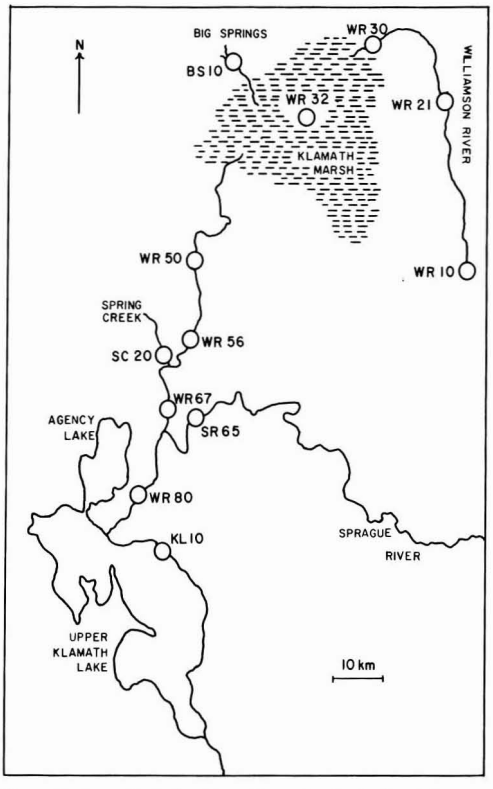

Figure 1. Approximate locations of sample sites in the study area.

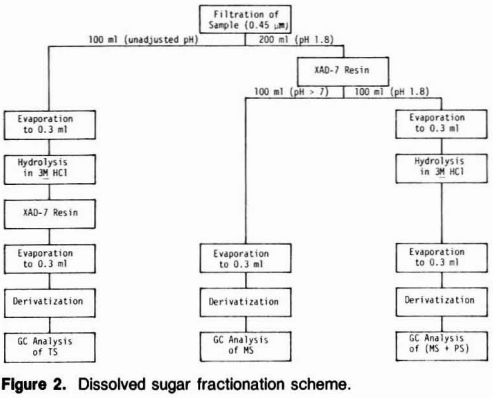

Figure 2. Dissolved sugar fractionation scheme.

high concentrations of humic substances which might interfere with subsequent derivatization and gas chromatographic analysis of MS. Humic substances were therefore removed from the acid hydrolyzates by adsorption on XAD-7 resin at pH 1.6–2.0 prior to derivatization. A typical gas chromatogram of alditol acetates from a river sample is given in Figure 3.

The fractionation scheme given on the right side of Figure 2 was used to estimate the relative contributions of MS, PS, and HS to the total concentration (TS) of each sugar in a water sample. In this scheme, an XAD-7 resin column was used to separate humic substances (and associated HS) at pH 1.8 from MS and PS prior to hydrolysis. A 220-mL water sample was passed through a

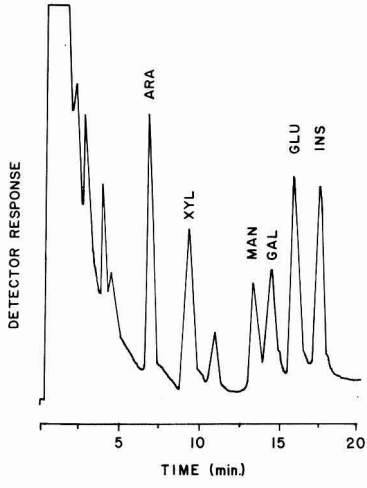

Figure 3. Gas chromatogram of alditol acetates (SR65, January 1979).

5-mL glass syringe "column" containing 4 mL of XAD-7, and the first 20 mL of eluent was discarded. The remaining 200 mL of eluent was divided into two fractions, one of which was derivatized directly to determine the MS content of the water sample. The other fraction was hydrolyzed by the previously described procedure, then derivatized to obtain the MS + PS content of the sample.

Losses of MS, PS, and HS were potentially significant during evaporation, acid hydrolysis, and passage through XAD-7 resin. An average 95% recovery of monosaccharides (MS) was obtained when 100-mL aliquots of standard sugar solutions were evaporated to near dryness under a stream of filtered air on a hot plate which maintained the aqueous solutions at approximately 30 °C. Significantly lower recoveries were obtained if the solutions became completely dry, due to the sudden increase in temperature to approximately 80 °C. Losses of PS and HS during the evaporation step could not be directly measured because of the necessity of an intermediate hydrolysis step that converts PS and HS into MS. As subsequent data will demonstrate, losses during hydrolysis are relatively high and therefore tend to obscure the small losses that occur during the evaporation step. On the assumption that losses of MS during the evaporation step are the result of air oxidation of aldoses, it was estimated that polysaccharides (PS) and humic-bound saccharides (HS) were unaffected by evaporation of aqueous solutions.

The successful recovery of submicromolar quantities of sugars after acid hydrolysis proved to be the most difficult step in the development of this analytical method. Polysaccharides (PS) and humic-bound saccharides (HS) in soils and sediments have most often been hydrolyzed with aqueous H_2SO_4 solutions. In one such procedure, samples were allowed to stand at room temperature for 16 h in 13 M H_2SO_4, followed by refluxing at 100 °C for 5 h in 0.5 M H_2SO_4 (*26*). Excess H_2SO_4 could be neutralized with $Ba(OH)_2$ or $BaCO_3$. In the present study, this method resulted in an almost complete loss of a 100-nmol sample of glucose. Alternatively, we attempted to remove SO_4^{2-} by ion exchange with a Cl^- resin. Again, large losses of glucose (50–75%) were observed.

Several investigators have used aqueous HCl solutions to hydrolyze PS and HS (*25*, *27*). Excess HCl can be removed by careful evaporation of the solution to dryness. In the present study, the yield of glucose vs. hydrolysis time was examined for solutions containing 100 nmol of glucose or an equivalent amount of dextrin in 3 M HCl. The results are summarized in Table I. These data indicate that glucose is rapidly destroyed under hydrolysis conditions. The hydrolysis of dextrin was quite rapid, with the optimum conditions for hydrolysis of dextrin being 1 h at 100 °C in 3 M HCl. Under these conditions, an 87% recovery of glucose was obtained from the dextrin solution. The results for dextrin hydrolysis were used to estimate recoveries during hydrolysis of PS and HS.

Table I. Glucose Recovery in Acid Hydrolysis Reactions

	% recovery	
time, h	glucose	dextrin
0	90	0
1	75	87
3	49	69
6		37
17		16

Table II. Percentage Recoveries for Sugar Species

treatment	monosaccharide	polysaccharide	humic-bound saccharide
evaporation	95	100	100
acid hydrolysis	75	87	87
XAD-7 adsorption	95	75	9

The average recovery of MS in the eluent passing through a column of XAD-7 resin was 95 ± 6% (as determined gas chromatographically). These results agree with the value of 99% obtained with [^{14}C]glucose. Polysaccharide recovery was estimated to be 75%, the percent recovery of [^{14}C]starch in the column eluent. From the decrease in absorbance (pH 10, 420 nm) of the water sample upon passage through XAD-7 resin, it was estimated that 8.8 ± 2.2% of humic substances was *not* adsorbed by the resin under our experimental conditions. The assumption that adsorbed and nonadsorbed fractions of humic substances contained equal sugar distributions is open to question.

The percent recoveries of MS, PS, and HS during evaporation, hydrolysis, and XAD-7 resin treatment are summarized in Table II. On the basis of these recoveries and the analytical scheme given in Figure 2, the overall concentrations of sugars in the fractions labeled TS, MS, and MS + PS can be related to the initial concentrations of monosaccharides, $(MS)_0$, polysaccharides, $(PS)_0$, and humic-bound saccharides, $(HS)_0$, by eq 1–3.

$$\text{fraction TS} = 0.64(MS)_0 + 0.79(PS)_0 + 0.79(HS)_0 \quad (1)$$

$$\text{fraction MS} = 0.90(MS)_0 \quad (2)$$

$$\text{fraction MS + PS} = 0.64(MS)_0 + 0.62(PS)_0 + 0.073(HS)_0 \quad (3)$$

The initial concentration of unfractionated sugar $(TS)_0$ in a sample can be calculated from the sum of $(MS)_0$, $(PS)_0$, and $(HS)_0$. In the data that are discussed below, it can be seen that, in general, $(PS)_0 + (HS)_0 >> (MS)_0$. Accordingly, $(TS)_0$ can be estimated from the concentration of sugar in the TS fraction alone with the equation

$$(TS)_0 = TS/0.79$$

Total organic carbon (TOC) results were obtained on a total carbon analyzer. The concentration of humic substances in river samples was estimated by absorbance of the solution at pH 10 at a wavelength of 420 nm. The calibration curve, which was obtained with solutions of

Table III. Total Concentrations (μM) of Individual Sugars

	WR10	WR21	WR30	WR32	WR50	WR56	SC20	WR67	SR65	WR80	KL10
					January 1979						
Ara	0.03	0.51	0.89	1.47	1.87	0.89	0.03	0.35	0.58	0.38	0.30
Xyl	0.01	0.56	0.99	2.15	2.38	1.39	0.00	0.58	0.51	0.46	0.43
Man	0.02	0.33	0.63	0.66	0.61	0.63	0.03	0.25	0.35	0.33	0.33
Gal	0.04	0.46	0.86	0.94	1.39	1.14	0.05	0.48	0.56	0.46	0.58
Glu	0.02	0.56	1.24	0.96	1.42	1.29	0.09	0.46	0.68	0.46	0.78
total	0.12	2.42	4.61	6.18	7.67	5.34	0.20	2.12	2.68	2.09	2.42
					February 1979						
Ara	0.01	0.07	0.46	1.52	1.79	0.78	0.05	0.44	1.39	1.13	0.27
Xyl	0.00	0.05	0.01	1.56	1.75	0.71	0.00	0.24	1.90	0.97	0.24
Man	0.00	0.06	0.04	0.49	0.41	0.26	0.00	0.08	0.58	0.32	0.29
Gal	0.07	0.00	0.51	2.30	2.55	0.78	0.01	0.70	1.63	1.01	0.41
Glu	0.00	0.04	0.05	0.76	0.96	0.47	0.05	0.26	1.09	0.57	0.43
total	0.08	0.22	1.06	6.63	7.46	3.00	0.11	1.72	6.59	4.00	1.64
					March 1979						
Ara	0.09	0.12	0.08	0.60	1.12	1.14	0.04	0.44	0.75	0.36	0.22
Xyl	0.07	0.09	0.08	0.75	1.55	0.96	0.01	0.37	0.58	0.51	0.38
Man	0.12	0.13	0.05	0.28	0.61	0.83	0.05	0.19	0.54	0.23	0.29
Gal	0.03	0.23	0.01	1.25	1.85	0.94	0.02	0.20	0.52	0.38	0.58
Glu	0.10	0.17	0.07	0.63	1.26	0.67	0.02	0.30	0.59	0.33	0.33
total	0.41	0.74	0.29	3.51	6.39	4.54	0.14	1.50	2.98	1.81	1.80
					May 1979						
Ara	0.08	0.06	0.07	0.73	1.53	0.73	0.15	0.34	0.18	0.16	0.17
Xyl	0.11	0.09	0.11	1.37	1.18	0.75	0.04	0.33	0.24	0.22	0.11
Man	0.10	0.05	0.03	0.57	0.62	0.48	0.00	0.08	0.09	0.08	0.25
Gal	0.07	0.10	0.07	1.19	1.00	0.43	0.00	0.15	0.18	0.19	0.24
Glu	0.16	0.07	0.07	1.06	0.77	0.44	0.04	0.36	0.17	0.18	0.21
total	0.52	0.37	0.35	4.92	5.10	2.83	0.23	1.26	0.86	0.83	0.98

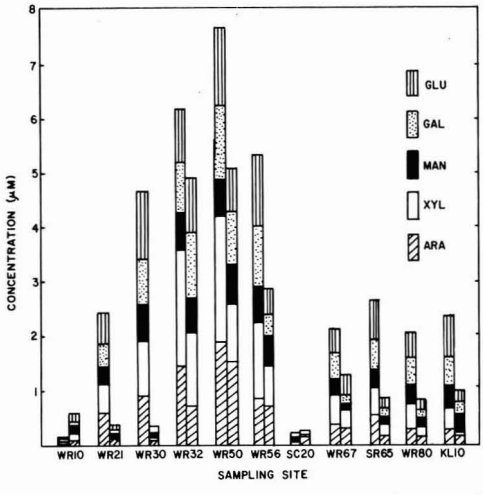

Figure 4. Total concentrations (μM) of individual sugars (January and March 1979).

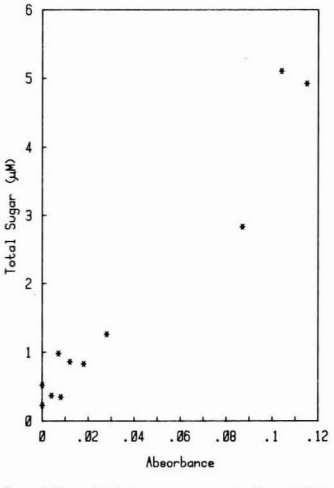

Figure 5. Correlation of total sugar concentrations (μM) with absorbance at 420 nm for the May 1979 data.

freeze-dried humic substances that were isolated from the Williamson River (WR50) by adsorption on XAD-7 resin, was linear over a concentration range 0–100 mg/L (28).

Results and Discussion

Analysis of River Water Samples. The spatial variations in total sugar concentrations are apparent from Table III and Figure 4. Spring waters (WR10, SC20) contain very low concentrations of dissolved sugars (4-month averages of 0.28 and 0.17 μM, respectively). Samples from Klamath Marsh (WR32) and the proximate downstream sites (WR50, WR56) had much higher concentrations of dissolved sugars (4-month averages of 5.31, 6.66, and 3.93 μM, respectively). Further downstream, the observed variation in dissolved sugars is consistent with approximately conservative mixing of streams containing different sugar concentrations. This spatial pattern is very similar to the previously reported distribution of amino acids in this river system (*24*).

A moderately good correlation between TS and TOC was observed, with sugar carbon accounting for an average of 2.0% of the TOC in this river system. These results are in excellent agreement with previously published values (*12–14*). Total dissolved sugar concentrations also correlate well with humic carbon (estimated by absorbance at 420 nm and pH 10), as illustrated in Figure 5 for the May 1979 data. For the 4 months of this study, correlation coefficients of 0.89, 0.80, 0.88, and 0.97 were observed, implying that dissolved sugars might be associated with humic substances.

Table IV. Concentrations (μM) of Dissolved Sugar Species

samples / sites	Ara			Xyl			Man			Gal			Glu		
	MS	PS	HS	MS	PS	HS	MS	PS	HS	MS	PS	HS	MS	PS	HS
WR10	0.06	0.02	0.00	0.05	0.06	0.00	0.04	0.06	0.00	0.03	0.04	0.00	0.03	0.13	0.00
WR10[a]	0.03	0.01	0.05	0.01	0.00	0.06	0.00	0.00	0.12	0.01	0.00	0.02	0.01	0.00	0.09
WR21	0.00	0.05	0.01	0.01	0.08	0.00	0.00	0.05	0.00	0.01	0.09	0.00	0.01	0.06	0.00
WR30	0.01	0.06	0.00	0.01	0.10	0.00	0.00	0.03	0.00	0.00	0.07	0.00	0.00	0.07	0.00
WR32	0.02	0.71	0.00	0.02	1.35	0.00	0.00	0.47	0.10	0.02	1.17	0.00	0.00	1.06	0.00
WR50	0.01	0.24	1.28	0.01	0.54	0.63	0.00	0.29	0.32	0.01	0.39	0.60	0.01	0.63	0.13
WR50[a]	0.07	0.42	0.64	0.01	0.40	1.15	0.00	0.61	0.00	0.02	0.90	0.93	0.03	0.68	0.55
WR56	0.01	0.49	0.23	0.02	0.73	0.00	0.01	0.19	0.28	0.00	0.42	0.01	0.00	0.44	0.00
WR56[a]	0.06	0.00	1.08	0.02	0.00	0.94	0.00	0.16	0.67	0.01	0.16	0.76	0.02	0.29	0.37
SC20	0.00	0.15	0.00	0.00	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.04	0.00
WR67	0.02	0.18	0.14	0.02	0.11	0.20	0.00	0.08	0.00	0.00	0.15	0.00	0.01	0.35	0.00
SR65	0.00	0.02	0.16	0.02	0.00	0.22	0.00	0.00	0.09	0.00	0.03	0.15	0.00	0.00	0.17
WR80	0.00	0.12	0.04	0.00	0.04	0.18	0.00	0.03	0.05	0.00	0.02	0.17	0.00	0.03	0.15
KL10	0.00	0.17	0.00	0.00	0.07	0.04	0.00	0.25	0.00	0.00	0.24	0.00	0.00	0.21	0.00

[a] Results obtained in March, 1979.

In most other studies of dissolved sugars in fresh waters, very similar sugar concentrations have been observed. For example, Semenov et al. (*13*), in a study of organic substances in several Soviet rivers, reported average MS and PS + HS concentrations of 1.2 and 3.2 μM, respectively. Stabel (*14*) reported an average hydrolyzable sugar concentration of 0.7 μM in Schösee, and Weinmann (*12*) reported an average hydrolyzable sugar concentration of 1.9 μM in the surface waters of Plusssee. Hirayama (*19*) reported a dissolved sugar concentration of 4.6 μM in Lake Biwa.

At most sample sites, total dissolved sugar concentrations decreased irregularly from January to May 1979. Perhaps this trend is indicative of increased microbial activity with increased water temperature. Without a long-term study of temporal variations in dissolved sugar concentrations, no solid conclusions can be drawn.

The relative abundances of arabinose, xylose, mannose, galactose, and glucose do not exhibit significant temporal or spatial variations. The 4-month average for the five sugars are 22, 24, 11, 24, and 19 mol %, respectively. These results agree reasonably well with the relative concentrations of individual sugars in other fresh waters (*12*, *14*) and with the sugar distribution in a sewage sludge derived fulvic acid (*29*) but are notably different from the results reported for monosaccharides in seawater (*16*, *17*). The approximately equimolar pentose:hexose ratio agrees well with the results of Hirayama (*19*). Prior studies have shown fructose to be present in natural waters (*14*, *17*, *20*). Since the alditol acetate method results in conversion of fructose to glucitol and mannitol acetates, the measured relative abundances of glucose and mannose are probably overestimated. It thus seems likely that mannose is a relatively minor fraction of dissolved sugars in the Williamson River system.

The distribution of sugars among MS, PS, and HS fractions is given in Table IV and Figure 6. Most of the data were obtained in May 1979, so temporal variations could not be ascertained. The MS fraction was uniformly low, averaging 2.6% for all sites and times. The remaining 97.4% of sugars was approximately equally distributed between PS and HS fractions. With respect to the individual sugars, the average PS/HS ratio varied from 0.7 to 2.8 in the following order: Ara < Xyl < Man < Gal < Glu. The higher percentage of PS for glucose (72%) is consistent with its ubiquitous occurrence in biopolymers. The relative enrichment of hexoses in the PS fraction is illustrated in Figure 7, in which the line of unit slope represents the hypothetical case where each sugar is uniformly distributed among MS, PS, and HS.

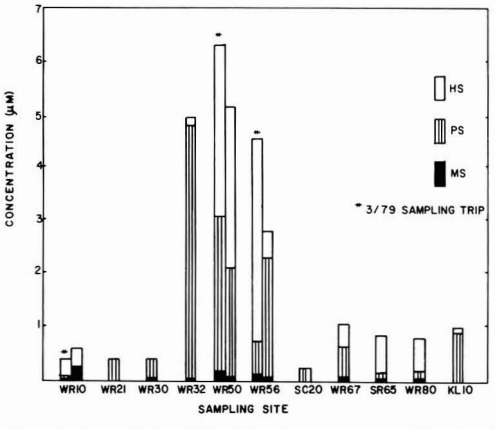

Figure 6. Concentrations (μM) of dissolved sugar species (March and May 1979).

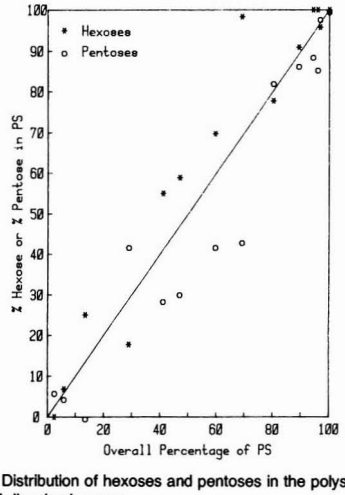

Figure 7. Distribution of hexoses and pentoses in the polysaccharide fraction of dissolved sugars.

The spatial variability of the PS/HS ratio is quite complex, probably due to the interplay of biological and geochemical processes. In a recent study of the distribution of amino acids in the Williamson River system (*24*), it was found that amino acid and humic carbon concen-

trations were positively correlated with discharge, suggesting concomitant mobilization of these components from soils during episodes of surface runoff. Similar mobilization of HS is expected; however, insufficient fractionation data were available to correlate HS with discharge. It is tempting to speculate that the PS/HS ratio may reflect the relative contributions of autochthonous and allochthonous sources to the total sugar concentration in a natural water. It would follow that lake water samples would have higher PS/HS ratios than stream samples, a prediction that is strongly supported by the data for Upper Klamath Lake (KL10) and Klamath Marsh (WR32), for which PS/HS ratios of 24 and 48 were observed. In contrast, an overall average PS/HS ratio of 0.82 was obtained for stream samples.

Sugar Content of Aquatic Humus. The probability that humic substances contain sugarlike structural components is intuitively quite high, considering the very high carbohydrate content of biomass from which humus is derived. It is certainly possible, however, that most carbohydrates are simply recycled in the biosphere through the action of microorganisms. The most comprehensively studied humic substance is the Prince Edward Island soil fulvic acid used by Schnitzer and co-workers (*1*). Using potentiometric titrations to estimate carboxyl and phenolic content and quantitative acetylation to measure the sum of phenolic and alcoholic hydroxyl groups, Schnitzer and co-workers have determined that their soil fulvic acid contains 7.7 mmol/g carboxyl groups, 3.3 mmol/g phenolic groups, and 3.6 mmol/g alcoholic hydroxyl groups. A summary of their work is given by Gamble and Schnitzer (*30*). Assuming that all alcoholic hydroxyl groups are present as sugar moieties with equal proportions of pentoses and hexoses (as observed in this study), it is possible to estimate the maximum fraction of carbohydrate carbon in their fulvic acid. The acetylation reaction detects only free hydroxyl groups. In a typical pyranose, there are 3–4 free hydroxyl groups/6 carbon atoms, depending on whether the pyranose is covalently bonded to 1 or 2 other structural units. Likewise, a furanose contains 2–3 free hydroxyl groups/5 carbon atoms. Therefore, the 3.6 mmol/g alcoholic hydroxyl groups in Schnitzer's soil fulvic acid corresponds to 5.7–8.1 mmol/g carbohydrate carbon, which is 13–19% (w/w) of the carbon content of the fulvic acid.

The probable presence of carbohydrate moieties in both soil and aquatic humus is also strongly suggested by several recent ^{1}H and ^{13}C NMR studies (*2–5*). Worobey and Webster (*2*) suggest that carbohydrates are very important structural components of humus and that these structural moieties are converted into aromatic structures by extraction procedures that utilize strong acid or base solutions. Hatcher et al. (*3*) and Wilson et al. (*4*) have concluded that aquatic humus from both marine and freshwater environments contains significant amounts of *O*-alkyl carbon, probably in the form of sugarlike moieties. Wilson et al. (*5*), using both ^{1}H and ^{13}C NMR, have concluded that 27% of the nonexchangeable H in a soil humus sample is bonded to the carbon atoms of sugarlike moieties. From their data regarding elemental ratios of C, H, and N, together with the reasonable assumptions that their sample of humus contains approximately 50% (w/w) carbon and approximately 12 mmol/g exchangeable H, the results of Wilson et al. (*5*) imply that about 15% of the carbon in their sample could be in the form of sugar moieties.

An even more directly quantitative determination of the carbohydrate content of a soil humus sample (Contech fulvic acid) was recently reported by Wershaw et al. (*6*), who used ^{13}C-enriched methylating agents to convert carboxyl, phenolic, and alcoholic hydroxyl groups into their respective methyl esters and methyl ethers. The relative abundances of carboxyl, phenolic, and alcoholic hydroxyl groups were estimated to be 2.5:1.0:1.1 by ^{13}C NMR spectroscopy on the ^{13}C-enriched methylated derivatives. According to Wershaw et al. (*6*), the Contech fulvic acid is equivalent to the Prince Edward Island soil fulvic acid used by Schnitzer and his co-workers. From the carboxyl content of the latter material (7.7 mmol/g), the alcoholic hydroxyl content of Contech fulvic acid is estimated to be 3.4 mmol/g, in excellent agreement with the value of 3.6 mmol/g for Schnitzer's fulvic acid. Like the acetylation method used by Schnitzer and co-workers, the methylation procedure of Wershaw et al. (*6*) detects only free hydroxyl groups, so the calculation procedure used earlier for Schnitzer's fulvic acid is also applicable to the data of Wershaw et al. (*6*). By assumption of a 1:1 ratio of pentoses to hexoses, the 3.4 mmol/g of alcoholic hydroxyl groups in Contech fulvic acid corresponds to 5.5–7.6 mmol/g carbohydrate carbon. Thus, about 13–18% (w/w) of the carbon in Contech fulvic acid could be in the form of carbohydrate moieties. These results are in excellent agreement with both the data of Gamble and Schnitzer (*30*) and the results of Wilson et al. (*5*).

The results obtained by wet-chemical and ^{1}H and ^{13}C NMR methods all indicate that approximately 15% of the carbon atoms in humus could be present as sugar moieties. It is of interest to compare this upper limit with the actual sugar concentrations obtained in this study. For example, the average TS at WR50 was 6.66 μM, consisting of approximately a 1:1 mixture of pentoses and hexoses. This concentration corresponds to a sugar carbon concentration of 0.44 mg/L, which is only 2.8% of the average TOC value at WR50 (16 mg/L). From absorbance measurements, approximately 60% of the TOC at WR50 is estimated to be humus carbon, and from the data in Table IV, a similar fraction of dissolved sugars at that sample site is humic-bound. Thus, about 2.8% of the aquatic humus carbon is identifiable as sugar carbon. This value is far less than the upper limit of 15% that was derived from measurements of alcoholic hydroxyl groups in humus. It is safe to assume that simple monosaccharide and polysaccharide fragments are not significant structural units in humus, because they would both be expected to yield sugars directly upon hydrolysis. At this time, the nature of the remaining four-fifths of the alcoholic hydroxyl groups is purely speculative. Certainly, the simple oxidation products of aldoses (aldonic acids, aldaric acids, and uronic acids) could account for both the relatively high alcoholic hydroxyl content and low sugar content of humus. None of the carboxylic acid derivatives of sugars can be reduced to alditols by $NaBH_4$ and thus could not be detected at all by the analytical methodology used in this study. Uronic acids have, in fact, been detected in soil humic substances (*31*) and in natural waters (*12*), but only in very low concentrations.

Conclusions

Total dissolved sugar concentrations ranged from 0.1 to 7.7 μM, with approximately equal concentrations of arabinose, xylose, galactose, and glucose, and with lower concentrations of mannose. Spring waters were quite low in dissolved sugars, while colored sample sites downstream from Klamath Marsh had much higher sugar concentrations.

Fractionation studies demonstrated that monosaccharide (MS) concentrations were quite low at all sam-

ple sites. The relative abundances of polysaccharides (PS) and humic-bound saccharides (HS) were highly variable. In lake and marsh waters, PS accounted for nearly all dissolved sugars, while in stream samples, PS and HS were almost equally abundant. Hexoses (particularly glucose) were relatively enriched in the PS fraction and relatively deficient in the HS fraction.

Identifiable sugars accounted for an average of 2.0% of the total organic carbon in the Williamson River system. This value is much lower than the carbohydrate contents of humic substances as estimated by analysis of alcoholic functional groups or by ^{13}C and ^{1}H NMR studies, suggesting that most of the sugarlike structural units in humic substances are probably not in the form of simple monosaccharide or polysaccharide moieties.

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Occurrence of Organotin Compounds in Ontario Lakes and Rivers

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■ The presence of butyltin and methyltin species is reported for the first time in lakes, rivers, and harbors in Ontario. Concentrations of tri-*n*-butyltin in Collingwood Harbor, a marina in Lake St. Clair, Toronto Harbor, and Ramsey Lake are 15–60% of the LC_{100}^{12d} value for a sensitive aquatic species, rainbow trout yolk sac fry. The species Bu_3Sn^+, Bu_2Sn^{2+}, and inorganic tin are concentrated by factors of up to 10^4 in the surface microlayer relative to subsurface water. Concentrations of methyltin and dimethyltin are high in Kingston Harbor and Whitby Harbor and in industrial areas such as Lake St. Clair.

Introduction

Organotin compounds are used in three major ways, viz., as stabilizers for polyvinyl chloride, as catalysts, and as biocides (*1*). The increasing annual use of organotin compounds raises the possibility of environmental pollution. Organotin compounds are a class of compounds about which more information is sought under Canada's Environmental Contaminants Act (*2*) regarding toxicology and environmental fate.

The toxicity of tin compounds to humans (*3*), terrestrial animals (*4*), and phytoplankton (*5*) has been extensively studied. In general, organotin compounds are more toxic than inorganic tin compounds. Progressive introduction of organic groups to the tin atom in any $R_nSn^{(4-n)+}$ series produces maximal biological activity against all species when $n = 3$, i.e., for the triorganotin compounds. However, within the class of trialkyltin compounds, there are considerable, and as yet unexplained, variations in toxicity with the nature of the alkyl group (*6*). For insects, trimethyltin compounds are most toxic; for mammals, the triethyltin compounds; for Gram-negative bacteria, the

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tri-*n*-propyltin compounds; for Gram-positive bacteria, fish, and fungi, the tri-*n*-butyltin compounds. For tributyltin compounds, LC_{100}^{12d} and LC_{50}^{24h} values for rainbow trout are ≤5 and 28 μg/L, respectively (*7*, *8*), and values in the range 30–75 μg/L have been reported for other fish, frogs, and gastropods (*8–10*). Further increase in the *n*-alkyl chain length produces a sharp drop in biological activity. Triphenyltin compounds are particularly toxic to phytoplankton (*5*) while tricyclohexyltin compounds show high acaricidal activity (*6*).

Variation of labile inorganic or organic anionic substituents, X, within any particular R_3SnX series has, in general, very little effect on biocidal activity in mammals (*6*), but there are not enough data to confirm whether or not this is true for fish.

The presence of butyltin (*11*) and methyltin (*12*, *13*) species at concentrations of ng/L to μg/L has been reported in a variety of natural waters as well as rain in the United States. Butyltin species probably occur as a result of anthropogenic activity, but methyltin species may result from anthropogenic activity or the methylation of tin, either biologically or abiotically: (a) increasing concentrations of methyltin species with increasing anthropogenic tin influx have been observed in the Chesapeake Bay (*14*); (b) several reports have now been published on the biomethylation (*13*, *15–19*) and chemical methylation (*20*, *21*) of inorganic and organic tin compounds.

Our research on organotin compounds attempts to determine (a) the aquatic environmental fate of tributyltin and dibutyltin compounds, (b) whether inorganic tin and organotin compounds can be methylated in aquatic environments, and (c) the toxicity of several commercially important organotin compounds to fish and algae. An integral part of this research is the determination of the extent of organotin contamination of Canada's fresh waters; this article reports the results of our investigations on the occurrence of organotin species in selected lakes, rivers, and harbors in Ontario.

Experimental Section

Determination of Butyltin Species in Water. Samples (8 L) of subsurface (0.5 m) water were collected in glass bottles, and the contents were acidified to pH 1 and stored at 4 °C until analysis. In addition, surface microlayer samples of 100-mL volume were collected with a glass plate sampler (*22*).

Analyses of the unfiltered water samples for butyltin species (Bu_3Sn^+, Bu_2Sn^{2+}, and $BuSn^{3+}$) and "total recoverable inorganic tin" (Sn(II) and Sn(IV)) were performed according to a method (*23*) that involved extraction from 8 L of acidified aqueous solution into benzene/0.5% tropolone, adjusting the pH of the water to 7, saturating with NaCl, and reextraction with benzene/0.5% tropolone, derivatization of the combined benzene/tropolone extracts with pentylmagnesium bromide, and cleanup and analysis of the $Bu_nPe_{4-n}Sn$ species by gas chromatography with a modified flame photometric detector. Appropriate reagent blanks were prepared. The detection limit for each of the $Bu_nPe_{4-n}Sn$ species is about 0.01 μg/L, and identities were confirmed by cochromatography with authentic standards on two different columns and, when possible, by gas chromatography–mass spectrometry (*23*). Recoveries of the butyltin species and Sn(IV) spiked at the 1 mg/L level in acidified water varied from 96% to 103% (*23*), and the standard deviation of concentrations of butyltin species at various locations was less than 15%.

Although Sn(IV) was the only inorganic tin species for which recoveries were determined in spiking experiments, the inorganic tin present in the environmental samples is reported as "total recoverable inorganic tin", since it has recently been shown that hydridization of either Sn(IV) or Sn(II) yields SnH_4 (*14*), and thus any Sn(II) that may be present in our water samples may similarly be alkylated to tetraalkyltin. Our results do show, however, that the yield of, e.g., Bu_4Sn from Sn(II) is almost negligible compared to that from Sn(IV).

Determination of Methyltin Species in Water. The sampling procedure was similar to that for the butyltin species except that the water was not acidified. After the sample was saturated with NaCl, it was extracted in 4–5-L aliquots with 100 mL of benzene/0.5% tropolone. Extracts were evaporated to a small volume, butylated with butylmagnesium bromide, and analyzed by gas chromatography–atomic absorption spectrophotometry (*24*). The detection limit for each of the $Bu_nMe_{4-n}Sn$ species is about 0.02 μg/L with 8-L samples. Recoveries of the methyltin species (Me_3Sn^{2+}, Me_2Sn^{2+}, $MeSn^{3+}$) and Sn(IV) spiked at the 0.05–1.0 mg/L level in water varied from 85% to 108%; six replicate analyses of samples spiked with 25 μg of the different methyltin species gave coefficients of variation between 5.4% and 11%. The surface microlayer was not examined for methyltin species.

Results and Discussion

Table I indicates the common occurrence of butyltin species (30 of 90 determinations) and inorganic tin (23 of 30 determinations) in subsurface water; to our knowledge these data are the first to be reported on organotin species in Canadian waters.

Table I shows concentrations of Bu_3Sn^+ in Collingwood Harbor, a marina in Lake St. Clair, Toronto Harbor, and Ramsey Lake, which are 15–60% of the LC_{100}^{12d} value for rainbow trout yolk sac fry (*7*). A possible source of Bu_3Sn^+ in these locations is boat or ship paint.

The species Bu_2Sn^{2+} occurs in 20 of 30 subsurface water samples; it may be derived from Bu_3Sn^+ or from polyvinyl chloride stabilizers such as dibutyltin diisooctylmercaptoacetate. The presence of Bu_2Sn^{2+} in water in remote areas such as the Turkey Lakes area, 50 km north of Sault Ste. Marie, is suggestive of atmospheric introduction.

The species $BuSn^{3+}$ occurs rarely in subsurface waters, but inorganic tin is widespread and especially concentrated in Collingwood Harbor and Ramsey Lake.

The presence of pollutants in high concentrations in surface microlayers is important to surface-dwelling biota and in considerations of air–water exchange. Table II shows the concentrations of Bu_3Sn^+, Bu_2Sn^{2+}, and inorganic tin in the surface microlayer, i.e., the top 60 μm of the water column as sampled with a glass plate (*22*). The species $BuSn^{3+}$ was not detected in any surface microlayer, but the other three species are concentrated by factors of up to 10^4 in the surface microlayer relative to subsurfacewater. To our knowledge this is the first report of organometallic species concentration in surface microlayers, although metal enrichment has been reported for surface microlayers, slicks, and foams in ocean and lake water (*25–31*).

The observation of surface microlayer concentrations 10^4 times greater than subsurface water concentrations prompted an estimation of the relative amounts of the various species in the surface microlayer and subsurface water. This was done by (i) considering a sample of water of length, width, and depth *A*, *B*, and *C* m, respectively, upon which rests a microlayer *D* m thick, (ii) supposing that the concentration of the compound of interest is *X* μg/L in the surface microlayer and *Y* μg/L in the subsurface water, and (iii) assuming that *Y* is invariant with

Table I. Concentrations (μg/L) of Butyltins and Total Recoverable Inorganic Tin (TRIT) in Unfiltered Subsurface Water[a]

location	depth, m	$[Bu_3Sn^+]$	$[Bu_2Sn^{2+}]$	$[BuSn^{3+}]$	[TRIT]
Lake Superior (Thunder Bay)	6				
Lake Superior (Red Rock)	4		0.01		
Lake Superior (Marathon)	5	0.02	0.56		0.73
Turkey Lake 1	6				
Turkey Lake 2	6				1.06
Turkey Lake 3	6				
Turkey Lake 4	6		0.08		0.04
Turkey Lake 5	6		0.02		
Sault Ste. Marie Harbor	5		0.03		2.43
Ramsey Lake (Sudbury)	25	0.75	0.02		48.7
Nepewassi Lake (Sudbury)	8		0.08		
Lake Nipissing (North Bay)	6		0.24		
Plastic Lake	3		0.05		0.49
Collingwood Harbor	3	1.0			50.1
Owen Sound Harbor	4		0.02		0.32
St. Clair River 1	5		0.01		0.12
St. Clair River 2	5		0.42		0.06
St. Clair River 3	5		0.30		0.06
Lake St. Clair (Mitchell Bay)	5		0.02		1.88
Lake St. Clair (marina)	2	2.91	7.30	8.48	6.0
Thames River (400 m upstream from mouth)	1				0.06
Port Dover Harbor	5				0.01
Grand River (mouth)	5				0.02
Hamilton Harbor	5	0.16	0.02	0.02	0.08
Toronto Harbor	5	0.84	0.27		1.04
Whitby Harbor	5	0.05	0.09		2.11
Belleville Harbor	5		0.01		0.53
Kingston Harbor	5	0.01	0.03		0.68
St. Lawrence River 1	8				0.01
St. Lawrence River 2	14				0.01

[a] Minimum detectable concentration of each species is approximately 0.01 μg/L; precise sampling locations are available upon request.

Table II. Concentrations (μg/L) of Butyltins and Total Recoverable Inorganic Tin (TRIT) in Unfiltered Surface Microlayer[a]

location	$[Bu_3Sn^+]$	$[Bu_2Sn^{2+}]$	[TRIT]
Lake Superior (Thunder Bay)	0.45		111
Lake Superior (Red Rock)	0.68	0.71	42
Lake Superior (Marathon)			11.6
Turkey Lake 1	0.29		81.4
Turkey Lake 2	0.85		424
Turkey Lake 3	0.48		27
Turkey Lake 4	0.29		42.2
Turkey Lake 5	0.15		83
Sault Ste. Marie Harbor	0.29		39
Ramsey Lake (Sudbury)	0.25		9.1
Nepewassi Lake (Sudbury)	3.81		502
Lake Nipissing (North Bay)	0.18		180
Collingwood Harbor			308
Owen Sound Harbor			208
St. Clair River 1	60.7	94	8.4
St. Clair River 2	11.9	2600	31
St. Clair River 3		2200	0.3
Lake St. Clair (Mitchell Bay)	8.7	119	125
Lake St. Clair (marina)	50.9	107	6.6
Thames River (400 m upstream from mouth)			12
Port Dover Harbor	11.8	50.5	2.5
Grand River (mouth)			
Toronto Harbor		1460	57.2
Whitby Harbor	1.4	2250	633
Belleville Harbor	54.6	195	80
Kingston Harbor	4.8	39	46
St. Lawrence River 1	9.7	38	1.4
St. Lawrence River 2			0.8

[a] $BuSn^{3+}$ not detected in any surface microlayer sample; minimum detectable concentration of each species is approximately 0.01 μg/L.

depth. The ratio, R, of the amount in the surface microlayer to the amount in subsurface water is XD/YC. Values of R were calculated with the data in Tables I and II and with $D = 6 \times 10^{-5}$ m (determined at several locations). In the majority of cases the carrying capacity of the surface microlayer is insignificant; however, the amount of material in the surface microlayer exceeded 5% of that in the whole depth of subsurface water at two locations for Bu_3Sn^+, eight locations for Bu_2Sn^{2+}, no location for $BuSn^{3+}$, and six locations for inorganic tin. The most notable results

Table III. Concentrations (μg/L) of Methyltin Species in Unfiltered Subsurface Water[a]

location	$[Me_3Sn^+]$	$[Me_2Sn^{2+}]$	$[MeSn^{3+}]$
Lake Superior (Thunder Bay)		0.03	0.15
Lake Superior (Red Rock)	0.05	0.03	0.23
Lake Superior (Marathon)		0.03	0.21
Turkey Lake 1		0.05	0.24
Turkey Lake 2		0.02	0.11
Turkey Lake 3		0.05	0.18
Turkey Lake 4		0.04	0.20
Turkey Lake 5		0.05	0.25
Sault Ste. Marie Harbor		0.04	0.25
Ramsey Lake (Sudbury)		0.04	0.22
Nepewassi Lake (Sudbury)		0.03	0.20
Lake Nipissing (North Bay)		0.09	0.23
Plastic Lake		0.04	0.17
Collingwood Harbor		0.05	0.20
Owen Sound Harbor		0.04	0.17
St. Clair River 1		0.18	0.64
St. Clair River 2		0.21	0.68
Lake St. Clair (Mitchell Bay)		0.10	0.35
Lake St. Clair (marina)		0.22	0.53
Thames River (400 m upstream from mouth)		0.21	0.67
Port Dover Harbor		0.16	0.61
Grand River (mouth)		0.14	0.37
Hamilton Harbor			0.06
Toronto Harbor		0.29	0.96
Whitby Harbor		0.28	1.20
Belleville Harbor		0.24	0.92
Kingston Harbor		0.40	1.22
St. Lawrence River 1		0.03	0.28

[a] Minimum detectable concentration of each species is approximately 0.02 μg/L; for concentrations of inorganic tin species, see Table I.

were (i) for Nepewassi Lake and Lake Nipissing, in which the amounts of inorganic tin in the surface microlayer were >38% and >18%, respectively, of the amounts in the whole depth of subsurface water, and (ii) for Whitby and Belleville Harbors, in which the amounts of dibutyltin species in the surface microlayer were 30% and 23%, respectively, of the amounts in the whole depth of subsurface water.

Anthropogenic sources of methyltin species are their use as polyvinyl chloride stabilizers or catalysts. Table III shows that higher concentrations of methyltin species are generally found near chemical plants or in harbors with heavy shipping traffic such as Kingston Harbor, Toronto Harbor, Port Dover, St. Clair River, and Sault Ste. Marie. In all of the samples, concentrations of $MeSn^{3+}$ are generally higher than those for Me_2Sn^{2+}, and Me_3Sn^+ is rarely found. There is no clear correlation between butyltin and methyltin species concentrations in the sites of Tables I–III, although both butyltin and methyltin species occurred in high concentrations in Lake St. Clair (marina) and Toronto Harbor.

Atmospheric transport could be the reason for the presence of methyltin species in areas remote from industrial activity such as Plastic Lake and North Bay; indeed, the presence of methyltin species in rainwater (*12*) lends support to the idea of atmospheric transport. Methyltin species, however, could also result from biotic or abiotic methylation of either organotin species or naturally occurring tin. The cleavage of Sn–C bonds in soils and sediments has been demonstrated (*32*). Successive cleavage of Sn–C bonds of compounds such as R_3Sn^+ ultimately produces inorganic tin, which may then be subject to microbial methylation. In a situation somewhat analogous to the formation–degradation equilibrium for methylmercury (*33*), concentrations of methyltin species may be at a steady state.

Analyses of butyltin and methyltin species and inorganic tin in sediments from these 30 locations are in progress, and investigations are planned on organotin contamination of water, sediment, fish, and algae from other locations in the Great Lakes.

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Mobility and Bioavailability of Uranium Mill Tailings Contaminants

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■ An evaluation of environmental transport and contamination resulting from the release of trace elements and radionuclides from uranium mill tailings was performed by utilizing both laboratory and field studies. The composition of tailings showed the enrichment of a suite of uranium analogue elements (As, Mo, Se, and V) as well as the frequent occurrence of heavy metals generally associated with sulfide minerals (Co, Cu, Ni, and Pb). Aqueous leaching of alkaline tailings mobilized base labile (anionic) species As, Mo, Se, and U, whereas acid tailings leachates contained appreciable Co and Ni. The assimilation of mobile constituents by the roots of native plant species was most evident for Mo and Se in alkaline tailings; levels of these contaminants reported to be toxic to grazing animals were found. The laboratory studies on contaminant mobility and bioavailability are compared with contamination of water, soil, and biota by Mo and U in the vicinity of an alkaline-leach uranium mill.

Introduction

The release of radionuclide contaminants from disposal sites for uranium mill tailings has received growing attention from the national press (*1*), the United States Congress (*2*), and federal regulatory agencies (*3*). This concern stems from a growing awareness that the hazards posed by uranium mining and milling comprise a substantial portion of the overall environmental risk of nuclear power production (*4*). The principal sources of radiation hazard in the uranium mining and milling industry are those associated with the progeny of ^{238}U. Of particular concern is the release of long-lived uranium isotopes from yellowcake drying and packaging, moderately long-lived ^{226}Ra and short-lived ^{210}Pb escaping as particulate or aqueous emissions from ore or tailings piles, and the very short-lived ^{222}Rn and progeny emanating from tailings (*3*). The presence of potentially toxic, nonradioactive elements in uranium ores, leach solutions, or mill effluents has not been acknowledged as a prime environmental problem posed by this industry. An evaluation of the ability of such toxic constituents to contaminate water resources, soil, and biota is required to determine whether these elements do indeed pose a threat to the environment.

A number of trace elements are frequently enriched in epigenetic sandstone uranium ore deposits, the predominant ore type presently being mined in the United States. Some deposits have As, Mo, Se, and V enriched along with U (*5*, *6*). This common geochemical behavior may result from the migration of these elements in ground waters as oxyanions or as anion complexes and deposition as reduced species in a zone containing humic substances and H_2S. Other trace metals such as Co, Cu, Ni, and Zn are often enriched in these uraniferous sandstones probably due to the presence of base metal sulfides associated with authigenic pyrite (*5*). In addition to these enriched ore constituents, high levels of inorganic species are present in spent leach solutions discharged from mills: SO_4^{2-} from acid leach solutions, Na^+ from carbonate leach solutions, Cl^- from sodium chlorate oxidant, and NH_4^+ used in yellowcake precipitation. In addition, many major and minor elements, for example, Fe and Mn, are solubilized during acid leaching of uranium ore. Organic chemicals

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such as tertiary amines, alkylphosphoric acids, isodecanol, and kerosene (as a carrier) used in solvent extraction circuits are also found in mill liquors disposed of in tailings ponds (*7*). Such a broad spectrum of nonradioactive species occurring at high concentrations in uranium mill residues poses a considerable threat to the environment if these contaminants are not contained.

Tailings contaminants can enter the environment by several pathways. Mobile constituents in tailings liquids can seep from tailings ponds or can be leached from tailings by ground water entering a disposal site. Contaminants present in shallow ground water can migrate to the soil surface as a result of evaporation and be deposited as salt encrustations. In addition, the accidental release of tailings into surface waters may release labile contaminants. Plants may assimilate bioavailable contaminants (a) by roots penetrating cover materials and coming into contact with tailings in a repository, (b) from soils contaminated with tailings transported by wind or water erosion, and (c) from soils irrigated with water contaminated by pollutants escaping from tailings ponds.

The objective of this paper is to examine the enrichment of potentially toxic constituents in uranium mill residues and the aqueous mobility and bioavailability of these contaminants in the environment. The extent of trace element transport and contamination will be demonstrated for tailings from Colorado Plateau ores. This evaluation will include laboratory studies on leaching tailings with water and on the plant uptake of contaminants and finally a comparison of these laboratory results with contamination found near an actual tailings pile.

Experimental Methods

Surface and near-surface (<50 cm deep) tailings samples were collected in bulk from inactive tailings sites at Ambrosia Lake, NM, Naturita, CO, and Mexican Hat, UT. Surface soils to be used as experimental controls were collected at three locations in the Grants Mineral Belt, NM, and represent a clay, a clay loam, and a sand. In addition, a contaminated sediment sample from Churchrock, NM, was provided by the New Mexico Environmental Improvement Division. This sample represents salts and surface sediments collected from an ephemeral streambed that had been saturated with liquids accidentally released from a tailings impoundment at an acid leach uranium mill. Tailings and soils were air-dried (20–25 °C) to prevent loss of volatile species such as Se. Aggregates in these solids were crushed to pass through a 20-mesh screen and then analyzed for selected trace elements.

Water extractions of trace contaminants were performed on the tailings, sediments, and soils described above. Air-dried solids were shaken with deionized water for 30 days at a solid to liquid mass ratio of 1:5. The suspensions were vacuum filtered through Whatman 42 filter paper and subsequently through 0.45-μm micropore filters. Carbonate slime tailings (Ambrosia Lake, NM) required centrifugation before filtering because of their high content of fines. The filtered extracts were acidified with concentrated HNO_3 (1% by volume) to a pH of 1.5 or less for trace element analysis. Aliquots of unacidified extracts were also taken for major anion analysis by ion chromatography.

A greenhouse experiment was performed to assess the uptake of contaminants from alkaline tailings (slimes from the Ambrosia Lake, NM, pile) by native plant species. A grass (*Sporobolus airoides*) and a shrub (*Atriplex canescens*) were grown for 6 months in soil-covered tailings or in control treatments with soils from the Grants Mineral Belt. Details on the experimental design can be found in ref 8. Above-ground plant parts were harvested, washed to remove any surficial particulate contamination, and air-dried. Dried samples were ground in a Wiley mill to less than 20 mesh in preparation for analysis.

Surface and ground waters, surface soils, and vegetation were collected (June and October 1979) from five general locations in the vicinity of the then operating alkaline (carbonate) leach uranium mill at Canon City, CO. At location 1, surface and ground-water samples were collected from a trench intercepting near-surface seepage from the tailings ponds and from observation wells near the tailings ponds. Soils and vegetation were collected from areas adjacent to ponds of seepage in the interception trench. At location 2, water samples were taken from a flood control reservoir that had accumulated runoff from the mill site and seepage from the tailings ponds; soils and vegetation were collected from the high-water shoreline of the reservoir. At location 3, ground water was collected from wells shown by the Colorado Department of Health records to contain elevated concentrations of Mo and U (and major ion pollutants, SO_4^{2-} and Cl^-). Soils and vegetation at sites in this location were sampled from gardens and small pastures irrigated with this contaminated ground water. Location 4 represents nearby areas that had not been irrigated with contaminated ground water or had used water from irrigation ditches. Thus, the soils and vegetation in these areas would be free of aqueous-borne contamination. Location 5 represents background areas at a distance of at least 3 km from the mill; these areas are assumed to be unaffected by mill operations. Waters from these background areas were collected from the Arkansas River, which supplies irrigation ditch water.

Water samples collected at Canon City, CO, were free of appreciable suspended solids and were preserved by acidification with concentrated HNO_3 to 1% by volume. Soils were oven-dried and ground in a Shatterbox pulverizer in preparation for analyses. Vegetation was also oven-dried and then ground in a Wiley mill in preparation for analysis. Oven-drying was utilized for these soils and vegetation because volatile species such as Se were not being determined in these samples.

Analytical Procedures. The analysis of major and trace constituents were performed as follows: (a) U by delayed neutron counting after thermal neutron irradiation for tailings, soils, vegetation, extracts, and waters (*9–11*); (b) V, Fe, and Mn by instrumental thermal neutron activation analysis for all matrices (*9*); (c) Mo, Se, As, Co, and Ni by instrumental epithermal neutron activation analysis for all matrices (*12*); (d) Cu and Pb by flameless atomic absorption spectrophotometry for all matrices; (e) SO_4^{2-}, Cl^-, and F^- by ion chromatography for waters; (f) ^{226}Ra by the ^{222}Rn deemanation technique for extracts; (g) ^{226}Ra by γ spectroscopy of ^{214}Bi and ^{214}Pb for encapsulated soils and tailings (*13*).

Results and Discussion

Uranium Ore of the Colorado Plateau. Sandstone uranium deposits of the Colorado Plateau (primarily the Morrison Formation) contain 50% of the uranium reserves in the United States and yield 59% of the annual U.S. yellowcake production (*14*). The composition of mineralized sandstone, mill pulp, barren sandstone, and surface soil from several uranium districts of the Colorado Plateau (*8*, *15*, *16*) are presented in Table I. These data illustrate enrichment in mineralized sandstone of a number of elements that may be geochemical analogues of uranium, i.e., V, Mo, Se, and As. Other base or heavy metals are somewhat enriched in mineralized sandstone; these Colorado Plateau ores contain elevated concentrations of Cu,

Table I. Trace Constituents in Geologic Materials from the Colorado Plateau[a]

element	mineralized sandstone[b]	mill pulp[c]	barren sandstone[c]	surface soil[d]	concn ratio of mill pulp/soil
U	3800-10400	2200	1-13	2.5	880
V	1500-16900	8500	18-578	34	250
Mo	100-400	60	0.5-26	0.9	67
Se	100-200	50	0.5	1.0	50
As	100-420	170	9-32	4.1	41
Cu	23-32	230	7-25	17	14
Co	36-59	19	5.5	6.7	2.8
Pb	52-170	190	1-4	37	5.1
Ni	23-35	16	16	9.4	1.7
S	5600-7300	1200	200-430		
^{226}Ra[e]	1270-3470	730	0.3-4.3	0.8	910

[a] Values in μg/g (pCi/g for ^{226}Ra). [b] Data represent range of mean values for Ambrosia Lake, NM, Uravan, CO, and Yellow Cat, UT, districts [from Squyres (*15*) and Cannon (*16*)]. [c] Average data reported by Cannon (*16*) from A. T. Miesch (written communication, 1961). [d] Mean of three soils from the Grants Mineral Belt, NM (*8*). [e] Calculated assuming secular equilibrium with U (surface soil activity based on measurements).

Table II. Elemental Composition of Tailings Fractions and Surface Soil[a]

sample	description	U	V	Mo	Se	As	Co	Ni	^{226}Ra
A	carbonate, sands, Ambrosia Lake, NM	60	360	14	46	18			290
B	carbonate, slimes, Ambrosia Lake, NM	180	960	66	33	29	4.4	4.5	610
C	carbonate, sands, Naturita, CO	280	1640	23	10	32			600
D	sulfuric acid, slimes, Mexican Hat, UT	100	330		2		21		
E	sulfuric acid, salts and sediments, Churchrock, NM	100	310	9	13	2			0.3
F	surface soil,[b] Grants Mineral Belt, NM	2.5	34	0.9	1.0	4.1	6.7	9.4	1.0
concn ratio (B/F)		72	28	73	33	7	0.7	0.5	610

[a] Values in μg/g air-dried tailings or soil or pCi/g for ^{226}Ra. [b] Mean concentration of three soils (*8*).

Co, Pb, and Ni, which are perhaps present with pyrite or as base metal sulfide minerals. Lead enrichement would also result from stable lead isotopes which are the final products of the ^{238}U and ^{235}U decay series. The enrichment of these accessory elements in ores has enabled byproduct recovery of V, Mo, Se, and Cu to be performed or considered for some ores (*7*, *17*).

The average composition of ore pulp from the Colorado Plateau (*16*) is generally less than the concentrations for mineralized sandstones, probably due to the mining of barren material along with mineralized sandstone. Elements including U, V, Mo, Se, and As are present in barren sandstone at very low concentrations compared with mineralized sandstone, whereas the difference in concentrations of the heavy metals (Cu, Co, and Ni) between the mineralized and barren sandstone is not as extreme. The concentration ratios comparing mill (ore) pulp with Grants Mineral Belt surface soils are reported in Table I. Again uranium and its analogue elements (V, Mo, Se, and As) are most enriched (concentration ratios >40) with heavy metals occuring at somewhat elevated concentrations.

Brookins et al. (*5*) describe mineral associations in a typical sandstone-type uranium ore from the San Juan Basin area of the Colorado Plateau as follows: U is present as coffinite or uraninite, Se as native selenium or ferroselite, Mo as jordisite, V as an oxyhydroxide or in clay minerals, and As in pyrite. The precipitation of mobile oxyanion forms of these elements occurs when Fe(III) and these oxidized species are reduced (*5*). Base metals are probably enriched in sulfides associated with the uranium ore but do not always occur in zones of uranium deposition (*5*).

The elevated concentrations of these accessory elements in reduced form in ores and adjacent sandstones indicate that exposure of these materials to oxidizing conditions during mining and milling may mobilize these elements. Unlike the slow reductive deposition of these elements in ore deposits, we might expect a rapid release of contaminants when exposed to oxidative aqueous leaching during mining and milling operations. In addition, aerated dumps of sub-ore-grade sandstones would be expected to release significant quantities of these species in a mobile form.

Composition of Uranium Mill Tailings. The fate of ore constituents in the milling process depends upon their solubility in the leaching solutions. The milling process primarily extracts uranium (at a few mills vanadium, also) and adds leaching reagents and oxidants. The tailings impoundments receive gangue material, spent leach solutions, and miscellaneous mill process waters. Tailings solids are presumed to be principally composed of sand (silica), clays (aluminosilicates), salts ($CaSO_4$, NaCl, etc.), and hydrous oxide coatings (Fe, Mn, Al, and Si). Soluble constituents in the tailings may precipitate, form salts upon loss of water via evaporation, seep into strata underlying the tailings pond, etc. The disposal of tailings as slurries provides for particle size fractionation as a result of differential sedimentation of sands and slimes (silts and clays). These physical and chemical processes (particle size separation, precipitation, and adsorption) give an initial heterogeneous distribution; they also provide means for the redistribution of ore constituents within the tailings pile. Thus, the overall elemental composition of the tailings corresponds closely to that of the ore (except for uranium and any other mineral values extracted); however, the distribution of the residual constituents within the pile may be quite different.

The elemental composition of a number of tailings and surface soil samples, as determined at Los Alamos by instrumental neutron activation analysis and atomic absorption spectrophotometry, are reported in Table II. The uranium analogue elements (V, Mo, Se, and As) are present in concentrations greatly exceeding surface soil content. Higher elemental concentrations are found in the slimes (sample B), the finer fraction, than in the sandy tailings

(sample A) from the carbonate leach mill in New Mexico. This enrichment in the finer fractions, which is widely acknowledged, may be related to the slimes containing (a) more surfaces for adsorption, (b) more finely divided precipitates, (c) most of the clays, and (d) more hydrous oxides of Fe and Mn for adsorbing trace elements than the coarse silica sand. Sample E in Table II represents salts that accumulated on surface sediments that were infiltrated by tailings liquids accidentally released from an acid tailings pond. The amount of solid tailings in these liquids is presumed to be very small; therefore, these liquids should represent the soluble constituents in the tailings pond solution. These salts contained high concentrations of trace elements (U, V, Mo, and Se) and major constituents (Fe, 4.4%; Mn, 0.6%). About 50% of the iron is presumed present as Fe(II) (see next section). Reduction of Fe is coupled with the oxidation of U(IV) to U(VI) during leaching in the mill circuit (*7*). Thus, milling processes can cause a redistribution of major and minor ore constituents such as Fe and Mn in the tailings.

The tailings whose analyses are presented in Table II represent a spectrum of mill processes, carbonate or sulfuric acid leach, and a range of ore types. The Ambrosia Lake and Churchrock mills in New Mexico processed ores from the Westwater Canyon member of the Morrison Formation (*15*); the Naturita, CO, mill processed ores from the Salt Wash member of the Morrison Formation; the ore input for the Mexican Hat, UT, mill was from the Shinarump member of the Chinle Formation in the White Canyon area, San Juan County, UT (*18, 19*). Thus, the wide variability in trace element composition of tailings is undoubtedly related to differences in ores and to some degree the type of milling process.

Aqueous Mobility of Tailings Contaminants. The concentration of trace elements in aqueous extracts of the tailings samples (see Table II) are reported in Table III along with the percentage of the constituent in the solid extractable by water. Mean extract concentrations for these elements are also presented for three local soils as sample F in Table III.

The alkaline leachates from carbonate sands and slimes from Ambrosia Lake (A and B, Table III) show appreciable mobility of Mo, Se, As, and U with more than 10% of the total content of these elements extractable from the slimes. The dissolution of these elements is most probably a result of the mobility of oxyanions or anion complexes of these elements in alkaline aqueous leachates. The concentrations of U, Mo, Se, and As in the slimes extract (B) greatly exceed that present in soil extracts (F); see concentration ratio (CR) II. Not only are these elements present in highly enriched concentrations in these tailings but they are also more extractable on a relative or percentage basis than from the soils. Nickel also appears to be more leachable from tailings (B) than from the soils (7.3% vs. 0.6%) even though Ni is depleted in these tailings vs. the soils. These differences in mobility between tailings and soil may be due to either different forms of the elements being present in these materials or the influence of major ions on the complexation of these elements in the leachates.

The tailings from the Naturita carbonate leach mill display a contrasting behavior to that of the Ambrosia Lake tailings. In general, trace elements in these tailings (denoted C in Table III) show little mobility on a percentage basis. However, the leachate concentrations are quite elevated compared with soil extracts, particularly for U and V. The low mobility of these elements may result from salt roasting these ores for vanadium recovery before

Table III. Trace Element Composition of Water Extracts and Percentage Extractable[a]

sample	description of material leached	pH of leachate	U	V	Mo	Se	As	Co	Ni	^{226}Ra
A	carbonate, sands, Ambrosia Lake, NM	7.8	2080 (17%)	290 (0.4%)	810 (29%)	640 (5.6%)	100 (2.8%)	18	74	125 (0.2%)
B	carbonate, slimes,[b] Ambrosia Lake, NM	9.5	3600 (10%)	3800 (2.0%)	5800 (44%)	2500 (30%)	1050 (18%)	37 (4.2%)	66 (7.3%)	8100 (6.6%)
C	carbonate, sands, Naturita, CO	8.1	1200 (2.1%)	6200 (1.9%)	410 (8.9%)	120 (6.0%)	190 (3.0%)	50	4	
D	sulfuric acid, slimes, Mexican Hat, UT	4.3	90 (0.5%)	30 (0.5%)	230	22	52	830 (20%)	1200	48 (0.3%)
E	sulfuric acid, salts and sediments, Churchrock, NM	2.7	8900 (45%)	47000 (76%)	1800 (100%)	2300 (88%)	100 (25%)			
F	surface soil,[c] Grants Mineral Belt, NM	8.4	12 (3.8%)	97 (2.0%)	180 (100%)	23 (9.6%)	38 (5.8%)	50	12 (0.6%)	
CRI	concn ratio[d]		300	64	32	110	28	17	100	
CRII	concn ratio[e]		300	39	32	110	28	0.7	5	

[a] Values in μg/L (pCi/L for ^{226}Ra); percentage extractable in parentheses. [b] Mean for two extractions. [c] Mean for three soils. [d] Maximum concentration of leachates A–D divided by mean soil extract concentration of F. [e] Concentration of leachate B/ concentration of leachate F.

Table IV. Mean Contaminant Concentration in the Above-Ground Portion of a Grass and a Shrub Grown in Soil-Covered Tailings and in Soil Controls[a,b]

	concn in grass (*Sporobolus airoides*)			concn in shrub (*Atriplex canescens*)		
element	soil-covered tailings	soil control	concn[c] ratio	soil-covered tailings	soil control	concn[c] ratio
Se	51	2.4	21[d]	57	1.8	32[d]
Mo	133	9.0	15[d]	200	8.0	25[d]
U	0.16	0.07	2[d]	1.8	0.04	45[d]
^{226}Ra	12	2.4	5	30	1.9	16
As	0.13	0.04	3	0.43	0.10	4
Ni	30	5.6	5	4.7	5.1	0.9
Co	0.55	0.30	2	0.40	0.49	0.8
Pb	27	12	2	0.4	2.0	0.2
Cu	33	35	1	16	17	0.9
V	0.34	0.76	0.5	0.70	1.06	0.7
Cu/Mo ratio	0.25	3.9		0.08	2.1	

[a] Concentrations in μg/g air-dried weight, except ^{226}Ra is given in pCi/g. [b] Data summarized from ref 8. [c] Concentration ratio = concentration of plant (tailings)/concentration of plant (control). [d] Means significantly different at $P = 0.05$ (Student's t test on means with unequal variances).

carbonate leaching at the mill (7). Calcium uranates and vanadates can form during salt roasting; these compounds are insoluble in water (7). Formation of insoluble forms of the other elements may also occur during the roasting process.

The water extracts of Mexican Hat tailings contain low concentrations of the measured elements except for Co and Ni. Since these ores contained appreciable Cu mineral content (chalcopyrite or covellite) and iron sulfides (pyrite) (*18*, *19*), it is reasonable to assume enriched levels of accessory elements such as Co and Ni in these sulfide minerals. The acidic and oxidizing conditions during U extraction in the mill would very likely change these minerals to more soluble forms. Thus, the mobility of Co and Ni is consistent with the presumed alteration of these minerals during milling.

The salt encrustation on sediments resulting from the evaporation of acid tailings solutions at Churchrock (sample E) are very soluble in water solutions as shown in Table III. In addition to the elements listed, Fe (5200 mg/L), Mn (1200 mg/L),$^{2-}$ SO_4 (90000 mg/L), Cl^- (400 mg/L), and F^- (280 mg/L) were present in large concentrations in the water extract of these salt-encrusted sediments. About 60% of the Fe was soluble, and most (80%) was present as Fe(II). Such movement and accumulation of salts illustrates one mechanism by which contaminants can be redistributed in tailings impoundments (*20*).

Vanadium does not appear to be very water soluble in the various tailings that have been examined. At the most basic pH (9.5), As, ^{226}Ra, and Se appear fairly mobile. Cobalt and possibly nickel appear to be most soluble in acidic solutions as expected. Thus, pH controls mobility to a large degree.

The results of these extractions indicate that a number of tailings constituents are mobile under aqueous leaching conditions. The mobility of some contaminants in tailings can be much greater than in soils on a relative basis and the leachate concentrations can be much greater (>100×). The ore and the milling process influence mobility as a result of the acidity of the residual material, the mineral form of the contaminants in the tailings, and the major ions present in leachates.

Uptake of Contaminants by Native Plants. The enriched levels of contaminants such as U, V, Mo, Se, and As in uranium mill tailings and their mobility in aqueous systems would cause concern if these contaminants enter biota. Of particular concern is the bioavailability of these elements through root absorption by plants growing in tailings or in soils contaminated with tailings (solid residues or aqueous effluents). A greenhouse experiment was carried out with a native grass (*Sporobolus airoides*) and shrub (*Atriplex canescens*) grown in soil-covered tailings or in soil alone to determine the uptake of these contaminants. (Details can be found in ref 8). The mean concentrations in above-ground plant materials are reported in Table IV for the grass and shrub grown in the three soils; these soils have been previously discussed in Tables I, II (F), and III (F). The concentrations of these elements in plants grown in soil-covered tailings (B, Ambrosia Lake slimes) are presented in Table IV along with concentration ratios.

When concentrations for the control and tailings treatments in Table IV are compared, Mo and Se are found to be assimilated readily from the tailings by both the grass and shrub. In addition, the concentrations of these elements exceed levels reported to be toxic to grazing animals. The lower threshold in forage for chronic selenium poisoning is reported to be about 5 μg/g (*21*); the threshold for molybdenosis (molybdenum toxicity) is 5–20 μg/g (*22*). A ratio of copper to molybdenum of less than 2 also indicates potential molybdenum toxicity (*22*). The grass and shrub grown in tailings both had Cu/Mo ratios much less than 2 (i.e., grass 0.25 and shrub 0.08). Other elements somewhat elevated in the grass grown in tailings were U, ^{226}Ra, As, Ni, Co, and Pb. The above-ground portion of the shrub grown in tailings was highly enriched in U and ^{226}Ra and somewhat enriched in As.

The tailings extract (sample B in Table III) concentrations for U, V, Mo, Se and As are at least 25 times the soil extract concentrations. In contrast, the mean plant concentrations grown in tailings are 15 times greater than those grown in soils for only three elements: U (shrub), Mo, and Se. Thus, the extract concentration of an element does not necessarily correspond to the quantity of that element present in the above-ground portion of the plant.

Table V presents assimilation factors comparing above-ground plant concentrations with either soil (A_{SE}) or tailings (A_{TE}) extracts or total soil (A_S) or total tailings (A_T) content. The A_{SE} factors range from 1.1 to 467, whereas the A_{TE} factors range from 0.044 to 455. Relatively small A_{SE} and A_{TE} factors (A_{SE} <10 and A_{TE} <1) for V, U, and As indicate that absorption and/or translocation of these elements in solution are limited by either chemically or biologically mediated processes in the root system. The elements Ni, Se, and Mo are much more readily assimilated from solution, as indicated by A_{SE} and A_{TE}

Table V. Assimilation of Trace Elements by the Grass and Shrub Relative to Water Extractable and Total Content

element	assimilation relative to water extracts of solids						assimilation relative to total content of solids					
	A_{SE}[a]		A_{TE}[a]		A_{SE}/A_{TE}		A_S[a]		A_T[a]		A_S/A_T	
	grass	shrub	grass	shrub	grass	shrub	grass	shrub	grass	shrub	grass	shrub
U	5.8	3.3	0.044	0.50	130	6.6	0.028	0.016	0.00089	0.010	31	1.6
V	7.8	10.9	0.089	0.18	88	61	0.022	0.031	0.00035	0.00073	63	42
As	1.1	2.6	0.12	0.41	9.2	6.3	0.0098	0.024	0.0045	0.015	2.2	1.6
Se	104	78	20	23	5.2	3.4	2.4	1.8	1.5	1.7	1.6	1.1
Ni	467	425	455	71	1.0	6.0	0.060	0.054	6.7	1.0	0.0090	0.054
Mo	50	44	23	34	2.2	1.3	10.0	8.9	2.0	3.0	5.0	3.0
Co	6.0	9.8	15	10.8	0.40	0.91	0.045	0.073	0.125	0.091	0.36	0.80

[a] A_{SE} (assimilation relative to soil extract) = concentration in plant grown in soil/concentration in soil extract ((μg/g)/(μg/mL)). A_{TE} (assimilation relative to tailings extract) = concentration in plant grown in tailings/concentration in tailings extract ((μg/g)/(μg/mL)). A_S (assimilation relative to soil) = concentration in plant grown in soil/concentration in soil ((μg/g)/(μg/g)). A_T (assimilation relative to tailings) = concentration in plant grown in tailings/concentration in tailings ((μg/g)/(μg/g)). Tailings = Ambrosia Lake slimes (sample B); soil = mean concentration for three Grants Mineral Belt Surface soil or soil extracts.

factors greater than 10. Ratios of assimilation factors (A_{SE}/A_{TE}) greater than 1 indicate greater relative absorption and translocation of elements derived from soil extracts than those derived from the tailings extract (e.g., V, As, U, and Se). Elements with ratios less than 1 (e.g., Co) exhibit greater assimilation from the tailings extract than from the soil extracts.

High A_S and A_T factors (>1) indicate high assimilation from soils and tailings and accumulation in plants of Mo, Se, and Ni (tailings only); in comparison, U, V, As, and Co exhibit low factors (<0.1). Large A_S/A_T ratios indicate greater relative uptake of U and V (ratios >30) and Mo, As, and Se ratios 1–5) from soils than from tailings. Ratios less than 1 show preferential uptake from tailings (e.g., Ni and Co).

Greater uptake of Ni from both the tailings and the tailings extract was found for the grass compared with the shrub; however, the assimilation results for the shrub compared with the grass shows preferential uptake of U from the tailings and its extract. As appears to be more readily assimilated by the shrub than by the grass for soils, tailings, and extracts.

Three criteria interdependently control the hazard posed by these tailings contaminants: (a) the contaminant level in the tailings, (b) its aqueous mobility, and (c) its assimilation by biota. With the particular tailings discussed in this section, As is not present in highly elevated concentrations in plants grown in tailings because of its low enrichment in tailings and low assimilation by plants even though it is fairly mobile. In contrast, even though V is highly enriched in tailings and fairly mobile, it is not assimilated. Molybdenum and selenium differ substantially from the other elements because they are highly enriched in tailings, easily extractable by water, and readily assimilated by plants.

This uptake experiment illustrates the need for biotic assimilation information in addition to leaching data to assess environmental hazard. It also shows that Mo and Se released from these tailings (Ambrosia Lake slimes) pose a hazard to consumer organisms because of their appreciable uptake by plants.

Environmental Contamination near an Active Uranium Mill. The results of laboratory experiments described in the preceeding sections illustrate potential environmental hazards that could result from the release of mobile contaminants in uranium mill tailings. A field validation of these concerns involving an actual case of environmental contamination near a uranium mill is presented in this section. Surface and ground water, surface soils, and vegetation were sampled in the vicinity of the then-operating carbonate leach uranium mill at Canon City, CO. The location of these sampling sites is described in the Experimental Methods section. The results of U and Mo analysis of these samples are summarized in Table VI.

Waters from locations 1–3 have elevated concentrations of Mo and U compared with those from locations 4 and 5. These elevated levels are most likely related to the presence of these elements in tailings pond seepage as the carbonate anion complex of the uranyl ion and the molybdate or polymolybdate anion. The presence of high concentrations of Mo along with the U in the ore input to this mill along with the expected solubility of these elements in the alkaline, oxidizing, carbonate-rich mill solutions (7) would confirm the potential for contaminant seepage. The chemical fixation of these aqueous anionic species after release would not be expected to occur in these alkaline geologic strata; thus, they could be transported long distances (>1 km) in a time span of several decades if sufficiently permeable strata were present. Thus, seepage from the mill tailings ponds provides the most obvious source of contaminants for these ground waters.

The soils and plants in contact with tailings pond seepage (locations 1 and 2) contain very high concentrations of Mo and U as would be expected. Also, the application of contaminated ground water during irrigation, as at sites in location 3, also produced appreciable enrichment of Mo and U in soils. Vegetation growing in these soils have, as might be expected from the uptake studies above, somewhat elevated U but highly elevated Mo levels. However, at one particular site in location 3, U and Mo levels in the soil were not elevated above uncontaminated soils, yet the grass showed high levels of Mo (72 μg/g) and U (2.0 μg/g). Thus, even though there was no apparent sign of soil accumulation of these elements, the application of contaminated irrigation water still seems to have increased levels of these contaminants in vegetation.

The plants from location 3 all have Cu/Mo ratios less than 2, which would indicate that this forage could cause molybdenosis if substantial amounts were consumed by grazing animals. Cattle with symptoms of molybdenum toxicity have been reported at this location in the past (22). As a comparison, molybdenosis in cattle has been reported near an open-pit uranium mine in Texas where Mo concentrations were from 15 to 45 μg/g in grasses, from 2.7 to 8.0 μg/g in soils, and from 0.14 to 0.70 mg/L in waters (23). The levels of Mo in the environmental samples at location 3 in Canon City, CO, either are in the same range

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1-Alkenes as Potential Indicators of Sediment Shale Oil Contamination

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■ Hydrocarbon fractions isolated from four shale oils, two petroleum oils, and one solvent-refined coal liquid product were analyzed by capillary gas chromatography/mass spectrometry for the presence of a homologous series of 1-alkenes. Of the liquid oil products examined, only the shale oils contained the 1-alkenes. 1-Alkenes were not detected in the hydrocarbon fractions of extracts from a raw oil shale or surface sediments collected in a drainage at locations above, adjacent to, and below the Department of Energy Anvil Points Oil Shale Facility, Rifle, CO. However, 1-alkenes were detected in retorted shale, sediment aggregates formed after oil transport downstream of the facility, and oil discharging from a shale pile. The absence of 1-alkenes in petroleum and a coal liquid product suggests that this class of compounds may be unique to shale oils, perhaps allowing their use as diagnostic indicators of sediments in contact with shale oils or their refined products.

Introduction

In the past, the United States has relied extensively on domestic sources of petroleum to supply its energy needs. With domestic supplies limited and the assurance of uninterrupted supplies of foreign crude uncertain, the U.S. has embarked on a plan to reinitiate development of fuels from oil shale and coal.

During production of shale oil, both waste water and retorted shale would be produced. The environmental consequences of ground disposal of these materials are largely unknown (*1*, *2*). Recent studies have identified one group of organic compounds (alkylpyridines) that have potential as indicators of impact to surface and ground waters by shale oils and retort waters (*3*). The alkylpyridines were shown to be mobile through substrata and thus useful for ground-water studies. However, little information is available regarding other chemical species that might be unique to shale oils and aid in the assessment of shale oil spills at sites of development or during transport (*4*, *5*). The need for such analytical approaches was recently exemplified by a spill of solvent-refined coal liquid at a pilot plant at Ft. Lewis, WA (*6*).

The purpose of this study was to examine the distribution and possible use of a homologous series of 1-alkenes as additional, confirmative indicators of shale oil contamination at a site of oil shale development.

Experimental Section

1. Substrate Materials. Samples of raw shale, retorted shale, and shale oil were obtained from the Department of Energy Anvil Points Oil Shale Facility, Rifle, CO. Over the period 1976–1977, shale oil was being produced by Development Engineering, Inc., from oil shale mined at the site (mahogany zone, Green River Formation). The shale was retorted by using the Paraho process operating in the direct heating mode, i.e., retort gases recycled to the retort and combustion of a portion of the carbonaceous fraction provided the heat for the process.

Product shale oil was sampled from the separation tank in a Teflon-lined stainless steel keg. The headspace was purged with N_2 and cooled by packing the keg in an ice bath for shipment to the laboratory and storage at 4 °C. Oil samples used in this study for comparative purposes included three other shale oils, a solvent-refined coal-blended distillate, and Prudhoe Bay and South Louisiana crude oils. Sampling and storage of the synthetic fuels materials have been previously described (*7*, *8*). In addition, oil, discharging from the bottom of a retorted shale and shale fines pile located adjacent to the facility, was collected and stored at 4 °C in glass bottles.

A 24-h composite of raw feed shale yielding 24–26 gallon/ton was obtained from the raw shale sampler installed in the semiworks retort. The sampler system removed a periodic sample from the raw shale conveyor belt running from the crusher to the retort by a timer-controlled flip gate. The composites (20–25 kg) were crushed to <6 mm in the sampler and were further ground to pass a 140-mesh sieve in aluminum jar mills. The ground raw shale was blended in a polyethylene mixer and split by using a riffle splitter into 50-g aliquots.

Retorted shale was sampled from a conveyor belt during the same run. The samples were ground to pass a 100-mesh screen and stored in 50-g aliquots as described for the raw shale.

2. Sediment Sampling. Samples of wet surface sediment were collected from West Sharrard stream (Figure 1) at streambed locations −1829, −762, and −244 m above, and +335, +549, +823, +1097, and +1676 m below a well used to monitor ground-water quality. Sediments were

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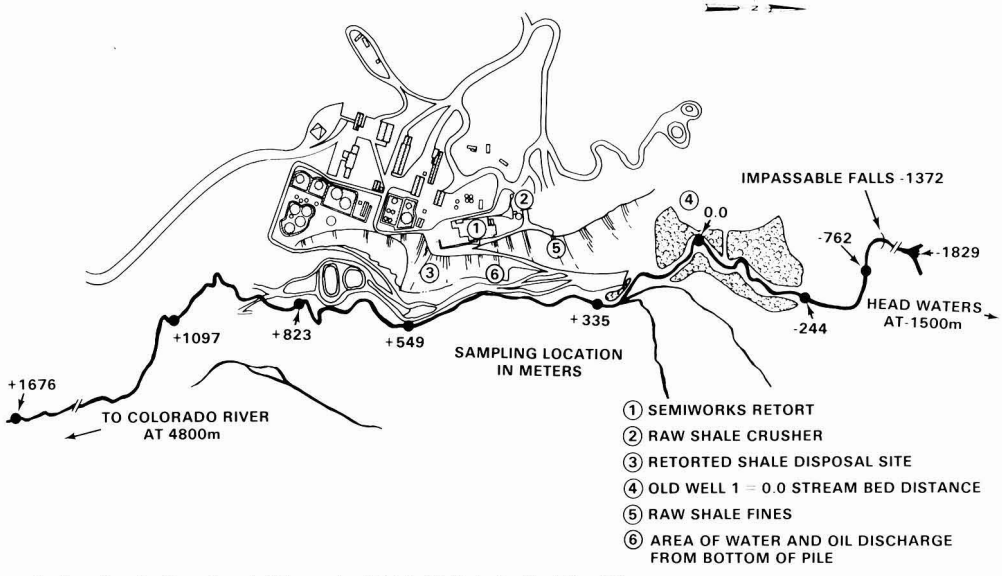

Figure 1. Sampling site (Department of Energy Anvil Points Oil Shale Facility, Rifle, CO).

placed in wide-mouth glass jars containing aluminum-foil-lined caps. Each sample of wet surface sediment represented an area approximately 200 cm^2 and a depth of 2.5 cm. In addition, dried sediment aggregates containing visual quantities of oil were collected at sampling location +1676 m after spring runoff water had receded. Separate aliquots of sediments were immediately Soxhlet extracted in the field laboratory and also immediately frozen (−20 °C) without extraction for transport to the Richland laboratory.

3. Sediment Extraction. Samples of raw shale, retorted shale, and sediment (50–100 g wet weight) were Soxhlet extracted with benzene/methanol, and the extract was prepared for column chromatography (*9*). The concentrated solvent extracts containing the saturate and olefinic hydrocarbons were separated from more polar components by elution of an extract-containing silica gel column (Grace Davision, 100–200 mesh, 15 g) with 40 mL of hexane. The eluted nonpolar fractions were concentrated under a stream of nitrogen in preparation for analysis by capillary gas chromatography (GC) and capillary gas chromatography/mass spectrometry (GC/MS) (*10*). All solvents used for sample preparation and analysis were Burdick and Jackson "distilled in glass".

4. Oil Fractionation. Samples of the individual oils (~10 mg) were dissolved in 1 mL of hexane and subjected to silica gel chromatography and analysis employing the methods described for sediment extracts.

5. Capillary Gas Chromatography. Samples containing the nonpolar hydrocarbons isolated from raw shale, retorted shale, sediment, or oil were quantified on a Hewlett-Packard 5840A gas chromatograph. Individual hydrocarbon components were separated on a 50-m quartz capillary column (J & W Scientific) employing a split ratio of approximately 10:1 and a flow rate of 1.5 mL/min helium through the column. Column conditions were initially at 65 °C with a 4-min hold followed by temperature programming at 4 °C/min to 250 °C with a 15–45 min hold at 250 °C prior to recycling. Individual *n*-alkanes were quantified by using known standards (Analabs) with 2,6,10-trimethyldodecane serving as the internal standard. Concentrations of 1-alkenes in Paraho oil were calculated based on the 1-alkene/*n*-alkane ratios, the concentration of the corresponding *n*-alkane, and the assumption that the detector response for 1-alkenes was comparable to the *n*-alkane counterpart. Individual concentrations of hydrocarbons reported in this study have been corrected for losses based on recovery experiments. Recovery of *n*-alkanes ranged from 81% to 100%.

6. Capillary Gas Chromatography/Mass Spectrometry. Prior to GC/MS analysis sample extracts were solvent exchanged into heptane. The heptane concentrates were analyzed on a Hewlett-Packard 5985 GC/MS operating in the electron-impact mode and equipped with 7900A and 7920 disc drives. A 50-m SP-2100 quartz capillary column with the gas chromatograph operating in the splitless mode was used to resolve the individual hydrocarbons in the complex mixture. Column conditions were initially at 60 °C with a 4-min hold followed by temperature programming at 4 °C to 250 °C. Three fragmentation ions characteristic of the homologous series of 1-alkenes (m/e 70, $C_5H_{10}^+$; 83, $C_6H_{11}^+$; 97, $C_7H_{13}^+$) (*11*) were monitored in the single-ion mode in hydrocarbon fractions isolated from raw shale, sediments, and oils of interest.

Results and Discussion

Oil derived from the pyrolysis of oil shale from the Green River Formation has been shown to contain 1-alkenes (*12*), whereas petroleum crude oils normally do not contain olefins (*13*). The few exceptions have been Pennsylvania crude petroleum in which the double bonds of hydrocarbons have been shown to be internal (*14*, *15*). Thus, a homologous series of 1-alkenes offered potential as a possible indicator for sediment shale oil contamination. For evaluation of this possibility, oil shale process materials derived from operation of the Department of Energy Anvil Points Oil Shale Facility and sediments from the adjacent West Sharrard Drainage were examined. The facility has been used for a number of oil shale studies over its 40-year history. Hydrocarbon sources would include terrestrial spillage or leaching from retorted shales followed by

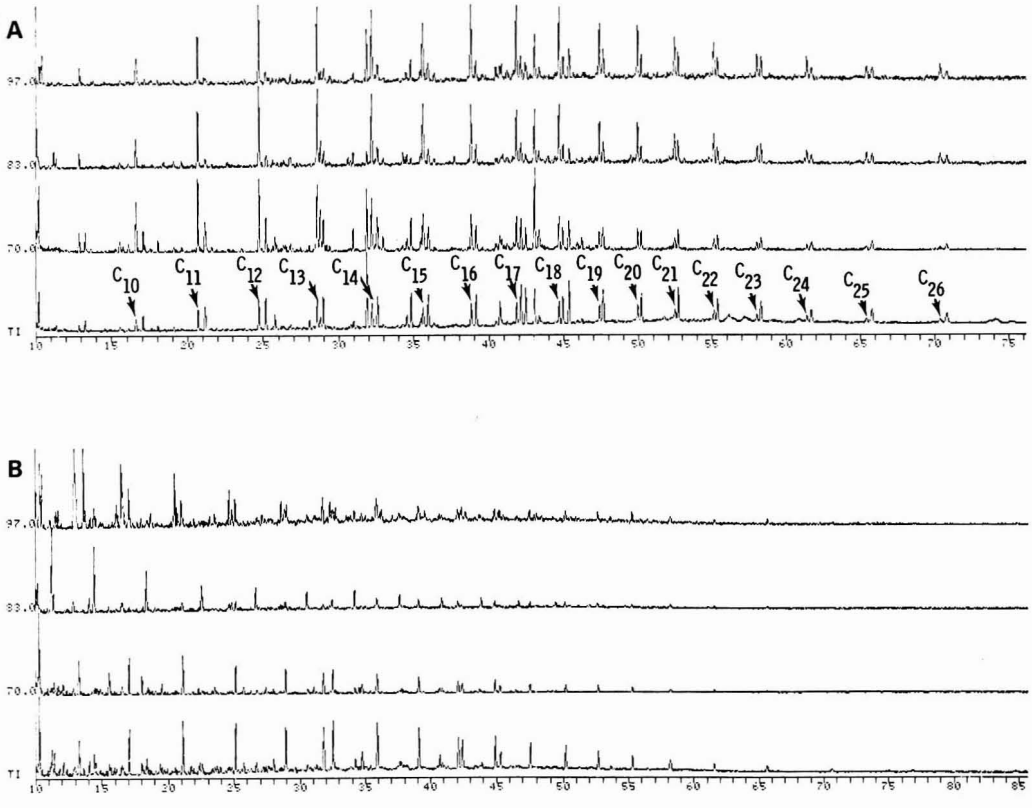

Figure 2. Total ion mass chromatogram of nonpolar hydrocarbon fractions isolated from (A) Paraho shale oil and (B) Prudhoe Bay crude oil. Labeled peaks correspond to homologous series of 1-alkenes. Homologous series of components to the immediate right of the 1-alkenes are the *n*-alkanes. Note intensity of fragment ions (*m/e* 70, 83, 97) for 1-alkene relative to *n*-alkane components.

transport through ground waters to the stream, as well as direct liquid spills. Due to periodic sediment scouring, hydrocarbons present in the sediments would likely have entered the drainage within 1 year. However, since the presence of hydrocarbons in the drainage would depend upon the initial source as well as possible undefined sorption and degradation processes controlling movement through substrata, the exact origin of hydrocarbons in the facility cannot be defined.

A good indicator of shale oil contamination must also be distinguishable from natural hydrocarbon sources in the region. Therefore, raw shale and natural sediments were also analyzed for 1-alkenes. This was of particular importance in the oil shale region since the sediment organic fraction is primarily derived from kerogen associated with the Green River oil shales. Native plant litter subject to degradation and secondary synthesis in local alluvial soils and sediments is more important than aquatic sources of organic matter in the West Sharrard Drainage because of the minimal development of an aquatic food web. Retorted shale was examined because of the possible contribution of leachates from the retorted shale disposal site located adjacent to the drainage (Figure 1).

Three fragment ions characteristic in the mass spectra of the homologous series of 1-alkenes were monitored in organic extracts of raw shale, retorted shale, and sediment (*11*). The fragment ions were *m/e* 70 ($C_5H_{10}^+$), 83 ($C_6H_{11}^+$), and 97 ($C_7H_{13}^+$). These fragment ions were found to be more intense in the 1-alkene series relative to the corresponding *n*-alkane series. In general, their intensity increased with the molecular weight of the fragment ion (i.e., *m/e* 97 > 83 > 70). The presence of 1-alkenes was also confirmed by congruency of GC retention times and comparison to published mass spectra (*11*). Confirmation of the presence of 1-alkenes in Paraho shale oil and their absence in Prudhoe Bay crude petroleum is illustrated in Figure 2. Of the four shale oils, two petroleums, and a coal liquid product examined, only the shale oils contained the 1-alkenes (Table I).

Table I. 1-Alkenes in Various Oils

oil type	presence (+) or absence (−) of 1-alkenes
shale oil A (surface retorting)	+[a,b]
shale oil B (surface retorting)	+[a]
shale oil C (modified in situ)	+[a,b]
shale oil D (modified in situ)	+[a]
Prudhoe Bay crude	−[a,b]
South Louisiana crude	−[a,b]
coal liquid product	−[a,b]

[a] GC analysis only. [b] GC and GC/MS analysis performed.

Sediments adjacent to the oil shale facility were examined by using the same techniques. The location of the sediment-sampling sites in West Sharrard Drainage are shown in Figure 1. The stream and drainage basin char-

Table II. 1-Alkenes in Process Materials and Sediments

sample type	presence (+) or absence (−) of 1-alkenes
raw shale	−[a,b]
retorted shale	+, trace[a]
sediment (−1829 m)	−[a,b]
sediment (−762 m)	−[a]
sediment (−244 m)	−[a]
sediment (+335 m)	−[a,b]
sediment (+549 m)	−[a]
sediment (+823 m)	−[a]
sediment (+1097 m)	−[a]
sediment (+1676 m)	−[a]
oil sediment aggregates (+1676 m)	+[a,b]
shale oil (oil shale pile)	+[a]

[a] GC analysis only. [b] GC and GC/MS analyses performed.

Table III. 1-Alkene/*n*-Alkane Ratios in Shale Oil Materials

carbon no.	shale oil	oil sediment aggregate	oil from pile
10	0.86	0.29	0.21
11	0.90	0.30	0.17
12	0.88	0.30	0.27
13	0.80	0.26	0.16
14	0.68	0.17	0.17
15	0.61	0.11	0.11
16	0.73	0.10	0.07
17	0.56	0.08	0.08
18	0.72	0.12	0.09
19	0.48	0.08	0.06
20	0.61	0.17	0.10
21	0.43	0.10	*a*
22	0.51	0.13	<0.01
23	0.36	0.07	<0.01
24	0.38	0.10	<0.01
25	0.24	0.15	<0.01
26	0.34	*a*	<0.02
27	0.21	0.25	<0.02
28	0.34	0.03	<0.03

[a] Not calculated due to peak interference.

Table IV. Concentrations of Total Selected *n*-Alkanes in Sediment and Raw Shale[a]

sample type	total selected *n*-alkane concentrations[b]
sediment (−1829 m)	3.0
sediment (−762 m)	0.7
sediment (−244 m)	1.0
sediment (+335 m)	13.4
sediment (+549 m)	2.2
sediment (+823 m)	0.8
sediment (+1097 m)	2.6
sediment (+1676 m)	12.7
raw shale	234

[a] Concentrations in μg/g dry weight. [b] C_{13}–C_{24}, pristane + phytane.

acteristics have been described (*16*). Sediments from bed distances located above the facility (−1829, −762, and −244 m) are not impacted by man's activities and served as indicators of possible natural levels of 1-alkenes. Sediments from bed distances located adjacent to or downstream of the shale pile and oil shale facility (+335, +549, +823, +1097, and +1676 m) have the potential for reflecting the effects of shale oil operations. These sediments were analyzed for the 1-alkenes and the results compared to (1) raw shale, (2) retorted shale, and (3) sediment aggregates containing visual quantities of oil collected downstream of the pile and most likely transported during high stream-discharge conditions 4 weeks prior to sampling.

Only retorted shale, oil sediment aggregate, and oil from the pile contained detectable levels of 1-alkenes (Table II). Trace amounts of 1-alkenes were present in the retorted shale, indicative of trace levels of residual oil adhering to the retorted shale following combustion of the raw shale. Oil from the sediment aggregates appeared weathered, as indicated by significant reductions in the more volatile components ($<C_{12}$) in the hydrocarbon fraction (not shown). Transport of these aggregates downstream probably dated from a May spring flood 30 days before. Thus, relatively rapid loss of these components may be expected, and compounds of carbon number >12 would serve as better indicators of the presence of oil over the longer term. In addition, 1-alkene/*n*-alkane ratios were lower in the oil isolated from sediment aggregates but similar to ratios determined in oil discharging from the shale pile as a result of shale combustion that occurred spontaneously 6 months previously (Table III). This difference arises from a lower and less consistent combustion temperature in the pile relative to that used in the Paraho process. 1-Alkene/*n*-alkane ratios in shale oil have been shown to vary considerably with the temperature of the retorting process and have been used as a measure of product yield (*12*). The concentrations of total selected *n*-alkanes in sediments collected from West Sharrard stream ranged from 0.7 μg/g at −762 m to 13.4 μg/g at +335 m. Concentrations of total selected *n*-alkanes from raw shale were 234 μg/g or factors of 20–400 more concentrated than West Sharrard stream sediments (Table IV). Except for two locations, *n*-alkane concentrations downstream were not significantly elevated relative to upstream locations. Sites at which concentrations were elevated were adjacent to or directly below the retorted shale pile. Estimated concentrations of 1-alkenes in Paraho shale oil in the C_{13}–C_{24} region ranged from 2 to 7 mg/g oil. On the basis of a 1-alkene with 24 carbons, the method could detect ~2 μg/g of Paraho shale oil in sediment.

Conclusions

Trace quantities of *n*-alkanes were detected in extracts from sediments in the stream sampled hydrologically above, adjacent to, and below shale extraction operations and shale pile at the Department of Energy Anvil Points Oil Shale Facility, Rifle, CO. Concentrations of selected *n*-alkanes in the stream sediments were markedly lower than primary sources at this site, i.e., native raw shales, retorted shales and shale oil (resulting from spillage or spontaneous combustion of the raw shale pile). Concentrations of *n*-alkanes were in the range of concentrations found in sediments typical of unpolluted near-shore marine and fresh-water environments (*10*, *17*) and considerably less than what has been observed for sediments from water bodies containing various anthropogenic hydrocarbon input (*18*, *19*) or that have been impacted as a result of a petroleum spill (*19–21*). Concentrations were elevated at several points adjacent to, or downstream of, the facility compared to upstream locations (Figure 1), likely reflecting raw shale (location +335 m) or process sources (location +1676 m).

Raw shale did not contain the 1-alkenes which were detected in retorted shale, Paraho shale oil, and sediment aggregates transported downstream. Thus, the 1-alkenes appeared to be formed during the retorting process and may serve as a relatively simple analytical tool for con-

firmation of the presence in stream sediments of residuals from shale oil alone or shale oil sorbed on retorted shale.

Due to the scouring of the stream during spring runoff, the period of impact on the stream sediments in the present study would be less than 1 year, except for areas of local sediment deposition or for materials of sufficient adhesiveness or density to retard hydrologic transport. This effect was exemplified by the detection of oil in sediment aggregates transported downstream of the pile during a recent flood and deposited as a material similar to pelagic tar (*22*). The 1-alkene/*n*-alkane ratios associated with oil from sediment aggregates and the pile were lower than those observed for Paraho shale oil, which suggests that the pile was the source of oil in this aggregate rather than other sources such as oil storage facilities. However, selective weathering of the 1-alkenes due to photochemical and microbiological processes cannot be ruled out as contributors to the observed ratios.

The absence of 1-alkenes in raw oil shale, petroleum, and a coal liquid product suggests that this class of compounds may be unique to shale oils, perhaps allowing their use as diagnostic indicators of sediments that have been in contact with shale oils or their refined products at sites of oil shale development or during transport of the crude or refined oils. However, further research is required to examine shale oils from other processes and the variability in the organic chemical composition of sediments as a function of geologic source and geographical location. This is exemplified by the presence of 1-alkenes in extracts of a bituminous coal (*23*) and in vegetation (*24*) that may have served as substrate material for the formation of coal (*25*).

Acknowledgments

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Determination of Polar Organic Solutes in Oil-Shale Retort Water

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■ A variety of analytical methods were used to quantitatively determine polar organic solutes in process retort water and a gas-condensate retort water produced in a modified in situ oil-shale retort. Specific compounds accounting for 50% of the dissolved organic carbon were identified in both retort waters. In the process water, 42% of the dissolved organic carbon consisted of a homologous series of fatty acids from C_2 to C_{10}. Dissolved organic carbon percentages for other identified compound classes were as follows: aliphatic dicarboxylic acids, 1.4%; phenols, 2.2%; hydroxypyridines, 1.1%; aliphatic amides, 1.2%. In the gas-condensate retort water, aromatic amines were most abundant at 19.3% of the dissolved organic carbon, followed by phenols (17.8%), nitriles (4.3%), aliphatic alcohols (3.5%), aliphatic ketones (2.4%), and lactones (1.3%). Steam-volatile organic solutes were enriched in the gas-condensate retort water, whereas nonvolatile acids and polyfunctional neutral compounds were predominant organic constituents of the process retort water.

Introduction

Oil-shale retort waste waters are coproduced with shale oil during retorting. The quantity and nature of retort water is dependent on the retorting process (*1*); in situ processes produced approximately equivalent quantities of retort water and shale oil, whereas above-ground retorting processes produce much less retort water.

Much research has been focused on the chemistry of oil-shale retort water because these waters must be treated for (1) ammonia and sulfur recovery, (2) boiler-feed water, (3) moistening of spent shale, and (4) disposal. Inorganic chemistry of an in situ produced retort water was extensively defined by Fox (*2*), and organic constituents also were determined for other retort waters (*3–5*). Ho et al. (*3*) found normal carboxylic acids are the principal components of retort water by using direct aqueous injection gas chromatography. Pellizzari et al. (*4*) and Raphaelian and Harrison (6) used solvent extraction followed by gas chromatography–mass spectrometry to identify a variety of organic compounds in retort water, but their reported concentrations were 1–3 orders of magnitude less than concentrations for same compounds reported by Ho et al. (*3*). Riley et al. (*5*) derivatized freeze-dried residue of a retort water with boron trifluoride–methanol to improve solvent solubilization of polar constituents, extracted with benzene, and determined both aliphatic monocarboxylic and dicarboxylic acids by gas chromatography–mass spectrometry. Although these four studies (*3–6*) were not intended to provide a comprehensive quantitative survey of organic solutes in retort water, they did indicate that a quantitative survey would be limited by: (1) minimal solvent-extraction efficiencies of polar organic solutes; (2) variety and large number of organic solutes requiring multiple analytical methods; (3) difficulty acquiring standards of more complex solutes for confirmation .

The primary objective of this study was to provide a quantitative survey of relatively simple, low molecular weight organic solutes in two retort waters. The solvent-extraction limitation was circumvented by using isolation procedures such as resin adsorption and steam distillation that were designed for polar organic solutes. A multimethod analytical approach was used to identify and measure as many compound types as possible; only those compounds confirmed by readily available standards were reported. A quantitative goal was to identify one-half of the dissolved organic carbon in two retort waters selected for study.

A secondary objective was to compare organic-solute composition of a process retort water, produced as an emulsion with shale oil, with organic-solute composition of a gas-condensate retort water, condensed from off-gases from an in situ oil-shale retort.

The two retort waters selected for study were produced from January to May, 1979, in the modified in situ retort 6 at the Occidental Oil Shale, Inc., facility at Logan Wash, CO. The water samples were analyzed for this study from November 1980 to June 1981. The history of these retort waters' collection, preservation, and storage is available from the Laramie Energy Technology Center (*7*). An extensive environmental research program is being conducted at retort 6, and a progress report describing the various studies is available from the Oil Shale Task Force (*8*).

Analytical Methods

A mass spectrometer used to confirm the various organic determinations was not available for this study. Therefore, the following criteria were used for identification and quantification of the various organic constituents in retort water:

1. Chemical and physical characteristics of organic solutes precessed through the following separation procedures: (a) fractionation of retort water organic solutes into more homogeneous compound groups by the dissolved organic carbon fractionation procedure (*9*) prior to specific compound analyses. This fractionation served as a sample cleanup procedure, limited the complexity and number of compounds in each fraction, permitted tailoring of the analytical procedure to the type of compounds found in each fraction, and gave a quantitative materials balance based on organic carbon; (b) gas chromatography; (c) liquid chromatography; (d) Separations based upon steam volatility.
2. Matching of retention times of an unknown with standards on two different column packings for both gas and liquid chromatographic procedures.
3. Specific derivatization procedures coupled with standard confirmation for gas and liquid chromatographic procedures and colorimetric analyses.
4. Comparison of the ultraviolet–visible spectra of an unknown with a standard spectra for liquid chromatography. This confirmatory test is more rigorous than absorbance ratioing commonly used for liquid chromatographic identification.
5. Quantitation agreement between multiple determinations and (or) methodologies to within an average deviation of 20% of the mean value for each constituent. Except for certain specific colorimetric analyses, each compound reported had to meet the quantitation agreement plus two or more of the previously listed criteria to be considered identified and quantified.

Although this analytical approach is much slower and more labor intensive than a mass spectrometric confirmatory procedure, it provides an equivalent degree of

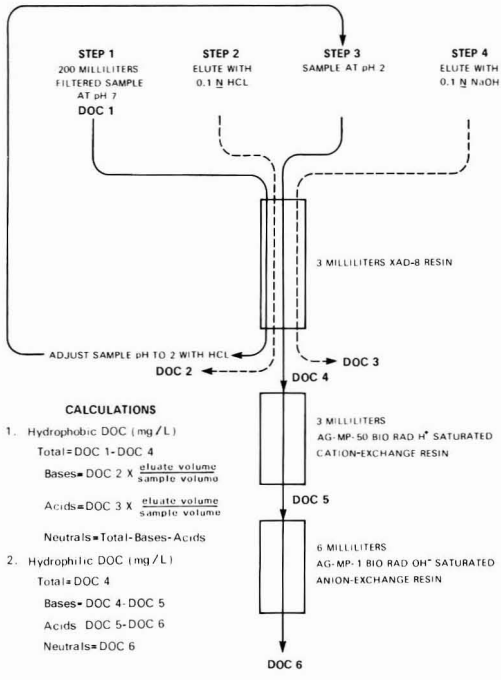

Figure 1. Analytical flow chart for dissolved organic carbon (DOC) fractionation.

confirmatory evidence through the multiple identification criteria and can determine those compounds not readily amenable to mass spectrometric analyses.

All gas chromatography reported in this study used flame ionization for detection; the liquid chromatograph had a scanning ultraviolet–visible on-line detector.

Dissolved Organic Carbon Fractionation. Dissolved organic carbon (DOC) fractionations were performed by Huffman Laboratories, Inc., Wheat Ridge, CO, according to the standardized procedure (*10*) shown in Figure 1. Parts of the DOC fractionation procedure also were used to isolate compound classes from retort water, and the theory and procedures of preparative DOC fractionation are given in a recent report (*9*).

Aromatic Amines. Aromatic amines were the predominant compound class found in the hydrophobic base fraction of DOC fractionation. They were isolated from retort water as follows. Purified Amberlite XAD-8 resin (*10*) was packed in a 0.9 cm i.d. × 30 cm glass chromatographic column and 20 mL of retort water pumped downward through the resin bed at 4 mL/min. A rinse consisting of 20 mL of 0.1 N NaOH, followed by 30 mL of distilled water, followed the retort water. This rinse is required to displace phenols, hydroxypyridines, and carboxylic acids from the column. Column flow was reversed, and aromatic amines were desorbed at 2.0 mL/min by 0.1 N HCl. There was no net concentration or dilution factor, as the aromatic amines were contained in 20 mL of column eluate, whose collection was started at the elution volume where acid breakthrough occurred.

After neutralization of the HCl with Na_3PO_4, the aromatic amine fraction was analyzed by liquid chromatography on a 0.4 cm i.d. × 25 cm column of 5-μm C-8 silica, with a 65% methanol/35% 0.05 N sodium phosphate buffer (pH 7) and a flow rate of 1.0 mL/min. Retention time and ultraviolet–visible spectra comparisons with standards were used to identify specific aromatic amines.

Aliphatic Amines. Steam-volatile aromatic amines, phenols, and neutral compounds were separated from aliphatic amines by vacuum rotary evaporation (to 20 mL) of 200 mL of retort water at 45 °C titrated to pH 7 with H_3PO_4. This 20-mL residue was titrated to pH 12 with NaOH and diluted to 200 mL with distilled water, and 160 mL of water was distilled off. This alkaline distillate was neutralized to pH 5 with HCl, vacuum evaporated to 20 mL, and gas chromatographed at 90 °C on a 2 mm i.d. × 183 cm glass gas chromatographic column containing 28% Pennwalt Amine 223 on 80/100 mesh Gas-Chrom R. Only the low molecular weight primary aliphatic amines were determined, and determinations were tentative, as a second column packing was not used. Low concentrations of aliphatic amines precluded additional confirmatory work.

Phenols. Phenols are the predominant compound class found in the hydrophobic weak-acid fraction of DOC fractionation. An Amberlite XAD-8 resin column was prepared in the same manner as for the aromatic amines, and 20 mL of retort water, acidified to pH 1 with H_2SO_4, was pumped downward through the resin bed at 4 mL/min. A rinse of 20 mL of 0.1 N sodium phosphate buffer (pH 7), followed by 30 mL of water, followed the retort water. Retort water was acidified to prevent adsorption of aromatic amines and hydroxypyridines, and adsorbed carboxylic acids were displaced from the column by the rinse. The column flow was reversed, and phenols were backflush desorbed at 2.0 mL/min with 0.1 N NaOH. A 20-mL portion of column eluate was collected from the point of NaOH breakthrough and immediately neutralized with H_3PO_4 to prevent phenol oxidation. Phenols were liquid chromatographed on the same column and conditions as the aromatic amines, except the mobile phase was 50% methanol/50% 0.05 N sodium phosphate buffer (pH 7). Retention time and ultraviolet–visible spectra comparisons with standards were used to identify specific phenols.

Aliphatic Monocarboxylic Acids. Aliphatic monocarboxylic acids occur in the hydrophobic and hydrophilic acid fractions of DOC fractionation. One liquid chromatographic and two gas chromatographic procedures were used to determine the entire suite of aliphatic monocarboxylic acids found in significant concentrations in retort water.

The best gas chromatographic procedure for determining aliphatic monocarboxylic acids C_2–C_5 was the direct aqueous injection procedure of Di Corcia et al. (*11*), which used acid-washed Carbopack B in a 2 mm i.d. × 50 cm glass column. For avoidance of acidification of retort water prior to injection, a glass-wool plug at the head of the column was coated with H_3PO_4, and retort-water samples were injected into the plug. Aliphatic monocarboxylic acids from C_2 to C_{10} also were determined by gas chromatography of the butyl esters. Aliphatic monocarboxylic acids were isolated from retort water by distillation of 100 mL acidified to pH 3 with H_3PO_4. An 80-mL sample of distillate was collected, and the condenser was washed with 20 mL of methanol to recover high molecular weight insoluble fatty acids. After the methanol rinse was combined with the distillate, the aliphatic monocarboxylic acid mixture was titrated to pH 8.5 with 40% tetrabutylammonium hydroxide, and the solution was freeze-dried. Butyl esters were formed by adding 20 mL of 14% BF_3/butanol to the freeze-dried salt and heating to 60 °C for 30 min. Butyl esters were extracted from the BF_3/butanol by adding 20 mL of 50% acetonitrile/water to the BF_3/butanol and extracting twice with 20 mL of *n*-hexane. The

combined 40-mL hexane extract was back-extracted twice with 40 mL of 50% acetonitrile/water to remove the last traces of butanol. The butyl esters may be concentrated further by hexane evaporation in a Kuderna–Danish evaporative concentrator. The butyl esters were analyzed by gas chromatography on 3% OV-17 and 3% OV-101 coatings on 100/120 mesh diatomaceous packings in 2 mm i.d. × 183 cm glass columns, temperature programmed from 60 to 260 °C at 6 °C/min. As this entire procedure involves many steps where losses can occur, it was calibrated by repeating the procedure with 100 mg/L of each fatty acid from C_2 to C_{10}, dissolved in water containing inorganic salts that approximate retort-water composition (*12*).

Formic acid could not be determined readily by the previous two gas chromatographic procedures; therefore, the *p*-bromophenacyl esters of C_1–C_5 acids were prepared according to the procedure of Barcelona et al. (*13*). Aliphatic monocarboxylic acids, isolated from retort water by distillation (as in the previous procedure), were titrated to pH 8.5 with KOH and freeze-dried. After derivatization of potassium salts (*13*), they were liquid chromatographed on a 0.4 cm i.d. × 20 cm column of 5-μm C-8 silica, by using 60% methanol/40% water heated to 60 °C (*14*) and a flow rate of 1.5 mL/min. This procedure also was calibrated by passing C_1–C_5 fatty acid standards dissolved in synthetic retort-water matrix through the entire procedure.

Aliphatic Dicarboxylic Acids. The procedure of Riley et al. (*5*) was modified to form butyl esters instead of methyl esters to enable determination of short-chain dicarboxylic acids, and tetrabutylammonium salts of freeze-dried retort water were derivatized with BF_3/butanol instead of straight freeze-dried retort-water salts, to aid in salt solublization in BF_3/butanol.

Dibutyl esters of aliphatic dicarboxylic acids were prepared and isolated from retort water as follows. Retort water (20 mL) followed by 50 mL of distilled water rinse was passed through an Amberlite XAD-8 column prepared as described previously for aromatic amines. The 70-mL portion of column eluate, acidified to pH 3 with H_3PO_4, was decreased to 20 mL by vacuum rotary evaporation at 45 °C. The 20-mL sample plus another 50 mL of water rinse was next passed through a column of hydrogen-saturated BioRad AG-MP-50 cation-exchange resin; column dimensions and flow rates were the same as the XAD-8 column used previously. The 70 mL of column eluate again was vacuum evaporated to 20 mL and titrated to pH 8.5 with tetrabutylammonium hydroxide. After being freeze-dried, tetrabutylammonium salts were derivatized with 10 mL of 14% BF_3/butanol heated to 80 °C for 2 h. Subsequent extractions and gas chromatography were the same as described previously for butyl esters of the fatty acids, except that the columns were temperature programmed from 120 to 260 °C at 4 °C/min. This procedure was calibrated by passing C_2–C_{10} dicarboxylic acid standards dissolved at 10 mg/L concentrations in a synthetic retort-water matrix through the entire procedure.

Aromatic Carboxylic Acids. Aromatic carboxylic acids are contained in the hydrophobic strong-acid fraction of DOC fractionation. Two Amberlite XAD-8 columns were prepared in the same manner as for the aromatic amines. Retort water (20 mL) followed by 50 mL of distilled water rinse was passed downward through the first column at 4 mL/min. The 70-mL eluate of retort water plus rinse was vacuum rotary evaporated at 45 °C to 20 mL and acidified to pH 2 with H_2SO_4. The 20-mL acidified sample next was passed through the second XAD-8 column followed by 50 mL of 0.01 N H_2SO_4 rinse. After direction of column flow was reversed, adsorbed carboxylic acids were desorbed with 5 mL of 0.1 N NaOH, followed by 15 mL of distilled water. This 20-mL fraction was titrated to pH 5 with H_2SO_4, and aromatic carboxylic acids were determined by inorganic ion-pair liquid chromatography as described by Jandera (*15*). A 40% methanol/0.2 N Na_2SO_4 ion-pair electrolyte mobile phase was used with a 0.4 cm i.d. × 20 cm column of 5-μm C-8 silica column heated to 60 °C (*14*) with a flow rate of 1.5 mL/min. Identification and confirmation of unknown peaks were by ultraviolet–visible spectroscopy and retention time matches.

Thiocyanate. Thiocyanate was determined colorimetrically in whole retort water as the ferric complex, by the method of Stuber et al. (*16*).

Hydroxypyridines. Hydroxypyridines are found in the hydrophilic base fraction of DOC fractionation and can be isolated from retort water as follows. Retort water (20 mL) was acidified to pH 1 with HCl, and the carbon dioxide was purged with nitrogen gas. This sample was passed through a 0.9 cm i.d. × 30 cm glass column of hydrogen-saturated BioRad AG-MP-50 cation exchange resin, followed by 50 mL of distilled water rinse at 4 mL/min. Hydroxypyridines and other amphoteric solutes are desorbed by downward elution of the column with 1.0 N NH_4OH. Column eluate collection started at the point of ammonia breakthrough, and 100 mL of 1.0 N NH_4OH eluant was collected. The volume was decreased and ammonia removed by vacuum rotary evaporation at 45 °C of this fraction to 2 mL.

Hydroxypyridines were liquid chromatographed on the same 5-μm C-8 silica column described previously with a 30% methanol/70% 0.05 N sodium phosphate buffer (pH 7) and a flow rate of 1.0 mL/min. Retention times and ultraviolet–visible spectral comparisons with standards were used to identify specific hydroxypyridines. The entire procedure was calibrated with hydroxypyridine standards dissolved in a synthetic retort-water matrix.

Pyridinecarboxylic Acids. The isolation procedure for pyridinecarboxylic acids was the same as for the hydroxypyridines (described previously), but short retention times and tailing peak shapes of pyridinecarboxylic acid standards by reverse-phase liquid chromatography indicated that their direct determination was not feasible. Methyl esters of the pyridinecarboxylic acids were determined readily by liquid chromatography and were formed as follows: the 1.0 N NH_4OH eluant from the cation-exchange resin was vacuum rotary evaporated to dryness. A 10-mL sample of 14% BF_3/methanol was added to the residue and boiled by using a reflux condenser for 16 h. A 5-mL sample of 29% aqueous ammonia was added to the BF_3/methanol, and the methyl esters were extracted by three successive 5-mL extractions with methylene chloride. Next, the slightly basic methyl esters of pyridinecarboxylic acids were back-extracted into 0.1 N H_2SO_4 by three successive 5-mL extractions of the combined methylene chloride extract. The acid extract was neutralized with K_3PO_4 and liquid chromatographed on the 5-μm C-8 silica column, described previously, by using a 60% methanol/40% 0.05 N sodium phosphate buffer (pH 7) and a flow rate of 1.0 mL/min. The entire procedure was calibrated with pyridinecarboxylic acid standards dissolved in a synthetic retort-water matrix.

Aliphatic Amides. Aliphatic amides occur in the hydrophilic neutral class of DOC fractionation. They were isolated from acid, volatile base, and volatile neutral solutes in retort water by passing 20 mL of retort water through a 0.9 cm i.d. × 30 cm glass column of hydroxide-saturated

BioRad AG-MP-50 anion-exchange resin, followed by a 50-mL rinse of distilled water. The combined retort water plus rinse column eluate was vacuum rotary evaporated at 45 °C to 10 mL and then titrated to pH 7 with HNO_3. The 10-mL volume then was reduced to 1 mL by vacuum rotary evaporation. Precautions were taken to ensure that the sample was not evaporated to dryness, as aliphatic amides will be lost by sublimation.

The amides acetamide through butyramide were determined by gas chromatography of the aqueous concentration on two 2 mm i.d. × 50 cm glass columns containing 60/80 mesh Tenax GC and 100/120 mesh Porapak Q. The Tenax column was operated isothermally at 130 °C, and the Porapak Q column was run at 200 °C.

Amides formamide through butyramide were determined by liquid chromatography of the aqueous concentration on the 5-μm C-8 silica column described previously. The mobile phase consisted of 5% acetonitrile and 95% water; the flow rate was 1.0 mL/min, and the detector was set at 214 nm. As with previous compounds, amide isolation and chromatography procedures were calibrated with amide standards dissolved in synthetic retort water.

Urea. Urea was isolated in the amide fraction and determined colorimetrically by reaction with diacetyl monoxime and thiosemicarbazide to form a red complex measured at 525 nm (*17*).

Volatile Nitriles, Alcohols, and Ketones. These compounds, which occur in the hydrophobic and hydrophilic neutral classes of DOC fractionation, were determined by direct aqueous injection of retort water into 2 mm i.d. × 183 cm glass chromatographic columns containing 100/120 mesh Porapak Q and 80/100 mesh Carbopak B. All gas chromatograms were generated under isothermal conditions at temperatures ranging from 75 to 200 °C. Standard recoveries and retention-time matches were determined by the method of standard additions to retort water.

Aldehydes. Formaldehyde cannot be detected by flame ionization gas chromatography, and the gas chromatography of higher molecular weight aldehydes in retort water was uncertain because of the possible formation of bisulfite addition products. Therefore, the procedure of Fung and Grosjean (*18*) was used, whereby carbonyl compounds are derivatized to form 2,4-dinitrophenylhydrazones that are separated by reverse-phase liquid chromatography and detected at 360 nm. The same 5-μm C-8 silica was used, as described previously. A 70% methanol/30% water mobile phase was used at a flow rate of 1 mL/min. The procedure was calibrated by recovery of various aldehyde and ketone standards dissolved in a synthetic retort water.

Lactones. Lactones in retort water were determined by direct aqueous injection gas chromatography on the same columns used to determine volatile nitriles, alcohols, and ketones discussed previously, except that the length of the Porapak Q column was decreased to 91 cm. An isothermal temperature of 230 °C was used for the Carbopak B column, and 235 °C was used for the Porapak Q column.

Pyrrole. Pyrrole was determined in whole retort water by liquid chromatography. The 5-μm C-8 silica column described previously was used with a 20% methanol/80% water mobile phase and a flow rate of 1 mL/min. Identification was by an ultraviolet–visible spectral scan; a pyrrole standard added to retort water was used for quantitation.

Results and Discussion

Organic analyses of the two retort waters studied are presented in Table I. Concentrations were calculated as the arithmetic mean of duplicate and, in a few instances, triplicate determinations and (or) methods for a specific compound. Recovery and precision data for each compound class determined are presented in Table II. Procedural standards dissolved in a synthetic retort-water matrix and standard additions to retort water were two techniques used to compensate for recovery losses.

The aliphatic monocarboxylic acids are by far the most abundant compound class in the process retort water, but they only consitute a trace of the DOC in the condensate retort water. Acetic acid constituted 15.8% of the process water DOC, and 37.6% of the aliphatic monocarboxylic acid DOC. The pH of 8.6–8.8 for retort water limited the volatility of aliphatic monocarboxylic acids, so that they did not steam distill into the condensate retort water. No significant concentrations of aliphatic monocarboxylic acids greater than C_{10} chain length were detected in retort water; longer chain monocarboxylic acids most likely partition into shale oil. Formic acid may not be stable in retort water, as it was not detected in process water and was present in small concentration in condensate water.

The aliphatic dicarboxylic acids were analyzed only in process retort water, because their extreme nonvolatility at retort water pH makes their presence in condensate retort water very unlikely. Their total concentration in process retort water was about 25 times less than the aliphatic monocarboxylic acids. Gas chromatograms of dibutyl esters indicated a homologous series of aliphatic dicarboxylic acids from C_2 through C_{12}, although only the series C_2–C_{10} was confirmed with standards. Pentanedioic acid was the most abundant, with nonanedioic acid second most abundant. Riley et al. (*5*) found the same relative abundances for aliphatic dicarboxylic acids found in retort water from the Paraho retorting process.

Benzoic acid was the only aromatic carboxylic acid detected in significant concentrations in the process retort water, although trace concentrations of monomethyl- and dimethylbenzoic acids were detected. The lack of aromatic carboxylic acids in retort water probably is a reflection of the aliphatic nature of kerogen from the Green River oil shale.

Thiocyanate, a nonvolatile anion, was detected in significant concentrations in both condensate and process retort waters. Its presence in the condensate water is evidence that if formed in secondary reactions from the volatile cyanide and sulfur species precursors in a manner similarly described by Luthy et al. (*19*) for coal-gasification waste waters.

Both phenols and aromatic amines are steam volatile, as shown by their greater concentrations in the condensate retort water . Phenol concentrations in oil-shale retort waters are much smaller than have been reported for coal-gasification waste waters (*20*), whereas aromatic amine concentrations are much greater in oil-shale retort waters. Aromatic amines and quinolines have been identified in kerogen from Green River Formation oil shale (*18*), and retorting releases these aromatic amines. For condensate water, 82% of the DOC isolated in the phenol fraction was identified as various phenols, whereas only 53% of the DOC isolated in the aromatic amine fraction was identified. Retention-time data and spectral data of unidentified aromatic amine peaks in the liquid chromatograms indicated that much of the unidentified aromatic amine DOC consisted of various C_3- and C_4-alkyl pyridines as reported in retort water by Riley et al. (*21*). Acridine and aminonaphthalenes assays were made with the limit of detection of 0.1 mg/L, but neither of these mutagenic aromatic amines were detected.

Table I. Retort Water Organic Analyses[a]

compound	DOC classification	condensate retort water (DOC = 790 mg/L) concn, mg/L	DOC, mg/L	DOC, %	process retort water (DOC = 3000 mg/L) concn, mg/L	DOC, mg/L	DOC, %
aliphatic monocarboxylic acids			2.87	0.36		1263.8	42.1
formic acid	HPI-A	1.0	0.26		ND		
acetic acid	HPI-A	3.4	1.36		1188	475	
propanoic acid	HPI-A	1.2	0.58		364	177	
2-methylpropanoic acid	HPI-A	0.5	0.27		119	64.9	
butanoic acid	HPI-A	0.4	0.22		117	63.8	
pentanoic acid	HPO-A	0.3	0.18		110	64.7	
2- and 3-methylbutanoic acid	HPO-A	NA			151	88.8	
hexanoic acid	HPO-A	NA			109	67.9	
heptanoic acid	HPO-A	NA			149	96.6	
octanoic acid	HPO-A	NA			131	87.6	
nonanoic acid	HPO-A	NA			81	55.5	
decanoic acid	HPO-A	NA			31	22.0	
aliphatic dicarboxylic acids		NA	NA			41.6	1.4
ethanedioic acid	HPI-A	NA			4.9	1.3	
propanedioic acid	HPI-A	NA			8.1	2.8	
butanedioic acid	HPI-A	NA			2.0	0.8	
pentanedioic acid	HPI-A	NA			21.2	10.0	
hexanedioic acid	HPI-A	NA			4.7	2.3	
heptanedioic acid	HPI-A	NA			7.2	3.8	
octanedioic acid	HPO-A	NA			11.5	6.2	
nonanedioic acid	HPO-A	NA			12.8	7.4	
decanedioic acid	HPO-A	NA			11.7	7.0	
aromatic carboxylic acids						16.6	0.6
benzoic acid	HPO-A	ND			25.4	16.6	
thiocyanate	HPI-A	8.1	1.68	0.2	78.6	16.1	0.5
phenols			140.2	17.8		64.5	2.2
phenol	HPO-A	54.3	41.8		26.0	20.0	
2-hydroxytoluene	HPO-A	23.2	18.1		7.1	5.5	
3- and 4-hydroxytoluene	HPO-A	42.6	33.1		9.6	7.4	
1,2-dimethyl-4-hydroxybenzene	HPO-A	5.6	4.4		4.6	3.6	
remaining dimethylhydroxybenzene isomers	HPO-A	54.5	42.8		36.1	28.3	
aromatic amines			152.1	19.3		9.74	0.3
aniline	HPO-B	21.3	16.5		1.6	1.24	
2-aminotoluene	HPO-B	3.4	2.7		0.2	0.16	
3- and 4-aminotoluene	HPO-B	5.2	4.1		NA		
pyridine	HPI-B	14.7	11.2		2.3	1.75	
2-methylpyridine	HPO-B	9.2	7.1		NA		
3-methylpyridine	HPO-B	6.5	5.0		NA		
4-methylpyridine	HPO-B	6.3	4.9		NA		
2,6-dimethylpyridine	HPO-B	9.5	7.5		1.8	1.41	
remaining dimethylpyridine isomers	HPO-B	37.6	29.5		NA		
2,4,6-trimethylpyridine	HPO-B	70.1	55.5		4.0	3.17	
quinoline	HPO-B	5.8	4.8		1.9	1.59	
isoquinoline	HPO-B	2.4	2.0		0.5	0.42	
2-methylquinoline	HPO-B	1.6	1.3		NA		
aliphatic amines[b]							
methylamine	HPI-B	1.8			1.8		
ethylamine	HPI-B	3.0			2.4		
hydroxypyridines		ND				31.5	1.1
2-hydroxypyridine	HPI-B	ND			13.6	8.6	
3-hydroxypyridine	HPI-B	ND			5.6	3.5	
4-hydroxypyridine	HPI-B	ND			4.0	2.5	
2-hydroxy-6-methylpyridine	HPI-B	ND			25.6	16.9	
pyridinecarboxylic acids		NA				0.70	tr[c]
2-pyridinecarboxylic acid	HPI-B	NA			0.3	0.18	
3-pyridinecarboxylic acid	HPI-B	NA			0.5	0.29	
4-pyridinecarboxylic acid	HPI-B	NA			0.4	0.23	
aliphatic amides			2.46	0.3		38.5	1.2
formamide	HPI-N	2.0	0.53		ND		
acetamide	HPI-N	4.0	1.63		52.7	21.4	
propionamide	HPI-N	0.6	0.30		23.2	11.4	
butyramide	HPI-N	ND			2.0	1.1	
urea	HPI-N	NA			22.8	4.6	
nitriles			34.3	4.3		3.4	0.1
acetonitrile	HPI-N	38.9	22.8		5.8	3.4	
propionitrile	HPI-N	8.5	5.6		ND		
isobutyronitrile	HPO-N	2.3	1.6		ND		
butyronitrile	HPO-N	2.5	1.7		ND		
valeronitrile	HPO-N	0.6	0.4		ND		
benzonitrile	HPO-N	2.7	2.2		ND		
aliphatic alcohols			27.26	3.5		1.5	tr
methanol	HPI-N	3.4	1.28		ND		

Table I (*Continued*)

compound	DOC classification	condensate retort water (DOC = 790 mg/L) concn, mg/L	DOC, mg/L	DOC, %	process retort water (DOC = 3000 mg/L) concn, mg/L	DOC, mg/L	DOC, %
ethanol	HPI-N	3.4	1.46		ND		
propanol	HPI-N	0.2	0.12		ND		
isopropyl alcohol	HPI-N	26.6	16.0		2.5	1.50	
sec-butyl alcohol	HPI-N	13.0	8.4		ND		
aliphatic ketones			20.7	2.6		2.42	0.1
acetone	HPI-N	19.5	12.1		3.9	2.42	
2-butanone	HPO-N	10.2	7.9				
2-pentanone	HPO-N	0.9	0.7				
aliphatic aldehydes						1.31	tr
acetaldehyde	HPI-N	ND			2.4	1.31	
lactones			12.1	1.3		16.7	0.6
γ-butyrolactone	HPO-N	9.6	5.4		13.7	7.6	
γ-valerolactone	HPO-N	11.3	6.8		15.2	9.1	
pyrrole	HPO-N	4.9	3.56	0.4	ND		
identified DOC			397.3	50.3		1508.4	50.3

[a] DOC = dissolved organic carbon; NA = not analyzed; ND = not detected; HPI-A = hydrophilic acid; HPO-A = hydrophobic acid; HPI-B = hydrophilic base; HPO-B = hydrophobic base; HPI-N = hydrophilic neutral; HPO-N = hydrophobic neutral. [b] Tentative data not included in carbon balance. [c] Trace.

The aliphatic amines methylamine and ethylamine were found in small concentrations in both retort waters despite the presence of 1000–10 000 mg/L of ammonia found in most retort waters. Luthy et al. (*19*) indicated that ammonia from coal gasification resulted from the pyrolytical cleavage of aliphatic carbon–amino linkages that would degrade most primary aliphatic amines. A similar process can be postulated for aliphatic amines in oil-shale retorting processes. Aromatic amines are much more refractory.

Hydroxypyridines are the major constituent of the hydrophilic base fraction of the process water and have not been reported previously in retort water. In retort water, the 2- and 4-hydroxypyridines exist in neutral lactam forms as pyridones, and the 3-hydroxypyridine exists as a mixture of the hydroxy compound and the corresponding zwitterion (*22*). Various methyl-substituted hydroxypyridines appear to be much more abundant than unsubstituted hydroxypyridines, but only the 2-hydroxy-6-methylpyridine could be confirmed and quantitated, because standards for the other methyl isomers were not available. The peak absorbance for the 2-hydroxypyridines is near 300 nm, which is a wavelength where other aromatic compounds in retort water show little absorbance. Therefore, 2-hydroxypyridine and its methyl-substituted isomers can be determined directly in unfractionated retort water injected into a liquid chromatograph with its detector set at 300 nm. Because of their hydrophilic nature, uniqueness, relative abundance, and ease of detection, the 2-hydroxypyridine class of compound might be considered as conservative tracer solutes for retort water. Hydroxypyridines are nonvolatile, and therefore were not detected in the condensate retort water.

Nonvolatile pyridinecarboxylic acids were found in trace amounts in the process retort water. Apparently little oxidation of alkyl pyridine to pyridinecarboxylic acids occurred.

Aliphatic amides, being nonvolatile when dissolved in water, were found primarily in the process retort water. Aliphatic amides most likely form from the reaction of fatty acids with ammonia, and urea forms from the reaction of carbon dioxide and ammonia. Finding formamide in the condensate, but not in the process water, parallels formic acid in these two waters and may point toward greater instability of formic acid in the process water compared to the condensate water.

Nitriles undoubtedly resulted from dehydration of amides produced in the retorting process, and nitrile volatility caused them to distill into the condensate retort water. Nitrile concentrations directly correspond to nitrile solubilities; therefore, more insoluble long-chain aliphatic nitriles may partition into shale oil associated with the gas-condensate fraction. Because of their toxicity (*23*), nitriles may be an important class of compounds contributing to the toxicity of retort water.

Volatile aliphatic alcohols and ketones occur in significant concentrations in the condensate retort water. Methyl ketones and alcohols were much more abundant than primary alcohols, aldehydes, or other isomers. Acetaldehyde is an interesting case; despite its volatility, it was not found in the condensate retort water but was found in the proces retort water. It likely formed a nonvolatile bisulfite addition complex in the process water, as retort waters are known to have significant concentrations of reduced sulfur species (*16*). Formaldehyde added to both retort waters at 10 mg/L concentration disappeared within 24 h, indicating a reactive process that degrades formaldehyde.

Lactones have been identified previously in retort water (*24*) and have been found in a Yugoslavia shale bitumen (*25*). For a test of the possibility that lactones may form in the heated injection port of the gas chromatograph by dehydration of the corresponding hydroxy acids, lactone standards were hydrolyzed with base, neutralized, and injected into the gas chromatograph. No detectable lactone peaks were found for the hydrolyzed lactones; thus, the reported lactones must exist as lactones in retort water. Lactones are borderline compounds with respect to steam volatility. Approximately equivalent amounts of lactones were detected in the condensate and process retort waters.

For a better illustration of the volatility partitioning of retort-water organic solutes into the process and gas-condensate waters, a histogram for compounds analyzed in both retort waters was plotted as the log of the concentration ratio shown in Figure 2.

Aliphatic monocarboxylic acids are 2.5 orders of magnitude more abundant in the process water; small concentrations of acids that occur in the condensate water may result from entrainment of these acids in mist or particulate constituents introduced into condensate water. Thiocyanate, although nonvolatile, can be formed from

Table II. Recovery and Precision Data for Determination of Polar Organic Solutes in Oil-Shale Retort Water[a]

compd class	analyt method	recovery	av dev from mean within a method	av dev from mean between methods
aromatic amines	resin adsorption isolation, liquid chromatographic separation, ultraviolet detection	85–97% for resin adsorption isolation procedure	6%[b] for resin adsorption isolation procedure. 2.4%* for liquid chromatography	
phenols	resin adsorption isolation, liquid chromatographic separation, ultraviolet detection	96% for phenol, 68% for hydroxytoluenes, and 41% for dimethylhydroxybenzenes for resin adsorption isolation procedure	12%[b] for resin adsorption procedure; 4.1%[b] for liquid chromatography	
aliphatic monocarboxylic acids	direct aqueous injection gas chromatography	100% relative to standards in synthetic retort water	2% for acetic acid, 6% for propanoic acid in Occi-6 process water	values for acids in Occi-6 process water: acetic acid, 7.3%; propanoic acid, 1.3%; 2-methylpropanoic acid, butanoic acid, 5.9%; pentanoic acid, 8.9%
	steam distillation isolation, butyl ester derivization, gas chromatography	a	2%[c] for pentanoic acid, 6%[c] for hexanoic acid in Occi-6 process water	
	steam distillation isolation, *p*-bromophenacyl ester derivatization, liquid chromatography	a	4–6% for C_1–C_5 acids in Occi-6 condensate water	
aliphatic dicarboxylic acids	removal of interferents by resin adsorption and steam distillation, butyl ester derivatization, solvent extraction, and gas chromatography	a	3–12%[c] for C_2–C_{10} alkanedioic acids in Occi-6 process water	
aromatic carboxylic acids	resin adsorption isolation, liquid chromatographic, separation, ultraviolet detection	98% for benzoic acid for resin adsorption isolation procedure	2% for resin adsorption isolation procedure; 3% for liquid chromatography (determined for 20 mg/L of benzoic acid)	
thiocyanate	resin adsorption of colored organic interferents, colorimetric determination of ferric thiocyonate complex	99%	3% for manual colorimetric determination; 1% for automated colorimetric determination	
hydroxypyridines	resin adsorption isolation, liquid chromatographic separation, chromatographic separation, ultraviolet detection	a	5–15% for hydroxypyridines in Occi-6 process water	
pyridine carboxylic acids	resin adsorption isolation, methyl ester derivatization, liquid chromatographic separation, ultraviolet detection	a	10–30% for pyridinecarboxylic acids in Occi-6 process water	
aliphatic amides	anion-exchange adsorption of acid interferents, vacuum evaporation of neutral and base interferents, gas-chromatographic separation, flame ionization detection	a	values for amides in Occi-6 process water determined between Tenax and Porapak Q GC-packings: acetamide, 6.3%; propionamide, 11.1%; butyramide, 30%	5% for acetamide in Occi-6 process water; 15% for acetamide in Occi-6 condensate water
	isolation procedure same as previous method; liquid chromatographic separation, ultraviolet detection	a	no precision data were obtained as only one run was performed	
urea	colorimetric determination in amide fraction as a thiosemicarbazide complex	100% relative to a reagent blank of synthetic retort water containing C_2–C_4 aliphatic amides	7.1% for Occi-6 process water	

volatile nitriles, alcohols, aldehydes, and ketones	direct aqueous injection of retort waste waters into Porapak Q and Carbopack C gas chromatographic columns with flame ionization detection	b	for determinations of 14 compounds in Occi-6 process water between two GC columns, the median av dev was 5.2% and the range was 0.7% to 40%	
aldehydes	derivatization in retort water to the 2,4-dinitrophenylhydrazone, solvent extraction, and liquid chromatography with visible light detection	a, b	a single determination was performed	16% for acetaldehyde in Occi-6 process water compared to data from the previous gas chromatographic method
lactones	direct aqueous injection of retort waste waters into Parapak A and Carbopack C gas chromatographic columns with flame ionization detection	b	2.5% for γ-butyrolactone, 39%[d] for γ-valerolactone for Occi-6 process water	
pyrrole	direct injection of retort water into a liquid chromatograph with ultraviolet detection	b	5.1% for pyrrole in Occi-6 condensate water	

[a] Key: a = quantitation of the retort water analyte was related to a standard dissolved in synthetic retort water that was run through the entire analytical procedure; b = the method of standard additions to retort water was used for quantitation. [b] Determined at 10 mg/L concentration level. [c] Deviations for determinations between OV-17 and OV-101 columns. [d] There is an interfering constituent for γ-valerolactone in Occi-6 process water.

Figure 2. Histogram showing relative concentrations of organic solutes in condensate and process retort waters.

Table III. Retort Water Dissolved Organic Carbon Fractionation[a]

	condensate retort water		process retort water	
fraction	DOC, %	identified DOC, %	DOC, %	identified DOC, %
hydrophobic bases	24	17.8	5	0.3
hydrophobic acids	19	17.8	28	19.5
hydrophobic neutrals	25	3.8	11	0.6
hydrophilic bases	12	11.4	9	1.1
hydrophilic acids	9	0.6	39	27.3
hydrophilic neutrals	11	8.9	8	1.5
total hydrophobic compounds	68	39.4	44	20.4
total hydrophobic compounds	32	10.9	56	29.9
total bases	36	19.2	14	1.4
total acids	28	18.4	67	46.8
total neutrals	36	12.7	19	2.1
total	100	50.3	100	50.3

[a] DOC = dissolved organic carbon.

volatile precursors, and aliphatic amides, nonvolatile in water, easily sublime when dry. Therefore, thiocyanate and aliphatic amides have phase-transfer mechanisms that result in the greater log concentration ratio in Figure 2 than for aliphatic moncarboxylic acids.

Aromatic amines, acetonitrile, isopropanol, and acetone are all steam-volatile compounds, existing as neutral solutes in retort water, and their retort-water log concentration ratios are quite similar, ranging from 0.7 to 1.0 (Figure 2). However, phenol has a smaller log concentration ratio than neutral solutes. Phenol probably has some slight ionic character at pH 8.6–8.8 of retort water, as the pK_a of phenols is near 10; this ionic character may decrease phenol volatility.

For a determination of which classes of organic compounds were not identified in retort water by this study, DOC fractionation of the two retort waters was compared with DOC identified in various classes of DOC fractionation. Specifically identified compounds were assigned to various DOC fractionation classes in Table I according to DOC fractionation theory (*10*), by using data for standards generated by Thurman (*26*) and Stuber (*27*); the results are shown in Table III.

In the condensate retort water, large percentages of hydrophobic bases were identified as aromatic amines, hydrophobic acids were identified as phenols, and hydrophilic neutrals were identified as nitriles, alcohols, and ketones. The percentage identification of hydrophobic neutrals, being the most nonpolar fraction, was not significant because this study focused upon polar solutes. Pellizzari et al. (*4*) and Raphaelian and Harrison (*6*) have identified many hydrophobic neutral solutes found in retort water. The small percentage of hydrophilic acids identified indicates that a noncarboxylic, nonphenolic class of acids likely exists in condensate water. One possibility is sulfonic acids formed from oxidation of volatile thiols that may be present initially in condensate water. Few hydrophilic bases also were identified, and the strong base fraction isolated by distillation for aliphatic amine analysis contained 6% of the DOC. Although methylamine and ethylamine are present in small concentrations, it is quite possible that higher molecular weight aliphatic amines, especially cyclic aliphatic amines, may exist in appreciable concentrations in retort water.

For the process retort water, most of the identified DOC occurred in the hydrophobic and hydrophilic acid fractions as monocarboxylic acids. Unidentified hydrophobic acid DOC likely consists of complex polyfunctional acids, and aromatic amine and phenol condensation products. Unidentified hydrophilic acid DOC very probably consists of simple hydroxy acids (a class not analyzed) and possibly sulfonic acids. A small percentage of both hydrophobic and hydrophilic base fractions were identified, but it is likely that most of the unidentified DOC in these classes is an extension of the hydroxypyridines into alkyl-substituted isomers for which confirming standards could not be obtained. Few hydrophobic neutrals were identified, because this study did not focus on neutral, nonpolar solutes. Few hydrophilic neutrals were identified, because of the difficulty of isolation, chromatography, and detection of neutral, nonvolatile, polyfunctional solutes in this fraction.

Finally, a number of negative assays were run for specific organic compounds in fractions isolated from both retort waters. For the hydrophilic base fraction, no detectable quantities of pyrazole, pyrimidine, pyrazine, or pyridazine were found. No thiophene, thiazole, or furan was found in the hydrophilic neutral fraction, *o,o'*- and *p,p'*-biphenols were not detected in the hydrophobic acid fraction, di- or trihydroxyphenols were not found in the phenol fraction, and carbamate anion and cyanuric acid were not detected in whole retort water. The iodine–azide decomposition reaction (*28*) was used to test for the presence of thiols, thioketones, and thiourea in various DOC fractions, none of these compound classes were detected.

Conclusions

On the basis of the results of this study, one can conclude that at least one-half and probably three-quarters of the DOC in retort water consist of low molecular weight polar organic solutes of fairly simple structures. If the analytical approach of this study were extended to the hydroxycarboxylic acids, cyclic aliphatic amines, sulfonic acids, and alkylhydroxypyridine classes, it is quite possible that a 75% of the DOC might be identified. Investigation of the hydrophobic neutral fraction by solvent extraction, gas chromatographic–mass spectrometric techniques might add another 10% as nonpolar DOC identified. The 50% of retort-water DOC identified by this study was distributed among only 71 compounds and compound isomer groups, whose concentrations in most instances were greater than 1 mg/L. The percentage of unidentified DOC accounted by summing trace constituent unknowns (<1 mg/L) in retort water is probably small, although trace constituents may outnumber major constituents by orders of magnitude. There also is a small percentage of the DOC in retort water that is so complex that structural identification is not feasible, but an exhaustive organic analysis of retort water might identify 80–90% of the DOC.

Comparison of the organic solute composition of a process retort water with a gas-condensate retort water has shown that condensate water organic solutes consist mainly of steam-volatile polar compounds, whereas, process water organic solutes are nonvolatile organic anions and polyfunctional neutral compounds. This knowledge of organic solute composition of retort water should aid in the design of retort water treatment systems and disposal practices.

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Gas Chromatographic Analysis of Glycols To Determine Biodegradability

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■ The biodegradability of propylene glycol, diethylene glycol, triethylene glycol and trimethylolethane, when challenged by activated or anaerobic sludge microorganisms, was investigated. The disappearance of the substrates was monitored by gas chromatography. Glycols are industrial pollutants also found as hydrolysis products from the corresponding nitrates, which are used as military propellants. Propylene glycol was readily degraded. The initial stage of decomposition of diethylene and triethylene glycol was nonbiological, but trimethylolethane was relatively stable under the conditions tested. A gas chromatographic method was developed for direct injections of the glycols in aqueous solutions having a limit of detection in the low-ppm range. This represents a significant improvement in sensitivity over previously reported methods for aqueous solutions of glycols.

Introduction

Glycols are used extensively in industry, and their biodegradability is of great importance due to the large quantities entering the environment.

Our interest in this area stems from the fact that four nitrate esters, propylene glycol dinitrates (PGDN), diethylene glycol dinitrate (DEGN), triethylene glycol dinitrate (TEGDN), and trimethylolethane trinitrate (TMETN), as military propellants may be found in waste streams from munition plants and loading operations and would therefore be pollutants if discharged into the environment. Initial studies have shown that these esters undergo microbial transformation via successive denitration steps leading to the formation of the corresponding glycols: propylene glycol (PG), diethylene glycol (DEG), triethylene glycol (TEG), and trimethylolethane (TME) (*1*).

Cox (*2*) summarized much of the work on the biodegradation of glycols and emphasized the use of indirect methods including biological oxygen demand (BOD), chemical oxygen demand (COD), manometry, and turbidity as indices of biodegradibility. Fincher and Payne (*3*) studied the degradation of PG, DEG, and TEG as sole carbon sources by using turbidity and manometry as evidence for growth. Haines and Alexander (*4*) investigated the biodegradation of DEG and TEG by using BOD as evidence of decomposition. Kawai et al. (*5*) reported tetraethylene glycol (10 000 ppm, μg/mL) to be biodegradable; metabolites were identified by gas chromatography/mass spectroscopy (GC/MS) after isolation by column chromatography, chloroform extraction, and derivatization (silylation), Jenkins et al. (*6*) showed 1000-ppm solutions of DEG and TEG to be biodegradable by using measurements of total organic carbon (TOC) and turbidity. These results were confirmed by gas chromatography (GC) after extraction and derivatization of the residual glycols. Shumilov et al. (*7*) used GC to determine the concentration of DEG and TEG between 600 and 2000 ppm in waste waters.

Alternative methods for analysis of glycols have also received attention. Oxidation of glycols to aldehydes followed by derivatization using 3-methylbenzothiazol-2-one hydrazone hydrochloride was developed to analyze for DEG and TEG (*8*). Ponder (*9*) employed direct injection of hydrolysates, which contained DEG down to 500 ppm, into a GC equipped with a thermal conductivity detector.

It is the purpose of this work to assess the biodegradability of the four glycols derived from the biological transformation of the corresponding nitrate esters. Detailed study of the biodegradation of glycols at low concentrations in aqueous solutions has not been investigated because of the lack of a suitable analytical method for direct determination of the substrates in the low-ppm range. In this connection, a GC method for the direct analysis of the four glycols of interest has been developed, which allows their determination in the low-ppm range from aqueous media.

PG, DEG, and TEG present minimal toxicological problems (*10*) and no carcinogenicity hazard. PG is the least toxic of the glycols and is commonly used in the pharmaceutical, cosmetic, and food industries. DEG and TEG are slightly toxic; repeated large doses are needed for the appearance of toxic effects (*10*). An estimate of the biohazard caused by the release of residual amounts of TME was obtained by determination of its mutagenic properties in the Ames test.

Experimental Section

Media. Basal salts medium consisted of 3.0 g of $NH_4H_2PO_4$, 1.25 g of K_2HPO_4, 0.75 g of KH_2PO_4, 0.2 g of $MgSO_4 \cdot 7H_2O$, 0.01 g of $CaCl_2$, and 0.01 g of NaCl per liter of distilled water adjusted to pH 7.0. Glucose was added at 1.0 g/L as indicated. The nutrient broth concentration was 4.0 g/L. The viscous nature of PG, DEG, and TEG required the preparation of initial solutions of 1000 ppm by weight, which were diluted to 100 ppm in the culture media for improved accuracy.

Sterile control flasks with the individual glycols in distilled water were filter sterilized by using a 0.2-μm membrane filter, PG and DEG (Baker grade) and TEG (practical grade) were purchased from J. T. Baker Chemical Co., Phillipsburg, NJ. TME (technical grade) was purchased

from Aldrich Chemical Co., Milwaukee, WI.

Culture Conditions. Aerobic batch cultures were incubated in 250-mL Erlenmeyer flasks containing 100 mL of media at 30 °C on an orbital shaker at 225 rpm. Anaerobic (unaerated) batch cultures were incubated at 37 °C in 250-mL Erlenmeyer flasks filled with media and loosely sealed.

Inocula. Aerobic nutrient broth cultures were inoculated with activated sludge from the Marlborough Easterly sewage treatment plant (Marlborough, MA), and anaerobic broth cultures were inoculated with anaerobic digest from the Nut Island sewage treatment plant (Boston, MA). Individual flasks contained 50 ppm of a glycol. Cell growth was harvested after 2 days. The cell mass was collected at 12 000 rpm on a Sorvall RC-5 centrifuge and washed three times with 0.85% KCl. These cells were used to inoculate corresponding flasks for biodegradation studies.

Lyophilization. Lyophilization was performed on 1000-ppm solutions of the four glycols. PG and DEG were resuspended in ether and TEG and TME in benzene. Residual glycols were derivatized with *N*-(trimethylsilyl)imidazole and injected into a Bendix Model 2500 gas chromatograph equipped with a flame ionization detector and a 183 cm × 0.64 cm stainless steel column packed with 5% OV1 on chromasorb W, 100–200 mesh. Nitrogen carrier gas flowed at 30 mL/min, and the detector and injector were at 225 °C. The column temperature was 100 °C for PG, DEG, and TME and 125 °C for TEG.

Gas Chromatography. Analyses of PG, DEG, and TEG were performed on a Perkin-Elmer Sigma 3B gas chromatograph equipped with a flame ionization detector and a Model 1021A electronic noise filter (Spectrum Scientific Corp.). Nitrogen carrier gas flowed at 25 or 30 mL/min through stainless steel columns, 46 cm × 0.32 cm packed with Poropak Super Q for PG and DEG and 51 cm × 0.32 cm packed with Poropak PS for TEG. Injection, oven, and detector temperatures were 185, 160, and 200 °C for PG, 250, 210, and 250 °C for DEG, and 250, 190, and 250 °C for TEG. Injection volumes were 1 or 2 μL. Analysis of TME was performed on a Bendix Model 2500 gas chromatograph equipped with a flame ionization detector and a glass column (183 cm × 0.64 cm) packed with Tenax GC, 80–100 mesh. Injection port and column were at 270 °C, and the detector was at 300 °C. Injection volumes were 5 μL, and nitrogen carrier gas flowed at 30 mL/min. TME was also analyzed on a Hewlett-Packard 5840 gas chromatograph under similar conditions except the Tenax column was 305 cm long and the carrier gas flowed at 15 mL/min. Detection limits were 3, 1.5, 10, and 3 ppm for PG, DEG, TEG, and TME respectively.

Mass Spectroscopy. Gas chromatographic mass spectral data were obtained on a Finnigan 4000 operating in the EI mode. Mixtures of the four compounds in methanol were separated by gas chromatography with a helium flow at 8 mL/min through an OV-17 (15.2 m × 0.05 cm) SCOT column. Injection port and feed lines were at 225 °C, and the oven temperature was programmed from 60 to 85 °C at 12 °C/min and then 85 to 200 °C at 20 °C/min.

The spectrometer scanned from m/z 17 to 160 at 3 ms/amu at 4 s/scan. The ionization energy was 70 eV, the source temperature 220 °C, and the emission current 300 μA.

Separations were also achieved with a Dexil (15.2 m × 0.05 cm) SCOT column with injection and feed lines at 250 °C, the oven programmed from 60 to 260 °C at 8 °C/min and a helium flow rate of 5 mL/min. However, TME and TEG were poorly resolved under these conditions.

Table I. Precision and Accuracy Data

compd	accuracy[a] × 10^{-3}	std error of estimate
PG[b]	2.41	0.12
DEG[c]	1.07	0.10
TEG[c]	1.37	0.12
TME[b]	−2.96	0.09

[a] Slope of regression line of the mean ratio of spiked distilled water vs. spiked salts or nutrient broth. [b] Spiked in 4 g/L nutrient broth. [c] Spiked in basal salts.

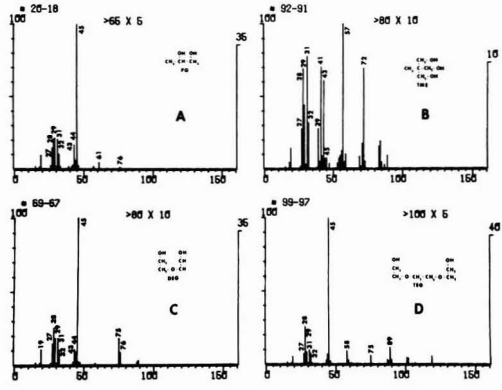

Figure 1. EI mass spectra of (A) PG, (B) TME, (C) DEG, and (D) TEG.

Mutagenicity Testing. A screening test for mutagenicity was performed with TME according to the standard procedures described by Ames (*11*, *12*). Five strains of *Salmonella typhimurium* (TA 98, TA 100, TA 1535, TA 1537, TA 1538) were used to test TME at concentrations ranging from 5 to 5000 μg/plate with and without metabolic activation.

Results

The precision and accuracy data for the method are presented in Table I. Figure 1 illustrates the fragmentation patterns for the four compounds; the major ions are labeled. The most prominent ions are 45, 45, 45 and 57; the most distinguishing ions are 61, 57 or 72, 75, and 58 (>75) for PG, TME, DEG, and TEG, respectively. Only the PG parent ion (m/z 76) is present under these conditions. The compounds eluted in the order PG first, then DEG, TME, and TEG, successively. Lyophilization and analysis of 1000-ppm solutions indicated a <1%, 4%, 24%, and 88% recovery of PG, DEG, TEG, and TME, respectively, as determined after derivatization and quantitation by GC. These solutions are 10-fold higher concentrations than those used in biological studies.

At initial concentrations of 100 ppm, PG rapidly disappears from culture flasks under both aerobic and anaerobic conditions, even as the sole carbon source (Figure 2). Some PG disappeared from the sterile controls. After 9 days, 8% and 16% of the PG was lost in sterile anaerobic and aerobic cultures, respectively. In active cultures, PG was not detectable after 2 days in aerobic nutrient broth. In basal salts supplemented with glucose, PG was undetectable after 4 days in aerobic and anaerobic cultures. As the sole carbon source, PG disappeared after 4 days under aerobic and 9 days under anaerobic conditions.

DEG was degraded under both aerobic and anaerobic conditions, but the decomposition appears to be nonbio-

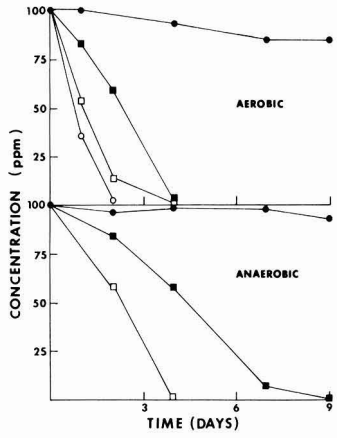

Figure 2. Decomposition of PG under aerobic and anerobic conditions: filter sterilized distilled water (●), nutrient broth (○), basal salts (■), and basal salts with glucose (□).

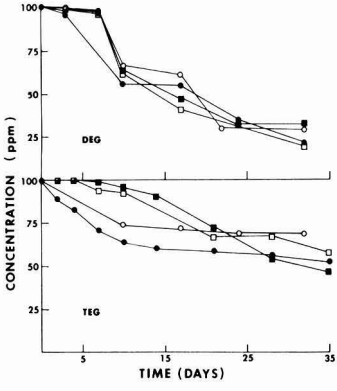

Figure 3. Decomposition of DEG and TEG in filter sterilized distilled water (●), aerobic nutrient broth (○), anaerobic basal salts (■), and anaerobic basal salts with glucose (□).

logical. The disappearance of the substrate in the sterile control (70–80%) was similar to that of the substrate in the inoculated cultures for a period of 32 days (Figure 3). The rate of disappearance was independent of culture media, as similar results were obtained whether nutrient broth, basal salts, or distilled water were used.

The pattern of TEG decomposition was similar to that of DEG (Figure 3), the major difference being the rate of disappearance. TEG was also nonbiologically transformed; after 35 days about 50% of the TEG remained, both in the sterile control and in the inoculated media, whether incubated aerobically or anaerobically.

TME was stable under the conditions tested and showed no evidence of chemical or physical instability during the 34 days. Microbiological results were variable but indicated at best only very slow rates of decomposition.

TME produced no toxic effects in the five *Salmonella* strains, up to 5000 μg/plate, and was negative as a potential mutagen in the Ames test. Toxicity would have been indicated by a decrease in background mutation rate.

Discussion

The low recovery of three of the four glycols by lyophilization illustrates the difficulty in attempting to extract glycols from aqueous solutions by conventional methods. Jenkins et al. (*6*) recovered 52% and 62% of DEG and TEG by rotary evaporation followed by chloroform extraction of residual solids, and much lower (<5%) recoveries were obtained by direct extraction with chloroform from solutions saturated with various salts. Similarly, derivatization using silylating agents for GC analysis (*13*) requires a nonaqueous preparation. Therefore, quantitative extraction of glycols from aqueous solution is extremely difficult.

In this work we successfully detected glycols in aqueous solutions in the low-ppm range. This was accomplished by direct injection into a GC without extraction or concentration steps for sample preparation. Quantitative analysis was successfully performed on samples containing glycols subjected to microbial activity. We have reported on the biodegradability of four glycols.

PG is relatively stable to nonbiological forces at low concentrations in aqueous solutions. Microbial decomposition occurs in rich media and as the sole carbon source. DEG and TEG decompose nonbiologically. No peaks other than the parent peaks were evidence by GC. Therefore, the fragments formed during the decomposition either were amenable to microbial degradation, subject to further nonbiological degradation, or were not detectable by the analytical method used. Cox (*2*) stressed the potential importance of chemical instability of polyethylene glycols, including factors of heat, peroxide, and acid contaminants formed during their production.

Relative rates of disappearance of the parent compounds indicate a sequence of PG > DEG > TEG > TME from high to low. This agrees with other reports where rates of biodegradation decrease with increasing degree of polymerization (*2*), but the rate difference may be due to chemical/physical factors affecting rates of depolymerization and not due to microbial factors. Ames testing indicates TME may not pose potential mutagenicity problems.

With the exception of TME, these glycols will undergo degradation under conditions suitable to a biological treatment facility. Degradation occurs through a combination of biological and chemical activities which varies with each glycol.

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Calculation of Evaporative Emissions from Multicomponent Liquid Spills

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■ A theoretical formulation is presented that enables the calculation of the evaporation rates of individual compounds in a multicomponent liquid mixture, as a function of time from a spill. The calculation of evaporation rates is based on conventional mass transfer theory and the assumption of a well-mixed liquid phase. The total evaporation rate, the liquid-phase composition, and the gas-phase composition can all be explicitly calculated as a function of time from the spill. Comparison of the theoretical results with experimental data on oil spill evaporation showed good agreement.

Introduction

For calculation of the air quality impact of volatile liquid spills, knowledge of the time-dependent evaporative emission rate is a necessary input for air quality simulation models. In a multicomponent liquid spill, the evaporative emission rate for each individual compound, as well as the total evaporation rate, may have to be estimated. The emission rates of individual components are necessary as input for both photochemical air quality modeling, which requires emission rates by hydrocarbon species class (*1*), and modeling for toxicity, hazard, or odor impacts of individual compounds from oil spills or hazardous material spills. Several studies have shown that evaporation is the primary mechanism of low-carbon-number hydrocarbon loss in an oil spill (*2*, *3*).

A relatively simple theoretical formulation is presented to calculate individual evaporation rates in a multicomponent liquid spill based on conventional convective mass transfer theory. The necessary inputs for the calculation are (1) initial mass of spill, (2) initial liquid composition, (3) spill area, (4) ambient air temperature, (5) windspeed, and (6) atmospheric stability. The mass transfer coefficient is based on an empirical fit to a solution of the steady-state atmospheric diffusion equation with power-law vertical velocity and eddy diffusivity profiles. Because of the mass transfer formulation, the analysis applies primarily to liquids with boiling points higher than ambient temperatures and does not necessarily apply to spills of liquified gases, where evaporation may be limited by heat transfer.

Evaporation Theory

The problem is to derive an expression for the time-dependent evaporation rate in a multicomponent liquid system. Application of the standard mass transfer rate equation for evaporation (*4*) to each component, with the assumptions of an ideal solution, a well-mixed liquid phase, and negligible atmospheric concentrations yields

$$dn_i/dt = -kp_i^s n_i \tag{1}$$

where

$$k = k_G A/n_T \tag{2}$$

and where dn_i/dt is the loss rate of moles of liquid component i per unit time, p_i^s is the saturation (pure) vapor pressure of component i, k_G is the mass transfer coefficient (mol m^{-2} atm^{-1} h^{-1}), A is the liquid surface area (m^2), and n_T is the total moles of liquid.

The above formulation requires the further assumption that the ratio n_T/A remains approximately constant; thus, the coefficient, k, can be considered a modified mass transfer coefficient, with units of atm^{-1} h^{-1}. Equation 1 is essentially identical with that used by Harrison et al. (*5*) in their experimental study of oil spill evaporation, and it presents the intuitive explanation that the evaporation loss of a compound is proportional to its vapor pressure and the amount of the compound remaining. The assumption that n_T/A remains constant is more appropriate for spills on land or close to shore than on open water, because oil spills on open water normally increase in area with time.

The solution of eq 1 is very straightforward:

$$n_i = n_i^0 e^{-kp_i^s t} \tag{3}$$

where n_i^0 is the initial number of moles of liquid component i. Thus, for a one-component system, the evaporation rate expression is very simple.

For a multicomponent liquid system, the individual evaporation rates must be summed to obtain a total evaporation rate. Summing eq 3 over all compounds, taking a derivative to obtain a total emission rate (mass/time), and using Raoult's law yield

$$\frac{dm_T}{dt} = -km_T^0 \sum_{i=1}^{N} [x_i^0 p_i^s M_i e^{-kp_i^s t}] / \sum_{i=1}^{N} x_i^0 M_i \tag{4}$$

where dm_T/dt is the total evaporative emission rate (mass/time), m_T^0 is the total initial mass of evaporable liquid, N is the number of components, x_i^0 is the initial liquid mole fraction of component i, and M_i is the molecular weight of component i.

Similarly, combining eq 3 and Raoult's law and summing over all components yield

$$p_i = x_i^0 p_i^s e^{-kp_i^s t} / \sum_{i=1}^{N} x_i^0 e^{-kp_i^s t} \tag{5}$$

where p_i is the partial pressure of component i as a function of time.

Equations 4 and 5 define the total evaporation loss rate and vapor composition as a function of time from the spill. The initial mole fraction x_i^0 can be derived from a knowledge of the initial liquid phase composition or can be estimated from a known vapor-phase composition over the liquid by using Raoult's law. An excellent summary of evaporative hydrocarbon emissions from a variety of sources is presented by the U.S. Environmental Protection Agency (*6*).

The mass transfer coefficient, k_G, in eq 2 is theoretically a function of windspeed and atmospheric stability (*7–9*). Current formulations for k_G are based primarily on the work of Sutton (*7*), who solved the steady-state atmospheric diffusion equation over a liquid pool with a power-law vertical velocity profile and a corresponding power-law eddy diffusivity profile. His resulting expression for k_G as a function of wind velocity, atmospheric stability, and liquid pool dimension has been used by Mackay and Matsugu (*8*) and Fleischer (*9*) to model evaporation rates from liquid spills. Liss and Slater (*10*) derived an average

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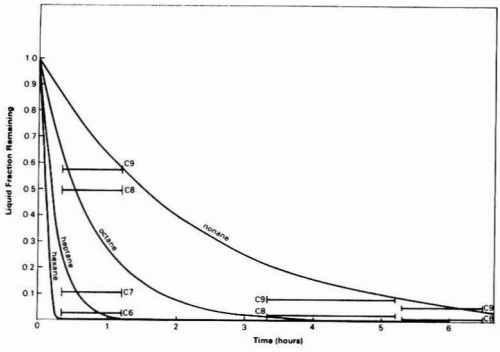

Figure 1. Comparison of single-component theoretical calculations (solid curves) with experimental data (horizontal bars) from a small oil spill (*3*). The experimental horizontal bars indicate the extent of time-averaged sample collection.

evaporation rate appropriate for the open sea surface but did not consider the effects of windspeed, stability, or liquid area.

The most detailed work has been that of Mackay and Matsugu (*8*), who used Sutton's theory for neutral atmospheric stability to analyze experimental cumene evaporation and formed the correlation

$$k_G = 0.0292u^{0.78}d_0^{-0.11}Sc^{-0.67}/(RT) \qquad (6)$$

where u is windspeed (m/h), d_0 is the spill equivalent diameter (m), Sc is the gas-phase Schmidt number (the ratio of kinematic viscosity to molecular diffusivity), R is the gas constant (8.206×10^{-5} atm m^3 mol^{-1} K^{-1}), and T is temperature (K). This expression can be easily used to calculate the modified mass transfer coefficient, k, in eq 4 and 5 during neutral stability conditions. Alternatively, k can be estimated empirically from experimental evaporation rates of individual compounds with eq 3.

Comparison of Theory with Experimental Data

For comparison with measured evaporation data, the theoretical analysis in eq 6 and 2 will be used to calculate a typical value of the modified mass transfer coefficient, k. With a windspeed of 5 m/s, an effective spill diameter of 100 m, a Schmidt number of 2.7, and a temperature of 20 °C, eq 6 results in a value of k_G = 780 mol m^{-2} atm^{-1} h^{-1}. To estimate an approximate value of n_T/A to use in eq 2, it will be assumed that a spill has a thickness of 0.001 m and the evaporable liquid has an average molecular weight of 134 g/mol and an average specific gravity of 0.6. These values result in n_T/A = 4.5 mol/m^2; Harrison et al. (*5*) used 5 mol/m^2 in the analysis of their experimental results. The resulting value of k, from eq 2, is about 170 atm^{-1} h^{-1}.

This value of k can be compared to measured evaporation rates of individual compounds from experimental oil spills, by using eq 3. Johnson et al. (*3*) present experimental data on the approximate evaporation rates of C_5–C_9 hydrocarbons in four actual oil spills on water. With the use of eq 3 and the appropriate vapor pressures, empirical values of k were derived. They ranged from 40 to 500 atm^{-1} h^{-1} (a typical value was 150 atm^{-1} h^{-1}). Somewhat higher values of k would be expected because of the relatively high windspeeds (4–14 m/s) during the experiments. Thus, empirical estimates for the modified mass transfer coefficient agree reasonably well with a theoretical calculation using eq 6 and 2. With the use of k = 150 atm^{-1} h^{-1}, the theoretical curves using eq 3 are compared with experimental data from one oil spill in Figure 1.

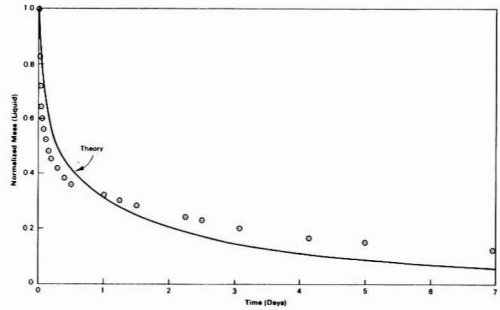

Figure 2. Comparison of multicomponent theoretical calculations (solid curve) with experimental data points (⊙) from long-term crude oil evaporation (*11*).

The multicomponent evaporation theory presented in eq 4 was compared with experimental data on crude oil evaporation in a wind tunnel. In these experiments, Matsugu (*11*) monitored the weight loss of crude oil over time periods of several days. Data points from Figure 22 of Matsugu (*11*) are reproduced in Figure 2 (with the assumption that 50% of the total weight of the oil was evaporable); these data were taken at 20 °C and a windspeed of 4.1 m/s. The experimental conditions resulted in a calculated value of k = 35 atm^{-1} h^{-1}, assuming an evaporable oil mass of 250 g and an average molecular weight of 130 g/mol. The initial liquid composition, although not stated, was assumed to be the average crude oil composition derived from the gas-phase composition presented in Kilgren and Hecht (*12*). From eq 4, the calculated evaporation loss is compared with the experimental data in Figure 2 and shows reasonably good agreement. The theory overpredicts evaporation after a few days, probably because the remaining oil becomes too viscous for the well-mixed assumption to apply.

Conclusions

A relatively simple theoretical formulation has been presented to calculate the time-dependent evaporation rates of individual components in a multicomponent liquid spill. Equations have been derived to calculate the total evaporation rate, the liquid-phase composition, and the gas-phase composition as a function of time from a spill. So that this theoretical formulation can be used in air quality simulation models, the total emission rate (eq 4) is multiplied by the gas mole fraction (eq 5) for the particular compounds of interest. This results in the time-dependent evaporative emission rate of a particular compound in a multicomponent liquid spill, for use in a toxicity, hazard, or air quality impact evaluation.

Acknowledgments

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Coal Gasification Solid Wastes: Physicochemical Characterization

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■ Physicochemical and morphological characteristics of coal gasification solid wastes produced by three different processes were investigated to assess the potential environmental impacts of disposal of these wastes. The wastes were composed of either calcic or ferruginous aluminosilicate glass with small amounts (1–7%) of magnetic particles. The calcic waste had relatively clean surfaces and a homogeneous matrix composition. The magnetic fraction of the waste was composed of metallic iron particles. The ferruginous wastes were occasionally covered by iron oxide or sulfide coatings. Magnetic particles in one ferruginous waste had immiscible iron oxide and sulfide phases in a silicate matrix. The magnetic fraction of the other waste was composed of iron sulfide particles. Some chalcophile elements displayed an association with the surface coatings and magnetic fractions. The gasification solid wastes were different from each other in almost every aspect as they represent products from extremely diverse process conditions.

Coal conversion technologies are being developed to utilize relatively abundant coal resources for the production of synthetic gas and liquid fuel. Evaluation of the technical, economic, and environmental viability of near commercial-scale gasification demonstration plants is in progress (*1*). Commercial gasification plants will consume vast amounts of coal and produce large volumes of solid wastes, the disposal of which could lead to health, environmental, and land-use problems (*2*). As part of the initial effort to assess the effects of solid waste disposal on the environment, the physicochemical characteristics of the wastes produced by three different pilot plants were investigated.

Experimental Methods

Gasification solid wastes (ash or slag) were obtained from three pilot plants that employed extremely diverse process conditions in terms of process pressure, temperature, redox condition, and reactor-bed type. The name of each individual process waste was coded as waste A, B, and C, because of the proprietary nature of the processes. Waste A was produced by a process using a high-pressure fixed-bed gasifier designed to provide low outlet gas temperature and to maintain the operating temperatures above the melting point of the coal ash at the bottom of the gasifier. As an ash-fluxing agent, crushed limestone was added to remove the ash as a molten slag. Waste B was a bottom ash of a process using a multistage fluidized-bed gasifier. After a series of pyrolysis and gasification stages, the solid waste was produced by a slagging combustor designed to utilized carbon in the residual char as a heat source for the process. The process producing waste C used an entrained-bed type gasifier. This type of gasifier is operated at high temperature with short residence time. The gasifier can process both finely pulverized coal and mineral slurry which contains significant amounts of residual carbon. Wastes collected from each gasifier were water quenched. The pilot gasification plants used Pittsburgh No. 8 (waste A), Illinois No. 5 and 6 (waste B), and Kentucky No. 9/14 (waste C) coal.

About 10 kg of solid wastes from each pilot plant were air-dried for characterization. The samples were mixed thoroughly and quartered. Scoopfuls were taken from each quarter until desired amounts were collected for the different analyses. Duplicate samples were collected for each analysis, and average values for the duplicates are presented in Table I. Physical properties such as bulk density, particle density, and particle size distribution were determined by standard methods (*3*). Ferromagnetic particles in the waste were separated by a horseshoe magnet. Morphology of the wastes was examined by scanning electron microscopy (SEM), and qualitative chemical composition of the surface and the cross-section surfaces of particles was determined by an energy-dispersive X-ray analyzer (EDX) attached to the SEM. A part of the bulk samples and magnetically separated fractions was ground with an agate mortar and used for X-ray diffraction (XRD) and neutron activation analysis (NAA). After acid dissolution of ground samples, selected elements were analyzed by atomic absorption and/or argon plasma atomic emission spectroscopy. Total sulfur and carbon contents were determined with an automatic LECO titrator and carbon combustion train analyzer, respectively.

Results and Discussion

The gasification wastes were composed of grey to brownish-black particles with a wide range of shapes and sizes. The mean particle size of waste A was 1.1 mm, and about 70% of the particles were between 0.5 and 2 mm in diameter. Waste B had the largest mean particle size (4.3 mm), and about 87% of the waste was composed of particle

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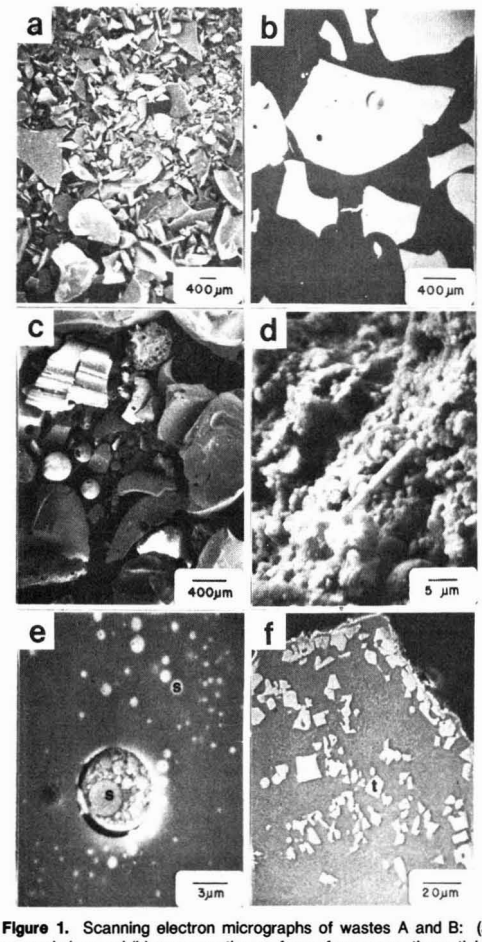

Figure 1. Scanning electron micrographs of wastes A and B: (a) general view and (b) cross-section surface of nonmagnetic particles of waste A; (c) general view, (d) surface coating, (e) iron sulfide inclusion, and (f) iron oxide inclusion of waste B.

sizes between 2 and 9.5 mm. Waste C was the finest of the three wastes, with the dominant sizes from 0.05 to 2 mm and a mean particle size of 0.6 mm. particle densities of the wastes were in the range of common silicate minerals (2.5–2.8 g/cm^3), and the bulk densities ranged from 1.4 to 1.7 g/cm^3. The texture of the wastes was much coarser than that of fly ashes produced by conventional coal combustion plants (*4*).

Waste A was composed of sharp-edged platy and blocky glass, and the surface of the glass was fairly clean and smooth (Figure 1a). The SEM–EDX analysis of the cross-section surface of nonmagnetic slag indicated that the matrix was relatively homogeneous calcic aluminosilicate. No evidence of phase separation was observed in the matrix (Figure 1b). About 1% of the waste by weight was magnetic particles having a metallic silver color and spherical shape appearing to be metallic iron. The mechanism of the metallic iron formation is not known with certainty, but the abundance of gas voids in the particles suggests that the iron particles would be formed by the reduction of iron-bearing sulfides and carbonates. XRD analysis of the waste did not reveal the presence of crystalline minerals.

The morphology of waste B was more complex than that of waste A. It was composed of relatively large, angular

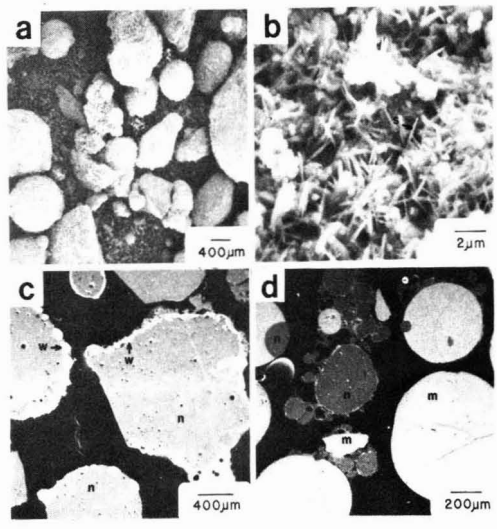

Figure 2. Scanning electron micrographs of waste C: (a) general view; (b) iron hydroxide formation on surface; (c) cross-section surface of nonmagnetic fraction; (d) cross-section surface of magnetic fraction.

blocky particles as a dominant component with smaller quantities of spherical, porous, and elongated particles (Figure 1c). The surface of the blocky particles was fairly clean, but the surfaces of the spherical and porous particles were frequently covered with powdery or crusty coatings (Figure 1d). The matrix of the waste was ferruginous aluminosilicate glass, and no phase separation was evident in the cross-section surface of nonmagnetic particles. Varying sizes of spherical and angular inclusions were, however, observed from the cross-section surface of magnetic particles, which comprised about 5% of the waste. The spherical inclusions and plerosphere-containing microspheres (marked s in Figure 1e) in the spherical particles were composed of iron and sulfur, and the angular inclusions (marked t in Figure 1f) in the blocky particles were composed of iron with chromium impurity. The XRD analysis identified the iron phase as ferromagnetic maghemite (γ-Fe_2O_3) from the 2.51-, 2.94-, and 2.03-Å diagnostic peaks. Although the XRD was unable to identify the iron sulfide phase, it was suspected to be ferromagnetic pyrrhotite.

Waste C was composed of about 30% large blocky particles and 70% smaller spherical particles. Aggregates of smaller particles were also common in the waste (Figure 2a). The surface of blocky particles was relatively clean, but the surface of spherical particles was extensively covered with crusty coatings. The SEM–EDX analysis showed that the coatings on the nonmagnetic particles (marked w in Figure 2c) were composed of iron and sulfur with varying intensity ratios. The blisterlike iron sulfide phase was probably formed by a diffusion of saturated iron sulfide as solidification of the melt progressed. On the other hand, the sparse sulfide coatings on the blocky particles appear to have formed after solidification of the glass phase. The magnetic fraction, about 7% of the waste, was a mixture of magnetic particles (marked m) and aggregated nonmagnetic particles (marked n) associated with magnetic particles (Figure 2d). A silicate-glass phase also occurred in the magnetic iron sulfide particles.

The XRD analysis of the nonmagnetic fraction in the waste C did not show crystalline mineral peaks, but the magnetic fraction showed strong 2.98-, 2.65-, and 2.09-Å

Table I. Chemical Composition of Whole Sample and Ferromagnetic Fraction of Gasification Solid Wastes

element	waste A whole waste	waste A magnetic fraction	waste B whole waste	waste B magnetic fraction	waste C whole waste	waste C magnetic fraction
			Major Elements (%)			
Al	8.8	0.4	10.1	10.2	8.8	6.3
Ca	18.5	0.8	2.9	2.7	2.2	1.4
Fe	3.8	89.6	13.4	14.1	17.2	34.1
K	0.6	<0.1	1.5	1.3	1.4	0.9
Mg	4.9	0.2	0.8	0.7	0.5	0.3
Na	0.3	<0.1	1.8	1.6	0.2	0.1
Ti	0.5	<0.1	0.6	0.5	0.6	0.4
Si	17.9	*a*	22.5	20.4	20.1	13.7
S	0.4	*a*	0.3	0.8	3.8	11.8
C	1.0	*a*	1.8	*a*	1.7	*a*
			Trace Elements (μg/g)			
Ag	1	*a*	<1	<1	<1	1
B	287	35	1302	1153	591	335
Ba	655	35	454	427	531	219
Be	10	<1	18	20	13	9
Cd	1	91	1	*a*	2	*a*
Ce	147	1	85	94	26	53
Co	7	765	137	140	34	117
Cr	78	93	386	360	643	435
Cu	30	1032	62	120	94	322
Li	86	6	81	69	64	38
Mn	3987	369	425	450	293	228
Mo	4	263	19	38	73	273
Ni	73	2516	254	348	150	488
P	467	9183	276	333	436	360
Sc	30	*a*	24	20	19	13
Sr	520	25	503	448	182	120
Th	29	1	16	20	16	15
V	154	61	237	220	450	408
Y	55	4	54	46	41	31
Zn	8	101	66	103	96	97
Zr	192	*a*	197	173	170	105

[a] Not determined.

peaks of pyrrhotite ($Fe_{1-x}S$) and very weak 6.24-, 3.29-, and 1.93-Å peaks of lepidocrocite (γ-FeOOH). The rod-shaped iron oxide mineral (marked s in Figure 2b) observed on the surface of magnetic particles could be lepidocrocite particles indicated by the XRD analysis. Pyrrhotite was probably formed from pyrite (FeS_2) by gradual reduction of sulfur during the process, and lepidocrocite was formed from the pyrrhotite by oxidation and hydration processes that occurred during storage.

The data in Table I show the average elemental composition of the whole samples and magnetic fractions of the wastes. The difference between duplicate analyses were less than 15% of the average values for most elements, but the differences increased up to 80% for the trace elements of which concentrations were less than 100 μg/g. Even wider variances of composition is expected among the samples produced under different test-run conditions for each process. The data presented, therefore, must be used with great care. In waste A, limestone flux added to the feed coal enriched Ca, Mg, and Mn concentrations but diluted the concentration of other major and minor elements contributed by the coal. About 90% of the magnetic fraction was elemental iron rather than iron oxide. These metallic iron particles were enriched in Cd, Co, Cu, Mo, Ni, P, and Zn compared to Ca-rich aluminosilicate particles.

Waste B was Fe-rich aluminosilicate, with most elements being derived from the feed coal. Boron content was significantly higher than in the other wastes (Table I). Only small differences in elemental composition between the whole sample and the magnetic fraction were noticed, which was expected, because the matrix composition of magnetic particles was very similar to the composition of the nonmagnetic particles. Compared with the whole sample, the magnetic fraction was slightly enriched with Cu, Fe, Mo, Ni, S, and Zn. The relationship between matrix composition and iron phases in the magnetic particles is not known, but the cooling history of individual molten particles would be a principal factor controlling the crystalline phases in the waste particles.

The elemental composition of waste C was comparable to that of waste B, except that Fe and S contents were significantly higher in waste C (Table I). As expected from the SEM–EDX results, the composition of the magnetic fraction was dramatically different from that of the whole sample. The concentrations of Fe and S among major elements and Co, Cu, Mo, and Ni among trace elements were significantly higher in the magnetic fraction. However, the analyses showed that about 50% of the magnetic fraction was nonmagnetic ferruginous aluminosilicate particles aggregated with the pyrrhotite particles (Figure 2d). Therefore, the concentration of the trace elements (Co, Cu, Mo, and Ni), which were frequently associated with the iron sulfide phase, would be even higher if one could remove the aluminosilicate particles from the magnetic fraction. Alkali, alkaline earth, and several other (B, Th, V, Y, Zr) elements were more concentrated in the whole wastes than in the magnetic fractions (Table I).

Conclusions

The results of physicochemical characterization indicate that the surface morphology, elemental composition and distribution, and crystallization of the solid wastes were controlled largely by the process conditions of the gasification pilot plants. There were some differences in chemical composition among the feed coals (umpublished data), but such differences are expected to contribute only a small part to the large differences observed among the wastes. For example, the limestone flux used in the process producing waste A diluted the concentration of major and trace elements originating from feed coal and produced chemically homogeneous calcic silicate glass. In wastes B and C, the iron contents relative to the other major elements were noticeably higher than in the ashes produced by coal combustion (*5*). Waste C also had considerable amounts of sulfur as iron sulfide and probably in part as sulfate and elemental sulfur. The calcic and ferruginous nature of the gasification wastes might be disadvantageous as compared with a silicious waste with respect to long-term weathering, particularly under acidic conditions. The iron- and sulfur-rich wastes produce acidic leachates which influence the solubility of most trace elements.

The trace element concentrations in the gasification wastes (Table I) were not significantly different from the average values in fly and bottom ashes generated by coal combustion power plants (*6*). However, the Co, Cu, Mo, and Ni contents were considerably higher in the magnetic fractions of wastes A and C than in fly ashes. The effects of the magnetic fractions should be further examined in terms of environmental impacts as well as recoverable metal resources. The surface coatings of iron oxide and sulfide appeared to have higher concentrations of trace elements than the silicate matrix, as was indicated by the presence of a Ni spectrum of the surface coating's SEM–EDX spectra. Such coatings were observed only occasionally in the waste B but somewhat more frequently in the waste C. The enrichment of trace elements was not detected on the surface of blocky aluminosilicate glass particles in the wastes.

The differences of morphological and physicochemical characteristics of the wastes will play an important role in long-term leaching of trace elements from the wastes after disposal, as seen from a short-term leaching experiment (7). Although the differences among the wastes are considerable, in a broad sense they are closer to bottom ashes than fly ashes produced by conventional coal power plants.

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CORRESPONDENCE

Comment on "Desorption Kinetics of Carbon Tetrachloride from Activated Carbon"

SIR: A recent paper by Jonas and Sansone (*1*) contains a number of serious errors. The errors can be broadly stated as follows: (1) an incorrectly derived basic equation was used in treating the data; (2) an erroneous rate model was used; (3) sample size was inadequate to eliminate flow maldistribution.

The desorption "kinetics" are purportedly described by an equation due to Wheeler (*2*). The reference cited is a government contract report of 16 years ago. The derivation has never appeared in the refereed literature. The Wheeler adsorption equation (*3*) is an asymptotic constant pattern solution that has been derived over the years by many other workers (*4*, *5*). The constant pattern or constant adsorption wave velocity is necessary to reduce the original system's partial differential equations to ordinary ones. The derivation of the Wheeler desorption equation *assumes by analogy* that a constant velocity wave is also obtained in desorption. However, Cooney and Lightfoot (*6*) have shown that constant pattern solutions will exist for *either* a saturation or elution process *but not for both*. If the equilibrium isotherm is favorable (type I or convex upward), a constant velocity wave can be obtained. An isotherm favorable in adsorption must be unfavorable in desorption, precluding the formation of a constant velocity desorption wave, as *assumed without proof* by Wheeler. It is also incorrect to apply *any* constant pattern solution to beds with nonuniform initial bed loading. Uniform bed preloading was explicitly assumed in Wheeler's desorption equation (*2*). Nonuniform initial bed adsorption requires solution of the original partial differential equations.

The rate model used by the authors is also erroneous. Physical adsorption with a "pseudo-first-order rate constant" was assumed. It has been well established that physical adsorption rates are important only for very small particle sizes or special cases where the adsorption rate is much smaller than normal due to steric or other unusual effects (*7*). Mass transfer by diffusion, both internal and external, is generally the rate-controlling process.

In other work (*8*) these same authors have found their "rate constants" to be a function of particle size and external flow velocity. Mass transfer is a distributed process and must be dependent on particle size. Adsorption is a point process and should be independent of particle size and flow external to the particle.

It is necessary in getting an analytical solution to a constant pattern differential equation to use a simple rate term. The solutions obtained by various workers with a linear rate function frequently conform well to experimental data for adsorption. However, this agreement is due to the mass transfer processes being approximately linear in the fluid concentration of the adsorbing species. The linearity of external mass transfer is an excellent and widely recognized approximation. It is perhaps not so widely known that internal diffusion also may often be approximately linear in a driving force involving the different of outer particle radius and average concentrations (see the appendix of ref 9).

The dependence of the observed rate parameter on bulk fluid velocity indicates the participation of external mass transfer. The dependence on particle size shows that external and/or internal mass transfer may be important. In any case, the net result *can be* an approximate linear dependence of the rate function on concentration. In some cases or experimental regimes the overall mass transfer rate may not be linear in concentration. In both adsorption and desorption, the authors reject data points that do not

fit their equations with a linear rate function. "Higher order kinetic regimes" are invoked to explain the departure. But no *independent* considerations are given for such a rejection.

Even if the authors' rate model and integrated column equation were correct, they err in using only bed exit conditions to judge application of their model. The breakthrough or bed exit concentration is a function of all previous fluid and adsorbent concentrations for the entire elapsed time. This situation is true regardless of whether the rate (dispersion) processes are of the point or distributed type. Whatever rate model is used must apply to the whole range of column conditions.

Finally, the dimensions of the carbon bed are too small for the particle size used. Cohen and Metzner (*10*) have recently shown that the column to particle diameter (CPD) ratio must be at least 30 to reduce flow nonuniformity errors to less than other errors. For Newtonian fluids, a CPD ratio of less than 30 results in appreciably greater flow near the column walls. This flow maldistribution is due to the small variations in bed porosity across the column.

From the authors' own figures of volumetric flow rate of 285 cm^3/min, superficial linear velocity of 323 cm/min, and mean particle diameter of 0.268 cm, a CPD ratio of 3.95 is found. The flow maldistribution error for a CPD value of 4 is too large to estimate from ref 10. Of course, there may be some compensation of errors in some circumstances. All such potential problems can be avoided by using adequate adsorbent bed diameters. For gas-phase work with commercially used sizes of activated carbon, this means column diameters of 8–10 cm.

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SIR: Wilde suggests that our desorption paper (*1*) is based on an incorrectly derived equation, an erroneous rate model, and a sample size inadequate to eliminate flow maldistribution. We believe he is mistaken on all counts.

In 1964, Wheeler derived an equation for adsorption kinetics from a continuity equation of mass balance per unit area (*2*). The derivation appears elsewhere (*3*, *4*) and is also available from us. The form was similar to that obtained by Bohart and Adams (*5*), Short and Pierce (*6*), and Klotz (*7*). The innovative feature of Wheeler's equation was the inclusion of a pseudo-first-order rate constant for adsorption, with units of reciprocal time, in the critical bed portion of the equation. Wheeler's derivation begins with four differential equations that require simultaneous solution and includes the concept of a constant velocity wave in the carbon bed. By selection of particular adsorption conditions, viz., on the plateau of a type 1 isotherm, past the linear portion, where the adsorption capacity is no longer dependent upon inlet concentration and exit concentration is much smaller than inlet concentration, the four differential equations were reduced to one that could be solved analytically. Without imposing these conditions, asymptotic solutions for the entire exit concentration vs. time curve have been obtained by Rosen (*8*), Masamune and Smith (*9*, *10*), and Schneider and Smith (*11*).

In studying the kinetics of desorption, Wheeler (*2*) considered the desorption curve (desorbing concentration as a function of time) to be a mirror image of the sigmoidally shaped adsorption curve and used four transformation equations to relate the adsorption and desorption equations. The equation Wheeler derived was eq 1 in our paper (*1*). The derivation is available from us.

The work of Cooney and Lightfoot (*12*) cited by Wilde is not applicable to the Wheeler adsorption and desorption equations, which are kinetic and in which exit concentration depends upon bed depth and time. Cooney and Lightfoot state that "x and y [dimensionless concentrations] can be expressed entirely as functions of the single distance variable z^* and independently of time, provided that t is very large".

The mirror image concept of adsorption–desorption can be visualized by the respective sigmoidal–antisigmoidal shapes of the concentration vs. time curves. In the adsorption cycle, the adsorption rate constant displays pseudo-first-order kinetics with respect to the decrease in gas molecules; in the desorption cycle, the desorption rate constant displays pseudo-first-order kinetics with respect to the reappearance (or regeneration) of active sites. In our experimental desorption tests we determined the maximum desorption rate from the carbon by waiting until the adsorption–desorption–adsorption wave had concentrated the adsorbed vapor at the exit of the bed. Thus, comments regarding elution processes or nonuniform initial bed loading are not applicable.

Physical adsorption can be considered to be second order in kinetics, involving the reaction between an active site and a free vapor molecule (*9*, *13*). However, when the rate of change of gas molecules is much greater than that of active sites (active sites $\gg$ gas molecules), the reaction is pseudo first order with respect to gas molecules. Likewise, when the rate of change (appearance or regeneration) of active sites is much greater than that of gas molecules (gas molecules $\gg$ active sites), the reaction is pseudo first order with respect to active sites. A rigorous derivation of pseudo-first-order kinetics reactions for generalized gas adsorption is available from us.

Wilde's statement that "Mass transfer is a distributive process and must be dependent upon particle size" is not applicable to our conditions. Mass transfer would affect the overall rate *only* if external diffusion itself, or in combination with another mechanism, were rate controlling. In our studies we have found internal or intraparticle diffusion to be rate controlling. Thus, if the total adsorption process were conceived to consist of the sequence

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(1) external diffusion (mass transfer), (2) internal diffusion, and (3) adsorption at the site (*9*, *11*, *14*), then the internal diffusion rate would control the overall adsorption rate constant. Our finding that internal diffusion controls the overall adsorption rate constant is in consonance with Masamune and Smith's conclusion, from their study of nitrogen adsorption rates, that surface adsorption was very rapid compared with intraparticle diffusion (internal diffusion) for spherical particles larger than 0.02 cm diameter (*9*).

In dynamic flow testing of packed beds, maintenance of the proper column to particle diameter ratio is not the only requirement for satisfactory contact of the gas–air stream with the gross surfaces of the particles. Other important considerations in eliminating flow maldistribution are the porosity and tortuosity of the bed, the bed depth or volume, and the mean residence time of the gas in the bed. In our studies, the mean residence time ranged from 0.35 to 0.79 s, 900–2000 times longer than has been found necessary for this type of activated carbon to adsorb organic vapors in the molecular weight range 140–160 (*15*). The true measure, however, of a flow maldistribution can be seen in deviations from the expected linear dependence of breakthrough time t_b (in the range $0 < C_x/C_0 \leq 0.04$) on carbon weight W. If flow maldistribution exists, deviations in the t_b vs. W plot would occur mostly at the low W values, tending to show more rapid bed breakthrough, resulting in shorter t_b values and causing deviations from linearity. No deviations from linearity were observed in our tests.

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Another Comment on "Desorption Kinetics of Carbon Tetrachloride from Activated Carbon"

SIR: In a recent paper on "Desorption Kinetics of Carbon Tetrachloride from Activated Carbon" (*Environ. Sci. Technol.* **1981**, *15*, 1367–1369), the authors claim to have demonstrated "a more fundamental relationship between the theoretical equations of adsorption and desorption kinetics than had previously been supposed". This demonstration rests on the observation that the "log of the desorption rate constant was a linear function of the percentage saturation of the bed...."

The purpose of this letter is to question how fundamental and generally significant the observed relationship is. In this reader's opinion, any truly fundamental relationship between desorption rate and adsorbate loading ought to account explicitly for the adsorption equilibrium relation, as done by Grubner and Burgess in a paper in the same issue (*Ibid.* **1981**, *15*, 1346–1351). The paper under discussion does not treat the equilibrium relation in any way, nor are the properties of the equilibrium isotherm of the system studied (CCl_4/BC-AC activated carbon) mentioned in the paper. This omission seems a serious shortcoming. Moreover, the reference cited (ref 3) for the derivation of the kinetic expression is an unpublished progress report, which is scarcely available to the scientific community.

I invite the authors to comment on the sensitivity of their model to the form of the equilibrium isotherm (i.e., favorable or linear).

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SIR: Roberts has misinterpreted us. He states that "the authors claim to have demonstrated 'a more fundamental relationship'" and understands us to have put forward eq 6 as that fundamental relationship. However, we said that the result (i.e., the linearity of the relationship between log k_d and percent CCl_4 saturation) "suggests that a more fundamental relationship exists". We did not claim to have found it.

We do not plan to respond to Roberts' other points concerning adsorption equilibrium and derivation of the kinetic expression at this time, because we believe that they are made moot by the preceding paragraph.

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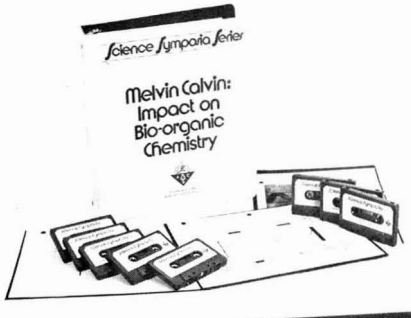

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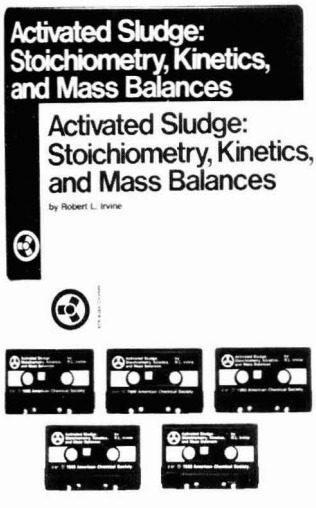

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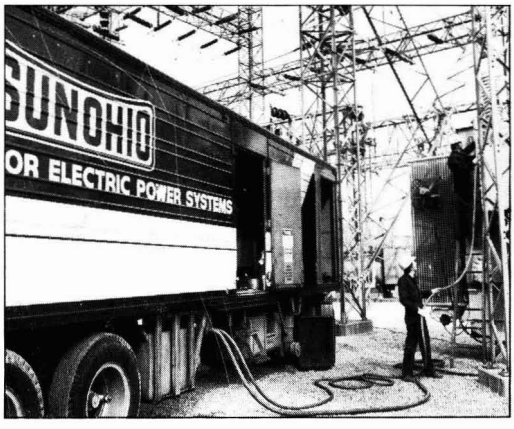

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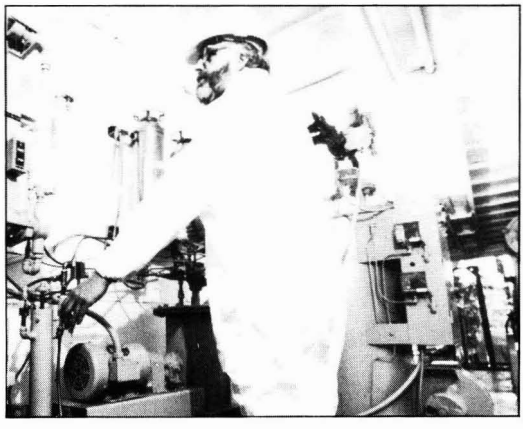

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