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ENVIRONMENTAL SCIENCE & TECHNOLOGY

ES&T

Tunable diode laser systems
352A

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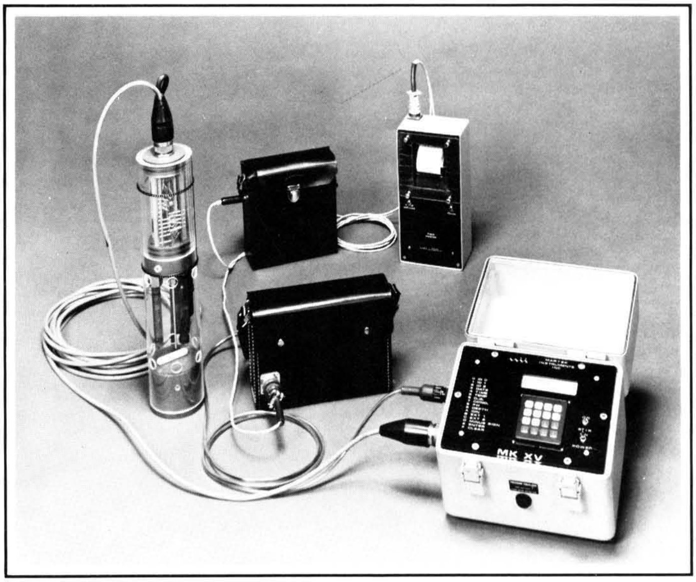

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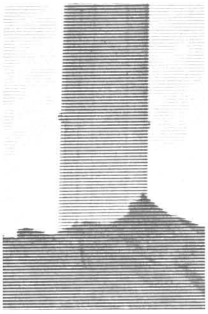

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ES&T LETTERS

How many PMNs?

Dear Sir: Julian Josephson's generally excellent article, "Introducing new chemicals," in the June issue of *ES&T* (p. 237A) misses an important point. This is the link between EEC's Sixth Amendment PMN exemptions and the estimated rate of PMN filings in the EEC. The latter is estimated by G. Dominguez to "run as high as 1000 per year."

Consider that the rate of pre-*manufacturing* notifications in this country is now passing 1000 per year, with an accumulated total of over 2200. At an EEC meeting in Rome, in December 1981, Dr. John Todhunter, then of the U.S. EPA, reported an EPA analysis that "80–90%" of substances notified under TSCA would have been exempt, if the EEC exemptions were to apply in the U.S. This is consistent with other analyses of the high proportion of low-risk polymers among U.S. PMNs. On this basis alone, 1000 U.S. PMNs would equate to about 150 EEC PMNs.

This major difference puts into better perspective NRDC's vigorous criticism of the entry of "most new chemicals into [U.S.] commerce with little or no toxicity testing." Consider also that the proposed U.S. exemptions are somewhat more restrictive than EEC's, in that these would exempt perhaps half those substances exempted by the Sixth Amendment. (This estimate remains too speculative to include in these projections but would immediately increase slightly the ratio of EEC to U.S. PMNs.)

But this is not all. As Josephson and EPA itself have indicated, present records show that only about 40% of substances PMN'd in the U.S. are so far actually marketed. Taking this factor into account, at the present time 1000 U.S. pre-*manufacturing* notifications will equate to about 60 EEC pre-*marketing* notifications. In short, for every six EEC substances notified, after testing via base set with some degree of flexibility yet to be established, there will be around 100 substances evaluated for risk by EPA. If current patterns continue, most of these will require no information beyond that identified in Section 5 of TSCA. A few, perhaps 5%, will require additional testing comparable to that defined by the base set, but a very few, perhaps 1%, will require far more if manufacturing is to proceed.

Thus, assuming that the frequency and the chemical identity of new chemical substances are roughly the same in the EEC and in the U.S., it will be a long time indeed before EEC PMNs run as high as 1000 per year.

Only time will tell which of these estimates is more accurate. What is more important, only time will tell whether the EEC, the U.S., or the Japanese system of notifying new substances will be the most cost-effective in eliminating unreasonable risks to health and the environment caused by new chemical substances.

George W. Ingle
Director, Association Liaison
Chemical Manufacturers Association

Errata[a]

Acidification of aquatic systems: A critique of chemical approaches

p. 607A, col. 2, line 2
by redox process

p. 607A, col. 2, line 20
produce alkalinity

608A, col. 2, 11 lines from bottom
replace with **than visual interest; and these graphs should be presented** . . .

p. 608A, Equation 20
$\ldots + [\mathrm{Mg}^{+2}])$

p. 612A, col. 3, line 13
$\mathrm{pH}_{\mathbf{e}}$

p. 613A, col. 2, line 2
, the sample H-ion concentration

p. 613A, Equation 35
$[\mathrm{H}^+]_s = [$

p. 613A, Equation 36

$$\frac{(V + v_i)}{V}[\mathrm{H}^+]_c + \frac{C_I v_I}{V}\left(\frac{[\mathrm{H}^+]_c}{[\mathrm{H}^+]_c + K_I}\right) = -[\mathrm{Alk}] + \left(\frac{K_I}{[\mathrm{H}^+]_c + K_I}\right) C_T \quad (36)$$

p. 614A, col. 1, line above Equation 39
solution of $[\mathrm{H}^+]_s$ gives

[a] *Environ. Sci. Technol.* **1982** *16*, (11), 606–614A

James R. Kramer
McMaster University
Hamilton, Ontario L8S 4M1, Canada

Five continuing crises at EPA

William Ruckelshaus will be judged by history by the skill and vigor with which he moves to address five EPA crises: those concerning confidence, competence, stability, fundamental environmental science, and the Science Advisory Board.

The public and the dedicated work force of EPA have little confidence that the Reagan administration is committed to serving the public interest. The appointment of Ruckelshaus, with his reputation for integrity and independence, gives cause for hope that the EPA will rise from the ashes, but he may be handcuffed by the Watt–Coors group.

The crisis in competence at EPA stems from the recent loss of some of its best professionals. Funds for research in EPA were cut 50% at a time when we faced problems of enormous complexity. The Reaganites argued that not enough was known about the causes of acid rain to institute regulations, while simultaneously uttering their infamous slogan: "We will do more with less."

Now Ruckelshaus has the support of Congress to do whatever is necessary to rebuild EPA, but the Reagan administration is dragging its feet. Ruckelshaus worried aloud recently that Congress would provide more than he could wisely use. Instead of fretting, he should seize this opportunity to rebuild the science base. This can be done in a multitude of ways, but two of the most important are to hire some of the bright young people now available in the job market and to restore funding for research to pre-Reagan levels. In particular, the fundamental environmental science base in universities should be strengthened. EPA has a miserable record in fostering long-term anticipatory research, because as a regulatory agency it focuses on fire fighting, which crowds out fundamental research that might lead to more cost-effective, long-term solutions.

The crisis in stability in EPA is as harmful to regulated industries as it is to the morale of EPA professionals. An inordinately large number of key positions are occupied on an "acting" basis. Ruckelshaus should restore permanence and predictability by quickly appointing competent people on a permanent basis, irrespective of political affiliation.

The Science Advisory Board "hit list" was apparently developed to mute the advice of some of the more independent scientists. Ruckelshaus promised there would be no "hit lists" under his administration, but he has so far not moved to fight off another more insidious crisis in the Science Advisory Board: The Reagan administration recently instructed EPA (and other agencies) to stop paying honoraria to scientists and consultants serving on advisory boards and proposal review panels. The stated reason is that dedicated patriotic scientists should be willing to work for free, rather than the $100 per day now provided. While the idea has popular appeal, it effectively discriminates against all but the independently wealthy and the hired guns of special interest groups. Resignations of professors and independent consultants are beginning because most cannot afford to consult without pay.

EPA will regain the scientists' confidence only if it is rejuvenated with adequate funding and competent personnel, and if it rebuilds the fundamental as well as the applied environmental sciences.

R. Sievers

__Robert Sievers__ is director of the Cooperative Institute for Research in Environmental Sciences and professor of chemistry at the University of Colorado. He is the author of 100 publications on environmental, analytical, and inorganic chemistry, and a former member of the EPA Science Advisory Board.

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ES&T CURRENTS

WASHINGTON

The U.S. Senate Appropriations Committee approved a $1.16 billion operating budget for EPA in fiscal 1984. This was $165 million more than the administration originally sought, but $200 million less than a group of senators thought was needed to restore the agency's effectiveness. Sen. Patrick Leahy (D-Vt.) wanted a $1.35 billion funding level, but Sen. Jake Garn (R-Utah) was able to have that request pared. Supporters of a higher EPA budget will try to have their funding goals restored on the Senate floor.

Howard: *introduced water bill*

A "strongly pro-environmental" Clean Water Act reauthorization bill was introduced by Rep. James Howard (D-N.J.). Sen. John Chafee introduced a parallel bill. Howard is House Public Works Committee chairman. His bill would allow industries facing a July 1, 1984, deadline for "best available technology" an extension of three years, but would leave most of the rest of the present law intact. Howard's bill also provides other antipollution requirements, including a cleanup of "toxic hot spots"—waters with high concentrations of toxic substances—within five years.

A government-wide process for assessing and managing risks to safety and health posed by contaminants is needed, said EPA Administrator William Ruckelshaus to a National Academy of Sciences meeting. He added that risk assessment should be differentiated from risk management much in the manner that an academy panel recommended (*ES&T*, May 1983, p. 199A). Ruckelshaus called for uniformity in the way risks are assessed and managed across federal regulatory agencies and for help in this direction from scientists. He proposed an interagency commission, with scientific peer review, to carry out risk assessment and to make the management decisions indicated by this assessment.

Tough federal action is needed to reduce acid precipitation, according to a report by the National Academy of Sciences (NAS). Although the report suggests that acid rain could be controlled if utilities and other industries were compelled to reduce their SO_x emissions sharply, it does not call for any specific legislation to that effect. It is, however, probably one of the strongest statements suggesting that SO_x is the principal acid precipitation culprit. The report also supports the Canadian government's belief that a 50% overall reduction of SO_x is needed to curtail damage to many lakes and streams in the U.S. and Canada.

EPA will allow limited production of synthetic crude oil from shale at Parachute, Colo., provided Union Oil Company of California, the producer, supplies the agency with chemical and toxicological data concerning the products. These data will be provided pursuant to a consent decree that Union Oil signed with EPA under Section 5(e) of the Toxic Substances Control Act. That section mandates a premanufacture notice before the manufacture of a new substance for commercial purposes. The consent decree also calls for worker protection and the treatment of certain process wastes as hazardous pending further evaluation.

STATES

Who pays for two canceled nuclear plants? The highest court of Washington State said that state's utilities need not pay the Washington Public Power Supply System the $2.25 billion in debt accumulated by two canceled plants. The debt is in the form of bond obligations. In the view of a state senator, default is assured, and bankruptcy is quite likely. The court said that utilities lacked authority to make agreements with the state power system. Attorneys for Chemical Bank, New York, trustee for many of the bonds, may study the Washington opinion to see if it can be appealed in federal court.

The Indian Point nuclear power plant, 35 miles north of New York City, was allowed to continue operating despite the lack of a proven emergency evacuation plan. The U.S. Nuclear Regulatory Commission (NRC), relying on the Federal Emergency Management Agency's opinion that enough improvements had been made, voted 3–2 to let the plant remain open. The New York Power Authority said that NRC's decision averts staggering economic consequences for New York City and Westchester County. But Rockland County officials, who sought to close the plant, and the Union of Concerned Scientists, decried the NRC decision.

The Love Canal (Niagara Falls, N.Y.) "emergency declaration area" (EDA): Is it now habitable, contingent upon leakage safeguards and contamination cleanup? A Congressional Office of Technology Assessment (OTA) Technical Memorandum suggests that, based on available information, it cannot be demonstrated with certainty that unsafe levels do or do not exist in the EDA, and that safety must be demonstrated "more unequivocally." The U.S. Department of Health and Human Services, in July 1982, had deemed the EDA safe, subject to safeguard and cleanup. OTA criticized monitoring at the canal and said that the strategy was inadequate to detect true toxic levels. OTA also said that the presence of dioxins at the site cannot be ruled out.

New Jersey authorities conducted tests for dioxins at eight sites in five northeastern counties in which Newark, Edison, and several other affected communities are located. For instance, at Clifton, 2,3,7,8-tetrachlorodibenzodioxin (TCDD), levels of 0.04–11 ppb were found, and other findings occurred in the Ironbound section of Newark and in Edison. One Newark site was said to contain about 50 parts per *million*. Approximately 1–5 ppb were found in Edison. The federal danger level is put at 1 ppb. New Jersey Gov. Thomas Kean expressed concern about the findings but also stated his belief that the health of nearby residents is not endangered.

Meanwhile, levels of 2,3,7,8-TCDD as high as 1.8 ppm—said to be six times as high as the Times Beach maximum—were reported at St. James, Mo. EPA offered temporary housing to three families living near the contaminated site and issued a general health warning for the area. And at Times Beach, after much haggling, federal, state, and local governments agreed to buy out the town. EPA will contribute $33 million for the buy-out, and the state of Missouri will pay $3.3 million. A buy-out is also slated for Minker-Stout, another contaminated area. The first offer is expected to be made in October.

A health threat assessment is being made at the Stringfellow Acid Pits (Riverside County) by the state of California. About 38 500 people live in the groundwater basin that authorities say is threatened by the site. Federal and state officials say that some carcinogens, mutagens, and teratogens are located there in very high concentrations. About 34 million gal of toxic industrial fluids were deposited at Stringfellow from 1956 to 1972—about six times that at Love Canal, N.Y.—with state approval. So far, however, no illnesses demonstrably related to exposure to the dump have been reported officially in the vicinity. The site is due for Superfund cleanup.

Sheffield: *favors "right-to-know"*

In Alaska, employers will have to inform workers what toxic or hazardous substances may be in their workplaces if, as expected, a "right to know" bill becomes law. Alaska's governor William Sheffield supports the bill, which is similar to laws already passed in 12 other states. Under the law, which would take effect Jan. 1, 1984, the state's Labor Department would be required to publish a list of toxic and hazardous substances each year, help employers get information about the substances, and develop guidelines for safety education. Employers would have to inform employees through posted notices where the substances are found and how to deal with them. About 800 OSHA-listed toxic and hazardous materials would be regulated.

SCIENCE

Can the body burden of persistent halogenated hydrocarbons such as polychlorinated and polybrominated biphenyls (PCBs and PBBs) be reduced? After all, they accumulate in fatty tissues. At the Foundation for Advancements in Science and Education (FASE, Los Angeles, Calif.), scientists announced significant reductions of these and certain other toxins through a detoxification program first tested on some Michigan residents who had ingested PBBs. The program consisted of exercise, sauna baths, and nutritional supplements emphasizing gradually increasing doses of niacin (vitamin B_3).

The effect of jet engine emissions on air is being studied at Battelle's Columbus Laboratories (Ohio) under a $992,000 contract with the U.S. Air Force, Navy, and Federal Aviation Administration. Researchers are examining two petroleum-based and one oil-shale-derived fuel. The objective is to identify and quantify the emissions and determine their potential for reacting with other environmental compounds to form photochemical smog and other hazardous pollutants. After sampling and analysis methodology evaluation, emissions will be analyzed in outdoor smog chambers. Results will be compared with emission figures from other combustion sources.

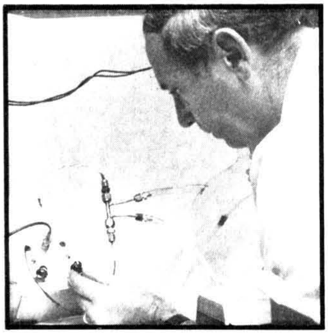
TECHNOLOGY

A "milestone" in liquid metal fast breeder reactor (LMFBR) technology was reached when a prototype sodium-to-water steam generator was run at its full 70-MW test power at Energy Technology Engineering Center in California. Breeder project engineers believe that this success shows that the transfer of heat from the LMFBR's sodium coolant to water for steam works according to a sound design. The liquid sodium is at pressures of 1550 psi and temperatures of more than 900 °F. It is isolated on a shell side, with water and steam on a tube side. The LMFBR itself—if it is ever built, for its funding prospects are presently very shaky—is supposed to make more nuclear fuel than it uses.

Specific species of mercury in the air can now be measured and quantified. The major forms of mercury in the air are elemental mercury, mercuric chloride, methylmercuric chloride, and dimethyl mercury. William Schroeder of Environment Canada told the APCA meeting in Atlanta, Ga., about the methodology for the speciation of these forms of mercury. Pyrolysis was found to be the method of choice for converting these forms to elemental mercury for detection and quantification by resonance atomic absorption or fluorescence spectrophotometry. Data were presented to establish the experimental conditions and pyrolyzer configuration for the complete conversion of the mercury compounds to the elemental form.

Some bacteria will "snack" on dioxins occasionally, says Fumio Matsumura, director of Michigan State University's Pesticide Research Center. *Bacillus megaterium* and a *Nocardiopsis* species can degrade dioxins "before they 'discover' that they made a mistake." he says. This bacterial degradation could detoxify dioxins, Matsumura believes, if the bacteria could be trained to "eat" them. To attain this situation, careful substrate preparation is important, and so is using solvents that can help the dioxins penetrate the bacterial cell walls. Degradation of dioxins seems to work even at concentrations as low as 5 ppb.

On-site analysis of hydrocarbons and chlorinated hydrocarbons in the air is possible with mobile monitoring systems. In a paper presented at the Air Pollution Control Association (APCA) meeting in June (Atlanta, Ga.), Radian Corporation scientists Randall Hall and Walter Crow described two different systems equipped with automated gas chromatographs, which can be used to sample and analyze suspected hazardous materials in the air on a continuous and unattended basis. The systems have been used to identify emissions from hazardous waste dumps, petrochemical plants, and hazardous spills. The use of ancillary techniques, such as GC/MS (gas chromatography/mass spectrometry), is recommended for absolute confirmation of compound identity.



Testing gas detector at NRL

Several new types of chemical vapor microsensors for detecting certain toxic gases have been developed by the U.S. Naval Research Laboratory (NRL) in Washington, D.C. The sensors are no larger than an ordinary pen. One uses an optical waveguide that is based on a coloration change to detect minute amounts of ammonia. The waveguide is basically a small dye-film-coated, glass capillary tube with a light-emitting diode and a phototransistor detector. The dye is oxazine perchlorate. Ammonia can be detected to less than 60 ppm, and the system is reusable. Another similar system can detect hydrazine.

In the manufacture of photovoltaic systems, no emission standards or data concerning wastes produced are available. Emission estimates are based on engineering studies of hypothetical facilities, according to EPA's Industrial Environmental Research Laboratory (IERL, Cincinnati, Ohio). However, some of the materials involved in this industry are used in other industries, so control experience and technologies under various environmental laws may ultimately be applied. Main environmental problems would probably come from larger, more centralized producers, according to an IERL study prepared by scientists at Brookhaven National Laboratory.

For determining suspended solids in water and wastewater, a new method involving homogenization of the sample was proposed by Enrico Cardarelli et al. of the University of Rome's Institute of Analytical Chemistry (Italy). They say that homogenization makes possible many such determinations on the same sample with a minimum of errors. Homogeneous samples are obtained through special approaches to mixing and pipetting. Cardarelli says that errors are always less than 1%. The work was supported by the Institute of Water Research in Rome.

INDUSTRY

The Dow Chemical Company (Midland, Mich.) has strongly replied to charges by Rep. Tom. Daschle (D-S.D.) that Dow kept confidential a British study on the effects of dioxin on the human immune system. Dow notes that the 1980 study by A. Milford Ward received wide public review. Dow also said that it never funded the Ward study and that it had no role in the report's distribution. Ward himself had said that while his research on a group of chemical workers found immune systems affected temporarily, in terms of susceptibility to cold, "flu," and similar illness, these workers did not contract serious health problems. Ward's work was reported by the U.K. Advisory Committee on Pesticides.

Despite a poor public image, a profitable future may be in the offing for the toxic waste disposal industry. By 1990, at least $12 billion will be spent each year on government-regulated hazardous waste disposal, according to an Office of Technology Assessment prediction. Present expenditures are less than $5 billion/y. Also, tighter standards covering a wide range of wastes may be expected. EPA presently regulates about 35 million metric tons (tonnes)/y of hazardous wastes of the 275 million tonnes/y produced annually. This amount will probably increase markedly. Also, generators are likely to seek responsible disposal companies to reduce liability risks.

Wanted: revisions to the Safe Drinking Water Act. The American Water Works Association (AWWA) wants to see deliberate contamination of water supplies made a federal offense. AWWA also calls for strengthening of the scientific basis of regulations and a focusing of EPA efforts on contaminants shown to present "unacceptable risks" to public health. AWWA also will advocate a strong federal program to promote continued monitoring of surface and groundwaters, expanded health effects research, and more training of water system operators.

"Metallic scrap is not a hazardous waste," the Institute of Scrap Iron and Steel, Inc. (ISIS, Washington, D.C.) told EPA. Herschel Cutler, ISIS executive director, expressed concern that a preamble to proposed regulations may lead to an inference that metal scrap is hazardous. Also, even if some individual items were hazardous if analyzed by EPA testing procedures, "such heavy metals detected in a laboratory would pose no hazard under real-world conditions. To regulate the generation, transportation, or storage of such scrap under [hazardous] requirements would create serious burdens for both industry and EPA with no environmental benefit," Cutler said.

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ES&T OUTLOOK

A monitoring report

Personal monitors are mandatory for health effects studies, biological monitoring is used in the occupational health field today, and genetic testing may be used in the future to reduce human exposure to chemicals in the workplace

For more than 10 years the World Health Organization (WHO) has been involved in the monitoring of ambient air quality as part of the United Nations Environment Programme (UNEP) Global Environmental Monitoring System (GEMS) now active in 50 countries. But the realization has emerged that a network of fixed monitoring stations does not adequately represent what people breathe. Studies in the U.S. and Europe have indicated that individuals spend up to 90% of their day indoors in residences, offices, schools, and shops. The exposure experienced inside residences, commercial buildings, and motor vehicles may be as important a component of total exposure as those components derived from occupational and outdoor environments.

There has always been the question of whether fixed outdoor monitoring stations can provide a fair estimate of what people breathe and of the pollutants to which they are exposed. A number of personal monitors are available, and many studies are being conducted that use such monitors to correlate indoor air pollution with outside ambient air pollution. However, general predictions of human exposure cannot be made from measurements made at ambient air stations, nor can they be made with an indoor sampler, even for homes free of major sources of pollution.

Personal monitors

Nevertheless, the use of personal monitors for air pollution studies has become widespread. Personal monitors are now also being used by the GEMS.

Recently, John D. Spengler of the Harvard School of Public Health chaired a session on personal monitors at the third annual National Symposium on Recent Advances in Pollution Monitoring of Ambient Air and Stationary Sources (Raleigh, N.C.) that was sponsored by the EPA Environmental Monitoring and Support Laboratory (EMSL). He said that personal monitoring in the field of air pollution is still relatively new. Since the early 1970s, there has been an increasing number of studies reporting personal exposures of carbon monoxide, sulfate, nitrogen dioxide, sulfur dioxide, respirable particles, aluminum, iron, and several volatile compounds. Urban exposures to particles and lead were reported in 1972, and studies of exposure of bicyclists and commuters to carbon monoxide were first published in the mid-seventies. In 1976, personal epidemiological studies to define home factors leading to different exposures among children were reported.

The field is developing rapidly. Personal monitoring is an important research area in the air category. All 50 states have representatives on indoor air quality. Next year, a third international conference on indoor air quality and climate will be held in

Stockholm, Sweden, Aug. 20–24. (A first international conference on indoor air pollution was held in Copenhagen in 1978 and a second one at Amherst, Mass., in 1981.)

Equipment

Meanwhile, the session at the recent Raleigh meeting was divided into two parts, one for the equipment and the second for the studies.

Basically, there are three types of personal monitoring equipment:

- analytical instruments that make the pollution measurement on the spot, including battery-operated instruments,
- collection devices that accummulate the pollutants for subsequent analysis in the laboratory, and
- passive detection devices that employ a chemical substance that reacts with the pollutant and changes its properties in some fashion.

Passive samplers were a main item of discussion at the meeting in Raleigh. Based on the principle of diffusion, these devices are simple, inexpensive, and easy to use. But they also have problems. Relative humidities of about 80% and insufficient ventilation (poor air movement over the devices) impair their performance. Despite these problems there are a number of good reasons why these passive devices are being investigated. For example, they are being used to check exposure of cleanup crews at hazardous waste sites. These devices are also useful in areas where there is no electricity—which is often the case at hazardous waste sites.

The simplest device that can be adapted to both personal and site monitoring is the Palmes tube. It is a cylindrical, hollow tube coated with a material sensitive to the pollutant being measured. Triethanolamine is the absorbent in the Palmes NO_2 sampler. The Palmes passive sampler was described by John R. Girman of the Lawrence Berkeley Laboratory.

There is a need for careful evaluation of passive samplers under controlled conditions that closely approximate use conditions. For example, the collection efficiency of the

Field-tested personal monitoring techniques

Pollutant group	Collection method	Analytical method	Commercial availability
Carbon monoxide	Pump	Electrochemical cell	General Electric, Aerospace Technology Division, 4Wilmington, Mass.
Nitrogen dioxide	Diffusion tube	Colorimetric	MDA Scientific Inc., Park Ridge, Ill.
Nitrogen dioxide	Badge	Colorimetric	Tokyo Roshi Co. Ltd., Tokyo, Japan
Respirable suspended particles	Cyclone and filter with pump	Gravimetric with microbalance	None (Harvard School of Public Health, Cambridge, Mass.)
Nonpolar volatile organic compounds	Tenax cartridge with pump	Thermal desorption coupled with gas chromatography or mass spectroscopy	None (Research Triangle Institute, Research Triangle Park, N.C.)
Vinyl chloride	Permeable membrane badge	Gas chromatography	REAL Inc., P.O. Box 3341, Baton Rouge, La.
Organochlorine pesticides and polychlorinated biphenyls	Polyurethane foam cartridge with pump	Gas chromatography	None (U.S. EPA Research Laboratory, Research Triangle Park, N.C.)
Radon	Track-Etch	Track counting	Terradex Corp., Walnut Creek, Calif.

Source: WHO Offset Publication No. 69, "Estimating Human Exposure to Air Pollutants," 1982

Laboratory-tested personal monitoring techniques

Pollutant group	Collection method	Analytical method	Commercial availability
Nitrogen dioxide	Impregnated filter	Colorimetric	None (National Bureau of Standards, Gaithersburg, Md.)
Respirable suspended particles	Pump	Piezoelectric principle	ThermoSystems Inc., St. Paul, Minn.
Respirable suspended particles	Pump	Light scattering	GCA Corp., Bedford, Mass.
Formaldehyde	Permeable membrane	Colorimetric	None (Oak Ridge National Laboratory, Oak Ridge, Tenn.)
Formaldehyde	Diffusion tube	Colorimetric	None (Lawrence Berkeley Laboratory, Berkeley, Calif.)
SO_2, NO_2, respirable suspended particles	Pump/impingers/filter	Colorimetric, gravimetric	None (Gage Institute, Toronto, Ontario, Canada)

Source: WHO Offset Publication No. 69, "Estimating Human Exposure to Air Pollutants," 1982

Palmes NO_2 sampler decreases by 15% when the temperature decreases from 27 to 15 °C. Other errors could be introduced because the absorbent triethanolamine is hygroscopic, so there may be a small effect caused by humidity.

Alfred T. Hodgson of the Lawrence Berkeley Laboratory (Berkeley, Calif.) reported the validation of a passive sampler for determining formaldehyde in residential indoor air. This sampler is capable of measuring one-week time-weighted average concentrations of formaldehyde. The performance of this passive sampler compared favorably with that of a reference pump-bubbler sampler. Hodgson reported that the concentration of formaldehyde varied with such factors as temperature, humidity, and ventilation.

Robert G. Lewis of the EPA EMSL (Research Triangle Park, N.C.) described the Du Pont and MRC (Monsanto Research Corporation) passive monitors for measuring volatile organic vapors in workplace environments. The Du Pont commercial device for measuring work-place exposure to organic chemicals uses activated charcoal as the adsorbent. Activated carbon irreversibly sorbs volatile organic carbons (VOCs). The VOCs cannot be quantitatively removed from the device by heat treatment. But a passive device with Tenax as the sorbent can be used to adsorb organic chemicals whose desorption from the device can be effected at 300 °C. The MRC personal monitor contains three adsorbents—Tenax for nonpolar organics, Ambersorb XE-340 for volatile organics, and Porapak-R for polar organic compounds.

Mary Lynn Woebkenberg of the National Institute for Occupational Safety and Health (NIOSH, Cincinnati, Ohio) described the federal facility for evaluating monitoring equipment. This facility consists of a gas and vapor generation system, a recirculating exposure chamber, and multiple variable sampler. Passive devices can be evaluated in its exposure chamber, which can house portable instruments as well. The total system can be used for the generation and sampling of complex atmospheres with trace chemicals down to the sub-ppm range.

Genetic testing

Some experts estimate that exposures to hazardous substances at work may play a role in 5% of all cancers. In 1980, NIOSH estimated that 8.9 million workers in the manufacturing sector were exposed to hazardous chemicals.

On the horizon is an emerging technology—genetic testing—that may prove useful in reducing occupational disease, especially disease arising from exposure to the two main workplace hazards. These are chemicals and ionizing radiation, according to a recent report from the Office of Technology Assessment, "The Role of Genetic Testing in the Prevention of Occupational Disease." The term *genetic testing* applies to several techniques used to examine workers for particular inherited genetic traits or environmentally induced changes in the genetic material of certain cells, on the assumption that the traits or changes may predispose them to illness. If individuals or groups predisposed to specific types of occupational illness could be identified, preventive measures could be specifically directed at these persons.

The possibility of genetic testing was first raised about one-and-one-half years ago, but the testing is still in its infancy and will not be available on a large scale until the end of the century, according to scientific experts. Another problem is that although genetic testing sounds good in theory its ability to identify people who are predisposed to occupational illness has not been demonstrated.

Genetic testing comprises two techniques—screening and monitoring. Genetic screening, when used in the workplace, is a one-time testing procedure to determine if a person has particular genetic traits, regardless of whether that person has been exposed to hazardous substances. With such screening, it may be possible to identify individual workers who are genetically at higher risk of disease.

Genetic monitoring involves periodically examining workers by collecting blood or other body fluids to assess whether genetic damage has occurred in certain cells. If the scientific validity of genetic monitoring were fully established, it could also serve as an early warning that exposure to hazardous substances in the workplace had occurred.

There are two types of genetic monitoring—the established cytogenetic methods, which detect major structural changes in chromosomes, and the new noncytogenetic methods, which detect damage to the DNA. According to the OTA report, the noncytogenic methods, for the most part, are still in the experimental stage, but eventually could lead to faster and less expensive monitoring methods.

There are other difficulties with genetic monitoring. In only a few cases has the relationship between worker exposure and genetic damage been documented, thereby making possible the establishment of a dose-response relationship. Moreover, when exposed populations are studied, rarely is there found more than a twofold increase in damage over the average of the unexposed population. In fact, in only one case did the correlation hold up. The correlation of induced genetic damage with risk for disease has been shown statistically only for the Japanese population exposed to ionizing radiation from the atomic bomb! Since genetic testing is so new and has not been widely used, there is little direct experience from which to make judgments regarding its use.

At a recent meeting entitled "Biological Monitoring and Genetic Screening in the Industrial Workplace," sponsored by the American Society of Law and Medicine (Boston, Mass.), the following questions were discussed: How do we reduce occupational disease risk? What are the means to this goal? How do we use the scientific techniques that are compatible with the legal structure?

But many factors besides genetic makeup can cause an individual to be predisposed to illness from environmental stress, the OTA report notes. Called confounders, these include age, sex, preexisting illnesses, nutritional status, personal habits including smoking, as well as prior exposure to environmental factors. The use of this technology also raises a highly controversial question: Could the use of such tests result in discrimination on the basis of race or national origin?

The bottom line: The science of genetic testing is not yet reliable; legislation requiring such testing is premature; the use of unvalidated tests is obviously unethical. One suggestion from Rep. Albert Gore (D-Tenn.) was that NIOSH develop criteria for valid scientific testing in this area.

Biological monitoring

Although genetic testing may be years away, certain biological monitoring is used in the occupational field today, according to a paper presented by P. Hughes, at a meeting of the American Society of Law and Medicine. Biological monitoring refers to evaluations of the absorption of chemicals or other agents by body systems. It often involves the examination of physiological materials, such as blood, urine, and breath. It has two main functions: first, the making of routine measurements on health and

Some useful definitions for monitoring studies

Exposure estimation of air pollutants is the determination of the pollutants to humans as a function of time and location. (The two major uses of exposure estimates are 1) as part of an exposure assessment, and 2) as a variable in a health effects study.)

Exposure assessments attempt to answer the question: Which populations (or subgroups) are or may be exposed to which pollutants and under what circumstances?

Health effects studies attempt to determine at what level a given exposure implies an unacceptable risk to human health.

Exposure to a given pollutant is a measure of the contact between the pollutant and the outer or inner surface of the human body.

Dose is the amount of air pollutant that crosses one of the body boundaries, e.g., the epithelium in the nose or lungs. Dose introduces physiological considerations.

Integrated exposure incorporates the duration of the exposure by integrating the concentration with the duration of exposure. This differentiates between a person exposed to a given air pollution concentration for 10 min and another exposed for 2 h.

Average exposure of a person is defined as the integrated exposure divided by the averaging time.

Total exposure refers to a 24-h exposure.

Occupational exposure refers to the 8-h work period.

Two ways to **estimate the exposure of a person, or a population,** to air pollution:
Field studies use personal air pollution monitoring devices to *measure* an individual exposure in members of a sufficiently large population.
Mathematical models consider both the exposure and activity of persons as a function of time to *estimate* the exposure.

Source: WHO Offset Publication No. 69

environmental indexes and the recording and transmission of data, and second, the collation and interpretation of such data with a view to detecting changes in the health status of populations and their environments.

Preemployment medical examinations are used widely today. They serve the purpose of proper job placement, in accord with the physical and mental capabilities of the worker.

With such examinations it is possible to identify persons likely to be vulnerable to certain types of exposure. For example, it is easy to identify those with chronic obstructive pulmonary disease so that they can be excluded from work in dusty environments. Although there is no complete agreement on the importance of such monitoring, biological monitoring is the main tool for evaluating environmental control measures and is the only means for detecting total health effects.

Using humans as biological monitors may give a better estimate of the magnitude of exposure than will direct measurement of environmental concentrations of contaminants. For example, changes in biochemical parameters, as measured in various biological fluids, are often among the more sensitive indicators of early changes in health due to hazardous chemicals in the work environment. In some cases, such changes indicate an actual effect on health. In other cases, they may indicate only homeostatic and compensatory mechanisms, which are reversible. The levels of these contaminants must be related quantitatively to an adverse health effect. Also, measurement of metabolites or biochemical changes resulting from inhalation of contaminants must be related quantitatively to an adverse health effect.

For example, in the monitoring of lead workers, use is made of clinical signs and symptoms of lead absorption such as levels of porphyrins, delta-amino-levulinic acid, and amino-levulinate dehyratase. In hearing conservation, temporary threshold shift of hearing acuity is used as an early indicator of permanent threshold shift.

Biological monitoring of exposed workers is also of value in maintaining surveillance of the health of those exposed to certain metals such as lead, mercury, cadmium, arsenic, selenium, tellurium, thallium, zinc, and manganese, as well as fluoride. The clinical evaluation of several types of chemical intoxication may include the determination of the concentration of the suspect toxin in blood, urine, or breath, its metabolites in urine, or an affected enzyme in serum.

Useful tests in emergency situations include carboxyhemoglobin for suspected carbon monoxide exposure, trichloracetic acid in urine for trichloroethylene exposure, and cholinesterase in serum for exposure to organophosphates. The detection of arsenic in hair and fingernails also is used for the evaluation of a suspected chronic exposure.

Only a few of the more basic tests are now used widely in occupational health practice. These include fluoride in urine and lead in blood and urine, for which there are well-validated procedures. The absorption, distribution, and excretion both of fluoride and of lead have been studied carefully over the past 40 years. The literature provides a sound basis for the interpretation of findings, and in turn, a reliable measure of the level of exposure of the individual to the substance.

Only a limited number of biological procedures have proven this useful, although many others have been proposed. For example, the practice of determining mercury in urine has not been entirely satisfactory; there is no generally accepted critical level of mercury in urine above which intoxication can be established. The same limitation applies to the interpretation of manganese levels in the urine.

So the search goes on for tests that are relatively simple to perform, yet highly specific, whose results may be interpreted as being health related.

—Stanton Miller

Restoration of aquifers

Methods for identifying, containing, and reclaiming contaminated groundwater are being developed and refined. But rehabilitation costs could remain high

Despite legislation aimed at protecting groundwater supplies, such as the Safe Drinking Water Act (SDWA) and the Resource Conservation and Recovery Act (RCRA) and related regulations, aquifers do become contaminated. When this occurs, there are three basic courses of action: Forbid use of the aquifer and obtain alternative water supplies, attempt to rehabilitate it, or continue to use the aquifer, but treat the water to remove the contaminants.

About 50% of the total of 3×10^{11} acre-ft (1 acre-ft = 325 900 gal) of groundwater estimated to be available in the U.S. is designated for drinking water. Presently, less than 1% of that total, or 3×10^{9} acre-ft, is believed to be contaminated. A national goal is to halt further groundwater contamination and, if and when feasible, to rehabilitate contaminated water supplies.

Abandoning a contaminated aquifer and procuring water supplies elsewhere might seem to be a more expedient way to solve the problem of contaminated groundwater. But this has disadvantages. Alternative supplies might be neither as cheap nor as abundant as one would hope. Moreover, if groundwater contamination ever threatened to become a national phenomenon, and more well systems were abandoned, alternative water supplies could become scarce, poorer in quality, and expensive. Kirk Brown of Texas A&M University told *ES&T* that once an aquifer used as a water supply is contaminated, 100% of its available groundwater must be considered contaminated. And rehabilitating groundwater is neither cheap nor easy.

Perceived limit of tolerance

Although the total amount of contaminated groundwater nationwide comprises only a small portion of available groundwater, a problem is that contamination incidents tend to occur near populated areas that depend upon this water for potable supplies. Significant episodes, some of which forced well abandonment, have occurred in parts of Long Island, New Jersey, Massachusetts, Tennessee, Florida, and several other states.

Jay Lehr, executive director of the National Water Well Association (NWWA, Worthington, Ohio), believes that the pendulum will swing from well abandonment toward aquifer rehabilitation in response to contamination incidents. "People have reached their perceived limit of tolerance to groundwater contamination," Lehr told *ES&T*. "That's not because of health threats; people are not dying. But they want to clean up this water just as they clean their houses or yards when they see a mess there." He added that in his view, "the U.S. has the technology and know-how to clean up groundwater supplies; aquifer restoration will be a major American industry within the next several years." Lehr noted that at present, about 75 reclamation or containment projects are under way or planned.

Whether Lehr's optimistic predictions concerning the growth of an aquifer restoration industry will materialize remains to be seen. One thing is certain—such restoration work will require major scientific and technological efforts and outlays of funds. Contamination plumes must be identified, mapped, monitored, and contained. Then a treatment and use or recharge scheme must be designed, installed, and operated. Costs could run into millions or tens of millions of dollars for each aquifer rehabilitation project.

Plume identification

The first step toward groundwater restoration is knowing the extent, thickness, rate of spread, and contents of a contamination plume. Until re-

Aquifer restoration: treatment alternatives

The first step in groundwater restoration is the quantitative identification of the problem. The next is identification and choice of treatment alternatives. The identification step includes:

- Defining the site's environmental setting
    - Surface
    - Subsurface
- Locating potential contamination sources
- Defining potential contaminant migration pathways
- Determining contaminant (plume) extent and concentration.

Candidate treatment processes include

- Physical treatment
    - Phase separation
    - Filtration
    - Gravity sedimentation
- Chemical or combined physical–chemical treatment
    - Chemical coagulation
    - pH adjustment
    - Carbon adsorption (liquid and vapor phase)
    - Air stripping
    - Steam stripping
    - Resin adsorption
    - Chemical oxidation
- Biological treatment
    - Aerobic fixed film
    - Aerobic suspended growth
    - Anaerobic
- Residuals treatment
    - Incineration
    - Sludge thickening and dewatering
    - Chemical recovery and reuse

Capabilities of candidate processes are tested through bench- and pilot-scale studies so that a conceptual treatment process for the specific problem(s) can be devised.

Source: Symposium presentation by John Absalon of Engineering-Science Inc.

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cently, about the only way to map the plume was to drill numerous monitoring wells around what is believed to be the plume's perimeter. Moreover, the plume's thickness might not be as great as that of the aquifer itself; so if a monitoring well is not screened properly, its intake might miss the contaminant plume altogether since groundwater flow and contaminant transport can be extremely stratified. Conceivably, the zone of contamination could be both overlain and underlain by clean water. That is why the utmost care must be taken, when wells are screened, to account for the three-dimensional aspect of the plume when a monitoring well network is planned.

In fact, in a sense, plume identification involves *four* dimensions. The monitoring scheme must consider plume spread in two horizontal and one vertical direction *over time.*

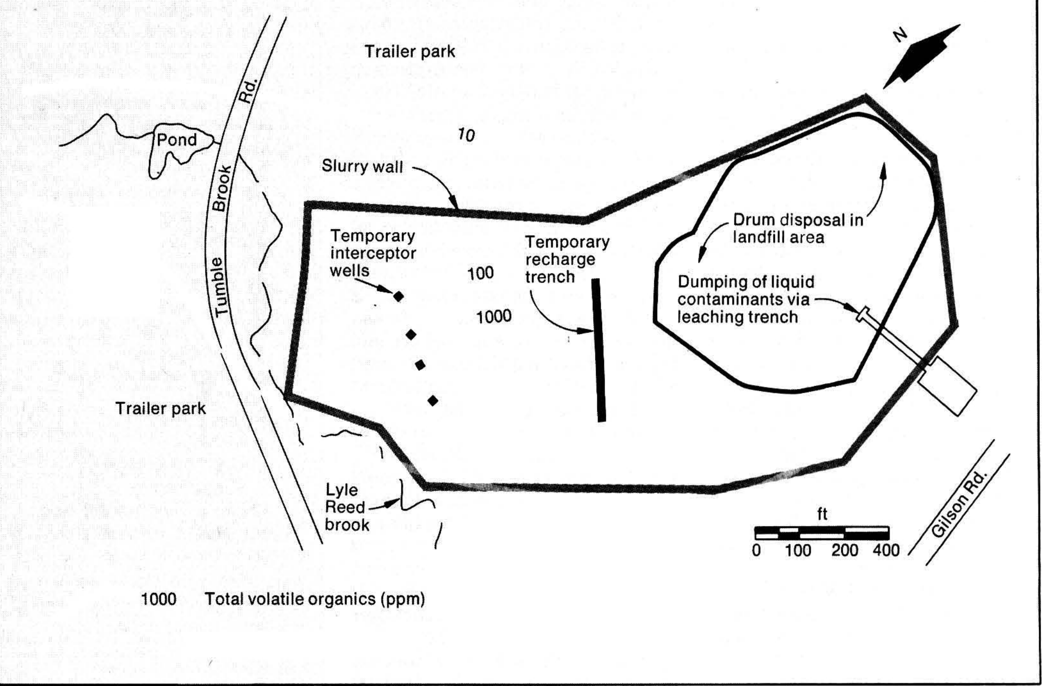
An example of a stratified contamination plume containing volatile organic solvents, in Nashua, N.H., was described at the Third National Symposium and Exposition on Aquifer Restoration and Groundwater Monitoring, held at Columbus, Ohio, in late May. Matthew Barvenik, a senior geotechnical engineer with Goldberg-Zoino & Associates, Inc., and a principal of Barcad Systems, Inc. (Mass.), spoke of a plume more than 450 m long, up to 33 m deep, covering about 1.2×10^5 m^2, and moving at about 7×10^{-4} cm/s. It originated from the disposal of drums, chemical sludges, demolition debris, and domestic rubbish in an abandoned 24 000-m^2 sand and gravel pit. In addition, more than an estimated 4×10^6 L of liquid chemical wastes had been discharged next to the pit by "midnight dumpers." Site cleanup is being carried out under the first cooperative agreement signed pursuant to the federal "Superfund" law. Total construction costs, including change orders, are \$2.4 million. Estimates of costs for the completed project come to \$10 million. Work on the site has been under way since 1980.

To define the plume, more than 60 single-level and multilevel monitoring wells were installed. A properly installed well system must monitor the entire thickness of the aquifer, while taking into account the stratified nature of water movement and contaminant transport. In this particular case, monitoring would have to go as deep as 33 m.

Typically, the cost of such wells could range from \$400 to \$3000 each. Add to these figures the costs associated with sampling and analysis, which might come to \$200-\$1500/sample. In estimating costs, one should also include the expenses of hiring a consulting firm, Kirk Brown suggests.

While monitoring wells will always have to be used to delineate groundwater contamination, other, less expensive methods might be employed to obtain at least a rough idea of where the wells can be placed most effectively and what substances they should monitor. In many situations, geophysical techniques can perform these tasks and can also provide profiling and area mapping and knowledge of the geological media through which groundwater and its contaminants migrate.

Donald Bruehl of Normandeau Associates Inc. (Bedford, N.H.) lists electrical resistivity sounding, seismic refraction profiling, and precision gravity surveys as "methods with which we have had much success in groundwater studies." Other techniques he mentions include magnetic and electromagnetic methods, earth conductivity, borehole geophysics, and remote sensing. He has used these techniques in groundwater surveys "in geologic conditions typical of the formerly glaciated Northeast." These conditions usually entail aquifers


The Nashua, N.H., site

consisting of stratified, glacially deposited sand and gravel. These materials are very permeable. Other contamination incidents have involved aquifers of glacial till (mixed clay, sand, gravel, and boulders) and fractured bedrock (permeable through the fractures or cracks in the rock).

Resistivity measurements have been used as a preliminary method of defining the horizontal and vertical extent of leachate plumes stemming from suspected hazardous waste drum burial areas in EPA Region 4 (southeastern U.S.). On the other hand, magnetometry can be useful for detecting contamination "source areas" in the form of buried steel drums. A. Shane Hitchcock of EPA Region 4 (Atlanta, Ga.) explains that where such technologies can be used, they reduce equipment costs, provide data immediately, and, with sufficient background information, can be very reliable.

Plume containment

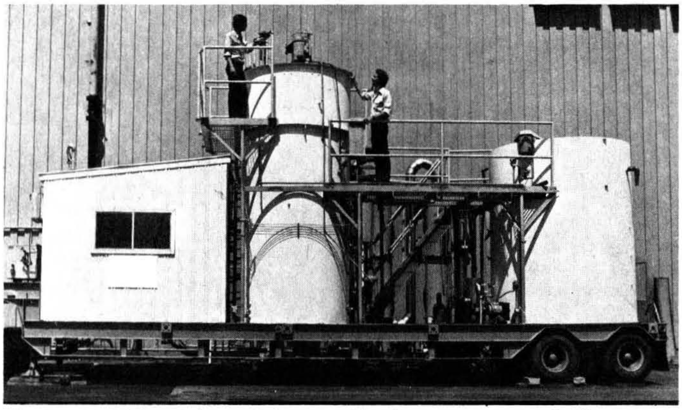
The strategy for containing the groundwater contaminants in Nashua, N.H., consisted of installing a 1-m-thick wall to surround them. The wall is a homogeneous soil-bentonite mixture constructed by a slurry technique; the material, keyed into bedrock at a maximum depth of 33 m is allowed to set. The wall is also keyed into a membrane surface cap.

After it has set, the wall's hydraulic conductivity is specified not to exceed 10^{-7} cm/s—the typical impermeability standard for hazardous waste sites—with leachate as permeant, Barvenik said. Moreover, since seepage under the wall through the rock was anticipated, a leachate collection and treatment plant has also been designed for the project; the design life of the containment system is 30 y.

But there are those who look askance at numbers indicating low hydraulic conductivity and permeability. Texas A&M's Kirk Brown maintains that under certain conditions, such as exposure to organic wastes, normally impermeable clays undergo structural changes and become more permeable, sometimes by several orders of magnitude (*ES&T*, September 1982, p. 503A). Perhaps this is one reason why EPA calls for synthetic impermeable materials in liners meant to protect groundwater from hazardous substances.

Treatment alternatives

Once a contamination plume is identified and mapped, a treatment scheme is needed. Treatment alternatives are considered, and then bench- and pilot-scale studies are conducted. Data from these studies help to establish design criteria for various treatment processes and to demonstrate performance capabilities of candidate processes, said John Absalon of Engineering-Science Inc. (Atlanta, Ga.). Treatability studies, in turn, can be used to develop a process aimed at specific problems, such as chlorinated solvents, hydrocarbons, heavy metals, and other contaminants.



Treatment: *Mobile unit for groundwater and leachate treatment uses PAC.*

The treatment of contaminated aquifer water could be carried out to prevent contamination spread (with purge wells) or to provide process water, or even potable water. Robert O'Brien of Calgon Carbon Corporation (Pittsburgh, Pa.) explains that granular activated carbon (GAC) is a frequently adopted treatment for contamination episodes involving organic chemicals. He says that his company installed GAC systems at 31 sites in the U.S. to treat contaminated groundwater flows of 5–2250 gallons per minute (gpm). In some cases, multimedia filtration was done before GAC treatment as a precaution; in others, air stripping was used to reduce the amount of volatile organics.

O'Brien says that for carbon tetrachloride (at four sites), influent concentrations of 130–10 000 $\mu g/L$ were reduced to below 1 $\mu g/L$, and 5–16 000 $\mu g/L$ of trichloroethylene (15 instances) were reduced to less than 1 $\mu g/L$. At one site, DDT, present at 4 $\mu g/L$, was curtailed to less than 0.05 $\mu g/L$. O'Brien notes that pre- and post-treatment analyses conformed to applicable EPA-published protocols for trace organics in water. He estimates that operating costs are \$0.22–\$2.52/1000 gal treated, depending upon the chemical(s) and their concentrations.

Donald Hager of Rubel and Hager, Inc. (Tucson, Ariz.) says that aeration, catalyzed chemical oxidation, and GAC adsorption will be used in a pilot system for removing organic solvents, including chloroform, carbon tetrachloride, and other low-molecular-weight chlorinated hydrocarbons. Pressurized gas aeration followed by direct incineration will be evaluated as an alternative to air stripping, he adds. In this way, discharge of contaminants from water to air is avoided. A 20-gpm plant will test ways to clean water for aquifer recharge at the Rocky Mountain Arsenal, Colo. The GAC portion will use carbon made by Westvaco.

Many experts note that there are problems with using GAC for low-molecular-weight chlorinated hydrocarbon removal from water. Hager says that chemical oxidation using ultraviolet-peroxide systems will address the destruction of nonadsorbable or nonvolatile organic contaminants in the water.

Zimpro Inc. (Rothschild, Wis.) is simultaneously using microbes and an organics removal approach involving *powdered* activated carbon (PAC) with activated sludge. The PAC adsorbs contaminants that the microbes cannot assimilate, while the microbes handle organics that otherwise would need an additional carbon step. Zimpro says that its units, presently in use at 15 U.S. sites, can remove hydrocarbons, pesticides, and certain other organics from groundwater, wastewater, or leachates, with a 95–99% removal efficiency reported for COD, total nitrogen, and various organics. Known by the trade name "PACT," the system is being used in a groundwater recharge project in El Paso, Tex., and for groundwater treatment at a chemical plant site in Michigan.

But not all contaminants are organic. Inorganics, such as heavy metals, silica, nitrate, and hardness, are also major groundwater contaminants, against which air stripping, carbon and polymer adsorption, and other approaches are generally of no avail. Removal approaches include pH adjustment, oxidation-reduction, and other adjustments necessary to accomplish insolubilization, filtration, ion exchange, electrodialysis, and reverse osmosis. Hager said that several inorganic treatment processes will be included in the Rocky Mountain Arsenal pilot study to assess heavy metal, silica, and hardness removal efficiencies.

At the Nashua, N.H., site, pilot field studies (20 gpm) are being conducted to evaluate metals removal by neutralization and precipitation. Organics (~0.2% by weight) removal and concentration for disposal or destruction through high-temperature air stripping, biological treatment, and distillation also are being studied, according to Bruce Lamarre of Roy F. Weston, Inc. (Concord, N.H.). Design parameters will lead to a 300-gpm treatment facility.

Reclamation problems

Both reclamation of contaminated groundwater and aquifer recharge can present technical and legal problems, warns Kenneth Schmidt, a groundwater quality consultant in Fresno, Calif. On the technical side, it often happens that the hydrogeologic system is misunderstood and not all contaminants are identified. These factors, Schmidt says, are especially troublesome for reclamation projects in the Southwest, a region particularly dependent on groundwater.

Schmidt spoke of a case involving vineyards south of Fresno, whose sandy soils were treated with dibromochloropropane (DBCP) to kill nematodes. That contaminant's concentration now exceeds 1 ppb in many wells. The amount of contaminated water involves about 3 million acre-ft near Fresno alone and could involve more than 20 million acre-ft of groundwater in all of California's San Joaquin Valley. The contamination is usually limited to the upper 200 ft of the aquifer. The problem with defining this contamination is that the source is so diffuse—DBCP was sprayed over many hundreds of thousands of acres of agricultural land from about 1955 to 1979.

Another difficulty, where contamination plumes are present, is that drawing a contaminant plume into a removal well for treatment can be inefficient. This is because large amounts of uncontaminated water are often drawn in with contaminated water. Schmidt says that at some reclamation projects, actual contaminated water accounts for less than 20% of the total water pumped. This situation is most likely to occur at sites at which the vertical and horizontal dimensions of the plume have not been precisely delineated before reclamation begins. Schmidt points out that heavy pumping can lead to substantial water table decline and changes in groundwater flow and quality, and in some cases, wells going dry.

An expired law

The SDWA expired last September; it remains in force under a simple reauthorization passed during the last session of Congress. But the law will most likely come up for a full reauthorization next year.

In any such reauthorization, industry would like to see EPA's authority to determine treatment technology removed and to have language in the law that would trigger standard setting if there were conclusive proof of harm from a contaminant. The betting is, however, that industry's proposals will not be considered.

The Senate Toxic Substances Subcommittee has asked the Congressional Research Service to compile a bibliography of groundwater information and to report data about groundwater contamination on a state-by-state basis.

Also, particularly in the Southwest, contamination plumes can comprise large volumes, sometimes in excess of 100 000 acre-ft. That is a tremendous amount of water to pump and can take a long time, often decades to handle. If large amounts of contaminated water cannot be treated and used, a major disposal problem could result. For example, land treatment by spray irrigation to remove volatile organics can lead to oxidation of ammonia to nitrate, another pollutant that could render the water unfit for use or aquifer recharge.

Pumping is not effective in removing contaminants from the vadose zone (the unsaturated zone between the surface and the water table). In wide areas, especially in the Southwest, the vadose zone is commonly several hundred feet thick. Substantial amounts of contaminants can be in this zone and can slowly drain downward to contaminate the "reclaimed" aquifer at a later time. Removal of contaminated soils and geologic materials at such depths is not feasible at many sites.

As if technical difficulties were not enough, Schmidt calls attention to legal problems. For instance, there are questions of water rights and adverse effects caused by pumping or disposal of treated water. This is especially true in the Southwest where water rights are embodied in a complex set of laws and traditions. Landowners may deny access even for monitoring, let alone groundwater recovery purposes. Siting wells at hydrogeologically preferred locations is often difficult, and the effectiveness of the reclamation program may be limited. Moreover, in some western states, such as Arizona, special permits are necessary for pumping or disposing of contaminated groundwater, and they are not always granted.

To compound all of the foregoing problems, there is a shortage of experienced and properly trained groundwater hydrologists, Schmidt observes. In addition, he notes that "unreasonble time constraints for implementing control measures are imposed by some regulatory agencies, often because of intense public pressure. This may cause plans to be implemented before the groundwater system is adequately understood. Serious pollution has resulted from implementing so-called control measures."

The cost factor

A major factor of the feasibility of groundwater reclamation is cost. One cost factor, that of delineating contamination plumes, may be reduced if various geophysical monitoring technologies are refined. Meanwhile, Schmidt points out that hundreds of thousands of dollars must be spent merely to define a plume. Then millions of dollars are required to construct facilities for reclamation. Operating costs are substantial, and many projects will go on for decades before completion. To all this, energy costs must be added.

Biological and physical-chemical technologies for treatment (filtration, carbon, reverse osmosis, and others) exist, but they are more effective when the contaminant(s) to be treated are properly identified and quantified and the treatment process does not involve dilution with clean fluid, which reduces treatment efficiency markedly. In the last analysis, the cheapest method of ensuring clean groundwater is, and will continue to be, contamination prevention.

—Julian Josephson

Clean Water Act revisited

Richard M. Dowd

The debate on the nation's water pollution laws continues this summer with a few interesting changes since last year. There are now three major items of legislation that have been developed: One that has been reported out of committee to the floor of the Senate by the Committee on Environment and Public Works (S. 5431); a bill that has been introduced into the House Committee on Public Works and Transportation (H.R. 3282); and a Reagan administration bill that was introduced last year. New additions to this legislation are as varied as the provisions that were introduced last year.

The debate over the implementation of best practicable technology/best available technology (BPT/BAT) and pretreatment of influents to publicly owned treatment works (POTWs) continues to focus on whether a technology- or water-based approach to attaining water quality standards should govern. Congress seems to be saying that control technology standards should be advanced one more notch; that more stringent control technology is needed to clean up the nation's rivers and streams. In any event, it is doubtful that there will be a waiver from BAT requirements in the final Clean Water Act amendments.

Pretreatment of influents to POTWs

Local and regional water quality managers are urging Congress to give them more flexibility in determining whether and when the pretreatment of influents is needed for proper operation of publicly owned treatment works. As a result, there has been serious consideration of a waiver from the categorical pretreatment requirements. Last year, the administration sponsored a provision to allow such waivers, and the Senate followed the proposal with interest. When EPA Administrator William Ruckelshaus appeared before the Congress recently, he indicated that EPA was still trying to define an appropriate waiver mechanism.

The viability of any pretreatment waiver hinges on EPA's ability to offer POTW operators a removal credit provision. Such a provision would permit operators the flexibility of evaluating each treatment works' needs for a pretreatment program. So far, a pretreatment waiver provision has not been included in the Senate or House bills, although such a provision is possible.

Deadlines for installing BAT

The Senate bill imposes a three-year deadline for installing BAT after the source-specific BAT guidelines have been issued by EPA; but in no case later than July 1, 1987. Under the present agency schedule for development of BAT guidelines, there are three years from issuance of the final guideline in June 1984 until July 1987. Should guideline development be further delayed in any way, this three-year period will be shortened. In some instances, industry would prefer to extend the deadlines, maintaining that three years will be insufficient because, when the guideline is set, the permit writer has yet to determine the level and type of controls for a source. Meanwhile, the environmental community believes that the guidelines will indicate the kind of controls that are necessary, and most industrial sources should be able to begin plant design and construction within a reasonable time.

The Senate and the House bills both focus on what will happen after the BAT guidelines have been established and controls have been installed. Both bills address the evolution from a technology-based approach to a water-quality-based approach to meeting standards. The bills require that EPA identify rivers and streams where installation of BAT was not sufficient to meet standards. Under these circumstances, EPA is given clear direction to establish new levels of control that would go beyond BAT in order to attain applicable standards.

Nonpoint sources

Senate committee members have expressed an interest in nonpoint sources of water pollution. As point source controls become more stringent, nonpoint sources will become more significant contributors of both conventional and toxic pollutants. While a nonpoint source provision is not presently in the Senate bill, it is likely to be reintroduced.

It is important to note what the bills do not cover. Although the bills suggest areas where more water quality data are needed, they do not identify the monitoring of pollutants as a key issue nor do they provide any direction to EPA to establish a comprehensive monitoring system for the nation's waters. In the late 1980s, the availability of adequate information will be critical to making decisions about water pollution control strategies. Without a significant monitoring effort, it is very likely that future debates will include discussion of the recurring need for information on direct-source contributions and the effectiveness of controls.

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ES&T FEATURES

Tunable diode laser systems for measuring trace gases in tropospheric air

A discussion of their use and the sampling and calibration procedures for NO, NO_2, and HNO_3

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Photochemical smog and acid deposition are two environmental problems in which the nitrogen oxides, NO, NO_2, and HNO_3 play a central role. Measurements of these constituents in the troposphere are therefore essential for understanding the chemistry of these problems.

NO, emitted mainly from automobile exhausts and thermal power plants, is the major anthropogenic source of the nitrogen oxides. It is oxidized in tropospheric air to NO_2 by reactions with O_3, HO_2, and organic peroxy radicals. NO_2 is an essential ingredient in the formation of photooxidants. It is rapidly photolyzed by solar radiation at wavelengths less than 420 nm to produce atomic oxygen, which combines rapidly with oxygen to form ozone. NO_2 is removed mainly by reaction with HO radicals to form HNO_3. It also reacts with organic radicals to form strong oxidants and irritants such as peroxy-acetyl nitrate (PAN). HNO_3, the major sink for the nitrogen oxides is, in turn, removed mainly by wet or dry deposition, often in the form of aerosol nitrate. The oxides of nitrogen, therefore, not only contribute directly to the production of photooxidants, but also control the concentrations of HO radicals, which are the major initiators of chain reactions involving hydrocarbons.

Wet chemical and filter methods have been used for many years to measure these compounds in the atmosphere. The reliability of these methods has not been high, and long collection times are required. For these reasons they have been largely supplanted by optical methods for measurement of NO and NO_2. Only indirect chemiluminescence methods have been reported for measuring HNO_3 with the sensitivity and the short response time required for tropospheric modeling (*1-4*).

Infrared absorption in the 2-15-μm region offers a number of advantages for atmospheric trace gas measurements; it is a passive technique, well adapted to in situ, real-time measurements. While virtually every minor or trace constituent absorbs in this spectral region the major gases, N_2 and O_2, do not. In fact, the absorption spectra for the trace gases are so rich that high resolution comparable to the line width, typically 2×10^{-3} cm^{-1} (60 MHz), is usually required to avoid mutual interferences. Such resolution can be obtained with a Fourier transform infrared (FTIR) spectrometer using a broadband light source. But because of its low sensitivity, path lengths of several kilometers are needed to detect constituents at the ppbv level.

Recently, tunable diode lasers have been developed that provide a wavelength-tunable source of extremely narrow line width. Techniques have been developed for measuring very small absorbances with these diodes. Reid and co-workers (*5-8*) have described optical systems for detecting tropospheric gases, but not the calibration methods or techniques for sampling real air into the system. This paper describes the use of tunable diode laser absorption spectrometers (TDLAS) for measuring nitrogen oxides in clean and polluted tropospheric air. We have used this spectrometer in a mobile system capable of in situ measurements of the oxides of nitrogen and other trace atmospheric gases.

Principles of TDL spectroscopy

Currently available tunable diode lasers (TDL) that operate in the mid-infrared are lead salt semiconductors of general composition $Pb_{1-x}Sn_xTe$, $PbS_{1-x}Se_x$, $Pb_{1-x}Sn_xSe$ and $Pb_{1-x}Cd_xS$. A p-n junction is formed by diffusion through an appropriate mask. The crystal is cut or cleaved to produce a diode of approximately 400 μm in length and 200 μm in width and height, with the crystal faces defining the cavity. Electrical contacts are evaporated onto the laser, which is then mounted on a rigid block. Application of an electric current (typically 0.5-2.0 A) causes lasing action by producing a population inversion between the almost filled valence band and the slightly populated conduction band in the active region. The frequency of the output laser radiation is given, to a first approximation, by the band gap of the semiconductor. Since this band gap depends on the metals that comprise the crystal and the composition parameter x, lasers can be manufactured to operate at a chosen frequency. Lasers are available for any frequency in the range of 500 to 3500 cm^{-1} (2.8-20 μm); frequencies outside this range are available on special order.

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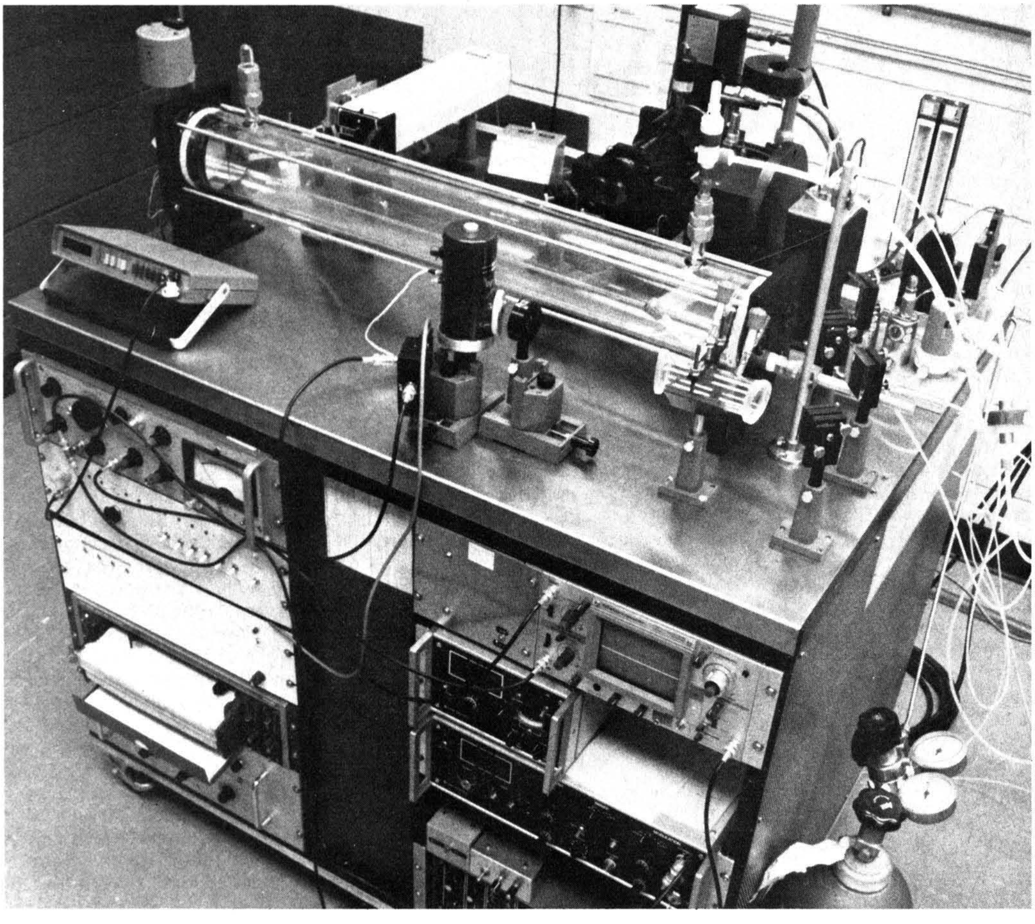
Tunability can be accomplished by subjecting the laser to a variable magnetic field (*9*), a variable hydrostatic pressure (*10*), or a variable temperature. Since these devices usually must be operated at a stable temperature below 50 K, temperature variation is the most convenient method for tuning the diode. Small temperature changes can be made by varying the current through the diode.

Early work was carried out with the diodes held in liquid helium Dewars. But this work was limited by problems with the supply, handling, and cost of liquid helium. More recently, reliable, closed-cycle refrigerators capable of achieving 12 K under fractional watt heat loads have become available. They have permitted lasers to be held at stable temperatures between 15 and 60 K, providing a wide frequency range for such lasers.

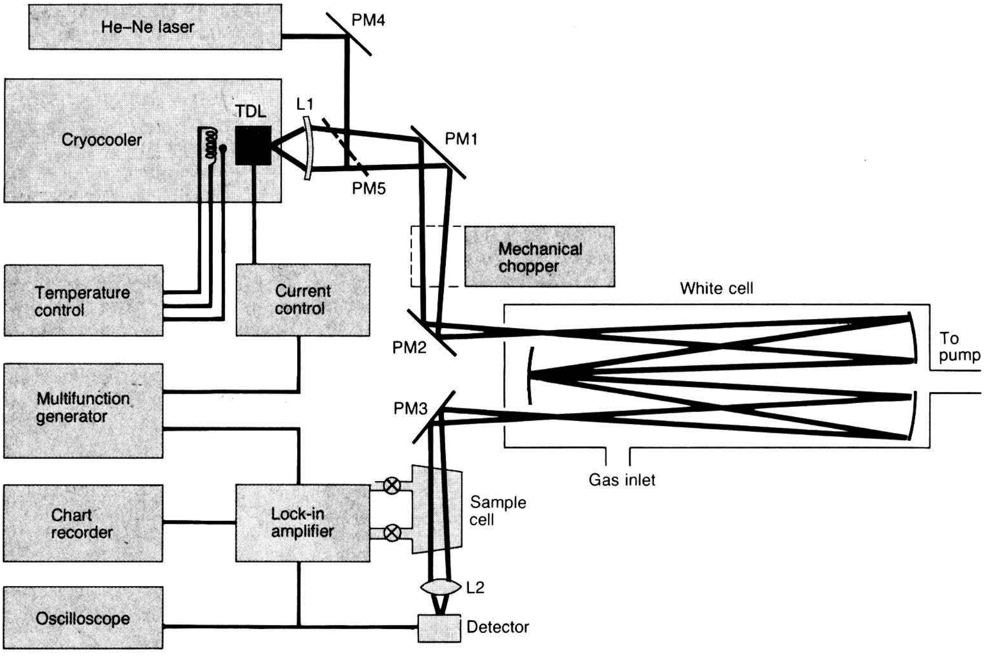
In principle, output frequencies corresponding to a number of well-defined longitudinal modes separated in frequency by $\Delta\nu \simeq c/2nl$ are possible, where c is the speed of light, l is the cavity length, and n is the refractive index of the laser material. The modes are not usually well defined and longitudinal, however, nor are the crystal faces exactly planar and parallel. Consequently, multimode operation, with variable frequency separation between modes, usually occurs. Since the intermodal separation is generally one wavenumber or greater, a laboratory monochromator is more than adequate to resolve the mode structure and is used, in some applications, to ensure passage of only a single mode through the system. Single mode performance often can be achieved by operating the laser at a suitable temperature and drive current. Under these conditions the frequency generally can be varied by 0.5 cm^{-1} for a current variation of 100 mA.

The line width of a TDL is extremely narrow. If a Dewar system is used to cool the diode the laser halfwidth can be as small as 27 kHz (*11*). The use of a refrigerator increases the noise because of piston vibration, and linewidths are typically between 1.6 and 50 MHz (*12*). Since gas-phase Doppler half widths are on the order of 60 MHz, TDL systems operating in single mode can obtain absorption spectra limited by Doppler broadening. The narrow line width and fast response of these diodes permit their frequency to be altered and



Air monitoring system. *The tunable-diode-laser-based Tropospheric Air Monitoring System (TAMS) as used for the Los Angeles measurement campaign. The optical system and gas control hardware are mounted on the bench with the White cell and detector in the foreground. The laser control, flow control, gas calibration, and signal processing and signal recording electronics are housed in the racks below the bench.*

FIGURE 1
A schematic of the laboratory tunable diode laser system[a]



[a] L1 and L2 are the lenses used to focus the beam onto the White cell entrance and the detector respectively, and PM1-5 are gold-coated plane mirrors used for beam alignment.

modulated. The laser can therefore be scanned rapidly over the spectral range of interest.

A TDLAS takes advantage of the narrow line width, tunability, and frequency modulation characteristics of these diodes to measure accurately small absorbances (10^{-3}–10^{-5}) due to a single rotational line in the vibrational band spectrum of a molecule. To measure this small absorbance, the absorption band must have a resolved rotational fine structure. Pressures less than 35 torr are used to substantially lower collisional broadening, but even at these pressures large molecules such as organic aromatics, PAN, N_2O_5, and $ClNO_3$ have so many rotational lines that the spectrum resembles a continuum. Most molecules with 5 atoms or less, however, as well as some larger molecules such as SF_6 and C_2H_4, have resolved fine structures.

All heteronuclear diatomics and some polyatomics have regions where the spectrum is resolved, even at atmospheric pressure; NO, NO_2, and HNO_3 fall into this category. Typical line strengths are in the range of 6×10^{-20} to 2×10^{-19} cm^{-1} $molec^{-1}$ cm^2, and therefore a path length of 20–50 m is sufficient to measure sub-ppbv levels of these molecules with a TDLAS capable of detecting absorbances of 10^{-5}. The long path length can be provided by directing the beam through the atmosphere and returning it to the detector by a retroreflector.

For molecules that do not have resolved absorption spectra at atmospheric pressure, or to avoid interferences by other species, reduced pressure is required, and the long path can be achieved with a multiple-reflection absorption cell.

Absorption relationships

The fraction of the power transmitted through an absorbing medium of length l cm can be related to the concentration of absorbing molecules, N molecules/cm^3, by the Beer Lambert law

$$\frac{I}{I_0} = \exp(-\sigma(\nu).N.l) \qquad (1)$$

where I and I_0 are the transmitted and incident powers and $\sigma(\nu)$ the frequency-dependent absorption coefficient in cm^2.

For a single isolated absorption line the absorption coefficient can be expressed as the product of an absorption coefficient at line center σ_0 and a line shape function $L(\nu)$

$$\sigma(\nu) = \sigma_0 L(\nu) \qquad (2)$$

At line center and for an optically thin system the Beer Lambert law reduces to

$$\frac{I_{abs}}{I_0} = \frac{I_0 - I}{I_0} = \sigma_0 N l \qquad (3)$$

Thus the power absorbed is always proportional to the concentration of the absorbing molecule. The functions $\sigma(\nu)$, $L(\nu)$ have three different forms, depending on the pressure. It can be shown, however, that for each of these cases the absorption signal remains linear with concentration for optically thin conditions.

TDL absorption spectrometers

The first TDLAS to be used as a trace gas detector was that of Hinkley et al. (*13-16*). Initially, it was used to measure ambient carbon monoxide in cities (*13*). A total path length of 610 m was achieved using a retroreflector. Since the P(1) to P(8) absorption lines of CO at around 2100 cm^{-1} are all resolved at atmospheric pressure it was possible to use the frequency modulation (FM) technique, with detection taking place at the fundamental frequency. They reported CO measurements of 400–1000 ppbv with an estimated noise equivalent of 5 ppbv. They later used these results to estimate sensitivities for C_2H_4, NH_3, O_3, Freon 11, Freon 12, and vinyl chloride based on their ability to measure absorbances of 10^{-3} over a 1-km path (*14*). Several improvements to this instrument have been proposed including line locking, 2f detection (*17*), and frequency stabilization using a tunable etalon (*18*).

Sachse et al. (*19*, *20*) have used a TDLAS of this type on an aircraft using 10 m on the outside of the fuselage as the absorption path. They measured carbon monoxide with an absorbance limit of 8×10^{-4}—about a fourfold-lower sensitivity than that achieved in the laboratory.

To overcome the problems of atmospheric turbulence and spectroscopic interferences, Reid et al. modified the TDLAS by using a multiple-reflection White cell in place of the atmospheric long path and ran the cell at reduced pressure (*5*). They also detected the absorption at twice the modulation frequency (2f), which had the advantage over detection at f of a "zero" baseline and a maximum at line center. By extrapolating observed absorbances in a 10-cm cell to those expected in a 300-m White cell they estimated their detection limit for SO_2 to be 3 ppbv in the ν_1 band at 1140 cm^{-1}. They estimated the absorbance detection limit to be 10^{-5}, corresponding to limits of 0.5 ppbv for O_3, 0.3 ppbv for SO_2 at 1370 cm^{-1}, 2 ppbv for N_2O, 0.01 ppbv for CO, 0.05 ppbv for NH_3, 0.03 ppbv for CH_4, 0.02 ppbv for NO_2, and 0.03 ppbv for NO. Later work by these authors showed that this limit could be improved by locking the laser frequency (*6*). They also showed the ability to measure SO_2 in a White cell but were unsuccessful in their attempts to measure NO_2 because of adsorption of the calibration gas on the cell walls (*8*).

Based on the results of Reid and co-workers, a number of TDLAS trace gas detectors have been built using their design and techniques. Connell et al. (*21*) have measured N_2O in air with an absorbance detection limit of 3×10^{-4}. Mankin et al. (*22*) have measured CO from an aircraft, and Pokrowski et al. (*23*) have measured HCl from on board a ship at sea.

A laboratory TDLAS

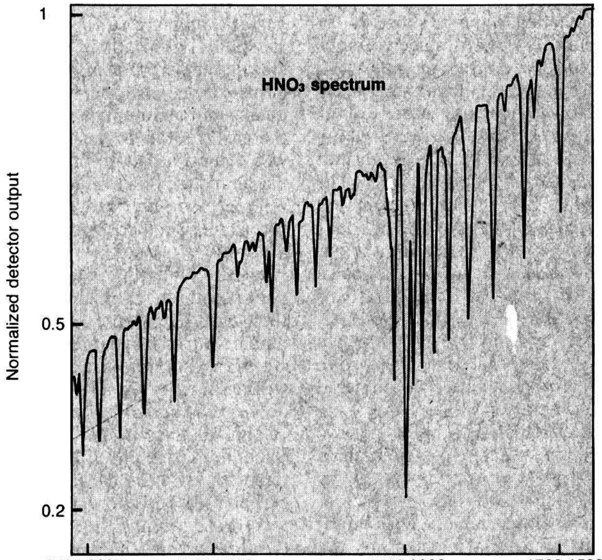
The laboratory TDLAS used in this work is based on the design of Reid et al. and is shown schematically in Figure 1. It routinely achieved absorbance detection limits of 2×10^{-5} or better, which—for the oxides of nitrogen—corresponds to mixing ratios below the 1-ppbv level.

The diode laser is held in a source assembly maintained to ±0.001 K at the operating temperature, which is in the 10–60-K range for the diodes used. Temperature control is provided by the combination of a closed-cycle, helium cryocooler, a heater, and a servo temperature control system. The current through the laser is supplied by a highly stabilized dc current control system. These items were supplied by Spectra Physics. The current can be changed or modulated by inputs received from a multiple-function generator. The laser radiation, which is generally emitted as a multilobe pattern within an f/1 cone, is collected and focused by an f/1 lens, L1. The plane fold mirrors, PM1 and PM2, permit maneuvering the beam for accurate entry into the White cell. The exiting beam is directed by a plane mirror, PM3, through a sample cell and another f/1 lens, L2, onto a liquid-nitrogen-cooled, mercury-cadmium-telluride detector, the output of which is fed into an oscilloscope for visual representation, then to a lock-in amplifier for processing. To aid in alignment of the optical path, it is convenient to pass a helium-neon laser beam through the center of the infrared beam. The red beam can be introduced into the optical train by inserting the folding mirror, PM5. The White cell can be replaced by a ¼-m monochromator for approximate frequency determination or for examining the mode structure of the laser output.

The spectrometer can be operated in either the amplitude modulation (AM) or the FM mode. In the AM mode the beam is chopped by the mechanical chopper and detected at this frequency by the lock-in amplifier to give a direct measure of the power incident on the detector. The absorption spectra are obtained as the laser frequency is varied. Figure 2 shows an example of the absorption spectrum of HNO_3 obtained in this way. The concentration of the absorbing species can be calculated directly from the spectrum, provided that the absorption coefficient in Equation 1 is known. This method of determining concentration is limited to the 1% absorbance level by the difficulty in measuring small differences between I and I_0.

This limitation can be circumvented by operating the system in the FM mode. The multiple-function generator

FIGURE 2
The HNO_3 absorption spectrum taken in the region of 1722 cm^{-1} using the 11-cm cell[a]



[a] Total pressure = 1.0 torr, HNO_3 partial pressure ≈ 0.01 torr, and laser power = 1 μW.

applies a 1–8-kHz sine wave to the laser current to give a current amplitude modulation that produces a frequency-modulated laser output. Measurement of the detector output at this frequency gives a signal related to the variation in power with frequency rather than the power incident on the detector itself. The signal obtained by scanning the modulated radiation over a single absorption line has a shape that is similar in appearance to the derivative of the absorption feature. This signal is a true derivative only if the modulation amplitude is much smaller than the absorption line width, but under these conditions the signal is relatively small. The signals are substantially larger for larger modulation amplitudes and it can be shown theoretically and experimentally that the maximum signal occurs when the peak-to-peak modulation amplitude is 2.2 times the half width (*24*). This determines the magnitude of the current modulation to be <1% of the total current. Under these conditions the derivative signal is severely broadened but still has the derivativelike shape that has given rise to the often used, although strictly incorrect, name of "derivative spectroscopy."

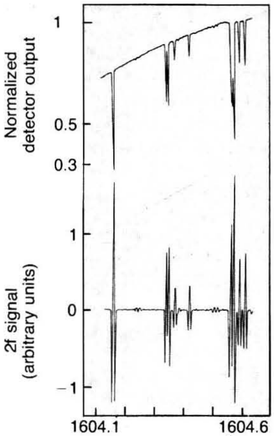
The modulated output signal often carries a substantial zero offset due to the variation in laser power with applied current. To reduce this offset and maximize the signal at the line center, the detector output is analyzed, not at the modulation frequency f itself, but at 2f. We shall refer to this technique as 2f detection. Figure 3 shows an example of the relationship between the AM and FM detection methods.

The measured 2f signal is proportional to the power absorbed by the target gas that can be measured accurately down to the 10^{-5} level since the power background is small. The total laser power is, however, not measured and therefore Equation 1 cannot be used to determine the gas concentration because of the unknown quantities I_0 and N. Consequently, it is necessary to calibrate the spectrometer by introducing a known concentration of the target gas and to use the proportionality between signal and concentration.

All spectrometers of this design have as the dominant noise contribution an interference pattern generated by scanning the laser across Fabry–Perot etalons resulting from the residual reflections of pairs of elements in the optical system. Our experience in dealing with this noise component is detailed in the following section, where the methods used to select the absorption lines and operating conditions for the nitrogen oxides also will be described.

FIGURE 3

The NO_2 spectrum in the region 1604.13–1604.65 cm^{-1}[a]



[a] Showing AM detection (top) and 2f detection (bottom) schemes for a high concentration (> 1%) mixture of NO_2 in air in the 11-cm cell. Pressure = 10 torr.

Measuring nitrogen oxides

The selection of a line was made by operating the spectrometer in the AM mode with a ¼-m monochromator in place of the White cell. A slit width of 100 μm is sufficient to permit the laser frequency output to be determined within ~1 cm^{-1}. For line identification the sample cell was filled with the pure gas at a pressure sufficient to give a substantial absorption. The laser operating temperature and current were adjusted for emission near the frequency of maximum line strength for the gas. The approximate frequency was determined with the monochromator and the exact value obtained by reference to published spectra. This procedure permitted the selection of an absorption feature with high line strength compatible with high laser power and single-mode output. Although all lasers were selected by the manufacturer to operate at the line strength maximum, selection of weaker lines was usually necessary to obtain good operating conditions.

The White cell was then placed in the optical path and filled to several torr with nitrogen. A mixture of several ppmv of the nitrogen oxide in N_2 was flowed through the sample cell at the same pressure. The instrument was operated in the FM mode and the 2f spectrum of the mixture was measured. The multiple-function generator was then programmed to scan the selected line repeatedly. This procedure permitted optimization of the system and the identification of the noise sources; interference fringes generated by etalons were always the first to be identified.

The frequency separation between fringe maximum generated by a Fabry–Perot etalon is given by $\Delta\nu = c/2nl$ where c is the speed of light and n is the refractive index of the material in the cavity of length, l. For typical lengths of 50 cm in the optical path, $\Delta\nu$ = 300 MHz, which is similar to the Doppler line width broadened by FM modulation. Consequently, an interference pattern caused by any Fabry–Perot etalon between 10 and 100 cm cannot be filtered out without affecting the signals. Most of these etalons were physically eliminated by using lenses slightly off axis and by using wedged windows or tilting them so they were no longer normal to the beam. By these means reflections off a transmissive element were not returned along the optical path.

Experience shows that etalon effects are easier to eliminate with some lasers than with others. This is related to the ease with which the radiation can be focused. Few etalons were encountered when the beam profile was close to Gaussian and could be focused within a 3-mm spot at 2 m using the single f/1 lens, L1 (Figure 1). Other lasers, whose far field patterns were either annular or multilobed, proved much more difficult to focus, and radiation was always observed well away from the beam center. In these cases the stray radiation often hit mirror mounts, particularly the field mirror mount of the White cell. When this scattered radiation fed back into the optical path an etalon could be set up with a transmissive element. These etalons often were impossible to eliminate. The obvious approach of restricting the beam with an aperture only served to introduce another element guaranteed to reflect this unwanted radiation and usually degraded, rather than improved, system performance.

Interference fringes also were generated within the White cell but had to be of different origin since the cell contained no refractive elements. The fringe periods indicated an optical path difference of four times the cell base path, and their amplitude depended strongly on optical alignment. The source of this interference appeared to be radiation scattered off the edge of the field mirror as the beam entered and left the cell. A good focus at the White cell entrance greatly lowered the magnitude of these fringes.

Since the base path of the cell was 1 m, the frequency maxima were all 75 MHz apart, which is less than the broadened absorption feature, and therefore filtering techniques could be used. To do this, an additional asynchronous modulation was applied to the laser current as described by Reid et al. (*8*).

Even for those cases in which all evidence of etalon-generated fringes had been removed, the residual noise was well in excess of the limiting detector noise. It was random and a function of the power hitting the detector but independent of any modulation applied to the laser. We call this "beam noise," which is inherent in the laser. Some lasers were of such low power ($<1\ \mu W$ received at the detector) that the beam noise was similar to the detector noise; these systems were considered to be detector noise limited.

Minimum detection limits

The detection limits for the nitrogen oxide trace gases were determined experimentally for the selected operating point and absorption feature. A sample of the gas at known concentration, C_s, at the ppmv level was flowed through the 11-cm sample cell. Since absorbance is directly proportional to path length, the measurements with the sample cell could be used to calculate the equivalent concentration in the White cell, C_W, by the simple relation: $C_W/C_s = L_s/L_W$, where L_s and L_W are the respective lengths of the sample and White cells. Since the White cell path length was usually adjusted to 40 m, a 10-ppmv sample in the 11-cm cell corresponded to a 27.5-ppbv concentration in the White cell.

The magnitude of the signal was measured, the gas was removed from the sample cell, and the remaining peak-to-peak noise was measured. The minimum detectable concentration (MDC) is defined as the equivalent White cell mixing ratio at which the signal-to-noise ratio would be unity.

If the trace gas can be introduced into the sample cell at a known mixing ratio, the MDC can be determined directly, without requiring knowledge of line widths or line strengths. On the other hand, if the concentration in the White cell itself is known, direct calibration is possible, without requiring the use of the sample cell. This could be done with NO and NO_2 but not conveniently with HNO_3.

Experiments were performed to test for possible sampling problems in introducing ambient air or calibration gases into the White cell. A gas mixture of known concentration (in the ppm range) was flowed through the sample cell and the signal measured. The same gas mixture was flowed through the White cell after being diluted by a known amount to a mixing ratio in the ppbv range. The signals should be related by the path length ratios in the two cells if no sampling errors occur. The results of these experiments are described separately for the three gases, since each required its own calibration procedure.

Sampling and calibration procedures

NO. Mixtures of NO in nitrogen were drawn from several cylinders that contained calibrated concentrations in the 4–20 ppmv range. These cylinders have been used by this group for some time, and comparisons have shown them to be consistent over several years. The calibration of one of the cylinders was compared with a flowing sample in which pure NO was diluted to 10 ppmv and found to be consistent within 5%. Parts per billion mixtures were prepared by flow dilution with air of these standards using calibrated flow meters. All flow meters, valves, and connecting plumbing were made of stainless steel or Teflon and were not found to affect the NO concentration.

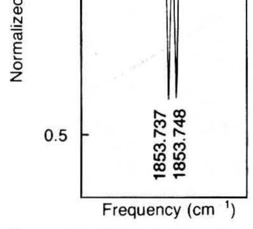
Spectroscopic identification of an observed NO feature is straightforward. The lines are more than 1 cm^{-1} apart and each is a Λ doublet, of which every second one is resolvable by the spectrometer, and may be identified from the literature (*25*). Figure 4a shows the AM scan of a high concentration of NO taken with a laser showing the $P_{1/2}$ (6.5) lines at 1853.737/1853.748 cm^{-1}. Figure 4b shows this doublet in 2f detection after the system had been optimized and the multiple-function generator reprogrammed to scan repeatedly over a smaller frequency range. The apparent broadening, due to the FM detection, is evident from the greater overlap between the two lines. The signal is from an 11-ppbv mixture of NO in N_2 flowing continuously through the White cell. The minimum detectable concentration is close to 0.5 ppbv with the limit being imposed by laser beam noise.

Of the three lasers tested only one gave an MDC of 0.3 ppbv at the beam noise limit. One was low powered, noisy, and difficult to focus, while the frequency of the third was unstable.

To test the sampling integrity of the system for NO at ppbv levels, a cylinder containing 4.00 ∓ 0.08 ppmv NO in N_2 was employed as a standard. Measured flows of this mixture in the 2–20 standard $cm^3\ min^{-1}$ (SCCM) range were introduced into various total flows of bottled air entering the White cell. Figure 5 shows a plot of the measured 2f signal as a function of the NO mixing ratio from the flow dilutions. The plot exhibits the expected linearity over the entire range of mixing ratios and shows no dependence on

FIGURE 4a

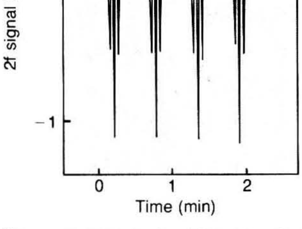
The Λ doublet of NO at 1853.737 cm^{-1} and 1853.748 cm^{-1}[a]



[a] Measured by AM detection for a high concentration (1%) of NO in the 11-cm cell. Pressure = 10 torr.

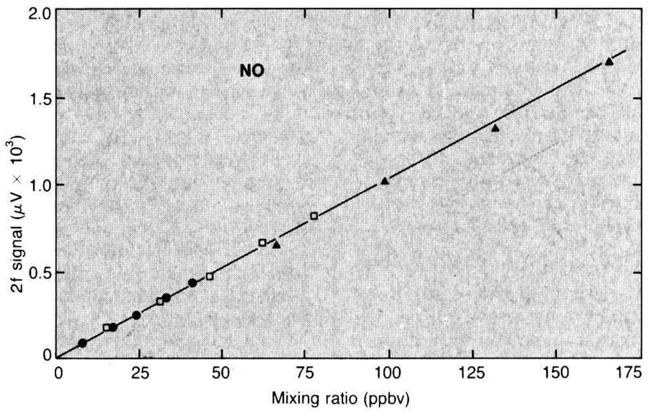
FIGURE 4b

A repetitive scan of the Λ doublet of NO at 1853.737 cm^{-1} and 1853.748 cm^{-1}[a]



[a] Measured in 2f detection for a NO:air mixing ratio of 11 ppbv in the White cell. Pressure = 10 torr. MDC = 0.5 ppbv.

FIGURE 5
The observed variation in the measured NO 2f signal vs. the expected mixing ratio[a]



[a] Obtained by introducing various flows of NO from a cylinder containing 4.00 ppmv NO in N_2 into several flows of bottled air. Pressure = 25 torr, temperature = 23 °C. Total flow (SLM) and residence times (s) respectively are: (▲) 0.5 and 27.6, (□) 1.0 and 13.8, (●) 2.0 and 6.9.

the residence time (7–27 s) in the White cell. Apparently, losses due to adsorption or reaction of NO at the walls are immeasurably small under these conditions.

NO_2. Since NO_2 is more polar than NO, problems were anticipated in maintaining sampling integrity at low concentrations. A cylinder containing a 10-ppmv mixture of NO_2 in oxygen was used as an NO_2 source for many of the experiments. But concern over the long-term stability of this source and possible surface effects on the regulators, valves, and flow meters used to take the mixture from the cylinder prompted cross calibration with an independent source. Passing known flows of nitrogen over a permeation tube was selected. Since the permeation rate is independent of the pressure outside the tube, mixtures can be made at low pressure and fed into the system without the gas contacting anything but transfer tubing. Permeation tubes are calibrated by the manufacturer from the weight loss as a function of time.

Four tubes were used, all of which had permeation rates in the 50–150-ng/min range. For N_2 flows of 10 SCCM, mixing ratios in the 2.5–7.5-ppmv range of NO_2 were produced. The mixtures could be further diluted to the tens of a ppbv range. Flow lines of Teflon or glass were found to be unreactive to NO_2.

A titration system was used to check the NO_2 sources. A known flow of NO mixture was oxidized to NO_2 by ozone:

$$NO + O_3 \rightarrow NO_2 + O_2 \quad (R1)$$

Reaction R1 provides quantitative amounts of NO_2 when carried out in an excess of NO or near its end point. Under these conditions the rate of the competing reaction:

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \quad (R2)$$

is negligible since $k_2 = 3.2 \times 10^{-17}$ $cm^3\,s^{-1}$ (*26*) and the O_3 concentration is small. The decrease in NO mixing ratio is then equal to the NO_2 mixing ratio produced. A series of experiments was performed in which this titration was used to calibrate the permeation tubes and to determine the MDC of NO_2. In some of these experiments the NO mixture was titrated to the end point and the signal due to the NO_2 generated was measured. The output of the permeation tube was then introduced to the flow and the measured signal compared with the signal from the titration source. For experiments involving an excess of NO, the residual NO was measured with a chemiluminescent instrument.

The permeation rates determined by these experiments were compared with those given by the manufacturer and with values obtained from independent weighings by the Atmospheric Environment Services (Canada). These comparisons are shown in Table 1. In all cases, the manufacturer's permeation rates were smaller than those obtained by the other methods, which suggests changes since shipment. The permeation rates appear to remain stable within ±5% provided the tubes are not subjected to large changes in pressure or temperature. However, care is needed in transportation since some changes were observed when we shipped tubes by air. One tube was found to have a white region in the plug indicating some damage, which perhaps explains its high permeation rate. Permeation tubes, therefore, provide satisfactory NO_2 calibration sources provided adequate care is taken in their handling.

As anticipated, problems were encountered in the handling of trace concentrations of NO_2 from the cylinder source. The measured concentration of 10 ppmv was found to agree within 5% of the manufacturer's figure only after the gas was run through the system for several minutes at high flows. The major source of the adsorption indicated by this observation appears to be the regulator, although it contained only stainless steel and Teflon. Low flow rates (<20 SCCM) also introduced adsorption problems that were not observed when the mixtures from the permeation tube were run directly into the sample cell. However, when the mixtures from the permeation tube were further diluted, indications of adsorption were obtained. Figure 6 shows a deviation from linearity at residence time greater than 14 s (required to generate the higher mixing ratios), which presumably is caused by surface adsorptions at long residence times. Measurements of mixtures made with high-rate permeation tubes showed that linearity is maintained at residence times <10 s up to at least 500 ppbv.

Three lasers were used for NO_2 detection. The approximate frequency of each was determined by comparing as large a section of the NO_2 spectrum as was possible with published spectra (*25*). Figure 7a shows part of the NO_2 spectrum between 1603.4 and 1603.8 cm^{-1} obtained with one of the lasers, while Figure 7b shows the 2f signals for a 25-ppbv sample for the lines 1603.593/.594 and 1603.632/.633. An MDC of about 0.5 ppbv is indicated, limited by beam noise, with some other absorption features also visible.

Another of the two lasers tested operated from 1600 to 1610 cm^{-1} and was beam noise limited at 0.2 ppbv. The third was found to have poor focusing properties.

A number of experiments have been performed that indicate that the TDLAS can resolve NO_2 absorption structure in this spectral region even at atmospheric pressure. Measurement of NO_2 with a retroreflector configuration should therefore be possible.

Development of such a system is now in progress in these laboratories, and tests of its sensitivity and MDC are being performed.

HNO_3. Nitric acid—the most polar of the three gases—was expected to present the worst sampling and calibration problems. Since prepared mixtures are not available, commercial permeation tubes and laboratory diffusion tubes were used as HNO_3 sources. In a diffusion tube the gas diffuses along a length of capillary tubing rather than through the porous Teflon plug of a permeation tube. The diffusion rate from a diffusion tube depends on the length and bore of the capillary and on the temperature of the reservoir.

Neither of these sources was stable for more than a few weeks and thus could not be used for absolute calibrations. Two independent calibration methods were used for HNO_3. In the first, the HNO_3 mixing ratio was calculated from the measured absorption and the known line strength. The second method involved the titration of HNO_3 against aqueous NaOH.

A schematic of the HNO_3 calibration system is shown in Figure 8. About 100 SCCM of air was flowed over 25 mL of a 2:3 mixture of HNO_3:H_2SO_4 held in a 250-mL flask at about 4 °C. The gas leaving the flask contained about 0.1% HNO_3 by volume and was split into two streams; one was passed through the 11-cm sample cell maintained at 25 torr, while the other was bubbled through a NaOH solution of known concentration and then through a bubble flow meter. The HNO_3 concentration was determined from the measured flow rate and the time required to neutralize the NaOH solution. While the titration was in progress the direct optical absorption of the HNO_3 flowing through the 11-cm cell and the 2f signals were measured. The mixing ratio in the 11-cm cell was determined from the direct absorption measurement and the known line strength. If unknown, the line strength could be calculated from the concentration determined by the titration.

Table 2 compares the mixing ratios determined by the titration with those calculated spectroscopically at 1720.3857 (cm^{-1}) using the line strength given by Bair and Brockman (*27*). The agreement between the two techniques is very good.

Since this line has a relatively low line strength, laser conditions were changed to measure a feature that would provide higher sensitivity. The line chosen was in the 1695-cm^{-1} region where no high-resolution spectra have been reported. Therefore, the line strength of this line had to be determined by the titration technique. It was checked regularly for more than six months and found to be reproducible over that period, as evidenced by the consistency of the data in the table.

The final row of Table 2 compares the mixing ratios determined by the two techniques when the White cell replaced the 11-cm cell for the absorption measurements. In this experiment, the HNO_3–air mixture was added to the main air stream at the sampling inlet to provide mixing ratios of 13 ppmv. The agreement between the two techniques attests to the absence of any serious sampling errors in the White cell at these concentrations.

Experiments were performed to check whether the 2f signal varied linearly with the HNO_3 mixing ratio. The flow system shown in Figure 9 was used to generate mixtures of HNO_3 in N_2 or in air. A constant flow of 1 standard liter per minute (SLM) of N_2 was passed over the HNO_3–H_2SO_4 diffusion source to provide mixtures containing ≈500 ppbv of HNO_3. Rotameter R_2 was used to introduce known amounts of this mixture to N_2 or air passing through rotameter R_3 to produce the desired mixture. Experiments were performed in which the mixture or the diluent was altered to give the range of mixing ratios. Figure 10 shows a plot of the 2f signal against mixing ratio obtained when the diluent was varied while the HNO_2–N_2 flow was held fixed. The mixing ratios shown on the right-hand axis of the figure were obtained by determining the sensitivity by a direct absorption measurement in the White cell.

These results, along with the titration experiments described above, show that sampling errors are not serious. Therefore, optical calibration using the 11-cm cell and the path

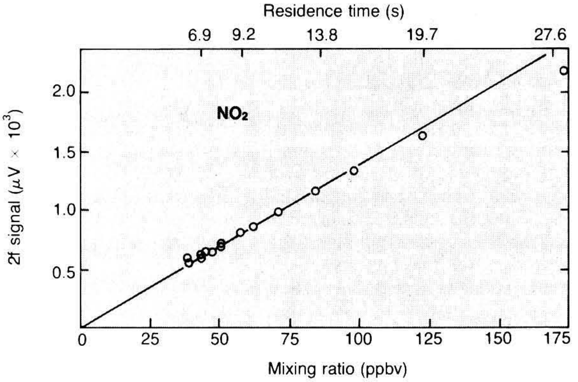
TABLE 1

Permeation rate in ng/min of NO_2 permeation tube

Tube number	Manufacturer weighing	Titration	Independent weighing	Independent titration
11367	140	166	152	153
11368	105	141	137	131
13390	85	176	175	—
11366	50	64	—	—

FIGURE 6

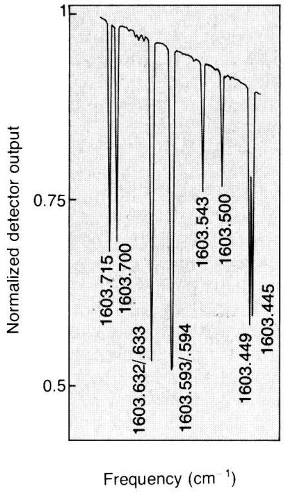
The observed variation in the measured NO_2 2f signal vs. the expected mixing ratios[a]



[a] Obtained by introducing the output of the permeation tube (176 ng/min) into various total flows of bottled air. Pressure = 25 torr, temperature = 23 °C.

FIGURE 7a

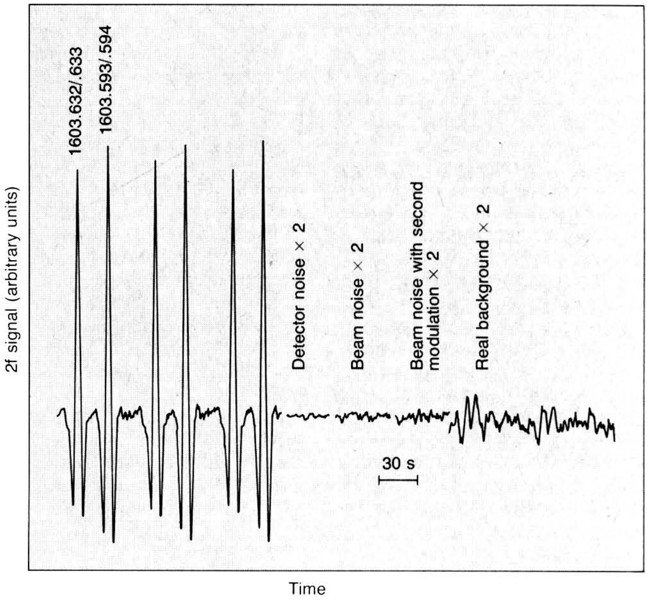
An example of the NO_2 spectrum in the region 1603.4–1603.8 cm^{-1}[a]



[a] Showing AM detection for a high concentration (> 1%) mixture of NO_2 in air in the 11-cm cell. Pressure = 10 torr.

FIGURE 7b

A repetitive scan of the 2f signals for a 25-ppbv sample of NO_2 in air[a]



[a] In the White cell for the lines at 1603.593/.594 and 1603.632/.633. Total pressure = 10 torr, temperature = 24 °C, and the MDC ≈ 0.5 ppbv.

length ratios should be applicable. Experience with the field instrument, described in the next section, showed that sampling conditions did not change appreciably over periods of more than two weeks.

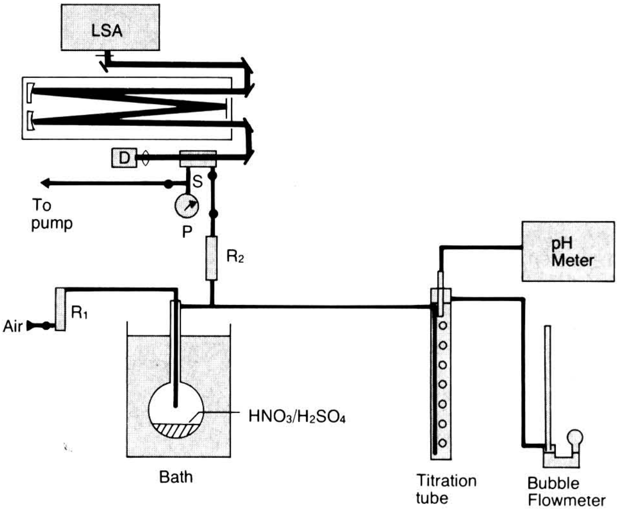
Two lasers were used for the HNO_3 measurements. Figure 2 shows the HNO_3 spectrum betweeen 1721.6 and 1722.2 cm^{-1} obtained with one laser. The spectral assignment was made from the data of Bair and Brockman (*27*). Figure 11 shows repetitively scanned 2f signals from the absorption feature at 1722.000 cm^{-1}. The slight overlap of adjacent lines due to modulation broadening accounts for the asymmetric line shape.

The figure shows 2f signals obtained at mixing ratios of 5.6 and 10 ppbv, which indicate a response time of about 5 min to the change in concentration. Since the residence time of the gas in the White cell is about 4 s, the longer response time suggests the occurrence of adsorption–desorption processes. Fluctuations of HNO_3 that occur in this system on time scales of less than 5 min can therefore not be followed.

The first laser would operate only at very low power (≈1 μW) and the MDC was detector-noise limited at

FIGURE 8

A schematic of the HNO_3 line strength/titration calibration apparatus[a]



[a] R_1, R_2: rotameter flowmeters, D: detector, S: 11-cm sample cell, P: pressure gauge.

≈0.6 ppbv. It was subsequently returned to the manufacturer for replacement.

Another laser was found to operate at several frequencies in the 1680–1720 cm^{-1} region with a laser power in the range of 15 to 30 μW. This one had an MDC of ≈0.35 ppbv, limited by beam noise.

A TDLAS for field measurements

Figure 12 is a diagram of a tropospheric air monitoring system (TAMS) designed for field operation in both clean and polluted air. The sampled air enters through a ¼-in.-o.d., 0.030-in.-wall Teflon tube. Particulates are removed from the air by a 0.2-μm Teflon filter located at the entrance of the tubing. A Teflon capillary downstream of the filter maintains the flow into the White cell at ≈2.5 SLM. The air traverses the inlet line in about 0.2 s while the residence time in the White cell is ≈4 s. The flow is monitored with a calibrated mass flow meter, FM2, and measured just before each calibration; it is adjusted, when necessary, by a Teflon needle valve situated at the inlet to the White cell. During a measurement the flow meter is isolated from the sampling line, since tests showed that it affected measurements of HNO_3 in the ppbv range. The motorized valve (MV), which is referenced to an MKS Baratron pressure gauge, controls the pressure in the White cell at 25 torr.

The NO and NO_2 calibration gases are added, in known amounts, upstream of the Teflon filter. The NO calibration standard is an Airco cylinder containing 4.00 ∓ 0.08 ppmv of NO in N_2. Flows of this calibration gas in the 0–20 SCCM are introduced into the air stream through a mass flow controller. This corresponds to additions of 0–32 ppbv of NO to the airstream.

The NO_2 calibration source is a Metronics permeation tube, calibrated by weighing and by NO–O_3 titration to permeate at a rate of 176 ng/min at 30 °C. The temperature of the tube is maintained at this temperature to ∓0.1 °C. A constant flow of 50 SCCM of N_2 over this tube adds 34 ppbv NO_2 to the air stream.

The calibration for HNO_3 is by the direct absorption technique described above. The 11-cm cell, containing HNO_3 in air at 25 torr, is placed in the laser beam, and the mixing ratio is determined by direct absorption and the known line strengths. The sensitivity for the White cell is calculated from the path length ratios. Mixtures containing known relative amounts of HNO_3 were also produced from the diffusion source and introduced upstream of the filter.

TABLE 2

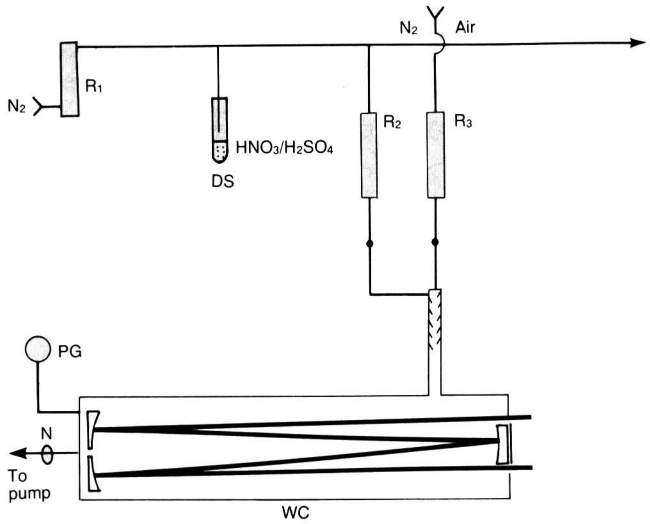
HNO_3 calibration results

Date of measurement	Mixing ratio in ppmv/10^3		Percent difference
	Titration	Optical	
Aug. 18, 1981	5.02	5.00[a]	0
Aug. 21, 1981	6.57	6.44[b]	−2
Aug. 26, 1981	5.53	5.53[b]	0
Sept. 4, 1981	4.51	4.51[b]	0
Feb. 9, 1981	0.0129	0.0128[c]	0

[a] Results obtained using line strength measurements of Bair and Brockman (*27*).
[b] Results obtained using the line strength determined from the average of several titration measurements.
[c] Results obtained using the White cell in place of the 11-cm cell.

FIGURE 9

The nitric acid flow dilution system[a]



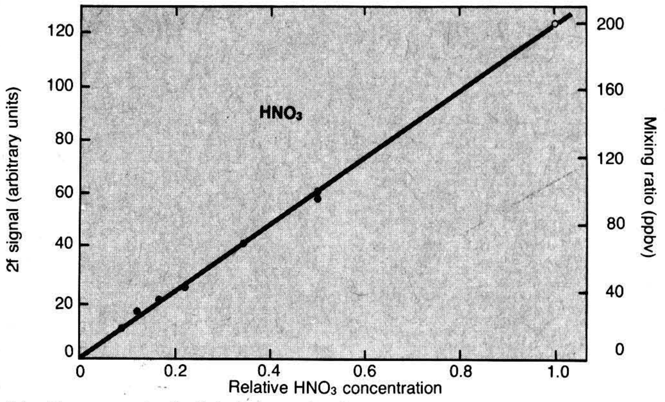
[a] R1-3: rotameter flow meters, DS: HNO_3 diffusion source, PG: pressure gauge, N: needle valve, WC: White cell.

The calibration of the TAMS for NO and NO_2 involved introduction of a known mixture of these gases at the entrance to the inlet tubing. The calibration procedure automatically compensates for losses in the system since they will be the same for the sampled air and for the calibration gas.

The optical method used for HNO_3 calibration does not account for losses that may occur in the system. Therefore, tests were performed to determine whether sample integrity was maintained through the Teflon inlet tubing and valve. A constant flow of HNO_3 in the ppbv range was passed into the system and the sampling tubing removed piece by piece. No variations in the 2f signals were detected when the stream was introduced directly into the White cell compared with it passing through 2.4 m of Teflon tubing, the Teflon filter, and the three-way Teflon solenoid valve that isolated the total gas flow meter from the sample line. Only when the stream passed through the flow meter was a (≈20%) change in the signal observed. The flow meter was therefore isolated from the inlet system when measurements were taken.

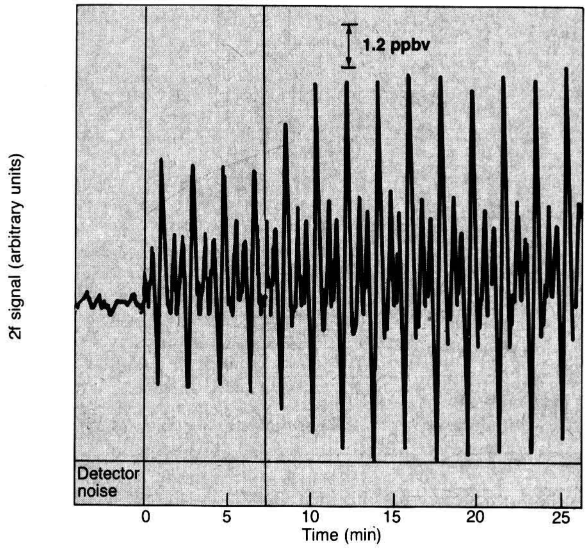
After several weeks of operation the Teflon filter became visibly dirty and was replaced, although no detectable

FIGURE 10
The observed variation in the measured HNO_3 2f signal as a function of HNO_3 concentration[a]



[a] The mixtures were produced by diluting the flow over the diffusion source with various flows of N_2. P = 29 torr, T = 24 °C, and the MDC = 0.9 ppbv. The mixing ratios were determined by direct absorption at the concentration shown (○).

FIGURE 11
A repetitive scan of the 2f signal for the HNO_3 absorption feature at 1722.000 cm^{-1}[a]



[a] Before time = 0 no HNO_3 added; for time = 0–7.5 mins.5.6 ppb HNO_3 added; after 7.5 mins.10 ppb HNO_3 added. The mixtures were made by diluting HNO_3/N_2 flows from a diffusion source in a fixed 4-SLM flow of room air. The sensitivity was determined by direct absorption in the 11-cm cell. Total pressure = 15 torr, temperature = 23 °C, and MDC = 0.6 ppbv.

change in the HNO_3 sensitivity had been observed.

Additional tests were conducted to determine the response time of the system to the nitrogen oxides. For NO and NO_2 the signals stabilized within ≈1 min after either an increase or a decrease in concentration. For HNO_3, on the other hand, the response time depended on the total flow through the system. Figure 13 shows that the time required to establish a stable signal for either an increasing or a decreasing concentration is substantially longer at low pressures and flows. Measurements over a range of test parameters showed that the optimum conditions at mixing ratios <20 ppbv were $P \simeq 25$ torr and total flows >2.0 SLM. For higher mixing ratios the response time was faster at all flows and pressures.

An interesting observation was that response time was faster with ambient air of normal humidity than with very dry cylinder air. This may have been the result of water vapor in the ambient air occupying some of the adsorption sites on the glass walls of the White cells.

Figure 14 shows some measurements of the three nitrogen oxides in ambient laboratory air. Also shown are the background signals made with bottled air, which is not supposed to contain any of these gases. The HNO_3 signal obtained with the bottled air may be the result of previously absorbed HNO_3 diffusing from the White cell walls. These measurements show that the MDC for each of the gases is better than 0.5 ppbv.

Figure 15 shows a plot of the 2f signal as a function of the flow rates of an HNO_3 mixture introduced into a constant 2.5 SLM flow of laboratory air. The mixing ratios shown on the right-hand ordinate were determined by the direct absorption technique. The plot is linear, establishing the ability of the TAMS to measure HNO_3 in ambient air below 10 ppbv. The intercept at ≈2 ppbv represents the HNO_3 mixing ratio in the ambient air that contained the exhausts from the diffusion source. Similar results were obtained for NO and NO_2.

The TAMS has been used in comparison studies with a chemiluminescence system and in measuring tropospheric air in the Los Angeles and southern Ontario regions. The results of these studies will be reported soon.

Acknowledgment

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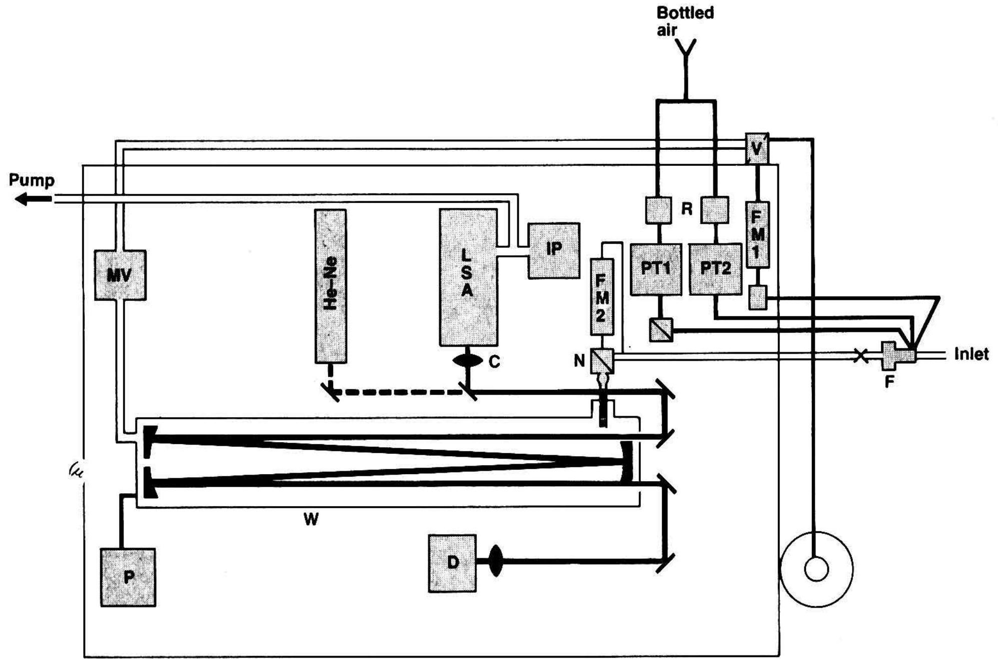
FIGURE 12
A schematic of the tropospheric air monitoring system (TAMS) designed for field operation



Key

MV	motorized valve
P	Baratron pressure
W	White cell
He-Ne	helium–neon alignment laser
LSA	laser source assembly
D	HgTeCd infrared detector
IP	ion pump
R	rotameter flowmeters
x	capillary
FM1	mass flow controller–NO flow
FM2	mass flow meter–total flow
PT 1	NO_2 permeation tube
PT 2	HNO_3 permeation tube
V	three-way valve
◪	solenoid valve
◎	4.00 ppm NO in N_2 spectral-seal cylinder
N	Teflon needle valve
C	collimating optics

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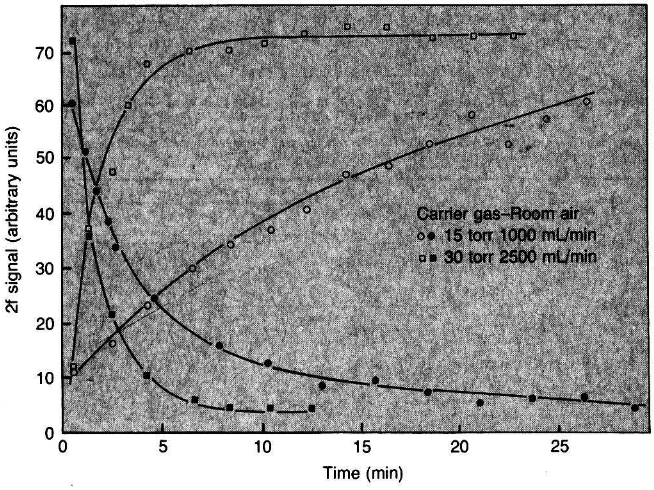
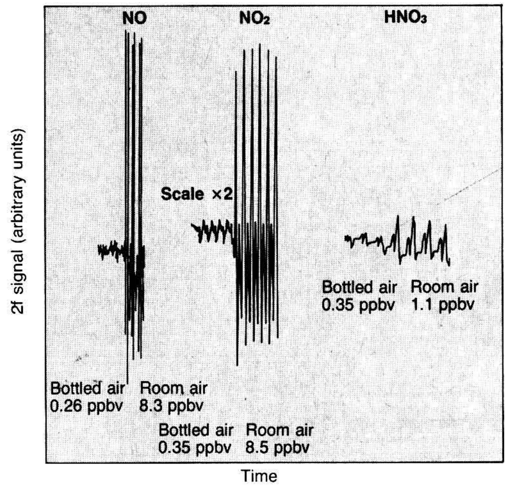
FIGURE 13
The variation in the observed HNO_3 signal as a function of time[a]



[a] 1) after the HNO_3 source has been removed, ■, ●.
2) after the HNO_3 source has been introduced to a flow of room air entering the White cell, □, ○.

FIGURE 14

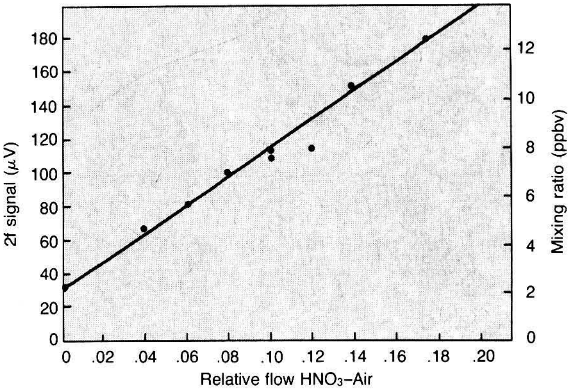
Observed 2f signals for NO, NO_2, and HNO_3 measured in ambient laboratory air[a]



[a] Also shown is the MDC for each species in bottled air. Pressure = 25 torr, temperature = 24 °C, and total flow = 2.5 SLM.

FIGURE 15

A plot of the variation in the observed signal as a function of the flow of an HNO_3–Air mixture[a]



[a] Introduced into a constant 2.5-SLM flow of room air. Mixing ratios presented on the right-hand side were determined by direct absorption using the 11-cm cell.

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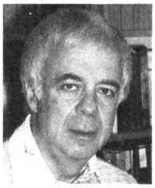

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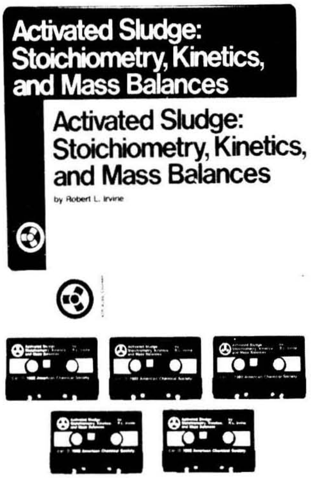

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International pollution control costs of coal-fired power plants

Here is a comparison of costs in the U.S., Europe, and Japan, a look at coal's competitiveness with other energy sources, and some thoughts on future technological developments

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In countries looking to coal as a major energy source for the generation of electricity, the cost of pollution abatement is a major concern. Such costs could affect coal's competitiveness with other energy sources. This problem was discussed extensively at an international symposium on costs of pollution abatement, held in Petten, The Netherlands, last year, and sponsored by the Organization for Economic Cooperation and Development (OECD) (*1*).

In general, pollution abatement costs depend on

- physical parameters related primarily to coal characteristics, power plant design, environmental control system design, and plant operation,
- applicable regulatory standards determined by public policy,
- economic and financial parameters such as interest rates, tax treatment, and raw materials' cost, and
- the definition of included and excluded items.

Differences in such factors are the principal cause of capital and operating cost variations across different studies. To compare the environmental control costs of coal-fired power plants, the specific pollutants being controlled should be carefully identified and any important differences in scope or definition made explicit. Unfortunately, many studies do not report their underlying assumptions in sufficient detail to permit rigorous comparisons for similar premises. The difficulties of making international comparisons can be further exacerbated by differences in nomenclature and costing methodology.

In this article, capital costs and annual revenue requirements reported in recent studies are presented together with a summary of key assumptions to illustrate the range of published costs for environmental control. All costs have been converted or adjusted to first-quarter 1982 U.S. dollars. Wherever possible, pollution abatement costs also are summarized as a fraction of total plant cost. Ranges of reported costs are given in terms of their mean value and uncertainty. Selected measures also are derived to show how different costs compare on the basis of similar levels of performance or effectiveness, and a simplified method is presented for estimating major pollution control costs for a range of user-specified assumptions.

Power plant pollution abatement systems may be characterized as controlling air pollutants, water pollutants, and solid wastes. Noise control systems also are considered an environmental control measure in a number of studies. However, the greatest attention is given to air pollution control, consistent with the concerns of the international community (*1*).

Sulfur oxide control

Control of sulfur oxide (SO_x) emissions most strongly dominates international discussions of environmental control costs since technological options are relatively expensive and not yet widely implemented in many countries. Control of SO_x emissions is achieved either by the use of low-sulfur fuels or by installation of a flue gas desulfurization (FGD) system. While the former remains the most prevalent method for existing power plants, FGD systems are increasingly being used at new installations, principally in Germany, Japan, and the U.S.

Where FGD is employed, wet lime or limestone scrubbing processes are used almost exclusively. In the U.S., a limestone scrubber producing a solid waste for disposal is the prevailing technology, while scrubbers in Germany and Japan typically use lime and produce gypsum as a by-product. Regenerative FGD systems producing by-product sulfur or sulfuric acid have been adopted only on a very limited scale where site-specific factors make it economical. The use of "dry" FGD systems currently is receiving considerable attention and development, but has not yet been widely implemented on a commercial scale. A number of major utility projects, however, are now in progress in the U.S.

Cleaning coal to reduce ash and sulfur content prior to coal combustion is also receiving significant attention in many countries. Techniques currently being developed in Germany and the U.S. involve better cleaning of small-sized, finely ground coal, with greater separation of mineral matter, including sulfur-laden pyrite.

However, costs increase considerably as finer coal sizes are treated. Currently, total costs for cleaning German coals (primarily for ash removal) are approximately \$3/metric ton (*2*). Estimated costs for new coal preparation plants in the U.S. range from approximately \$1-2/metric ton of cleaned coal for a relatively simple plant with no appreciable sulfur removal, to approximately \$4-6/metric ton for more complex plants able to

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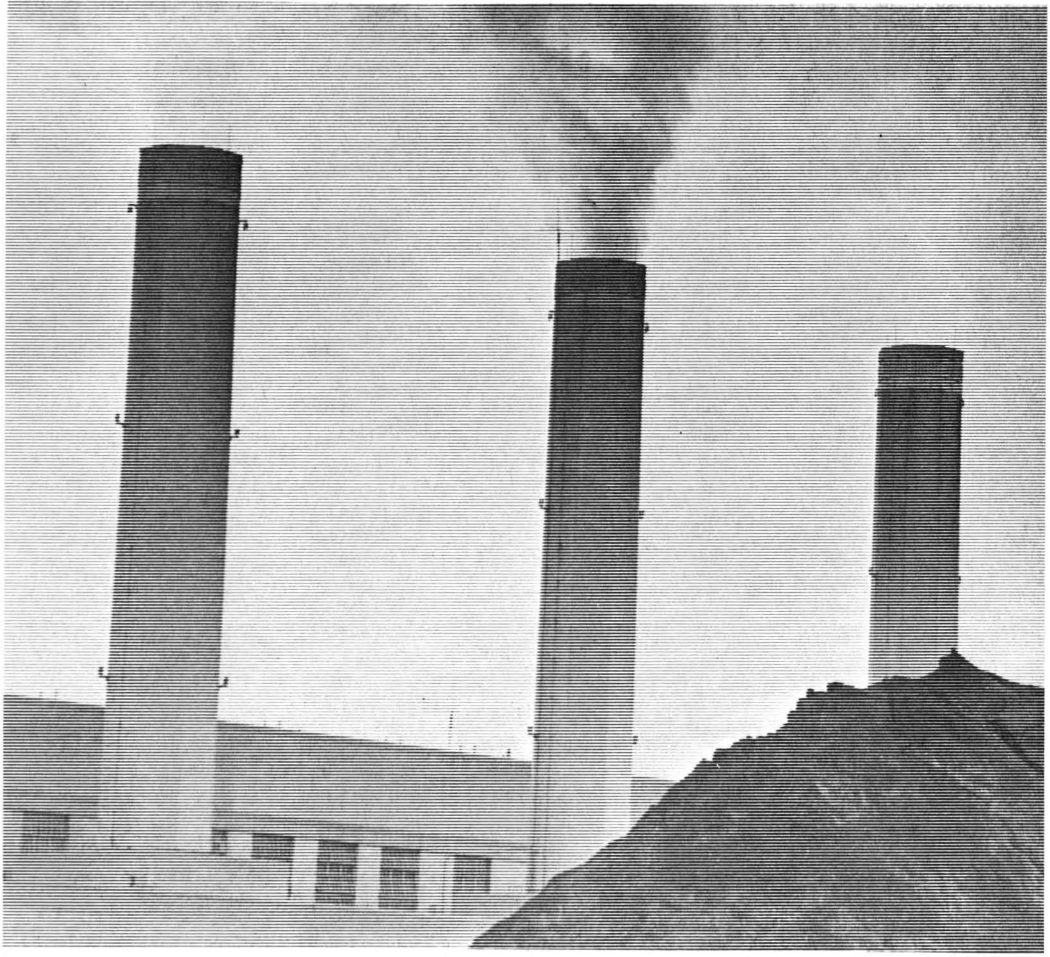

remove 20% to 40% of the total sulfur as well as significant amounts of ash (*3*). The value of coal lost with the cleaning plant refuse would add approximately 5-20% of the raw coal cost to these figures, depending on the level of cleaning. Currently, commercial processes employ physical cleaning and can only remove sulfur present in the form of mineral pyrite. Chemical processes able to remove organic sulfur are still under development. In many cases, however, clean coal alone is insufficient to meet environmental regulations, and FGD systems are required.

Tables 1 and 2 summarize the capital costs and revenue requirements, respectively, reported in recent studies (*3-15*). Table 1 shows reported capital costs of a wet lime or limestone FGD system for SO_x control (in 1982 dollars) ranging from \$72 to \$184/kW of installed capacity for plants in Germany, Japan, and the U.S. These values represent 11-18% of total power plant cost, with an average value of 13%, corresponding to approximately \$140/kW, excluding sludge disposal costs. Case studies on which these capital costs are based, however, reflect plant sizes ranging from 150 to 2000 MW, coals of different quality, and differences in environmental standards, FGD system design, and economic assumptions.

While a comprehensive analysis of the effect of such differences is limited by available information, some key insights are possible. Table 3 summarizes analytical models for simplified cost calculations that show the effect of key variables on pollution control costs (*16*). For a lime or limestone FGD system at a moderate-to-large-sized plant (500 MW or more), the variation in capital cost per kilowatt at a given location is primarily a function of the maximum sulfur or sulfur dioxide removal rate. This, in turn, depends principally on the coal sulfur content and the required SO_2 removal efficiency, as determined by the applicable emission standard. For the cases in Table 1, the maximum sulfur removal rates vary from approximately 1 to 16 metric tons of sulfur per million kWh (that is, coals of 0.5% to 4.0% S with net removal efficiencies of 30% to 95%). This accounts for a significant portion of the cost variations in Table 1. Some economies of scale also are achieved for larger units with lower heat rates.

More significant are design considerations such as full vs. partial scrubbing and the inclusion of redundant scrubber trains to enhance system reliability (common in U.S. plants but not in Japan or Germany). In addition, differences in key economic parameters and assumptions, such as interest rates and facility lifetime, also are pronounced (see footnotes to Tables 1 and 2). For example, FGD systems in

TABLE 1

Capital costs for pollution control at a new coal-fired power plant[a] (1982 U.S. $)

		Capital cost ($/kW)				% of total plant cost			
Reference no.	Plant size (MW)	SO_x	TSP	NO_x	Total env. control	SO_x	TSP	NO_x	Total env. control
Federal Republic of Germany									
(*4*)[b,c]	750	109	22						
(*5*)[b,d]	600		13						
(*6*)[b,e]	150	117 ± 18[f]				12–15			
	750	72 ± 8[f]							
(*7*)	(Not given)								27[g]
Japan									
(*8*)[h]	2000[i]	134	29	9	172[l]	11.8	2.6	0.8	15.2[l]
	2000[j]	154	31	29	214[l]	13.1	2.6	2.5	18.2[l]
	2000[k]	182	31	42	256[l]	15.0	2.6	3.5	21.1[l]
(*9*)[m]	2000[n]	0	12	5	56[q]	0	1.2	0.5	5.4[q]
	2000[o]	131	12–20	7–12	236–249[q]	10.9	1.0–1.6	0.6–0.9	20 ± 0.2[q]
	2000[p]	131	12–20	38	271–278[q]	10.6	1.0–1.6	3.1	22 ± 0.3[q]
U.S.									
(*3*)[r]	1000	143	45		218[s]	11.6	3.7		17.7
(*10*)	500[t]	175[w]	40						
	500[u]				176[s]				
	500[v]				244[s]				
(*11*)[x]	500[y]	90				11.3			
	500[z]	120 ± 10			165 ± 15[v]	14.5			20.0[v]
	500[aa]	180				20.6			
(*12*)[bb]	1000[cc]	121 ± 16	96 ± 11	14 ± 7	329 ± 57[ee]	11.6 ± 0.1	9.3 ± 0.1	1.3 ± 0.5	31.5 ± 1.5[ee]
	1000[dd]	184 ± 23	56 ± 6	13 ± 7	385 ± 71[ee]	17.5 ± 0.2	5.3 ± 0.1	1.2 ± 0.5	36 ± 2[ee]

Footnotes to Tables 1 and 2

[a] Unless otherwise specified, environmental control systems are assumed to be: a wet lime or limestone scrubber for SO_x, an ESP for particulates (TSP), and combustion modifications for NO_x.

[b] Calculated assuming 2.40 DM/U.S. $ and 5% inflation of reported costs to 1982.

[c] Assumes designs currently going on-line in Germany; SO_2 removal of 50–80%, fly ash removal above 99%, with plant operating 4000 h/y.

[d] Costs are based on a South African coal and include supplies, erection, and start-up, but not ducts, dust-handling system, or engineering. Plant operates 8000 h/y.

[e] Coal has 1.5% S. SO_2 emission limit is 650 mg/Nm^3. Plant operates 5000 h/y. Credit is taken for by-product gypsum.

[f] Excludes land cost. Equipment cost based on manufacturer's estimates. Details of project scope not reported.

[g] Details not reported. Appears to include all environmental controls for air, water, and land.

[h] Plant with two units. Coal of 1.2% S, 15–20% ash, $70/metric ton. Reported costs are adjusted to 240 yen/U.S. $. Plant capacity factor is 0.70. Discount rate is 10%.

[i] Level II emissions: 200 ppm, SO_2 (80% removal); 100 mg TSP/Nm^3 (hot-side ESP); 300 ppm NO_x.

[j] Level III emissions: 100 ppm SO_2 (90% removal); 30 mg TSP/Nm^3 (hot-side ESP); 150 ppm NO_x [combustion modifications plus 50% selective catalytic reduction (SCR)].

[k] Level IV emissions: 50 ppm SO_2 (95% removal); 30 mg TSP/Nm^3 (hot ESP); 60 ppm NO_x (combustion modifications plus full SCR).

[l] Only costs related to air pollution control were reported. No FGD sludge disposal costs or credits are included with SO_2 control.

[m] Plant with two units. Capacity factor 0.70. Coal of 1.2% S, 15–20% ash, 1.8% N_2, $70/metric ton. Costs at 240 yen/U.S. $. Reported 1981 costs inflated 5% to 1982. Interest rate 10%, inflation rate 5%, fuel escalation rate 8%.

[n] Model I emission levels: 1000 ppm SO_2 (no control); 400 mg TSP/Nm^3; 400 ppm NO_x.

[o] Model II emission levels: 100 ppm SO_2; 30–50 mg TSP/Nm^3 (ESP + FGD); (a) 300 or (b) 170 ppm NO_x (combustion modifications, gas recirculation).

[p] Model III emission levels: 100 ppm SO_2; 30–50 mg TSP/Nm^3; 60 ppm NO_x (Model II + SCR).

[q] Includes effluent control at 9, 15, and 17 $/kW for Models I, II, and III, respectively, plus "others" at 29, 71, and 72 $/kW accounting for 2%, 6%, and 9% of total generating cost for Models I, II, and III, respectively. This category includes dust control, noise control, ash disposal, and other miscellaneous costs.

[r] Reported 1981 costs inflated 5% to 1982. Coal of 2.0% S, 15% ash, $30/U.S. ton. Emission levels of 0.6 lb SO_2/MBtu and 0.03 lb TSP/MBtu. Plant capacity factor of 0.65.

[s] Includes cost of solid waste disposal, SO_2, and particulate control.

[t] FGD costs based on 4% S coal, 90% SO_2 removal. ESP costs based on 99.7% efficiency and 5×10^{10} ohm-cm resistivity, with 1980 costs inflated 20% to 1982. Plant operates 5500 h/y. Reported 1984 FGD operating costs adjusted to 1982 assuming 13.5% deflation of O&M costs, which were assumed to be approximately 50% of total revenue requirement.

[u] 0.7% S western coal. 1984 operating costs adjusted as in (*t*).

[v] 3.5% S eastern coal. 1984 operating costs adjusted as in (*t*).

[w] Waste sludge disposal excluded from capital cost but included in annual revenue requirement.

TABLE 2

Contribution of pollution control cost to total annual revenue requirement (1982 U.S. $)

Ref. no.	Cost basis*	Plant size (MW)	Reported annual cost (mills/kWh)				% of total annual electricity cost			
			SO_x	TSP	NO_x	Total env. control	SO_x	TSP	NO_x	Total env. control
Federal Republic of Germany										
(4)[b,c]	(F)	750	(8.7)	(1.0)						
(5)[b,d]	(F)	600		(0.4)						
(6)[b,e]	(F)	150	(6.6 ± 0.9)							
		750	(4.7 ± 0.5)							
Japan										
(8)[h]	(L)	2000[i]	8.7	1.5	0.4	10.6[l]	12.6	2.2	0.6	15.4[l]
		2000[j]	9.6	1.6	2.6	13.8[l]	13.3	2.2	3.6	19.1[l]
		2000[k]	10.9	1.6	4.3	16.8[l]	14.6	2.1	5.8	22.5[l]
(9)[m]	(L)	2000[n]	0	0.6	0.7	4.8[q]	0	0.7	0.3	5.6[q]
		2000[o]	8.9	1.0	0.7	16.0[q]	9.1	1.0	0.6	16.1[q]
		2000[p]	8.9	1.0	5.8	26.8[q]	8.1	0.9	5.3	24.3[q]
U.S.										
(3)[r]	(F)	1000	(8.5)	(1.5)		(11.2)[s]	(13.4)	(2.8)		(18.1)
(10)	(F)	500[t]	(9.4)[w]	(1.6)						
	(L)	500[u]				10.0[s]				
		500[v]				15.3[s]				
(11)[x]	(F)	500[z]	(5.5 ± 0.5)			(7 ± 1)[v]	(10.3)			(13.0)[v]
(12)[bb]	(L)	1000[cc]	10.6 ± 0.5	3.5 ± 0.3	0.4 ± 0.2	21.2 ± 2.7[ee]	11.8 ± 0.5	3.9	0.5 ± 0.1	23.5 ± 0.5[ee]
		1000[ee]	17.1 ± 0.6	2.0 ± 0.2	0.4 ± 0.1	31.2 ± 4.5[ee]	17.7 ± 1.1	2.1	0.4 ± 0.1	31.5 ± 1.5[ee]
Denmark										
(13)[ff]	(F)	400[gg]	(2.5)[jj]							
		400[hh]	(3.3)[jj]							
		400[ii]	(4.3)[jj]							
The Netherlands										
(14)	(F)	600				(6.7)[kk]				(12.7)[kk]
Sweden										
(15)[ll]	(F)	200	(2.9)[mm]							
		200	(5.7)[nn]							

* (F) = First-year cost basis (shown in parentheses)
(L) = Levelized cost basis

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[x] All cases meet emission standards of 1.08 lb SO_2/MBtu and 0.03 lb TSP/MBtu. Plant capacity factor of 0.63. Base case coal of 1.5% S, 15% ash, costing $70/metric ton (Europe). Reported FGD costs include solid waste disposal by landfill.

[y] 1.0% S coal.

[z] 1.5% S coal (base case).

[aa] 3.5% S coal.

[bb] Plant with two 500-MW units, capacity factor of 0.65. 1981 EPRI Economic Premises. 1982 environmental standards. Reported costs inflated 5% to 1982.

[cc] Wyoming coal (0.48% S).

[dd] Illinois coal (4% S).

[ee] Includes solid waste disposal, plant cooling, water treatment, and noise control.

[ff] Base case plant using coal of 1.2% S, 10.7% ash, operating 6500 h/y (full load).

[gg] 1.0% S coal.

[hh] 2.0% S coal.

[ii] 3.0% S coal.

[jj] Dry spray tower scrubber removing 85% SO_2 with ESP particulate collector. Costs do not include ESP, land, engineering costs, administration, or taxes.

[kk] Includes full FGD, low-NO_x burners, advanced particulate control, noise and dust abatement. Urban area. Coal characteristics and emission levels not specified.

[ll] Costs assume 5.9 kroner/U.S. $. Reported 1981 costs inflated 5% to 1982. SO_2 removal via a wet-dry method. Details of coal and plant operation not specified.

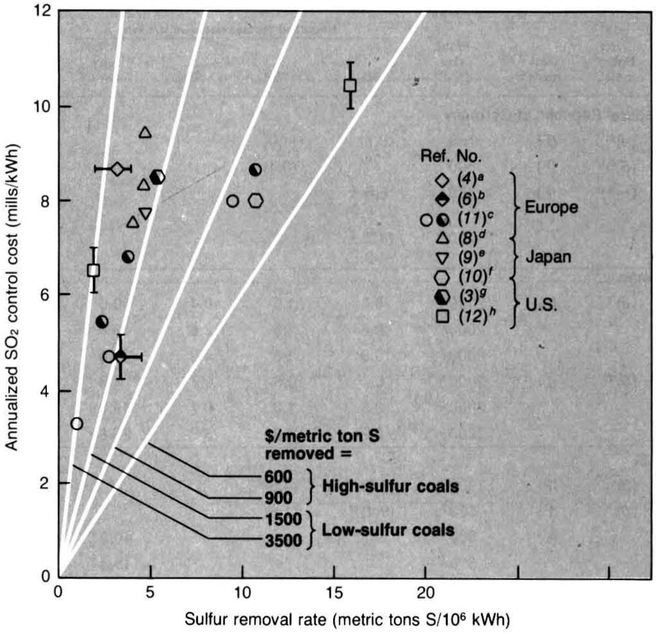
[mm] Estimate by Swedish Coal Project (KHM).

[nn] Estimate by Fläkt Company.

Japan are assumed to have a seven-year life (*8*), while in many U.S. studies, a life of 30 y is assumed (*3*, *10*, *11*).

FIGURE 1

Cost-effectiveness of wet FGD systems for sulfur removal



[a] Assumes a nominal coal heating value of 31.4 MJ/kg (13 500 Btu/lb), net plant heat rate of 9500 Btu/kWh, 5% sulfur retention in ash.

[b] Same as (a), plus 80% SO_2 removal.

[c] Assumes 8% retention of sulfur in ash.

[d] Assumes net plant heat rate of 9500 Btu/kWh, 5% sulfur retention in ash. First-year cost assumed to be 87% of reported levelized cost.

[e] Assumes 9500 Btu/kWh, 5% sulfur retention in ash. First-year cost obtained from private communication.

[f] Assumes coal of 3.5% S, 11 700 Btu/lb based on private communication. Heat rate, sulfur retention, and cost indexes based on premises for TVA computer model.

[g] Assumes 5% retention of sulfur in ash.

[h] Coal characteristics, plant characteristics, and first-year cost estimates obtained from private communication.

Annual costs

Table 2 summarizes the annual revenue requirement for pollution abatement reported in various studies. This includes certain fixed costs—principally the cost of capital—plus variable costs, such as utilities, labor, and maintenance, associated with system operation. Note that there are two different methods of presenting results. In the majority of cases, annual costs are reported for the first year of power plant operation (shown in parentheses). Other studies report a "levelized" annual cost, a measure of the lifetime annual average revenue requirement calculated from projected price escalations in various cost components. The calculation for both methods is presented in Table 3.

Levelized pollution control costs are typically 20–50% greater than corresponding first-year costs and more heavily reflect the contribution of variable costs to total revenue requirements. For most of the studies in Table 2, detailed information regarding the assumptions for levelized cost calculations is not available, so direct comparisons across all studies are not possible. Table 2, however, does show available data on the annual cost of pollution control systems as a percentage of the total annual cost of power plant operation, thereby permitting somewhat broader comparisons. SO_2 control costs for lime/limestone FGD systems range from 8% to 18% of total plant cost (excluding solid waste disposal), with the average of reported values being 12%. The highest relative costs are incurred at higher levels of SO_2 removal.

A comparison of annual cost data for comparable levels of performance is shown in Figure 1. Here, estimates of first-year revenue requirements in mills/kWh (1 mill = $0.001) were derived and plotted against the calculated or estimated sulfur removal rate in tons/unit of electricity generated. The slope of a line through the origin then reflects the average cost of sulfur removal in dollars/ton of sulfur removed. This is a common measure of cost-effectiveness, useful for comparing different sulfur removal systems.

Studies reported to the OECD generally involved plants using either low-sulfur bituminous coals of about 1.0–1.5% sulfur, or high-sulfur coals of about 3.5–4.0% sulfur. For the latter cases the annual average FGD cost was equivalent to approximately $750/metric ton S removed, while for the former cases the average cost was approximately $2150/metric ton S removed. The analytical models in Table 3 indicate that with all other factors held constant, the FGD cost per unit of sulfur removed varies inversely with coal sulfur content. This is the principal factor responsible for the three-fold variation in the average cost between studies concerning high-sulfur and low-sulfur coals.

However, the allowable SO_2 emission rate, as well as certain FGD design parameters, particularly the scrubber removal efficiency and the ratio of spare scrubber trains to operating trains, also influences the cost-effectiveness of FGD systems. Again, a systematic assessment of the importance of such factors across different studies using similar coals was precluded by data limitations. Nonetheless, Figure 1 suggests a much greater degree of similarity among national studies when data are viewed in terms of cost-effectiveness for a given coal quality. Overall, the cost-effectiveness of sulfur removal seen in Figure 1 ranges from approximately $700 to $3500/metric ton S removed, or $350–1750/metric ton of SO_2.

Reported capital and operating costs for SO_2 removal systems other than wet lime/limestone scrubbing are based on relatively limited commercial applications. Hence, they are less representative than lime/limestone costs. For dry FGD systems, capital costs reported in a Danish study (*13*) are only about one-third the average costs reported for wet FGD systems, but do not include the costs of particulate collection, land, engineering, and other items typically included in the cost estimates of other dry systems.

A study by the U.S. EPA (*10*)

comparing wet and dry FGD systems indicates a lower cost for the dry system at sulfur contents of up to nearly 3.5% for U.S. bituminous coal, though other studies indicate cost advantages for dry FGD only at much lower sulfur contents, typically about 2% or less. For low-sulfur coals in the EPA study, dry FGD annual revenue requirements were up to 20% less than for a wet FGD system for comparable levels of sulfur removal plus total suspended particulate (TSP) control. Combined SO_2/TSP capital costs were 13% to 18% lower with dry FGD. Similarly, lower operating costs were reported for a spray dryer in Germany (*6*), while in Japan (*8*) levelized annual costs for SO_2/TSP control were 16% lower for an advanced dry FGD system than for a comparable wet FGD system. Dry FGD systems thus offer the potential for significantly reduced SO_2 control costs at coal-fired power plants using low-sulfur coal. But further demonstration of this technology at the commercial scale is needed so that more reliable estimates of capital and operating costs can be developed and refined.

Similar experience is needed for SO_2 removal using adipic acid or other organic acids in conjunction with wet limestone systems. This technique offers potential savings of about 5% and 7% on capital and operating costs, respectively, when it is used with high-sulfur U.S. coals (*10*). Less expensive reagents, such as dibasic acid (DBA), may offer still larger cost reductions with high SO_2 removal efficiencies. Alternative technologies such as limestone injection multistage burners (LIMB) are not yet sufficiently advanced to offer definitive economic estimates, though current expectations for LIMB are encouraging (*10*).

Particulate control

Electrostatic precipitators (ESP) are the most universally employed devices for fly ash control. Table 1 summarizes current capital costs reported by various sources. These range from \$12 to \$96/kW (1982 basis), with a typical value of \$35 ± \$10/kW for plants meeting current standards with coals of 1.2% S or more. Analytical models for a cold-side ESP (Table 3) suggest that the capital cost for a particular plant depends primarily on the coal ash content, sulfur content, and required particulate removal efficiency, with costs increasing significantly for low-sulfur coals. However, Table 1 also shows that on the average, particulate collection costs are less than 4% of total plant capital costs, and less than one-fourth the capital investment for FGD.

From Table 2, the annual revenue requirements for particulate removal are seen to be only about 10–30% of the values reported for SO_2 removal in any given study. As a percent of the total annual cost of electric power generation, particulate removal accounted for 1–4%, with an average reported cost of 2%.

For plants using low-sulfur coal, the use of flue gas conditioning can further reduce particulate operating costs by a modest amount when cold-side electric precipitators are employed (*5*). Advanced two-stage ESP designs also may reduce future cost by up to 10% for high-resistivity coals (*10*). Hot-side ESPs have been installed in a number of U.S. power plants burning low-sulfur coal and are incorporated into the Japanese plant designs cited above. While a hot ESP is generally less costly than a cold ESP for low-sulfur coal applications, operating difficulties at several existing units have brought a halt to their use at new plants in the U.S. At the same time, capital and operating costs for full-sized fabric filter systems, which are now coming into greater use in the western U.S., appear preferable to ESPs for low-sulfur coals (*3*). Current estimates of fabric filter costs also appear comparable to those for a hot-side ESP in advanced environmental control system designs in Japan (*8*). Firmer figures on fabric filter costs must await additional operating experience with full-scale utility operations. Based on current research, it appears that future fabric filter costs may be reduced about 10% with advanced design using electrical stimulation (*10*), in which dust particles are electrically precharged to enhance their capture in fabric filters.

Nitrogen oxide control

The cost of nitrogen oxide (NO_x) control depends significantly upon applicable regulatory requirements. For moderate NO_x reductions (up to about 50%), which are achievable through combustion modifications plus low-NO_x burners, Table 1 shows that capital costs for coal-fired power plants average about \$10/kW, or less than 1% of total plant capital costs. Similarly, Table 2 shows that annualized costs amount to about 0.4 mills/kWh, or an average of 0.5% of total plant operating costs.

Costs are substantially higher if flue gas treatment systems are required to achieve higher levels of control. Data reported for Japanese power plants employing selective catalytic reduction (SCR) systems, in addition to combustion modifications, indicate total capital costs on the order of \$40/kW, or a little more than 3% of total plant capital requirements (*8*, *9*). This would make SCR costs comparable to those for an ESP. Corresponding operating costs for advanced NO_x control are 4–6 mills/kWh, or almost 6% of total plant generating costs, when full SCR treatment is employed.

While SCR costs in Reference 1 come only from Japanese studies, at least one recent study in the U.S. (*17*) reports substantially higher capital costs (ranging from \$53 to \$95/kW on a 1982 basis) as well as higher levelized annual costs (6.5–13.0 mills/kWh) for two Japanese SCR processes. These cost differences appear to be attributable primarily to differences in economic premises, such as the treatment of contingencies and other cost factors; project scope, such as the effects of an SCR system on fan costs and construction of downstream components; and detailed process design, including removal efficiency and flue gas dust loading. It should be recalled, however, that experience with SCR on full-scale coal-fired power plants is still quite limited and remains to be commercially demonstrated in all countries other than Japan.

Solid waste disposal

Disposal of FGD sludge and fly ash may incur additional capital and operating costs, which often are included with the cost of air pollution control. For example, European FGD costs developed for the OECD (*11*) include landfill disposal of oxidized sludge, which accounts for approximately \$15/kW, or 12% of FGD capital costs (equivalent to approximately 2% of total power plant costs). U.S. capital cost estimates for total solid wastes—sludge plus ash—ranged from \$30/kW (*3*) to values of \$22 ± \$7/kW and \$56 ± \$18/kW (*12*). These corresponded to approximately 2%, 2%, and 5% of total plant capital costs, respectively.

Total annual revenue requirements for solid waste disposal by untreated ponding were reported in one U.S. study (*3*) to be 1.2 mills/kWh, or about 2% of total plant revenue requirements. In another (*12*), average solid waste disposal costs accounted for approximately 4% and 8% of total levelized costs for plants using low-sulfur coal and high-sulfur coal, respectively. Solid waste disposal costs depend on the quantities of sulfur and ash being disposed of (see Table 3), as well as on

TABLE 3

A simplified method for estimating environmental control costs for a new coal-fired power plant [a]

Part I: Identification of independent variables affecting cost

(1) **Environmental control systems design** [b]
  Boiler combustion modifications (low-NO_x burners)
  Electrostatic precipitator (cold-side)
  Limestone FGD system (with forced oxidation and partial bypass); η_{FGD}
  Landfill disposal of solid wastes

(2) **Power plant characteristics:** P, H, K
(3) **Coal properties (as burned):** a, s, h
(4) **Emission limitations:** S_{TSP}, S_{SO_2} (or η_{SO_2})
(5) **Economic factors:** C_e, C_l, C_R, F_f (optional: F_i, i, n, r_i,

Part II: Calculation of key plant and performance parameters [c]

(1) **Pollutant removal efficiencies** [d]	
η_{TSP}	$1 - [(h \cdot S_{TSP} \cdot 10^{-6})/0.80a]$
η_{SO_2}	$1 - \frac{1}{2}[(h \cdot S_{SO_2} \cdot 10^{-6})/(0.95s)]$
η_{FGD}	$\geq \eta_{SO_2}$
(2) **Plant flow rates** [d,e]	
m_A	$[0.80 \times 10^6(a/h) - S_{TSP}](5 \times 10^{-7}\,P\,H)$
m_S	$[0.95 \times 10^6(2s/h) - S_{SO_2}](5 \times 10^{-7}P\,H)$
G	$0.347\,P\,H$
α_S	η_{SO_2}/η_{FGD}
G_S	$\alpha_s\,G$
(3) **ESP parameters** [f]	
A_S	$k_1[-\ln(1-\eta_{TSP})]^{1.55}$ where, $k_1 \approx \begin{cases} 0.0470\ (s < 1.0\%) \\ 0.0364\ (1.0\% \leq s \leq 2.0\%) \\ 0.0244\ (s > 2.0\%) \end{cases}$
A	A_sG
P_{ESP}	$2.5 \times 10^{-6}\,A + 1.55 \times 10^{-7}G$
(4) **FGD system parameters** [g]	
R_m	$\begin{cases} 1.10\ (\eta_{FGD} < 0.67) \\ 1.10 + 16.3(\eta_{FGD} - 0.67)^{2.5}\ (0.67 < \eta_{FGD} \leq 0.90) \end{cases}$
m_L	$1.5625\,m_sR_m$
N_o	$\alpha_s\,P/125$ (nearest integer)
N_s	$1, (N_o \leq 4)$ $0.25\,N_o$, (truncated integer, $N_o > 4$)
P_{FGD}	$(1 + 3.5s)(0.332 + 0.217m_s + 4.20 \times 10^{-6}G_s)$ $+ \begin{cases} 3.63 \times 10^{-2}(G/H)(3.50\alpha - 2.50), (\alpha_s 70.715) \\ 0.0, (\alpha_s \leq 0.715) \end{cases}$

Part III: Calculations of total capital and variable costs (million 1982 $) [h]

System or component	Total capital cost (TCC) [i]	Annual variable cost (AVC) [j]
(1) **Low-NO_x burners** [k]	$0.006\,P_g$	nil
(2) **Electrostatic precipitator** [l]	$78.51 \times 10^{-6}A^{0.91} + 10.16 \times 10^{-3}P$	$K(12.84 \times 10^{-8}A + 0.00876P_{ESP}C_e)$
(3) **Limestone FGD system** [m]	$(N_o + N_s)[5.508 + \frac{1}{N_o}(0.0803\,m_s +$ $2.057 \times 10^{-5}G_s)] +$ $\begin{cases} 0.315m_L + 5.148, (m_L < 28) \\ 0.140m_L + 10.094, (m_L \geq 28) \end{cases}$	$K(0.00911\,m_LC_R + 0.143\,m_s +$ $3.65 \times 10^{-6}G_s + 2.00 +$ $0.00876P_{FGD}C_e)$
(4) **Solid waste disposal** [n]	$C_l \times 10^{-6}(6.90\,m_s^{1.017} + 1.80\,m_A^{0.9})$ $+ (1.557m_s^{0.8} + 0.945m_A^{0.6} + 4.032)$	$0.154(m_sK)^{0.7} + 0.095(m_aK)^{0.6} + 1.275$

[a] Based on Reference 3. A more complete treatment of these models appears in Reference 16.

[b] These are selected as typical of current practice. Simplified cost models for other options also are presented in Reference 16.

[c] Other methods of calculating these parameters may be employed without affecting the cost of calculations in Parts III and IV.

[d] Assumes 80% of the ash and 95% of the sulfur in coal enters the flue gas stream (based on combustion of bituminous coal in a pulverized coal boiler). Other fractions may be directly substituted for other cases or assumptions.

[e] Gas flow rate estimation based on typical bituminous coals with 35% excess air (including leakage) and a temperature of 300 °F (149 °C). For other gas temperatures, multiply by T (°R)/760 or T (K)/422.

[f] Equations in Reference 16 give SCA as a continuous function of sulfur content, but have been simplified here to reduce algebraic complexity.

[g] Limestone stoichiometry assumes a constant liquid-to-gas (l/g) ratio of 90 gal/ft^3. However, FGD costs do not vary significantly for other l/g values (and corresponding stoichiometries) within ±20% of this.

[h] Costs for other years may be estimated using the Chemical Engineering Plant Cost Index.

[i] This is the sum of direct capital costs plus indirect capital costs. The former includes equipment, materials, land, labor, and structures. The latter includes engineering, contractor fees, construction expense, startup costs, contingencies, working capital, and interest during construction. Reference 16 represents indirect costs as a fraction, f_i, of total direct cost. The total capital costs shown here assume $f_i = 0.5$ for combustion modifications and ESP, and $f_i = 0.8$ for the FGD and solid waste disposal systems. To use other values of f_i multiply the total cost shown here by $(1 + f_i)/1.5$ (or 1.8), except for solid waste and land cost (C_l) for which $f_i = 0.0$.

Part IV: Calculation of revenue requirement, levelized cost, and electricity cost

(1) **Annual revenue requirement** [o]	$ARR = F_f\,(TCC) + (AVC)$
(2) **Levelized revenue requirement** [o,p]	$LRR = F_f\,(TCC) + f_l(AVC)$
	where, $f_l = \frac{k(1-k^n)}{1-k}\left[\frac{i(1+i)^n}{(1+i)^n-1}\right]$ and $k = \frac{(1+r_i)(1+r_r)}{1+i}$
(3) **Cost of electricity (annual or levelized)**	$C_{e,j} = \frac{(ARR)\text{ or }(LRR)}{8760\ P\ K}$

Part V: Illustrative example

Input parameters

(1) **Control system design**	$\eta_{FGD} = 0.90$ (with allowable bypass)
(2) **Power plant characteristics**	$P = 1000$ MW $H = 9500$ Btu/kWh (10 016 kJ/kWh) $K = 0.65$
(3) **Coal properties (as fired)**	$a = 0.120$ $s = 0.030$ $h = 12\,500$ Btu/lb (27 905 kJ/kg)
(4) **Emission limitations**	$S_{TSP} = 0.03$ lb/10^6 Btu (12.9 ng/J) $S_{SO_2} = 0.60$ lb/10^6 Btu (258 ng/J)
(5) **Economic factors**	$C_e = 60.0$ mills/kWh (\$0.60/kWh) $C_l = \$5000$/acre (\$12,355/hectare) $C_R = \$8.50$/ton (\$9.37/mton) $F_f = 0.15$ ($i = 0.10$, $n = 30$, $r_i = 0.06$, $r_r = 0.0$)

Part VI: Calculated Costs

Component	Million 1982 \$ (also \$/kW for 1000-MW plant)				$C_{e,j}$ (mills/kWh)	
	TCC	AVC	ARR	LRR	1982	Levelized
Low-NO_x burners	6.0	0.00	0.9	0.9	0.2	0.2
ESP	35.8	1.25	6.6	7.7	1.2	1.4
FGD system	168.9	23.32	57.7	69.3	10.1	12.2
Solid waste	29.4	3.78	8.2	11.5	1.4	2.0
Total	240.1	28.35	73.4	89.5	12.9	15.7

a = coal ash content, as fired (fraction)
A = electrostatic precipitator collector area (ft^2)
ARR = annual revenue requirement (\$)
A_s = specific collection area (ft^2/acfm)
AVC = annual variable cost (\$)
C_e = total cost of electricity (mills/kWh)
$C_{e,j}$ = electricity cost due to component j (mills/kWh)
C_l = waste disposal land cost (\$/acre)
C_R = limestone reagent cost (\$/ton)
F_f = fixed charge factor (fraction)
f_i = indirect cost factor (fraction)
f_l = levelization factor (dimensionless)
G_s = flue gas flow rate capacity through scrubber (acfm)
h = coal higher heating value, as fired (Btu/lb)
H = power plant heat rate (Btu/kWh)
i = nominal discount rate (fraction)
K = annual plant capacity factor (fraction)
LRR = levelized revenue requirement (\$)
m_a = fly ash removal capacity (tons/h)
m_L = limestone reagent capacity (tons/h)
m_s = scrubber SO_2 removal capacity (tons SO_2/h)
n = book life of equipment (years)
N_o = number of operating scrubber trains (integer)
N_s = number of spare scrubber trains (integer)
P = net power plant capacity (MWe)
P_j = power requirement of component j (MWe)
r_i = inflation rate (fraction)
r_r = real-cost escalation rate (fraction)
s = coal sulfur content, as fired (fraction)
S_{SO_2} = sulfur dioxide emission standard (lb/10^6Btu)
S_{TSP} = particulate emission standard (lb/10^6Btu)
TCC = total capital cost (\$)
α_s = fraction of flue gas being scrubbed
η_{FGD} = specified scrubber removal efficiency (fraction)
η_{SO_2} = required SO_2 removal efficiency (fraction)
η_{TSP} = required particulate removal efficiency (fraction)

Metric conversion factors

1 acfm = 4.719×10^{-4} m^3/s (actual)
1 acre = 0.405 hectare
1 Btu/kWh = 1.054 kJ/kWh
1 Btu/lb = 2.324 kJ/kg
1 ft^2 = 0.0929 m^2
1 lb/10^6 Btu = 430 ng/J (g/10^6 kJ)
1 ton = 0.9074 mton

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[j] Includes the cost of raw materials, operations, maintenance, plant overhead, administration, supervision, and utilities. The recommended electricity cost is the marginal cost for new capacity (with environmental controls), which is taken as an independent parameter here for simplicity. Reference 16 derives this value.

[k] Additional combustion modifications could increase capital costs by approximately a factor of two, with small increases in variable costs.

[l] Includes flange-to-flange costs plus ash-handling equipment.

[m] Models are based on a computer program developed by the Tennessee Valley Authority (TVA). Costs assume a midwestern U.S. location.

[n] Assumes codisposal of all fly ash and scrubber wastes (gypsum).

[o] Applies to any system or component. The fixed charge factor, F_f, includes the cost of capital, depreciation, income tax (including tax credits), insurance, ad valorem tax, and interim replacements. Typical values for U.S. power plants are approximately 0.15 ± 0.03. Calculation procedures for F_f are beyond the scope of this paper.

[p] The levelization factor f_l applies to variable cost items, which are assumed to escalate at a real rate, r_r, over inflation (r_i). If r_r and r_i are zero, the levelization factor is unity.

the method of waste disposal (*3*). Other site-specific factors also can affect disposal costs considerably. Limited data reported to the OECD indicate substantially higher waste disposal costs for plants outside the U.S., so that the figures cited above should not be generalized. Recovery of by-product gypsum from FGD systems, the prevailing practice in Germany and Japan, substantially reduces total waste disposal costs and may even generate an economic credit (*6*). There is general uncertainty, however, as to whether by-product markets can be maintained if worldwide coal use increases significantly in the future.

Other controls

The costs of water-related pollution control may include thermal and chemical effluent treatment. Reported capital costs in Japan (*9*) ranged from \$9 to \$17/kW (1–2% of total plant costs) for increasingly stringent levels of chemical control. Costs reported by the Electric Power Research Institute (EPRI) (*12*) for meeting current U.S. effluent standards were \$64 ± \$10/kW (6% of total plant costs) for plants using either high-sulfur or low-sulfur coal. This included \$40 ± \$6/kW for cooling towers, which were not included in the Japanese plant design. Corresponding annualized costs (in 1982 dollars) were approximately 0.7 mills/kWh for the model plant in Japan (*9*) and 2 mills/kWh for the new plants in the U.S. (*12*).

Noise control costs were included by EPRI (*12*) and the Japan Environment Agency (*9*) as a component of environmental costs. Capital costs in the former case averaged \$12/kW (about 1% of total plant cost), with annual operating costs of about 0.4 mills/kWh (0.5% of total generation costs). Slightly higher costs of \$12 to \$22/kW were assumed for the model plants in Japan.

Miscellaneous costs for the Japanese plant also included dust control measures. These had a negligible cost impact except for the most stringent control level, which involved the construction of coal storage silos at a 1982-dollar cost of approximately \$70/kW. Plant operating costs also included a small charge (0.5–1.5 mills/kWh) levied in Japan for the compensation of pollution-related health damage.

Total cost of control

In Tables 1 and 2, values of total environmental control costs reported in various studies are summarized. At face value, capital costs range from approximately 5% to 36% of total plant capital costs, while annual costs are 5% to 32% of total plant revenue requirements. As seen previously, however, these figures reflect not only different definitions of total environmental control, but also widely differing coals, plant configurations, and regulatory requirements.

FIGURE 2

Capital and operating costs for pollution control systems at a new coal-fired power plant

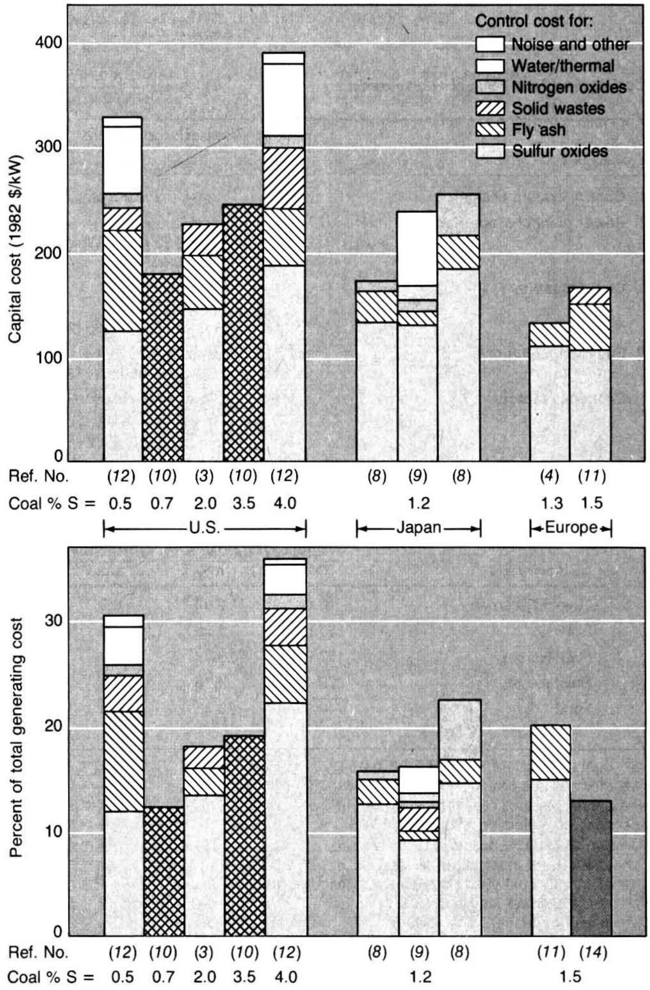

Figure 2 gives a better picture of how various system components contribute to total costs at a well-controlled coal-fired power plant equipped with a wet FGD system for SO_x control, an ESP for particulate control, and combustion modifications for NO_x control. For these systems, a representative cost of air pollution control (excluding solid waste disposal) is approximately \$185 ± \$50/kW for capital costs, equivalent to 18% of total plant cost, and 15 ± 4% of total annual power-generating costs, according to data from selected studies for Europe, Japan, and the U.S. Approximately 75% of the air pollution control cost is for FGD, 20% for the ESP and 5% for NO_x control. In general, the high end of the range applies to U.S. plants using high-sulfur coals with high pollutant removal efficiencies, while the lower end applies to European plants using low-sulfur coals with moderate removal efficiencies. Solid waste disposal costs for fly ash and FGD sludge add approximately

$30 ± $15/kW to capital costs and 5 ± 3% to annual costs unless recovery and reuse are feasible.

The additional costs of water pollution control are $16 ± $8/kW for treatment of chemical wastes, plus $40 ± $6/kW if cooling towers are required for thermal effluent control. Corresponding increases in annual costs are approximately 1–3% of total generating cost. Pollution abatement costs, including air, water, and solid wastes, thus amount to approximately $270 ± $80/kW (26 ± 8% of total plant) for capital costs and 23 ± 7% of total generating costs for new plants meeting current environmental standards in Europe, Japan, and the U.S. The cost of noise control adds at least $10/kW to capital costs and 0.5% to annual costs if noise is defined as a part of total environmental control. Miscellaneous costs for fugitive dust control remain negligibly small, but could become sizable under extremely stringent local standards requiring construction of coal storage silos. Similarly, more stringent requirements for NO_x control also would add significantly to these costs, as indicated earlier.

Competitiveness of coal

The competitiveness of coal relative to other fuels for electric power generation is of key international concern, particularly the relative costs of coal-based and oil-based electricity. While the importance of nuclear power is also clearly recognized, the essential conclusion drawn is that the average cost of a nuclear plant in OECD countries may vary by nearly a factor of two (from about $1200 to $2000/kW), thus making nuclear power either the cheapest or the most expensive option relative to fossil fuels (*11*). For the near term, new nuclear plants have been removed from consideration in some countries and therefore may not even be an alternative in many cases. Thus, there is high worldwide interest in coal vs. other conventional fossil fuels.

Two options are the most commonly considered for converting from oil or gas to coal for power generation. One is the construction of a new coal-fired unit, either in lieu of a new oil or gas unit, or as a replacement for an existing oil or gas unit that would be retired prematurely. The other is the physical modification of an existing boiler to accept coal as a fuel. For technical and economic reasons, physical modifications (boiler retrofits) are usually limited to units originally designed for coal.

Other options for burning coal in boilers designed for oil firing include the use of coal–oil or coal–water mixtures. The ability to use coal–oil mixtures (COM) has been demonstrated technically, and continued development and some commercialization are proceeding. Implementation, however, generally has been limited by economics and other factors. Coal–water mixture (CWM) fuels hold the potential of far more favorable economics since fuel oil expenses are totally avoided. Here, however, the results of current research and development projects are awaited so that the technical, environmental, and economic viability of CWM for commercial applications can be assessed more rigorously.

Comparisons with new plants

Table 4 summarizes several electricity cost comparisons between new coal-fired plants and new or existing plants using other fossil fuels, (*8*, *9*, *11*, *14*, *18*, *19*). In all cases, there is agreement that at prevailing 1981–82 fuel prices (when most of these costs were derived), electricity costs were lower for a new coal-fired plant than for a comparable new oil-fired plant. More recent drops in world oil prices during 1983 now indicate a less favorable economic climate for coal, at least in Europe and Japan where coal prices are approximately twice those in the U.S. In those regions, environmental control costs could have a more significant effect on coal's competitiveness with oil since they raise the breakeven oil price by several dollars per barrel in the generally sensitive price range.

Thus, in the absence of environmental control requirements, a new coal-fired power plant in Japan might cost less than a comparable oil-fired plant for oil prices above $25/bbl, whereas oil prices might have to rise above $30/bbl before a coal plant with strict environmental controls could be competitive. This would be just above current world prices. For the U.S., coal still remains economically preferable to oil for new plant construction, even with high environmental control costs, because of substantially lower coal prices.

In comparisons with existing facilities, a study for OECD (*11*) reported a 15% lower cost of electricity from a new coal-fired power plant in Europe with full environmental controls (including FGD) compared to an existing oil-fired plant at fuel prices of $36/bbl for oil and $70/metric ton for coal (see Table 4). These prices would favor early retirement of the oil plant and its replacement by a new coal-fired plant. This situation, however, contrasts with a Japanese power company study (*8*) indicating that at similar oil and coal prices electricity from a new coal-fired plant would still be about 15% more expensive than that from an existing oil-fired plant, making early retirement of the oil plant unattractive.

This qualitative difference results primarily from a $340/kW difference in the "base" cost of the coal-fired power plant assumed in the two studies. Additional differences in pollution control costs produce a total capital cost difference of approximately $400/kW. Thus, in the Japanese study, oil prices would have to rise above $44/bbl before it would be economical to retire an existing oil-fired plant, as compared with $31/bbl for the OECD European study. In this case, the cost of environmental control had a much less significant influence on the fuel choice decision than did differences in the estimated cost of the base power plant.

Table 4 also shows data comparing the costs of a proposed new coal-fired facility with existing gas-fired power plants in The Netherlands (*14*). Recent rises in gas prices have led to a situation in which coal-fired plants are now economically more attractive, with the magnitude of cost differences depending on environmental standards and other site-specific factors. Table 4 shows that the total annualized cost of one proposed new coal plant with full environmental controls would be 12% less than the average fuel plus operating costs for existing gas-fired plants.

Comparisons for retrofit plants

Comparative costs of oil- and coal-based electricity for boilers retrofitted to coal firing also are indicated in Table 4. A U.S. EPA study (*19*) considered boiler conversions with and without FGD systems for base-load and intermediate-load plants with remaining amortized lives of 10 and 20 y. In all but one case, the converted boilers yielded significantly lower electricity costs than the oil-fired plant. Despite the prevailing economic advantages, such replacements are not occurring at a rapid rate because of such factors as uncertainty over future oil prices, capital availability, and difficulties in finding acceptable sites (*19*).

One case of a recent conversion from oil to coal in the U.S. involves the Brayton Point Station in Massachusetts (three units totaling 1150 MW).

TABLE 4

Comparative electricity costs for conversions from oil or gas to coal

Country	Reference No.	Case Description	Percent savings in electricity cost with a coal-fired plant instead of: new oil plant	Percent savings in electricity cost with a coal-fired plant instead of: existing oil (gas)
Replacement by a new coal-fired power plant				
Japan	(*8*)[a]	Coal @ $70/mton, Level III Control		
		+ Oil @ $30/bbl	−1	−21
		$35/bbl	7	15
		$40/bbl	16	7
		Coal @ $90/mton, Level III Control		
		+ Oil @ $30/bbl	−10	−25
		$35/bbl	−2	−20
		$40/bbl	7	−14
	(*9*)[b]	Coal @ $67/mton, oil @ $39–$42/bbl		
		w/ Model I Control	32	
		w/ Model II Control	25	
		w/ Model III Control	17	
The Netherlands	(*14*)[c]	Case 3 plant w/ full env. control		(11)
Europe	(*11*)[d]	Coal @ $70/mton, with FGD		
		+ Oil @ $36/bbl		15
Conversion of an existing plant to coal firing				
The Netherlands	(*14*)[c]	Case 4 plant with full env. control		(21)
U.S	(*18*)[e]	Brayton Point Station without FGD		37
	(*19*)[f]	Low-cost conversion without FGD		
		Base load, 20-y life		40
		Int. load, 10-y life		34
		High-cost conversion, with FGD		
		Base load, 20-y life		18
		Base load, 10-y life		7
		Int. load, 20-y life		7
		Int. load, 10-y life		−7

[a] See footnotes h and j, Table 1, for key assumptions.

[b] See footnotes m–p, Table 1, for key assumptions.

[c] See footnote kk, Table 1; for key assumptions.

[d] See footnotes x and z, Table 1 for key assumptions.

[e] Cost savings based only on 1982 fuel costs of 4.11¢/kWh for oil and 2.58¢/kWh for coal. Breakeven cost of entire project estimated to be $6/bbl of oil (equivalent) price difference between coal and oil.

[f] Based on an oil price of $29/bbl and levelized coal prices of $1.70–$2.05/10^6 Btu, with capital costs of $200/kW for FGD retrofit and $140–$410/kW for converting a boiler and upgrading a precipitator.

In this case, retrofitting of an FGD system was not required. The total project cost amounted to $167/kW, of which approximately one-half was for environmental control equipment (*18*). The savings realized from reduced fuel costs were expected to result in a project payback period of less than two years, with continued cost savings thereafter.

Finally, Table 4 shows the case of a proposed conversion from natural gas to coal in The Netherlands. This unit was initially designed to burn low-calorific-value gases, as well as mixtures of fuels; hence it was suitable for conversion to coal. Even with full environmental controls (including FGD), the electricity produced by this unit was estimated to be 25% cheaper than that from existing gas-fired plants.

Summary of findings

Significant differences in reported capital and operating costs for pollution control are seen to be derived from markedly different premises regarding applicable environmental regulations, coal characteristics, plant design parameters, project scope, and economic and financial assumptions. However, in examining the case of SO_2 control, one finds that cost estimates in different countries exhibit much greater similarity when expressed in terms of the cost-effectiveness of pollutant removal for similar fuels and environmental constraints. Typical 1982 costs for a well-controlled power plant, including air pollution control, water pollution control, and solid waste disposal, are on the order of 26% ± 8% of total plant capital cost ($270 ± $80/kW) for plants in Europe, Japan, and the U.S. Air pollution control and disposal of associated solid wastes account for approximately 80% of this figure, with FGD systems contributing the major share (approximately $140 ± $35/kW, excluding waste disposal). Corresponding annual revenue requirements for environmental control are approximately 23% ± 7% of total power-generating costs, of which approximately 85% is attributable to air pollution control and solid waste disposal.

In general, the high end of the cost range reflects air pollution control levels of 90% or more for SO_2, up to 50% for NO_x, 99.5% or more for fly ash (particulate matter), plus stringent control of both chemical and thermal water pollutants. In contrast, the low end of the cost range generally represents less stringent SO_2 removal requirements (permitting only partial flue gas treatment), coupled with moderate NO_x controls, by-product use of solid wastes, and minimal water treatment requirements.

For SO_2 removal requirements below about 40%, the use of physical coal cleaning might allow emission limits to be met without the need for

FGD, reducing costs substantially. On the other hand, a need for more stringent NO$_x$ controls, requiring flue gas treatment systems such as those now beginning to emerge in Japan, would increase capital costs and revenue requirements by at least an additional 3% and 5%, respectively, of total plant costs cited above, although significant uncertainty still remains as to the actual cost of such systems. In the future, advanced control technologies, as well as advanced processes using coal either for direct combustion or for conversion to other liquid and gaseous fuels, holds the promise of higher degrees of pollution control at relative costs comparable to or less than those for conventional systems (*20–25*).

Electricity cost comparisons

Comparisons between electricity costs for new coal-fired plants and new oil- or gas-fired plants indicate that at a coal price of $70/metric ton, typical of Europe and Japan, a new coal-fired power plant with strict environmental controls is more economical than a new oil-fired plant for oil prices about equal to the current world price. At the much lower U.S. coal prices, however, coal is clearly the fuel of choice relative to oil.

Indeed, new coal plants may generate electricity even more economically than existing oil-fired plants, making early retirement of such facilities economically attractive in some locations. Such comparisons are strongly dependent on the local prices of oil and coal, which have continued to fluctuate in recent years. Breakeven oil prices of approximately $35/bbl or more are indicated at coal prices of $70/metric ton, with capital cost estimates for the base power plant, as well as environmental control equipment, also seen to be key factors in decisions to replace oil with new coal facilities.

Conversion from oil or gas to coal by retrofitting existing coal-capable boilers, where technically feasible, also appears economically attractive in a number of situations. The actual rate of such conversions, however, is still low. Among the reasons cited for this are uncertainty over future oil prices, unavailability of capital, lack of suitable sites, regulatory or permitting delays, and the lack of appropriate infrastructure for the delivery and handling of coal and associated solid wastes.

Finally, cost comparisons performed for the OECD between new coal-fired plants and new nuclear plants indicate nuclear power to be either the least expensive or most expensive option for electricity production because of the nearly twofold range in costs associated with current nuclear plant designs in various countries. Moreover, social and political factors also continue to inhibit or preclude nuclear power in many locations. Thus, an expanded use of coal in compliance with strict environmental standards is foreseen for many countries in the coming decades.

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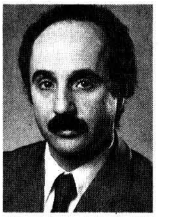

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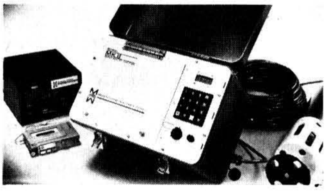

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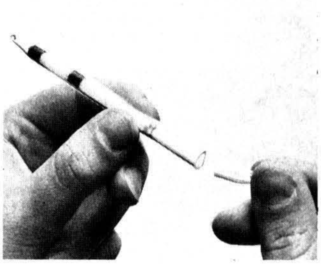

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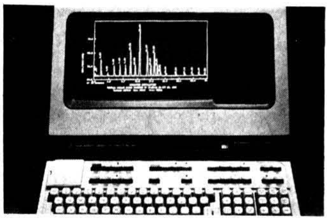

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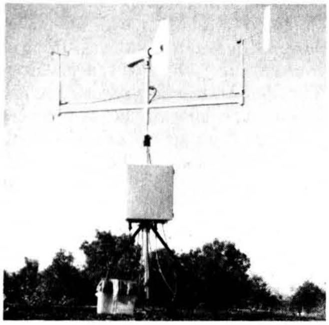

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Self-contained weather system can be used for air pollution monitoring. It measures wind speed and direction, temperature, relative humidity, precipitation, barometric pressure, and solar radiation. An RS-232 interface output is optional. Met One **114**

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Field sample fixation kit
This portable kit is designed to preserve water samples collected on location by lab personnel. It contains PVC-coated bottles for transporting hazardous corrosive solutions. Included are storage jars, theromometer with case, pH paper, disposable 5 mL glass pipets, pipetter, and pipet disposal tubes. Wheaton Chem-Tec **119**

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Monitors are made for a wide range of pressure and level control applications. Digital adjustment for high and low alarms and pump control for ascending and descending set points provide flexibility. Pressure is displayed on a digital meter. Ivek **120**

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The product is designed for the microbiological analyses of water and wastewater. Individual plastic packs each contain a 47-mm membrane with a nutrient absorbent pad. The filters have pore sizes of 0.45 μm and 0.7 μm. Micron Separations **123**

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Field fluorometer (Model 10) can be used as groundwater and oil-in-water monitor. Flow patterns are traced with nontoxic fluorescent tracers on a continuous-flow or grab-sample basis. Multiple sampling wells allow rapid contamination mapping, and petroleum is detectable to 5 ppb. Turner Designs **125**

In-bag decontamination
Autoclavable bag of impervious, sturdy plastic allows biohazardous materials to be decontaminated in the bag during the autoclave process. Autoclave indicator is on the inside of the bag. Hazard warnings are printed in English and Spanish. M.D. Industries **126**

Research GC/MS system
This system is designed for research applications in analytical chemistry. It includes the Incos data system with new software and an extensive assortment of sample introduction and ionization methods. The model performs chemical ionization, electron ionization, discharge ionization, and pulsed positive ion–negative ion chemical ionization. Finnigan MAT **127**

pH electrode
Gel-filled electrode has a chemically resistant and virtually indestructible polymer body and dimensions of $\frac{1}{2} \times 6$ in. It provides fast responses over the 0–14 pH range at temperatures from 0 to 100 °C. Chemtrix **128**

Dust collector control
This controls large baghouse dust collectors with 32 outputs to monitor 32 rows of cleaning. It is available in 220 or 120 V ac, 50 or 60 Hz, and with a temperature rating of 40–135 °F. It will fit in standard enclosures 14 in. high by 12 in. wide. Special Timer **129**

Magnetic stirrer
Electronic parts rather than electric motors create its magnetic field. The lack of moving parts eliminates heat from sources other than chemical reactions in an experiment. A magnetic follower rotates in the vessel that contains the medium to be stirred. The stirring speed is infinitely variable from 200 to 1000 rpm. Scientific Glass Laboratories **130**

Nonwoven filter matrix
Patented method now allows nonwoven filter matrix to be as strong or even stronger than woven matrices. The filter, from which particulates and residue can be cleaned, can remove particles down to 0.3 μm with minimum efficiencies of 99.97%. Multi-Fab 131

Respirator
Blue 1 air-purifying respirator uses new silicone technology and respirator design for maximum safety in hazardous atmospheres. Tufel silicone rubber allows detergent cleaning, sanitizing, and drying with no evident deterioration. Meets NIOSH exhalation criteria; does not react with ozone or skin barriers used against paint overspray. Survivair 132

Water flow velocity monitor
Lightweight portable monitor now has gold sensing electrodes not affected by most acids, corrosive liquids, or industrial wastewater. Measures velocity in open channels with ±1% accuracy. Montedoro-Whitney 133

Hi-vol air sampler programmer
Digital programmer is retrofittable on any standard high-volume air sampler. The Model 352 programmer can work 1-24 h on a repeatable 1-10-day schedule. Has digital clock, meets upcoming EPA reference method standards. Sierra Instruments 134

Baghouse leak detection
Model 109 baghouse monitor will detect open holes, seams, and breaks that cause leaks, and meets all EPA specifications for visible emissions. Measures sub-micron particles and spans ducts up to 10 ft. Alarms at 0-100% opacity as desired. Datatest 135

Ethylene oxide monitor
Environmental chromatograph monitors ethylene oxide (EtO) at the proposed OSHA limit of 0.5 ppm (1 ppm averages during 8 h) and detects EtO below 0.1 ppm. Control by microprocessor; analyses in real time. HNU Systems 136

Sediment penetrometer
Instrument determines types of sediment, erosion, accumulation, and transportation. It can be used for lake, waterway, and coastal area bottom investigations. Its weight is 7.5 kg. Samplers and traps are included. It is known as System Borg. C. H. Borgs Mekaniska AB, Lars Borg, Box 89, S-199 02 Enköping, Sweden (write direct).

ES&T

LITERATURE

Water for trace analysis. Booklet explains ultrapure, ion-free, organic-free water for trace analysis, and reviews several analytical methods. Continental Water Systems **151**

Small-scale fume scrubber. Brochure describes laboratory-scale fume scrubber for droplets, mists, vapors, gases, odors. Heat Systems–Ultrasonics **152**

Energy planning and engineering. April issue of *Synectics* describes firm's capabilities in planning and engineering for "soft" (i.e., solar) and "hard" (such as coal) energy, and work with the regulators and the regulated. Synergic Resources **153**

Field and laboratory items. 1983 Chemtrix catalog lists pH meters, water test devices, ovens, and many other items. Chemtrix **154**

High-volume air samplers. Brochure describes TFIA and TFIA-2 line-powered, and TFIA-4 battery-powered high-volume air samplers, which are used for indoor and outdoor air quality tests. Staplex **155**

Formaldehyde monitoring. Report LAD 001-014 describes ambient air monitor with special application to the monitoring of formaldehyde. Foxboro **156**

Particle counters. Brochure describes two airborne particle counters, one for 0.5 and 5.0 μm, and one for 0.3, 0.5, 1.0, 2.0, and 5.0 μm. Applications include work station, clean room, and others. Faley International **157**

Solvent recovery. Publication describes modular process units for solvent recovery, pollution control, and other uses. Glitsch **158**

***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*

Laboratory supplies. Catalog lists lines of chemicals and laboratory supplies, including "hard-to-get" research items. Water testing equipment is included. Daigger Scientific **159**

Wastewater reuse. April 1983 issue of *Reactor* contains a view from California on wastewater reuse: how much, how soon? There is also an article on powdered, activated carbon for groundwater restoration. Zimpro **160**

Gas chromatograph for air. Bulletin 4189B describes a gas chromatograph system for air monitoring applications that is microprocessor-based with sample conditioning. Beckman Instruments **161**

Spectrometers. Brochure describes the 3500 AES series of optical emission spectrometers. Bausch & Lomb **162**

Pollution control services. Brochure TR81-9000132 describes worldwide air and water pollution control services, systems, and equipment. Andersen 2000 **163**

Hazardous waste screening. Announcement discusses Haloscan, using EPA Proposed Method 9022, to scan hazardous waste samples for the presence of organic halogens. Environmental Research Group **164**

Chemicals. Brochure lists chemicals, many of which are for standard substances and solutions of very high purity. G. Frederick Smith Chemical **165**

Air purifier. Flyer sheet describes the series ET-35 industrial air purifier, which has an adjustable 8-ft, 4-way capture arm with 360-degree flexibility. Ecology Tech **166**

Septic system survey. Literature describes innovative aerial photographic–ground survey approach for locating failing septic systems for "201" wastewater facilities planning studies, and other needs. Resource Technologies **167**

Liquid chromatography (LC). Brochure features new line of threaded easy-disconnect LC columns. Other high-performance LC systems and items are also listed. Ace Glass **168**

Wastewater services. Brochure No. 1100 describes company's services for designing and installing specialized wastewater treatment systems as well as standard products. Lancy International **169**

Industrial hygiene. Catalog features industrial hygiene items, such as ORBO adsorption tubes for monitoring industrial atmospheres in accordance with all NIOSH specifications. Supelco **170**

Trihalomethanes (THMs). "The Deadly THMs" is a brochure reviewing facts about the chemicals found in drinking water supplies, and suspected of causing cancer. Environmental Purification Systems **171**

Arsenic detection. Technical paper AA-22 explains how to determine trace levels of arsenic by means of hydride generation. Varian **172**

Solvent recovery. Booklet F-48668A explains how solvent recovery can be an income-producing system. Solvent recovery is effected mainly through a continuous fluidized-bed adsorption system. Union Carbide **173**

Trace analysis. 1983 catalog lists standards and accessories for trace analysis by gas chromatography. Ultra Scientific **174**

Groundwater monitoring. Brochure explains how groundwater monitoring in conformity with RCRA regulations may be done at the site of a waste management facility. ERT **175**

Biomolecule isolation. Biotechnology brochure highlights a phase in the process of generating and isolating biomolecules through biotechnology. LKB Instruments **176**

Gas chromatography. Bulletin No. 52 lists GC applications, resins, chromatograms, packings, and other information. Alltech **177**

Air sampling equipment. Catalog lists more than 800 air sampling items, such as pumps, vapor badges, bags, impingers, accessories, many other devices. SKC **178**

Gas sampler. Brochure describes SS 12-12 environmental gas sampler, which works by positive displacement and is fully automated. The device is portable and rugged, and can be powered with batteries. D&S Instrument Ltd. **179**

Carbon column testing. Brochure 27-29 describes accelerated column test (ACT) that tests carbon for effectiveness of removal of organic impurities. The speed of isotherm tests is combined with the accuracy of a pilot column. Calgon **180**

Injection wells. Brochure describes practices, permitting requirements, investigations, design and installation, and monitoring requirements. Geraghty & Miller **181**

Gas chromatography (GC). *GC Technology Newletters* discuss advances in analysis by GC with use of microcomputer control and data handling. Environmental laboratory work is featured. Technicon **182**

Water quality control. Catalog No. 783 lists a line of instrumentation for water quality and process control. pH, redox, and other parameters are covered. Energy management is also featured. Great Lakes Instruments **183**

Safety supplies. June 1983 catalog lists safety supplies necessary or helpful for meeting OSHA regulations. Interex **184**

Hydrological testing. Brochure introduces two new hydrological test tools used for determining the permeability of subsurface formations to groundwater and fluids. Special application to nuclear waste disposal site testing. Lynes, Inc. **185**

Sample preparation. Announcement describes "BAKER"-10 SPE Applications Guide Vol. I and System. Applications include sample preparation for pesticides, PCBs, trace metals, and aflatoxins. J.T. Baker Chemical **186**

Dissolved oxygen. YSI Industrial catalog introduces a low-cost dissolved oxygen system line and a temperature-to-frequency transmitter. Both autoclavable and general purpose sensors can be used. Yellow Springs Instrument **187**

Environmental analysis. 1983–84 catalog, "Products for Analysis," lists items for laboratory analysts, plant engineers, ecologists, and other professional and technical workers. Hach **188**

Acoustic microscope. Brochure describes a scanning laser acoustic microscope (SLAM) and tells how flaws, voids, and other conditions are discovered in a nondestructive manner. Sonoscan **189**

NSF announcements. The *Bulletin* from the National Science Foundation (NSF) announces NSF activities and reports and is published monthly, except in July and August. National Science Foundation, 1800 G St., N.W., Washington, D.C. 20550 (write direct)

Chemical substances reporting. Booklet sets forth rules and regulations for reporting chemical substances in the Commonwealth of Virginia as of 1977, but updated through Feb. 28, 1983. Toxic Substances Information, Department of Health, 109 Governor St., Richmond, Va. 23219 (write direct)

Nuclear fuel and waste. Publication, "Book Two—Fuel/Waste," answers more than 100 questions on this topic. Cost is $8, prepaid. American Nuclear Society, 555 North Kensington Ave., La Grange Park, Ill. 60525 (write direct)

Wastewater treatment markets. Brochure announces comprehensive industrial market study. Carol A. Wilt, WWEMA, P.O. Box 17402, Dulles International Airport, Washington, D.C. 20041 (write direct)

Standards. Catalog lists ANSI-approved standards—about 10 000 of them. Free to ASNI members, $10 to nonmembers. American National Standards Institute, 1430 Broadway, New York, N.Y. 10018 (write direct)

Iron-55 SRM. *NBS Update* for Feb. 7, 1983, (back page) announces standard reference material for iron-55 (^{55}Fe), available at a cost of $313. Pamela Gelfield, Radioactivity Group, C114 Radiation Physics, National Bureau of Standards, Washington, D.C. 20234 (write direct).

Submersible pumps. Brochure explains submersible solids-handling and sewage pumps. Submersible Wastewater Pump Association, 221 North LaSalle St., Chicago, Ill. 60601 (write direct)

Nonpoint sources. Report EPA 600/3-82-021 selects agricultural nonpoint source pollution control methods. Environmental Research Laboratory, U.S. Environmental Protection Agency, Athens, Ga. 30605 (write direct)

Health aspects of lubricants. This is the title and subject of Report No. 1/83. CONCAWE, Babylon-Kantoren A, Koningin Julianaplein 30-9, 2595 Den Haag, The Netherlands (write direct)

Threatened drinking water. Pamphlet (costing 50¢) is entitled, "Our Drinking Water: A Threatened Resource," and says that the main threat is chemical. Public Affairs Committee, Inc., 381 Park Ave. S., New York, N.Y. 10016 (write direct)

The breeder reactor. "Breeder Basics" explains how the breeder reactor produces more fuel than it uses while it generates power. Neil Gabbert, Information Officer, Breeder Reactor Corp., P.O. Box U, Oak Ridge, Tenn. 37830 (write direct)

Treating contaminated soils. Manual tells how to treat soils contaminated with hazardous chemicals. Aquarius, Utah Water Research Laboratory, UMC 82, Utah State University, Logan, Utah 84322 (write direct)

Environmental books. "Agricultural-Veterinary Food and Environmental Sciences Catalogue 1983." Elsevier Science Publishing Co., Inc., 52 Vanderbilt Ave., New York, N.Y. 10017 (write direct)

Need more information about any items? If so, just circle the appropriate numbers on one of the reader service cards bound into this issue and mail in the card. No stamp is necessary.

BOOKS

Water Supply and Sanitation in Developing Countries. Eric J. Schiller, Ronald L. Droste, Eds. xi + 368 pages. Ann Arbor Science Publishers, Inc., P.O. Box 1425, Ann Arbor, Mich. 48106. 1982. $29.95, hardcover.

The social, management, and economic aspects of water supply and sanitation in developing countries are treated. The authors suggest that those involved in this field should consider renewable energy technologies. The book arises from a short course on the subject given in June 1981 at the University of Ottawa, Canada.

The Law and Practice Relating to Pollution Control in the Member States of the European Communities: A Comparative Survey. 10 volumes. Graham & Trotman Ltd., Sterling House, 66 Wilton Rd., London SW1V 1DE, England. 1982. $370, set.

These volumes cover air, water, waste, nuclear energy, and many other environmental subjects governed by law in Europe. A volume is devoted to each of the countries (Belgium and Luxembourg are combined in one), and one volume compares the nations.

An Introduction to Solar Energy for Scientists and Engineers. Sol Wieder. xii + 301 pages. John Wiley & Sons Inc., 605 Third Ave., New York, N.Y. 10016. 1982. $24.95, hardcover.

This book includes the mathematical derivations and justifications necessary to explain the various workings of solar energy and its use. It deals with energy received by earth, heat transfer and optics, space heating, hot water supply, collectors, systems, and conversion of energy to useful work.

The Two Faces of Chemistry. Luciano Caglioti. xvi + 218 pages. MIT Press, 28 Carleton St., Cambridge, Mass. 02142. 1983. $17.50, hardcover.

Chemistry may have brought better living, but there have been problems. This book looks into the advantages and liabilities of pesticides, detergents, drugs, fluorocarbons, and many other substances. The author traces the stages of development of some chemicals and how it was determined that they might have adverse effects.

Biological Monitoring of Heavy Metal Pollution: Land and Air. M. H. Martin, P. J. Coughtrey. xi + 475 pages. Elsevier Science Publishing Co., Inc., 52 Vanderbilt Ave., New York, N.Y. 10017. 1982. $80, hardcover.

This book aims at integrating information concerning the use of plants and animals as indicators of heavy-metal pollution. It combines background material with specific, detailed information, which indicates that biological monitoring could be recognized as a technique in its own right for assessing heavy metal pollution.

Indicators of Genotoxic Exposure: Banbury Report 13. Bryn A. Bridges et al., Eds. xiv + 880 pages. Cold Spring Harbor Laboratory, Cold Spring Harbor, N.Y. 11724. 1982. $62.50, hardcover.

What damages occur if the body is insulated by genotoxic substances? Are there repair mechanisms? What are the biochemical pathways by which injury occurs and repairs are accomplished? The papers in this book cover clinical perspectives, mutagen detection, DNA damage and repair, DNA adducts, sister chromatid exchange, germ cell effects, and mutagenesis.

Of Mice and Molecules: Technology & Human Survival. Eric Skjei, M. Donald Whorton. xv + 347 pages. The Dial Press, 245 East 47th St., New York, N.Y. 10017. 1983. $18.95, hardcover.

The authors present accounts of health dangers the products of modern technology pose; however, they do not make their book a polemic. They discuss hazards to air, water, and food, such as asbestos, polychlorinated biphenyls, lead, benzene, Agent Orange, toxic wastes, and cigarette smoke, among many others. Routes by which the body is exposed to such substances and how it attempts to protect itself are discussed.

Waterworks: An Owner–Builder Guide to Rural Water Systems. Michael Hackleman. xiv + 172 pages. Doubleday & Co., Inc., 245 Park Ave., New York, N.Y. 10167. 1983. $14.95, paper.

In many parts of the world, even in the U.S., city water systems do not exist. The author discusses water sources and their evaluation, sources of energy for obtaining it, hardware, siting, reuse if necessary, capacity, and many other aspects of the "do-it-yourself" water supply.

Incentives for Environmental Protection. Thomas Schelling, Ed. xix + 365 pages. MIT Press, 28 Carleton St., Cambridge, Mass. 02142. 1983. $32.50, hardcover.

This book examines the extent to which pricing incentives (charges on emissions, for example) rather than regulatory standards might be shaped into a technically effective, politically enactable, enforceable, and equitable policy. It also compares that approach and that of regulatory standards with regard to advantages and disadvantages. Case studies are presented.

Pollution and the Biological Resources of the Oceans. S. A. Patin. xi + 287 pages. Butterworth, 10 Tower Office Park, Woburn, Mass. 01801. 1982. $95.95, hardcover.

This book looks at the world's oceans as a whole and considers general pollution patterns. Some topics it reviews are pollutant migration within marine ecosystems, accumulation of pollutants in commercial marine products, ecotoxicological control, and chemical toxicant effects. The author is deputy director of the All-Union Research Institute of Marine Fisheries and Oceanography, Moscow, U.S.S.R.

Settling Things: Six Case Studies in Environmental Mediation. Allan Talbot. The Conservation Foundation, 1717 Massachusetts Ave., N.W., Washington, D.C. 20036. 1983. Inquire as to price.

This work is a report to the Ford Foundation. It shows how mediation was used to resolve six environmental disputes that otherwise would have gone to court. Examples of mediation include a hydroelectric plant at Storm King Mountain, N.Y., a garbage disposal site in Wisconsin, and a ferry terminal site in Port Townsend, Wash.

The Role of Genetic Testing in the Prevention of Occupational Disease. GPO Stock Number 052-003-00906-4. x + 243 pages. Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402. 1983. $6.50, paper.

Should some people be excluded from certain types of employment because of a proven or perceived genetic pattern that indicates susceptibility to occupational diseases? Or should the workplace be made so safe that this question need not arise? The U.S. Congress's Office of Technology Assessment wrestles with the scientific, ethical, and other aspects of this highly controversial topic.

The Treatment and Handling of Radioactive Wastes. A. G. Blasewitz, et al., Eds. 656 pages. Battelle Press, 505 King Ave., Columbus, Ohio 43201. 1983. $65, hardcover.

This work explores the current state of technology, and compares various countries' approaches to the problem. Also discussed are decontamination, size reduction, high- and low-level waste handling, transport, disposal, and lower-level waste immobilization.

Proceedings of the Seminar on Development and Assessment of Environmental Standards. 135 pages. American Academy of Environmental Engineers, P.O. Box 269, Annapolis, Md. 21404. 1983. $12, paper.

These proceedings include insights concerning data bases used in conjunction with standards development. They look into dissolved oxygen, trihalomethanes, trichloroethylene, particulate matter, and general considerations involved in standard setting.

A Directory of 181 Organic Chemical Plants in New Jersey. David Sarokin, Sebastian Sperber. 21 pages. INFORM, 381 Park Ave. S., New York, N.Y. 10016. 1983. $15 ($5 for nonprofit groups), paper.

New Jersey has a large chemical industry. The compilers listed 181 plants and locations, some "from unpublished sources," as INFORM explains. Locations, addresses, and telephone numbers are given; the organic chemical industry is concentrated mainly in the northeastern corner of the state.

EPA Guidebook. 232 pages. Government Institutes, Inc., 966 Hungerford Drive, No. 24, Rockville, Md. 20850. 1983. $35.

This second edition updates the guide to EPA through May of this year, thereby reflecting some major personnel changes made by EPA Administrator William Ruckelshaus. It gives an office and official responsible for enforcement activities; explains whether a problem should be taken to a regional office or to headquarters; provides information about technical and regulatory assistance; and addresses questions concerning contracts. Telephone and "hotline" numbers are given.

Resource Recycling. Jerry Powell, Ed. Periodical. Resource Recycling, P.O. Box 10540, Portland, Ore. 97210. Inquire as to subscription price.

This magazine is aimed at covering all aspects of recycling. Treatment of waste paper, glass, and other materials is discussed, as are state and provincial programs, market development, and the like.

Women and Occupational Health Risks. 41 pages. WHO Publications Centre U.S.A., 49 Sheridan Ave., Albany, N.Y. 12210. 1983. 4 Swiss francs (about $2.50), paper.

This book reports on a meeting on the subject that took place in Budapest, Hungary, last year. It considers current attitudes and legislation in various European countries, mutagenicity, teratogenicity, mental health, and other factors.

The Solar Energy Directory. Sandra Oddo, Martin McPhillips, Eds. 350 pages. Grey House Publishing, Inc., 360 Park Ave. S., New York, N.Y. 10010. 1982. $50, hardcover.

This directory lists professional, private, regional, and government organizations; manufacturers and utilities; educational, training, and research institutions; and sources of information pertaining to the solar energy field.

Handbook of Environmental Data on Organic Chemicals, Second Edition. Karel Verschueren. 1336 pages. Van Nostrand Reinhold, 135 W. 50th St., New York, N.Y. 10020. 1983. $99.50.

This book provides detailed coverage on individual substances, mixtures, and preparations, as well as control methods now in use. Pesticides, detergents, phthalates, polynuclear aromatics, and polychlorinated biphenyls are investigated in detail. Threshold values, natural and manmade sources, emission control methods, and other pertinent topics are examined.

Siting Hazardous Waste Management Facilities: A Handbook. 84 pages. National Audubon Society, 115 Indian Mound Trail, Tavernier, Fla. 33070. 1983. $3, paper.

This book was published by the Conservation Foundation, Chemical Manufacturers Association, and National Audubon Society. Its aim is to promote understanding, public participation, and education in siting hazardous waste facilities, and to act as a guide to the important issues. Waste analysis, storage, regulation enforcement, closure, and treatment are among the topics discussed.

The World Environmental Handbook—A Directory of Natural Management Agencies in 144 Countries. World Environment Center, 17th Floor, 605 Third Ave., New York, N.Y. 10158. 1983. $25 (add $2 for postage in North America, $4.50 elsewhere).

There are now environment agencies in 144 countries, 500% of the number existing in 1972. In the Third World, 105 countries have environment agencies. This book lists agencies from Afghanistan to Zimbabwe, and gives addresses and names of people in charge, along with telephone numbers.

Procedures Manual: Organics Detection System, Analysis of River Water for Volatile Organics by the Purge-and-Trap Procedure. 93 pages. Ohio River Valley Water Sanitation Commission, 414 Walnut St., Cincinnati, Ohio 45202. 1983. $4 (add $2.50 for postage); single copies free to public agencies and nonprofit organizations.

This manual gives step-by-step instructions in operating gas chromatography systems for detecting and identifying volatile halogenated hydrocarbons, such as chloroform, in river water. It also reviews the commission's organics detection system methodologies.

Waste Management & Research. R. B. Dean, T. H. Christensen, Eds. Periodical, quarterly. Subscription Fulfillment Department, Academic Press Inc., 111 Fifth Ave., New York, N.Y. 10003. $95/year.

This periodical (initiated this year) covers (but is not to be limited to) topics such as city cleansing, recycling, health effects, correction of "bad" or "harmful" practices, new technologies, engineering, and social and policy considerations.

ES&T
MEETINGS

Sept. 14–15 Raleigh, N.C.
Oct. 25–26 Charlotte, N.C.
Dec. 7–8 Raleigh, N.C.
Hazardous Waste Management under RCRA. North Carolina State University

Write: Woody Fairbrother, North Carolina State University, Division of Continuing Education, P.O. Box 5125, Raleigh, N.C. 27650; 919-737-2261

Sept. 16 Raleigh, N.C.
Oct. 27 Charlotte, N.C.
Dec. 9 Raleigh, N.C.
Applied Spill Prevention, Control, and Countermeasures. North Carolina State University

Write: Woody Fairbrother, North Carolina State University, Division of Continuing Education, P.O. Box 5125, Raleigh, N.C. 27650; 919-737-2261

Sept. 19–22 Oklahoma City, Okla.
Interstate Conference on Water Problems. Oklahoma Water Resources Board

Write: James R. Barnett, Oklahoma Water Resources Board, P.O. Box 53585, Oklahoma City, Okla. 73152; 405-271-2551

Sept. 21–22 Chicago, Ill.
Toxic Air Pollutants: An Analysis of Regulatory Strategies. State and Territorial Air Pollution Program Administrators and Association of Local Air Pollution Control Officials

Fee: $125; $75 for government officials. *Write:* Ann Renauer, 444 North Capitol St., N.W., Washington, D.C. 20001; 202-624-7864

Sept. 22–23 Schaumburg, Ill.
Groundwater Compliance: Designing, Installing, and Operating Groundwater Wells. Center for Energy and Environmental Management

Write: Mary Jo Russell, CEEM, P.O. Box 536, Fairfax, Va. 22030; 800-424-9068

Sept. 25–30 White Haven, Pa.
7th International Conference on Enzyme Engineering. Engineering Foundation

Write: The Engineering Foundation Conferences, 345 East 47th St., New York, N.Y. 10017; 212-705-7835

Sept. 26–28 Miamisburg, Ohio
8th Annual Inland Spills Conference. Ohio Environmental Protection Agency and Spill Control Association of America

Fee: $30 (full conference). *Write:* Sara E. Games, Conference Coordinator, Ohio EPA, 361 E. Broad St., Columbus, Ohio 43216-1049; 614-466-8820

Sept. 25–30 Philadelphia, Pa.
10th Annual Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies (FACSS). Society for Applied Spectroscopy, the ACS Division of Analytical Chemistry, and others

Write: Richard J. Knauer, Publicity Chairman, Armco, Inc., P.O. Box 1697, Baltimore, Md. 21203

Sept. 27–29 New Haven, Conn.
Spill Control and Hazardous Materials Conference–Workshop. New Haven Harbor Petroleum Cooperative

Write: Sal Brancato, Spill Control and Hazardous Materials Conference, P.O. Box 8831, New Haven, Conn. 06532; 203-236-4382

Sept. 30–Oct. 5 Ypsilanti, Mich.
12th Annual Conference of the National Association for Environmental Education: "Crossroads: Society and Technology." National Association of Environmental Education

Write: John H. Baldwin, 156 Hendricks, University of Oregon, Eugene, Ore. 97403; 503-686-3698

Oct. 2–5 Philadelphia, Pa.
1st Symposium on Industrial Resource Management. Journal of Resource Management and Technology

Write: Iraj Zandi, University of Pennsylvania, Philadelphia, Pa. 19104; 215-898-8368

Oct. 5–6 Washington, D.C.
Oct. 18–19 Denver, Colo.
The Fundamentals of Groundwater Quality Protection. American Ecology Services, Inc. and Geraghty & Miller, Inc.

Write: Richard M. Miller, American Ecology Services, Inc., 127 East 59th St., New York, N.Y. 10022; 212-371-1620

Oct. 9–13 San Antonio, Tex.
19th Annual Conference and Symposium: "Analysis and Management of Land Drainage and Flood Waters." American Water Resources Association

Write: American Water Resources Association, 5410 Grosvenor Lane, Suite 220, Bethesda, Md. 20814; 301-493-8600

Oct. 9–14 Santa Fe, N.M.
6th International Symposium on Environmental Biogeochemistry. International Symposia on Environmental Biogeochemistry, Inc.

Write: Douglas E. Caldwell, Department of Applied Microbiology and Food Science, John Mitchell Building, University of Saskatchewan, Saskatoon, Saskatchewan S7N 0W0, Canada

Oct. 18–19 Chicago, Ill.
Symposium on Iron and Steel Pollution Abatement Technology. U.S. EPA, Industrial Environmental Research Laboratory, and Iron and Steel Committee (TS-4.1) of the Air Pollution Control Association

Fee: $90. *Write:* John S. Ruppersberger, Industrial Processes Branch (MD-63), EPA, Industrial Environmental Research Laboratory, Research Triangle Park, N.C. 27711; 919-541-2733

Oct. 24–27 Tulsa, Okla.
National Water Resources Association Annual Conference and Seminar. Oklahoma Water Resources Board

Write: J. W. O'Meara, 955 L'Enfant Plaza S.W., Washington, D.C. 20024; 202-488-0610

Oct. 25–27 Dallas, Tex.
2nd QualTest Conference and Exposition. American Society for Nondestructive Testing, Inc., and others

Write: Beth Risinger, Director of Marketing and Membership, 4153 Arlingate Plaza, Caller No. 28518, Columbus, Ohio 43228; 614-274-6003

Oct. 31–Nov. 2 Washington, D.C.
4th National Conference and Exhibition on Management of Uncontrolled Hazardous Wastes Sites. Hazardous Materials Control Research Institute (HMCRI), U.S. EPA, U.S. Army Corps of Engineers, American Society of Civil Engineers, and the U.S. Geological Survey

Write: Beverly Walcoff, HMCRI, Columbia Blvd., Silver Spring, Md. 20910; 301-587-9390

Nov. 1–4 New Orleans, La.
Joint Conference on Occupational Health. American Academy of Industrial Hygiene and the American Academy of Occupational Medicine

Write: Joint Conference on Occupational Health, 2340 S. Arlington Heights Rd., Arlington Heights, Ill. 60005

COURSES

Aug. 23–26 Research Triangle Park, N.C.
Ambient Air Quality Monitoring Systems: Course 63. Northrop Environmental Training

Fee: $585. *Write:* Carolyn Jenkins, Registrar, Northrop Environmental Training, P.O. Box 12313, Research Triangle Park, N.C. 27709; 919-549-0652

Sept. 12–13 Chicago, Ill.
Ion-Exchange Water Softening and Demineralization. Center for Professional Advancement

Fee: $490. *Write:* Center for Professional Advancement, Dept. NR, P.O. Box H, East Brunswick, N.J. 08816-0257; 201-249-1400

Sept. 12–14 East Brunswick, N.J.
High Purity Process Water. Center for Professional Advancement

Fee: $700. *Write:* Center for Professional Advancement, Dept. NR, P.O. Box H, East Brunswick, N.J. 08816-0257; 201-249-1400

Sept. 12–15 Dayton, Ohio
Safety Management Techniques. Dayton/Miami Valley Safety Council

Write: James C. Schaffner, Director, Dayton/Miami Valley Safety Council, 1980 Winters Bank Tower, Dayton, Ohio 45423; 513-226-1444

Sept. 19–21 Nashville, Tenn.
Management of Leachate and Groundwater at Hazardous Waste Disposal Sites. Vanderbilt University

Fee: $225. *Write:* Director, Continuing Engineering Education, Vanderbilt University, Box 1525, Sta. B., Nashville, Tenn. 37232; 615-322-2924

Sept. 19–23 Chicago, Ill.
Microchemical Analysis. McCrone Research Institute

Fee: $650. *Write:* Nancy B. Daerr, McCrone Research Institute, 2508 South Michigan Ave., Chicago, Ill. 60616; 312-842-7105

Sept. 19–23 Chicago, Ill.
Basic Principles of Chemical Engineering. Center for Professional Advancement

Fee: $995. *Write:* Center for Professional Advancement, Dept. NR, P.O. Box H, East Brunswick, N.J. 08816-0257; 201-249-1400

Oct. 3–5 Phoenix, Ariz.
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Triple-Quadrupole Mass Spectrometry Studies of Nitroaromatic Emissions from Different Diesel Engines

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■ Triple-quadrupole mass spectrometry (MS/MS) has been used to compare nitroaromatic emissions from two different types of diesel engines, a direct-injection, single-cylinder engine and an indirect-injection V-8 engine. The low level of nitropyrenes/nitrofluoranthenes in exhaust extracts may be due in part to the low pyrene content of the reference fuel used. Addition of pyrene to reference fuel resulted in increased pyrene in exhaust extracts, but only minor differences in mutagenicity. Only about 1/1000 of the total mutagenicity from complete reaction with NO_2 appeared to have occurred during diesel exhaust and soot collection on filters. Fractionation with Me_2SO was found to be useful in separating aliphatic hydrocarbons from mutagenic activities and in concentrating nitroaromatic compounds for MS/MS analysis. Concentration of certain nitroaromatic compounds was necessary for isobutane chemical ionization MS/MS, while atmospheric pressure MS/MS appeared capable of detecting nitroaromatic compounds even in unfractionated extracts. MS/MS comparisons of concentrated samples of differing mutagenicities showed the main differences were increased ion intensities of dinitro compounds in more mutagenic samples. It is concluded that the polynitro compounds may be of more significance than mononitro compounds in the mutagenic activities that have been found associated with diesel soot.

Introduction

Use of diesel engines in light-duty vehicles has been increasing because of increased fuel efficiency, the ability of diesel engines to utilize a wide range of fuels, and the lower taxation on diesel fuels in certain countries. The presence of direct-acting mutagens in diesel exhaust emissions (*1–4*) has generated concern over potential health effects that may occur from increased diesel emissions. Correlations between the presence of nitro polycyclic aromatic hydrocarbons (nitro-PAHs) in environmental extracts and mutagenic activity have been observed (*5–8*).

New analytical approaches are needed to identify the mutagenic activities in exhaust extracts and measure the effects of different diesel engine designs and fuel formulations. Schuetzle et al. (*9*) have used triple-quadrupole mass spectrometry (MS/MS), high-resolution MS, and HPLC to compare exhaust extracts from three different makes of light-duty diesel vehicles. The differences in exhaust mutagenicity were quantitatively linked to the differences in mononitropyrene concentrations in each exhaust extract. However, only 10–20% of the exhaust mutagenicity was relatable to the mononitropyrenes. The exhaust sample studied in detail was from a malfunctioning prototype Nissan engine (*10*) and thus did not represent emissions from a production line engine.

Clark et al. (*11*) have shown that exhaust mutagenicity varied 2–4-fold when one engine type was operated on fuels of differing aromaticity. Other engines of differing designs showed less than a 2-fold variation in mutagenicity when operated on the same range of fuels. Fuel variations as well as engine design may affect exhaust mutagenicity, but new methods are needed to elucidate the nature of these differences.

Comparison of diesel soot extracts by MS/MS may be a useful initial approach to evaluate the relationships between mutagenicity of diesel exhaust and nitro-PAHs. MS/MS spectra showed that nitro-PAHs of similar molecular weights were present in soot extracts and fuel PAHs treated with NO_2, suggesting a contribution of unburned fuel to exhaust mutagenicity (*7*).

In the studies reported here, MS/MS analyses were used to compare diesel soot extracts and chemical fractions from two different types of diesel engines. Determination of the type of nitro-PAHs present in soot extracts enables selection of nitro-PAH compounds for synthesis as standards and for more quantitative estimates of the contribution of individual nitro compounds to mutagenicities present in exhaust.

Methods

A standard no. 2 diesel reference fuel was utilized in the experiments reported here. The PAH composition of this fuel has been reported previously (*7*). The one-cylinder diesel was a Swan engine (Jintang Diesel Engine works, The Peoples Republic of China) and the eight-cylinder

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Table I. Samples Utilized for MS/MS Analysis

sample	TA 98 direct Mutagenicity, revertants/μg	source and preparation conditions	% of total wt	% of total Mutagenicity
I	435	aromatic fraction from no. 2 reference diesel fuel treated with excess NO_2	100	100
Ia	1086	Sephadex chromatographic fraction 3 of sample I	27	51
Ib	702	Sephadex chromatographic fraction 4 of sample I	34	43
II	9.7	CH_2Cl_2 extract of exhaust particles from Swann single-cylinder diesel engine running on no. 2 reference fuel	100	100
IIa	57.4	aromatic fraction of II prepared by Me_2SO extraction, dilution with water, and back-extraction into hexane	8.5	50
IIb	16.7	polar fraction of II prepared by Me_2SO extraction, dilution with water, and back-extraction with CH_2Cl_2	2.7	4.7
IIc	<0.1	aliphatic fraction of II; residue after Me_2SO	73	–0–
III	5.2	CH_2Cl_2 extract of exhaust particles from Oldsmobile V-8 diesel engine running on standard no. 2 diesel fuel	100	100
IIIa	20.9	aromatic fraction of III; prepared by Me_2SO extraction, dilution with water, and back-extraction into hexane	12	49
IIIb	9.5	polar fraction of III prepared by Me_2SO extraction, dilution with water, and back-extraction into CH_2Cl_2	8.1	30
IIIc	<0.1	aliphatic fraction of III; residue after Me_2SO extraction	46	–0–

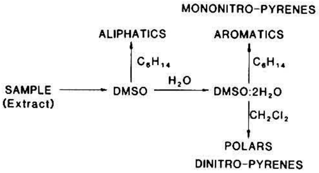

Figure 1. Fractionation of diesel soot extracts with Me_2SO. The solvents were mixed with extracts and the phases separated in a separatory funnel. The *n*-hexane and methylene chloride extractions were repeated three times. After washing with water, the extracts were concentrated by rotary evaporation and the final few milliliters removed in a stream of flowing N_2.

diesel was a standard Oldsmobile 5.7-L V-8 engine. Diesel exhaust particles were collected at the Inhalation Toxicology Research Institute from the above engines in which the one-cylinder engine was operated at 2000 rpm (75% of maximum) and 900 W (75% of maximum) engine load (electrical alternator), and the 8-cylinder engine was operated on the EPA Federal Test Procedure Cycle. Soot samples were collected on Pallflex T60A20 filters after a 10-fold dilution in a tunnel and extracted with methylene chloride as described previously (*7*).

The PAH fraction from the above reference fuel was extracted as described previously (*6, 7*) and fractionated as outlined in Figure 1. The hexane–PAH extract was washed with 5% NaOH and 5% HCl to remove ionic impurities. After evaporation of the solvent, 1–5 g samples were converted to nitro-PAHs by reaction with NO_2 as described previously (*6*). The resulting fuel nitro-PAH mixtures were fractionated by Sephadex LH-20 chromatography (*7*) and subfractionated by thin-layer chromatography on Analtech silica gel G plates (250-μm thickness) using 1:1 hexane–CH_2Cl_2 solvent. The mass and mutagenic activities of the two most active Sephadex fractions (Ia and Ib) are given in Table I.

The PAHs extracted from this fuel were predominantly methylated naphthalenes (*7*). This is in contrast to other reference diesel fuels where phenanthrenes and methylated phenanthrenes were the major PAHs (*6, 11*).

The methylene chloride extracts of diesel exhaust particles were also fractionated with Me_2SO as described in Figure 1 (*6, 7*). The samples and fractions used in these studies are summarized in Table I.

Standards of 1-nitropyrene and mixed dinitropyrene isomers were partitioned between the Me_2SO/H_2O and hexane or CH_2Cl_2 phases to confirm the separation shown in Figure 1. Analysis by solid-probe MS of the hexane and CH_2Cl_2 extracts showed that the separation was quantitative.

GC/MS (gas chromatography/mass spectrometry) analyses were performed with a Finnigan Model 4023 instrument operated in the electron impact mode. The instrument was equipped with a 20-m SP 2100 fused-silica column, with the column inserted directly into the ion source. The transfer and separator ovens were maintained at 250 °C, as were the injectors. The GC oven temperature was programmed 50–250 °C (2 °C/min) in which 1 μL of samples was injected with a 2-min hold at 50 °C. The instrument was interfaced to a Finnigan INCOS data system by using standard 3.1C software and NBS–NIH–EPA Mass Spectral Library. The MS was calibrated daily with perfluorotributylamine.

MS/MS analyses were performed at the University of Virginia by using a modified Finnigan 3200 instrument (*12*). Samples of 10–50 μg were injected into a thermal desorber, with a temperature program of 25–350 °C in 10 min which was started after the solvent was vented. The instrument was tuned by using standard 1-nitropyrene, synthesized as described previously (*13*), and the m/z 231^+ (M − 17) ion signal optimized. The ionizer was operated under isobutane chemical ionization conditions with a 0.4-torr isobutane source pressure. The first quadrupole was operated with a 1.3-s scan time over a mass range 80–450. The second quadrupole was operated with RF voltage only, with N_2 collision gas pressure adjusted for maximum m/z 231 ion intensity. The third quadrupole was set to scan 17 amu behind quadrupole no. 1. The specific reaction monitored was

$$R\text{–}NO_2 \rightarrow R\text{–}NO_2\text{–}H^+ \rightarrow R\text{–}N^+O$$

Thus only ions selected in quadrupole no. 1 that lost 17 amu upon collision in quadrupole no. 2 and separated in quadrupole no. 3 were detected. This loss is relatively specific for nitro compounds. The nitro-PAH masses observed in MS/MS spectra were interpreted from the molecular weights of the PAHs present in diesel fuels (*7*). The nitro-PAHs have a mass gain of 45 over the parent PAH and the R–N$^+$O ion observed in MS/MS spectra had a mass of 16 less than the parent nitro-PAH.

The specificity of the M + H$^+$ − 17 reaction for nitro-PAHs has been studied with over 100 PAHs reacted with NO_2 on the solid probe (*21*). Of the known PAHs, 92%

gave predominantly M + H^+ − 17 fragments. The other 8% of compounds gave M + H^+ − 30 ions as the predominant fragment in addition to M − 17 ions. The brief reaction of PAHs with NO_2 has been found to be specific and quantitative enough to allow semiquantitative analyses of environmental samples for PAHs (*21*), though the MS/MS procedure does not differentiate between PAHs of the same molecular weight. The formation of M + H^+ − 17 ions by other compounds (such as aldehydes, amines, phenols, carboxylic acids, etc.) is 20–40fold less prevalent than for nitro compounds. Selected samples in this study were also reacted with methyl isocyanate, which reacts with phenols, amines, and aldehydes (*21*), but no significant changes in the MS/MS spectra were observed. The reproducibility of MS/MS analyses for nitro-PAHs has been found to be ±20% by internal standards (*17*, *19*, *21*).

Atmospheric pressure ionization MS/MS (API/MS/MS) analyses were performed on a TAGA 6000 instrument at the laboratories of Sciex (Toronto, Canada) (*14*). Samples of 10–25 μg of extract were evaporated on the solid probe grid and thermally desorbed (in the ion source) over a 20-min period. The reagent gas was zero air. In this case, the specific reaction monitored was

$$\text{R-NO}_2 + \text{O}_2^- \rightarrow \text{R-NO}_2^- \xrightarrow{\text{Ar}} \text{R} + \text{NO}_2^-$$

The ions that were detected were those separated in quadrupole no. 1, which yielded NO_2^- upon collision with argon in quadrupole no. 2. Quadrupole no. 3 was set to detect only m/z 46^- ions. The ion energy was 65 eV.

An exact comparison of results obtained in the Sciex and Finnigan instruments on the same samples were not possible because the Sciex software is designed for air monitoring measurements and the Finnigan software for GC/MS analysis. It was thus not possible to present data in the same format for close comparison.

Salmonella mutagenicity assays were conducted as described by Ames et al. (*15*) with strains TA98 and TA100. Sodium azide (1 μg/plate), 2-aminoanthracene (0.5 μg/plate), 2-nitrofluorene (1.5 μg/plate), and benzo[*a*]pyrene (2.5 μg/plate) were used as positive controls to verify the activity of Aroclor 1254 induced liver homogenates and the reversion properties of the test strains. *Salmonella* in the plateau phase of growth (overnight culture, approximately 10^9 cells/mL) were used as starting culture. Cultures were incubated in the dark for 48 h, and revertant colonies were counted with an Artek colony counter. Assays were run in triplicate and averaged, and the specific activity in revertants/microgram of extract was calculated by linear regression analyses of data at regions of linear dose–response. Triplicate assays averaged less than 10% in standard deviation. When samples were compared, they are assayed on the same day by using the same starting culture. The mutagenicity of the positive controls in different experiments had the following range of activities: 2-aminoanthracene, 500–800 revertants/plate (TA100), 400–800 revertants/plate (TA98); 2-nitrofluorene, 150–250 revertants/plate (TA98); sodium azide, 350–550 revertants/plate (TA100); benzo[*a*]pyrene, 150–300 revertants/plate (TA98) and 500–700 revertants/plate (TA100).

Results

The exhaust extract samples and chemical fractions used for MS/MS analysis and Ames bioassay comparisons are summarized in Table I. The single-cylinder diesel soot extract (sample II) was 2-fold higher in mutagenic activity than extracts from the Oldsmobile V-8 engine (sample III). This was an Oldsmobile V-8 engine different from the one sampled previously (*7*). The aromatic fractions recovered from the two engines (samples IIa and IIIa) were similar to previous samples in the aromatic fractions contained ca. 50% of the total mutagenic activity of the whole extracts. The aliphatic fractions (IIc and IIIc) were devoid of mutagenic activity although they contained more than 45% of the mass in each extract. The polar fractions contained about 30% of the total mutagenic activity from the Oldsmobile (sample IIIb) but only 5% of the total activity from the single-cylinder exhaust (IIb). The residual activity in the Me_2SO/H_2O fractions was not analyzed in these studies. Previously, only nonvolatile tars and gums were found in these fractions.

MS/MS analyses for nitro-PAHs were performed on NO_2-treated fuel PAH samples I, Ia, and Ib in Table I. Table II shows a comparison of the ions observed on MS/MS between fuel nitro-PAHs and two Sephadex LH20 fractions derived therefrom. The ion intensities showed that sample Ia was somewhat depleted of mononitro-PAHs (odd masses) compared to sample Ib and was enriched in certain dinitro-PAHs (even masses).

Sample Ib was further fractionated by TLC to confirm the identity of the nitro-PAHs detected from MS/MS. A yellow band was separated from the slower moving orange material. Analysis of this material by GC/MS analyses showed the predominant compounds in this fraction were isomeric mono-, di-, tri-, and tetramethyldinitronaphthalenes. The direct mutagenic activity of this yellow band was approximately 15000 revertants/μg. No standards were available to identify the specific isomers present.

Figure 2 shows a comparison of the mutagenicity and MS/MS ion intensities of the fuel nitro-PAHs (sample I) and the exhaust aromatic fractions between the two engine types (samples IIa and IIIa). The even mass ions appeared to be positively correlated with mutagenicity in several instances, but the odd mass ions show only a few correlations such as m/z 171. The m/z 231 ion, corresponding to mononitropyrenes, shows little correlation with changing mutagenicity. The interpretation of individual ions whose intensities showed correlations with mutagenicity activity is shown in Table III. Interpretations of MS/MS ions were based on the known presence of the parent PAHs in this reference fuel (*7*) and assumed direct conversion of fuel PAHs to exhaust nitro-PAHs. The quantity of extracts was not adequate to allow further concentration of biologically active compounds for GC/MS analyses.

Table IV compares the MS/MS analyses for nitro-PAHs in the other fractions of diesel soot extracts between the single-cylinder and V-8 engine. These fractions all had less than 20 revertants/μg, which limited meaningful comparisons. The polar fraction from the single-cylinder engine (IIb) appeared to be the only sample that contained detectible dinitropyrene/dinitrofluoranthene ions. The unfractionated extracts showed nitro-PAH type ions similar to the aromatic fractions in Figure 2. However, the intensities were so low that comparison was difficult. The aliphatic fractions (IIc and IIIc) were very low in nitro-PAH ions, which correlated with their lack of mutagenic activity.

The Swan single-cylinder engine was run on reference diesel fuel supplemented with pyrene to confirm the contribution of fuel PAHs to PAHs in diesel exhaust. Figure 3 shows that pyrene addition to the fuel resulted in increased pyrene/phenanthrene ratios in the exhaust aromatic fraction. However, analysis of these extracts by API/MS/MS shows that the ion intensities of nitropyrenes and dinitropyrenes were not increased.

Internal standards of 1-nitropyrene were added to soot extract to verify that the nitropyrenes being measured by

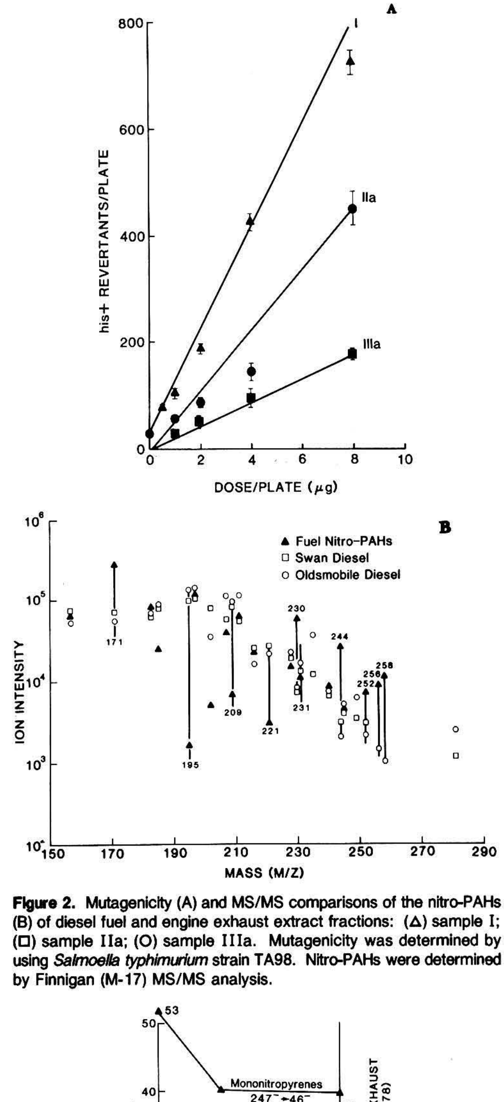

Figure 2. Mutagenicity (A) and MS/MS comparisons of the nitro-PAHs (B) of diesel fuel and engine exhaust extract fractions: (Δ) sample I; (□) sample IIa; (O) sample IIIa. Mutagenicity was determined by using *Salmoella typhimurium* strain TA98. Nitro-PAHs were determined by Finnigan (M-17) MS/MS analysis.

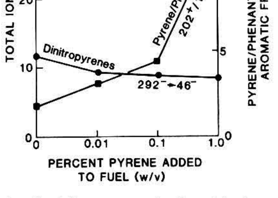

Figure 3. Effects of adding pyrene to diesel fuel on single-cylinder diesel exhaust extracts: MS/MS results. Pyrene was added to reference diesel fuel in the indicated grams/100 mL (w/v). The exhaust extracts were fractionated with Me_2SO and analyzed by GC/MS for PAHs. The unfractionated extracts were analyzed by API/MS/MS for nitropyrenes (m/z 247⁻ → 46⁻) and dinitropyrene (m/z 292⁻ → 46⁻).

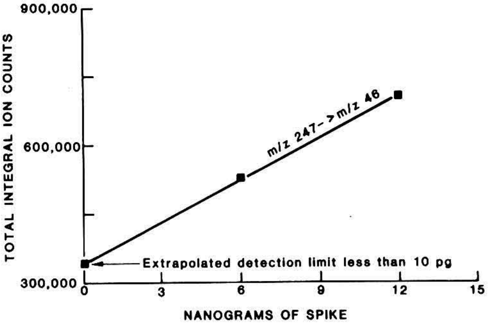

Figure 4. Calibration curve for nitropyrenes in diesel exhaust extracts. A 25-μg sample was applied to the solid-probe grid of the Taga 6000 API/MS/MS. Duplicate samples were spiked with 6 and 12 ng of 1-nitropyrene, and the intensity of the NO_2^- ion was measured after collision of the nitro-PAHs with Ar.

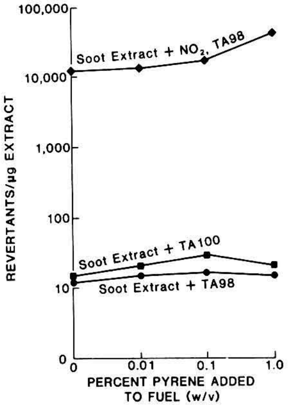

Figure 5. Effects of adding pyrene to diesel fuel: mutagenicity. The conditions were as in Figure 3. The unfractionated extracts were assayed with *Salmonella* strains TA98 and TA100. The extracts were also reacted with excess NO_2 to determine the mutagenic activity after all PAHs had reacted.

API/MS/MS were in the linear response range of the instrument and to quantitate nitropyrene concentrations. These results are shown in Figure 4. The response to standard nitropyrene additions was linear. The detection limit of the instrument for nitropyrenes was in the picogram range. The calculated nitropyrene concentration was 432 ppm or <10% contribution to the total mutagenicity of the single-cylinder extract (based on <2000 revertants/μg for nitropyrene) (*18*).

Figure 5 shows that supplementation of diesel fuel with pyrene also did not result in major changes in the mutagenicity of extracts. TA100 detected some increases in mutagenicity, but only slight increases were noted when extracts were assayed with TA98. A 3-fold increase in mutagenicity was observed from the exhaust from pyrene-supplemented fuel compared to the unsupplemented fuel exhaust when these extracts were treated with NO_2. In all cases, the mutagenicity of each exhaust extract was only about $^1/_{1000}$ of the mutagenicity observed when extracts were reacted with excess NO_2.

Discussion

These studies illustrate the difficulties in analyzing nitro-PAHs in diesel exhaust or other types of atmospheric particulate samples. MS/MS procedures or extensive

Table II. MS/MS Comparison of Sephadex LH-20 Fractions of Fuel Nitro-PAHs

m/z	sample I	sample Ia	sample Ib	possible compound
157	677[a]	35	467	nitronaphthalenes
171	2836	39	4086	nitromethylnaphthalenes
183	878	78	1370	nitrobiphenyls
185	256	61	424	nitrodimethylnaphthalenes
195	17	28	48	nitrofluorenes
197	1174	304	1516	nitromethylbiphenyls
202	53	40	76	dinitronaphthalenes
207	408	48	456	nitrophenanthrenes
209	71	56	66	nitromethylfluorenes
211	616	246	768	nitroethylbiphenyls
216	231	86	268	dinitromethylnaphthalenes
221	32	24	35	nitromethylphenanthrenes
228	150	148	194	dinitrobiphenyls
230	584	289	543	dinitrodimethylnaphthalenes
231	116	66	74	nitropyrenes
235	b	b	b	nitrodimethylphenanthrenes
240	84	233	55	dinitrofluorenes
244	274	278	153	dinitrotrimethylnaphthalenes
245	48	46	21	nitromethylpyrenes
249	b	b	b	nitrotrimethylphenanthrenes
252	73	159	22	dinitrophenanthrenes
256	93	174	42	dinitromethylbiphenyls
258	129	122	42	dinitrotetramethylnaphthalenes
276	b	b	b	dinitropyrenes
281	b	b	b	nitrobenzopyrenes
mutagenicity, revertants/μg	435	1086	702	

[a] Ion intensities $\times 10^{-2}$. [b] None detected.

Table III. Tentative Identification of Selected M − 17 MS/MS Ions in Figure 2

m/z	tentative identification
171	nitromethylnaphthalenes[a]
195	nitrofluorenes[a]
209	nitromethylfluorenes[a]
221	nitromethylphenanthrenes[a]
230	dinitrodimethylnaphthalenes[a]
231	nitropyrenes[b]
244	dinitrotrimethylnaphthalenes[a]
252	dinitrophenanthrenes[a]
256	dinitromethylbiphenyls[a]
258	dinitrotetramethylnaphthalenes[a]

[a] Parent PAH detected in reference diesel fuel. [b] Pyrene present in fuel at 25 ppm (*7*).

fractionation prior to GC/MS analysis were required to detect low levels of nitro compounds present. Treatment of exhaust extracts with NO$_2$ (Figure 5) indicated that only a small fraction of the total possible reactions with NO$_2$ had occurred, which would make detection of the original nitro-PAHs in unfractionated extract difficult. Even with MS/MS analyses, a preliminary concentration step (e.g., isolation of an aromatic fraction) was necessary for rigorous comparison of samples from different sources. For maximum concentration of fuel nitro compounds, both initial isolation of an aromatic fraction and silica chromatography were necessary. This approach had also been shown to concentrate the nitropyrene in exhaust extracts ca. 200-fold (*19*).

Comparison of diesel soot extracts from different engines was first reported by Schuetzle et al. (*9*). A moderately polar fraction (γ_1) isolated by HPLC was used for analysis. This fraction was shown by MS/MS to contain mononitro-PAHs and dinitro-PAHs containing two fused rings. A second more polar fraction (γ_2) was the fraction in which dinitropyrene standards eluted. About 50–75% of the total mutagenicity was associated with the first fraction and 20% with the second. Most of the data reported was from an EPA-collected sample from a malfunctioning Nissan engine that had been stored for several years (*9*).

The studies reported here showed that a similar concentration and fractionation can be accomplished by Me$_2$SO partitioning. Me$_2$SO fractionation required less time and instrumentation than HPLC procedures, and the mutagenic activity was concentrated more (*7*). Separation of aliphatic hydrocarbons and tars from the aromatic fractions was readily accomplished by Me$_2$SO fractionation.

Both isobutane chemical ionization (CI) MS/MS and atmospheric pressure ionization (API) MS/MS appeared to be satisfactory for detection of nitro-PAHs. The isobutane chemical ionization instrument appeared to exhibit somewhat better resolution than the API instrument, possibly because of the higher collision energies involved in the API instrument (30 vs. 65 eV). The negative ion analysis for NO$_2^-$ appeared to be somewhat more specific and sensitive for nitro-PAHs. This may in part be due to reaction of dinitro-PAHs in isobutane chemical ionization resulting in $(M - 30)^+$ ions as well as molecular ions, $(M + H)^+$. In the results reported here, masses corresponding to dinitropyrenes were detectable in single-cylinder exhaust extracts by CI/MS/MS only after fractionation, whereas they were directly detectable by API/MS/MS (Figure 3).

With the exception of low levels of dinitropyrenes in the single-cylinder exhaust, but not in the Oldsmobile V-8 exhaust, the molecular weight range of nitro-PAHs were similar to each other and to the PAHs derived from fuel treated with NO$_2$. The exceptions were traces of nitrobenzopyrenes that were absent in fuel nitro-PAHs but present in emissions. Thus, comparing complex samples of differing mutagenicities by MS/MS appears to be a useful initial approach in estimating which nitro-PAHs may be present and the qualitative contribution to the total mutagenicity of particulates. These interpretations may also suggest which compounds need to be synthesized for evaluation of biological activity and analytical quantitation. However, MS/MS analyses do not differentiate between isomers of individual nitro-PAHs such as nitropyrenes/nitrofluoranthenes. The intensity of daughter ion

Table IV. MS/MS Comparisons of Diesel Fractions[a]

	sample						
m/z	IIb	IIIb	II	III	IIc	IIIc	possible compound
157	656	575	136	212	71	16	nitronaphthalene
171	588	479	130	238	66	24	nitromethylnaphthalenes
183	708	768	145	284	103	49	nitrobiphenyls
185	819	756	139	335	26	24	nitrodimethylnaphthalenes
195	864	602	332	552	199	219	nitrofluorenes
197	989	933	258	637	132	209	nitromethylbiphenyls
202	627	316	176	164	31	23	dinitronaphthalenes
207	490	532	148	472	83	182	nitrophenanthrenes
209	1088	415	199	360	60	84	nitromethylfluorenes
211	401	429	104	364	32	90	nitroethylbiphenyls
216	203	114	64	82	15	8	dinitromethylnaphthalenes
221	151	266	45	289	6	15	nitromethylphenanthrenes
228	157	66	26	40	2	1	dinitrobiphenyls
230	62	38	13	32	2	5	dinitrodimethylnaphthalenes
231	53	58	17	49	1	3	nitropyrenes
235	58	162	16	122	2	3	nitrodimethylphenanthrenes
240	43	23	9	19			dinitrofluorenes
244	10	8	5	8	1		dinitrotrimethylnaphthalenes
245	14	16	4	10			nitromethylpyrenes
249	19	34	2	30		1	nitrotrimethylphenanthrenes
252	28	8	5	6	1	1	dinitrophenanthrenes
256	6		2	4			dinitromethylbiphenyls
258	5		1	3		1	dinitrotetramethylnaphthalenes
276	4						dinitropyrenes
281	39	33	3	9	11	2	nitrobenzopyrenes
mutagenicity, revertants/μg	16.7	9.5	9.7	5.2	<0.1	<0.1	

spectra was too low to allow tentative identification by this approach.

The combustion of pyrene-supplemented reference fuel in the single-cylinder engine provides additional evidence that certain fuel PAHs may increase PAH concentrations in exhaust streams. These results have been confirmed with 1% pyrene/99% hexadecane fuel, where the major organic components associated with exhaust particles were found to be pyrene and hexadecane (*17*). Since only minimal changes in exhaust mutagenicity were detected from addition of pyrene to diesel fuel, it was hypothesized that the availability of reactive NO_x species in exhaust streams might be the limiting factor. Studies with the addition of nitric oxide to undiluted single-cylinder exhaust streams have shown that the mutagenicity of particulate extracts increased several-fold by this procedure (*17*). Yergey et al. (*16*) have reported that the mutagenicity of diesel exhaust was reduced when nitrogen-free combustion gases were used.

While mononitropyrenes have been discussed extensively as major contributors to the mutagenicity of diesel exhaust soot, this study suggests a number of components may be significant. The differences may be due in part to the very low pyrene content of the reference fuel used (25 ppm), which contrasts with commerical diesel fuels, which may range up to several hundred ppm in pyrene content (*17*). Studies with aromatic-free hexadecane fuel show that pyrene emissions from diesel combustion are increased 35% by the addition of even 100 ppm pyrene to fuel. The possible contribution of fuel-derived pyrene to exhaust pyrene and nitropyrenes may be particularly significant in emissions from the prototype Nissan engine (*10*), where the injectors were leaking intermittently during the combustion cycle. Also, in normal diesel engine operation, where acceleration involves increased fuel injection, the pyrene content of the fuel may influence exhaust mutagenicity.

While many of the compounds detected by MS/MS are not available in pure form for evaluation of the relative biological activity, it appears that PAHs readily react to form polynitro derivatives, and some of these have enhanced mutagenic activity. Comparison of the mutagenic response to nitropyrenes in Chinese hamster ovary cells with *Salmonella* showed that certain dinitropyrene isomers and trinitriopyrenes were more active mutagens than 1-nitropyrene in the mammalian cells (*20*).

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Registry No. Pyrene, 129-00-0.

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Characterization of PCB Components in Clophen Formulations by Capillary GC–MS and GC–ECD Techniques

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■ Clophen A30, A40, A50, and A60 technical formulations were analyzed by electron capture (ECD) and mass spectrometric (MS) detection techniques, after gas chromatographic separation on one fused silica capillary column (SE-54). On the basis of combined ECD and MS data, most of the strong and many of the weaker peaks were identified on the basis of 102 individual PCB components, available as reference compounds. Several differences from previously published assignments that were based on retention index calculations were found. The available individual components accounted for 82–85% of the total PCB content in A30 and A40 and 91–100% in A50 and A60.

Introduction

Polychlorinated biphenyls are ubiquitous environmental contaminants (*1*). They have been produced since the 1920s as technical formulations with varying degrees of overall chlorine content (20–80%). The formulations are complex mixtures of many (out of the 209 theoretically possible) components, differing in the number and the relative positions of the 1–10 chlorine atoms in the biphenyl molecular framework. They do not behave identically in the environment. For accurate information on sources, transport mechanisms, sinks, accumulation, degradation, and other relevant processes, analyses of polychlorinated biphenyls should therefore be made in terms of individual components rather than of technical formulations, which are, however, the dominant sources of PCB in the environment. It is thus essential to have detailed information on their composition.

Sissons and Welti (*2*) were among the first to realize the need for this approach. They separated and identified the major components in Aroclor 1254, using various analytical techniques. The retention properties of these components as well as those of 40 other components that were synthesized by them, were used to predict a complete analysis of Aroclor 1242, 1254, and 1260. Jensen and Sundström (*3*) synthesized 90 components and identified, in Clophen A50 and A60, almost 60 components, each containing four or more chlorine atoms per molecule. Most reports in the literature have been concerned with formulations of either low (*4–7*) or high (*8–13*) overall chlorine content, but also of both (*14–16*). The number of individual components available to these authors (except in ref 2 and 3) has been up to about 40 and in several cases considerably less.

Attempting to obtain information on nonavailable components in order to account for unidentified peaks, some authors have used the chromatographic retention indices of available components to calculate such data for missing ones. This approach has been applied to predict the composition of formulations with lower (Aroclor 1016, 1242, Clophen A30, A40 (*2, 5–7, 14, 15, 17, 18*)) and higher (Aroclor 1248, 1254, 1260, Clophen A50 and A60 (*2, 13*–15)) degrees of chlorination. According to some of these authors, the identity of many peaks could not however be unambiguously determined.

Some of these uncertainities have been resolved by application of other techniques than comparison of retention times, e.g., MS (*6, 7, 19*), NMR (*2, 8*), and IR (*2, 7–9*).

Generally, the efficiency of packed columns in GLC is unsufficient to allow their use for accurate analysis of the complex PCB mixtures in technical formulations and environmental samples (*20*). However, they have been used successfully in the analysis of Aroclor 1254 fractions that were preseparated on alumina columns (*2*) and of Clophen A50 and A60 fractions containing four, three, and less than three, respectively, *o,o′*-chlorines in the molecular framework that were preseparated on charcoal columns (*3*). Another approach to the use of packed columns involves the use of columns with varying selectivities. In this way, complete analysis of all components in Aroclors 1242 and 1016 has been claimed with use of up to 12 columns (*6, 13, 18*). The strongly increased GLC separation offered by capillary columns has been used to advantage in the

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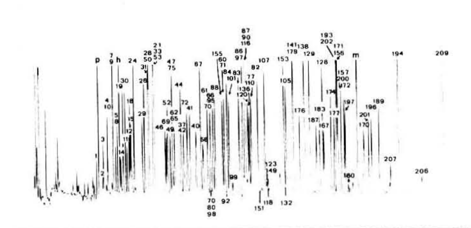

Figure 1. Temperature-programmed capillary column ECD chromatogram of a mixture of PCB components that were available in sufficiently pure form. Also included are pentachlorobenzene (p), hexachlorobenzene (h), and mirex (m). Relative amounts were selected to obtain similar peak heights in the mixture. However, some components were available only as stock solutions in low concentrations (e.g., 123, 149, 118, and 180). Peaks are identified by the IUPAC numbers of components giving rise to that particular peak (coeluting peaks given in a vertical column). Components 132, 92, 151, 141, 157, and 193 were not present in the mixture at this stage because of elution close to other components. The separation of some of these components from adjacent ones is demonstrated in technical formulations (Figure 4). Chromatographic conditions are as in the Experimental Section.

analysis of technical formulations (*2, 5, 7, 11, 12, 14–17*); in some cases the eluate was also analyzed by MS (*2, 5, 7, 11*).

We have studied the composition of PCB formulations, both qualitatively and quantitatively, by analyzing the eluate of the same capillary column by electron capture detection (ECD) and by directly coupled computerized mass spectrometry (MS).

Results will be presented for a characteristic series of formulations with chlorine contents in the 30–60% range. We have observed only minor differences in chromatograms of Clophen and Aroclor formulations with the same chlorine contents, e.g., Clophen A50 and Aroclor 1254. Data will be reported here in detail for the Clophen series, i.e., A30, A40, A50, and A60. The number of individual components available to us as reference compounds (102) was larger than in earlier reports. This allows a detailed comparison with the existing literature data on predicted compositions of such mixtures that have been based on retention index calculations that were, in turn, derived from a relatively limited number of available components.

Experimental Section

Clophens-, labeled 16571 (A30), 16557 (A40), 16572 (50), and 16573 (A60), and chlorobiphenyl standards were gifts from Bayer (Leverkussen FRG), from Analabs Inc. (Northhaven, CT) and from Dr. Palmork, Bergen, Norway. A Hewlett-Packard gas chromatograph Model 5880A equipped with a pulsed ^{63}Ni electron capture detector was used for GLC–ECD analysis in the splitless mode. The solvent was *n*-hexane (Nanograde, Mallinckrodt Inc., St. Louis, MO). All individual components were injected individually to determine response factors and retention times. Synthetic mixtures of various compositions were made to determine temperature-programmed conditions for optimum separation. The best conditions for the capillary WCOT (50 m × 0.33 mm) SE-54 fused silica column, compromising between the various chromatographic regions, were as follows: carrier gas, He (130 kPa); autosampler injection 1 μL splitless; makeup gas, N_2 (30 mL min^{-1}); detector, 320 °C; injector, 230 °C; septum purge, 5 mL min^{-1}; injector purge, 20 mL min^{-1} He; temperature program, isothermal phases at 60 (2 min), 180 (15 min), 210 (5 min), and 250 °C (10 min), intermediate temperature increase rates 10, 4, and 4 °C min^{-1}, respectively. The separation and coelution of the available components under these conditions are represented in Figure 1. Retention times were very reproducible (within 0.000–0.05 min over prolonged periods for retention times up to 1 h). This allowed accurate correlations.

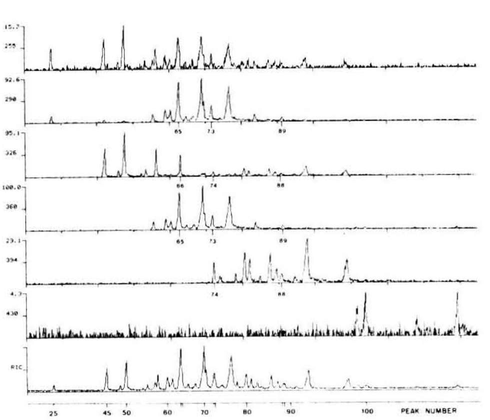

Figure 2. Relative abundances of mass peaks in reconstructed single ion and total ion current mass chromatograms of Clophen A60. Peak numbers have been defined in Figure 3.

A Finnigan 1020 automated GC–MS system with a Data General Nova 3 computer was used to obtain the mass spectral data; column as above (156 000 theoretical plates, C_{14}); injector, 230 °C; inlet, 60 °C (1 min); 6 °C min^{-1} up to 240 °C; separator oven at 240 °C and analyzer at 90 °C; electron energy 70 eV; scan range 150–550 amu, 1-s scan time.

Results

Mass Spectral Analysis. Reconstructed single ion mass chromatograms in combination with the reconstructed total ion current chromatogram (RIC) are shown for Clophen A60 in Figure 2. The selected ions characterize strong peaks in each of the clusters M^+, $(M - 35)^+$, and $(M - 70)^+$. Usually for PCB components, the strongest peaks belong to even masses in M^+, followed by even ones in $(M - 70)^+$; much weaker peaks characterize the $(M - 35)^+$ cluster (odd masses). The chlorine number of the component(s) in each peak of the RIC was evaluated by comparing the relative contributions of strong peaks characterizing the various clusters. For example, the characteristic ratio of peaks with m/e 360, 326, and 290 for hexachloro components can be observed for several well-separated peaks in Figure 2 (These define the peak numbers given completely in Figure 3. These should not be confused with scan numbers). Any significant contribution from a pentachloro component results in a larger contribution of m/e 326. The distinction between such components is illustrated in Figure 2 for the practically coeluting pairs of components in peak numbers 65, 66 (hexa, penta), 73, 74 (hexa, hepta), and 88, 89 (hepta, hexa). Distinction is still possible in cases where the peak maxima coincide, provided that the chlorine numbers differ by one. Two peaks originating from components with equal chlorine numbers could only be distinguished if the peak maxima were separated by at least 2–3 scan numbers in cases of similar contribution or by at least 5 scan numbers in cases of very dissimilar contributions, where one peak appeared as a weak shoulder on the other one.

Single ion mass chromatograms have also been analyzed for the other formulations (using m/e 220, 221, 222, 254, 255, 256, etc.). The total number of positions throughout

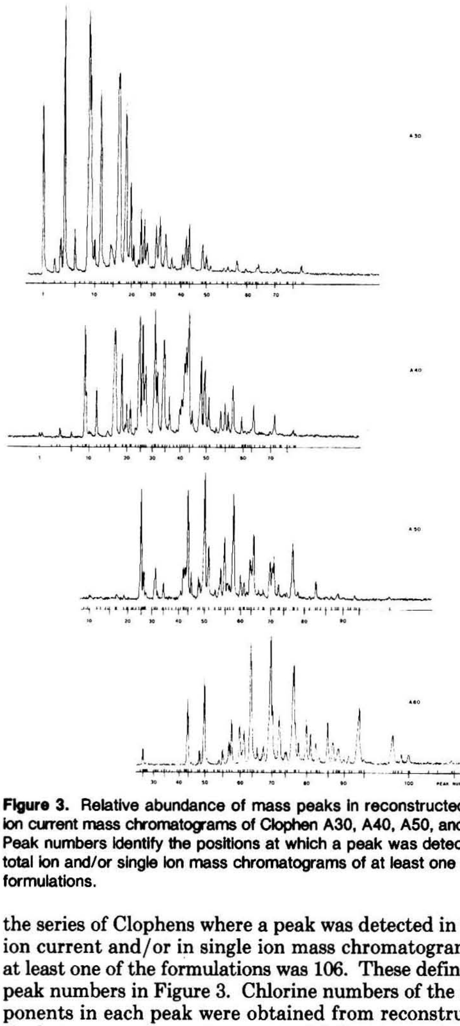

Figure 3. Relative abundance of mass peaks in reconstructed total ion current mass chromatograms of Clophen A30, A40, A50, and A60. Peak numbers identify the positions at which a peak was detected in total ion and/or single ion mass chromatograms of at least one of the formulations.

the series of Clophens where a peak was detected in total ion current and/or in single ion mass chromatograms of at least one of the formulations was 106. These define the peak numbers in Figure 3. Chlorine numbers of the components in each peak were obtained from reconstructed single ion mass chromatograms and full mass spectra and in addition, in more complex situations with more than one component contributing to a peak, from a study of the evolution of mass spectral details around each peak. This information could also be used as proof that the peaks of interest were actually derived from PCB components. For closely eluting (or coeluting) components with different chlorine numbers, the relative contributions of such components were evaluated (semiquantitatively) from single ion mass chromatograms. Chlorine numbers and relative contributions of components in each peak are given in Table I. In the following, some specific findings will be considered. The chlorine numbers of the major constituents are 2 and 4 but mainly 3 in A30, 3 and 5 but mainly 4 in A40, 4 and 6 but mainly 5 in A50, and 5 and 7 but mainly 6 (and also significant contributions of 8 and 9) in A60. Several peaks (e.g., 7 and 13, Figure 3) appeared only as minor contributions in one or more formulations. Early eluting peaks are strong in A30 and very weak in A60 while late peaks are strong in A60 and very weak in A30. The contributions of all peaks show systematic trends within the series A30–A60 but with considerably different rates of change. Some peaks have maximum contributions in A30 (e.g., peak 4), others in A40 (e.g., 27) etc. The structure of partly resolved and composite peaks (i.e., with proven contributions of two or more coeluting components) are therefore also expected to differ appreciably between the formulations. The single ion mass chromatographic data are essential in this respect. For instance, whereas peak 9 has similar contributions from chlorine numbers 2 and 3 in A30, the contribution of 3 dominates in A40; peak 45 changes its composition from 90% tetrachloro–10% pentachloro in A30 to practically 100% pentachloro in A60. The practically coeluting peaks 65 (hexa) and 66 (penta) increase and decrease strongly in the Clophen series and the contributions of peaks 70–72 (hexa-, hexa-, and pentachloro) increase, remain constant, and decrease in the series. Similar observations were also made for weaker peaks. For example, peaks 75, 76, and 78 showed the presence of hexachloro in A50 and heptachloro in A60.

Finally, it was determined which of the available individual PCB components could be assigned to each Clophen peak, taking into account both chromatographic retention and chlorine number constraints. Individual components and the synthetic mixture were subjected to GC–MS under the same conditions as the Clophens. Although temperature-programmed conditions during GC–MS were different from those in GLC–ECD analysis (Figure 1), the order of elution was identical, and the separation of adjacent components only differed slightly, for a few pairs of peaks. Thus, the analysis of the synthetic mixture by GC–MS was fairly straightforward. For each peak, the number of chlorine atoms actually found agreed with the assumed content of the sample vials. It is still possible that some components have not been labeled correctly. However, no errors were found in the chlorine numbers. The components listed in the first column of Table I satisfy retention and chlorine number constraints.

GLC–ECD Data. ECD chromatograms of the Clophen series are represented in Figure 4. All peaks observed in at least one of the Clophens have been listed in order of elution in Table I. Individual PCB components with retention times compatible with the chromatograms of the formulations within 0.01 min are identified for each peak by their IUPAC number(s) or by u if no component with the appropriate properties was available. Components with inappropriate chlorine numbers, as determined by GC–MS, are given in the last column. One of these numbers or the symbol u is given at the apex of the corresponding peak in Figure 4. It is interesting to note that ECD chromatograms of the Aroclor formulations that are available to us were practically identical with those of the Clophens with corresponding chlorine contents. The elution order of the PCB components is identical with and the relative peak heights are very similar to the total ion current mass chromatograms presented in Figure 3. However, monochloro components are characterized by a considerably lower response on ECD.

Figure 4 shows that several components eluting at close intervals can be distinguished at least qualitatively, such as the groups 18–15, 31–28, 60–92–84, 82–151, 149–123–118, and 153–132–105. Strong variations can be observed in the ratios between 149 and 118 and between 153, 132, and 105 within the Clophen series. Whereas 118 is the dominant peak in A30–A50, 149 dominates in A60. Components 153 and 132 increase in the series A30–A60; 105 dominates in A40 and is practically absent in A60. On the basis of missing (or very weak) peaks at the expected retention times, the absence (or presence in only trace amounts) of several components can be determined (Table II).

Table I. Composition of Peaks in ECD Chromatograms of Clophen A30–A60 As Represented in Figure 4[a]

components[b,h]	rel peak heights[c] A30	A40	A50	A60	Cl no.[a]	peak no.[e]	coeluting components[f]
4, 10	+				2	1	
7, 9	+				2	2	
u	+				2	3	2 (1)
5, 8	++++	(+)	(+)		2	4	
19	+	(+)			3	5	
18	++++	++	(+)		3	8	
15	++ 50	+ 20	(+)		2	9	
u	50	80			3		
24	+	tr			3	10	
u	++++	++	tr		3	11	
u	tr				3	12	
29	(+)				3	13	
26	+	(+)			3	14	
u	+	tr			3	15	
31	++++	++++	(+)		3	16	
28	++++	++++	(+)		3	17	50 (4)
21, 33	++++ 90	++ 70	(+) 50		3	18	
53	10	30	50		4		
u	tr	tr			4	19	
u	++++	+			3	20	
u	+	+	tr		4	21	
46	(+)	(+)			4	23	
52	++	++++	++++	+	4	25	
49	++	++++	+	(+)	4	27	
47	+ 30	++ 30	(+)	(+)	4	28	
75	70	70			4	29	
u	tr				5	30	
44	++	+++	++	(+)	4	32	
37	++ 90	++ 50			3	33	
42	10	50			4		
u	++ 50	++++ 40	+ 20		4	34	
41	50	60	80		4	35	
u		tr	tr		4	36	
40[g]	+	+	(+)		4	37	
67	(+)	(+)			4	38	
u	tr	(+)	tr	tr	4	39	
61	+	+++	+		4	41	
70	–	++++ 30	+++ 30	(+)	4	42	
80	++100	30	30		4	43	
98	–	30	30		5	44	
66	++ 90	++++ 90	++++ 40		4	45	
95	10	10	60	+	5		
88	(+)	+	+	(+)	5	46	
u	tr	–			5		
60[g]	++	++++	+		4	48	
92	+(sh)	+(sh)	++	(+)	5		
84	(+)	+	++	(+)	5	49	
101	+	++	++++	++	5	50	
99	(+)	+	+++	(+)	5	51	
83		(+)	+		5	52	
86, 97	tr	(+)	++		5	54	
87, 90, 116	+	++	++++	+	5	55	
120	(+)	+	++	(+)	5	56	
136	(+)	(+)	+	+	6	57	
77	+ 20	+++ 20	++++ 10	++	4	58	
110	80	80	90		5		
82	+	+	+	(+) 100	5	59	
151			(+)	+	6	60	
u	tr	tr	(+)	+	6	61	
u	tr	tr	(+)		6	62	
u	tr	tr	(+)	tr	6	63	107 (5)
149	(+)	(+)	+++	++++	6	65	
118	(+)	++	++++	+	5	66	
u	tr	tr	(+)	(+)	6	67	
u	tr	tr	tr	tr	6	68	
u	tr	tr	tr	tr	6	69	
153	(+) 20	(+) 10	+++ 30	++++ 60	6	70	
132	(+) 20	(+) 30	++ 30	++ 30	6	71	
105	(+) 60	+ 60	+++ 30	(+) 10	5	72	
141	tr	tr	+	++	6	73	
179	tr	tr		+	7	74	
u			(+)		6	75	
u				tr	7		
u			(+)		6	76	
176				(+)	7		

Table I (*Continued*)

components[b]	rel peak heights[c]				Cl no.[a]	peak no.[e]	coeluting components[f]
	A30	A40	A50	A60			
138	+	(+)	++++	++++	6	77	
u	tr	tr	(+)	+	6	78	
129			(+)	(+) 50	6	79	
u			tr	(+) 50	7		
187			tr	++	7	80	
183			tr	+	7	81	
128			+	+	6	82	
167			tr	tr	6	83	
u				tr	7	84	
174			tr	+	7	85	
177			tr	(+)	7	86	
u			+		6	87, 88	
193				+	7		
202				tr	8		
156			+	+	6	89	171 (7)
200				tr	8	90	157 (7)
u				tr	8		
172			(+)	(+)	7	91	
197				tr	8	92	
180			+	++++	7	93	
u				tr	7	94	
u	tr	tr	tr	tr	8	95	
170			+	+++	7	96	
u				tr	7	98	
201				+	8	99	
196				+	8	100	
189				(+)	7	102	
u				+	8	103	
194				(+)	8	104	
u				tr	8	105	
206				tr	9	106	
209				+	10		

[a] PCB components with retention times corresponding to each Clophen peak within ±0.005 min are listed in order of elution. Well-separated components are given in consecutive lines. At least partly separated components are given in consecutive lines, connected by a brace. Exactly coeluting components are given in the same line. In some cases, such components could be distinguished by MS: for clarity, these are also given in consecutive lines, connected by a bracket. [b] IUPAC numbers of PCB components (u if yet unidentified). [c] For each formulation, peak heights relative to the highest peak: ++++, ≃100%; +++, ≃75%; ++, ≃50%; +, ≃25%; (+), ≃10%; tr, trace. Information, derived from MS, is included as percentage contributions for each set of closely eluting or coeluting components. [d] Chlorine number(s) of component(s) detected by MS. [e] The corresponding peak number(s) as defined in the mass chromatograms (Figure 3). [f] IUPAC numbers of coeluting components with the inappropriate chlorine number in parentheses. [g] Component no. 56 resulted in two strong peaks, coeluting with 40 and 60. [h] IUPAC numbers in this and subsequent tables are identified in ref 15.

Table II. Components (IUPAC Numbers) in the Clophen Mixtures, Detected at Only Trace Concentrations or below the Detection Limit of Mass Spectrometry (MS) and Electron Capture Detection (ECD) Techniques in This Work[a]

component	MS	ECD	component	MS	ECD
1	–	–	62	–	–
2	–	–	65	–	–
3	–		67	–	tr
7	tr	tr	69	–	–
9	tr	tr	71	tr	–
11	–	–	72	tr	–
12	–	–	107	–	–
14	–	–	123	–	*
29	tr	tr	155	–	–
30	–	–	157	–	*
46	tr	tr	171	–	*
50	–	*	197	tr	tr
58	–	–	207	tr	tr

[a] –, absent; tr, in trace amounts; asterisk, no distinction from coeluting component by ECD.

These findings are supported by the GC–MS data, where in addition the absence of three more components was established (Table I).

Combination of MS and ECD Data. The good agreement between both the elution patterns and relative peak heights of all four Clophens in the ECD and total ion current mass chromatograms allowed a relatively straightforward correlation between the results of the two detection techniques (Table I). Several ECD peaks include possible contributions from coeluting components with equal chlorine number. The relative contributions of at least partly separated components with equal and different chlorine numbers and of coeluting components with different chlorine numbers were evaluated from single ion mass chromatograms. These were taken into account when considering the composition of peaks that are labeled 15, 21, 47, 37, 70, 95, and 110 in the ECD chromatograms. This has assisted in obtaining a quantitative estimate of the contributions of as many individual components as was possible in each of the Clophen formulations (Table III), on the basis of ECD response and compositional data obtained from GC–MS analyses.

Comparison with Literature Data

Qualitative Analyses. Sissons and Welti (2), using NMR, MS, and IR and solid–liquid chromatographic preseparation techniques, identified the major components of Aroclor 1254, 52, 44, 95, 84, 70, 101, 99, 97, 87, 110, 149, 132, 118, 105, 153, and 138, and, using solely NMR, components with smaller contributions, 128, 156, and 170. Their major components also appear in the presently reported assignment of the strongest peaks in Clophen A50.

Table III. Percentage Contents of Individual Components (Identified by Their IUPAC Numbers) in Clophen A30–A60 Formulations, Taken from the Literature and Evaluated in the Present Work on the Basis of Single-Component ECD Response Factors

		this work				ref 3	
IUPAC no.	comment	A30	A40	A50	A60	A50	A60
4 + 10	*a*	1.5					
7 + 9	*a*	0.6					
5 + 8	*a*	6.1	0.2				
19		1.2					
18		9.9	3.8				
15	*b*	9.0	0.8				
24		0.5					
29		0.2					
26		2.1	0.4				
31	*b*	6.8	2.4	0.1			
28	*b*	9.9	4.0				
21 + 33	*a*	4.6	1.3				
53		0.5	0.5				
46		0.5	0.8				
52		3.1	7.3	6.8	1.1	5.0	
49		1.2	4.1	1.5		1.4	
47[c]	*b*	0.4	0.7	0.1			
75[c]	*b*	0.9	1.7	0.2			
44		3.0	6.6	3.3		1.9	
37	*b*	3.2	1.2				
42	*b*	0.4	1.2	0.3			
41		1.6	3.5	0.7		1.29	
40		0.7	1.2	0.2			
67		0.2	0.2				
61		0.9	2.2	0.8			
70	*b*		1.9	1.2		3.9	
80	*b*	2.5	1.8	1.2			
98	*b*		1.8	1.1			
95	*b*	0.3	0.6	2.3	3.9	4.4	2.9
66	*b*	2.3	5.7	1.6			
88		0.2	0.4	0.4	0.1		
60		1.5	3.1	1.6	0.8		
92				1.3	0.5		
84		0.4	1.3	2.7	0.4	2.5	0.3
101		0.7	2.3	6.1	4.1	7.0	5.6
99		0.3	1.1	2.5	0.2	1.8	
83		0.2	0.3	0.7			
86 + 97	*a*	0.2	0.6	1.3	0.2		
87 + 90 + 116	*a*	0.4	1.1	3.5	0.9		
120		0.3	1.0	1.9	0.01		
136		0.1	0.1	0.7	1.5	0.50	1.0
77	*b*	0.3	0.7	1.1			
110	*b*	1.0	2.8	9.7	3.6	7.6	2.9
82		0.2	0.9	1.4	0.1	1.0	
151		0.1	0.1	0.6	4.7	1.3	3.3
149		0.5	0.4	4.1	9.6	2.0	6.5
118		2.5	6.7	10.5	1.0	5.0	1.6
153	*b*	0.5	0.3	3.2	8.6	4.2	12.9
132	*b*	0.2	0.5	3.1	4.6	1.8	3.2
105	*b*	0.5	1.5	0.7	0.2	3.6	
141	*b*			0.7	1.8		
179	*b*				0.7		
176				0.7	1.3	0.05	0.37
138		0.8	0.5	6.0	11.3	5.1	11.3
129				0.6	1.1		
187		0.1		0.3	3.8		
183				0.3	3.1	0.39	3.3
128				1.4	1.2	1.3	2.0
167				tr	tr	0.47	1.0
174				0.3	4.9	0.33	3.7
177				0.3	3.4	0.27	2.1
202	*b*				0.8	0.005	0.07
193	*b*				0.8		
156				0.8	0.8	0.81	1.5
200				0.2	0.8	0.007	0.09
172				0.1	1.1	0.23	0.9
197					tr	tr	0.03
180		0.3	0.2	0.2	8.9	0.98	7.6
170		tr	tr	0.6	5.2	0.72	4.1
201					1.4	0.08	0.74
196					1.4	0.06	0.44
189					0.4		
194					1.3	0.35	0.67

Table III (*Continued*)

		this work				ref 3	
IUPAC no.	comment	A30	A40	A50	A60	A50	A60
206					0.1		
209					0.2		
sum		85.4	81.8	91.0	100.2		

[a] Average response factors used for coeluting components with equal chlorine numbers. [b] Response factors evaluated with the use of GC-MS data as given in Table I. [c] 47 and 75 were not fully separated.

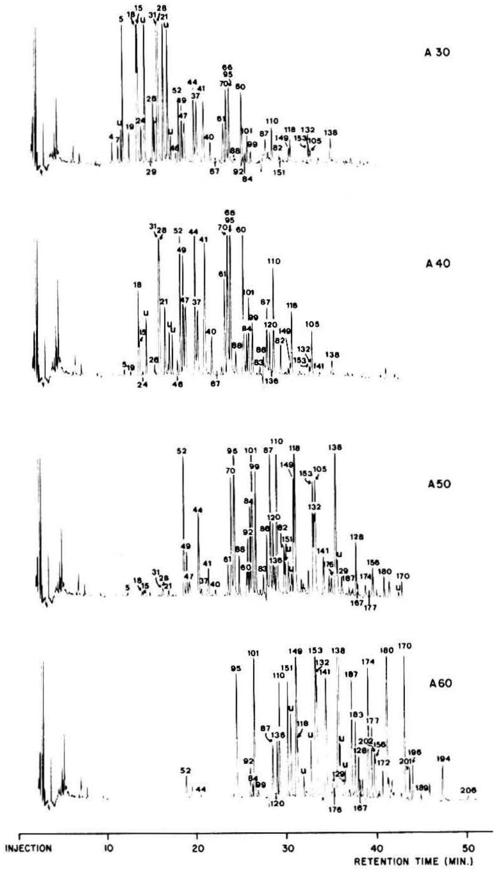

Figure 4. Temperature-programmed capillary ECD chromatograms of Clophen A30, A40, A50, and A60. Peaks are identified in terms of individual PCB components by the IUPAC number of the component or one of the components (if applicable, with the largest contribution) with appropriate retention time; u = unknown. Full details are presented in Table I. Experimental conditions as in Figure 1.

The present assignments also include 66 (coeluting with 95), 80 and 98 (with 70), 86 (with 97), 116 (with 87), and 77 (with 110).

Jensen and Sundström (*3*), using 90 components synthesized by them and some literature data, were able to calculate the percentage contributions of 46 components in Clophen A50 and A60. There is reasonably good agreement between their assignment and ours with respect to component that were available as reference compounds both to them and to us. Webb and McCall (*7*) separated 27 PCB components in Aroclor 1221, 1242, and 1254; the GLC retention times and IR spectra were compared with known, prepared compounds. The identification of components eluting from their SCOT SE-30 column agrees with our findings for the components that were available to them. These authors also reported 20 components to be absent from Aroclors 1221–1254, including 37, 42, 26, 90, 92, and 120. However, these components appear in our assignments. Tas and de Vos (*8*) and Tas and Kleipool (*9*) synthesized seven components (153, 138, 180, 170, 136, 149, and 174) and proved their presence in Phenoclor DP6 by application of NMR, IR, and GLC techniques. Schulte and Acker (*11*) analyzed Aroclor 1254 on a 60-m SE-30 capillary column with ECD. Their elution pattern was identical with that reported here for the 20 components that they identified by GLC and GLC–MS analysis. The reported elution order is different, however, for 128, 187, 202, and 200.

Recently, some authors have made extensive use of retention indices of available components to obtain estimates of retention data of unavailable components. Thus, complete quantitative characterization of the Aroclor series 1016–1260 has been claimed (*6, 13, 18*). With the use of retention indices of all PCB components computed for 13 GLC phases, six packed columns with liquid phases of varying selectivities were needed for 1221 and twelve for 1242 and 1016, on the basis of 38 available components. Four capillary columns with different selectivities were needed for Aroclor 1248, 1254, and 1260, using 45 available components (*13*). It is difficult to compare their data because no detailed information on chromatograms and available components was presented. Ballschmiter et al. presented the most recent and detailed results for the analysis of technical formulations (*14, 15*), as a basis for analyses for various types of environmental samples (*21, 22*). They have presented chromatograms obtained with ECD on SE-30 columns, resulting in the same elution pattern as on the present SE-54 column. The chromatograms differ little from those presented here, except for a few details in separation. With use of calculated retention indices and experimental data for 45 available components, detailed assignments of the Clophen series were given (*14, 15*). The agreement between their assignment and our assignment is good, but not perfect, for these 45 components. Significant differences exist for other components. Because it is the most recent and detailed assignment presently available in the literature and it has been applied to various types of environmental samples (*21, 22*), it may be useful to specify where differences exist on the basis of experimentally determined retention times and chlorine number constraints. This then applies to components 14, 29, 33, 36, 42, 51, 54, 62, 79, 86, 90, 128, 130, 132, 137, 160, 163, 165, 167, 173, 174, 177, 196, 200, 201–202, and 208. For these components, bottles may have been wrongly labeled, or alternatively, calculated retention times may not be sufficiently reliable. Future work in different laboratories will assist in distinguishing between these possibilities.

Quantitative Analyses. Table III summarizes the results of quantitative estimates of available components in Clophen formulations A30–A60 evaluated in the present

Table IV. Relative ECD Response Factors of Individual PCB Components, Given as Range of Peak Heights per Picograms of Component Injected, for n Available Components with Chlorine Number n_{Cl}[a]

n_{Cl}	n	rel factors	n_{Cl}	n	rel factors
1	3	0.07-2.2	6	11	7.1-16.5
2	8	1.4-7.7	7	10	4.9-10.6
3	9	4.7-14.3	8	6	6.1-10.9
4	22	4.4-11.1	9	2	2.0-18.1
5	18	8.0-31.2[a]	10	1	41

[a] The range is 8.0-15.3 when the data for component 97 are deleted.

work and those in A50 and A60 analyzed by Jensen and Sundström (*3*). Generally, the agreement is good, diferences being within a factor 2, with the exception of component 105 in A50. The sum of all contributions that we were able to determine is not too different from 100%, particularly if the contribution of the few strong and unidentified peaks in A30 and A40 are taken into account (their aggregate contribution was estimated to be 10% on the basis of estimated response factors, Table IV). A comparison with other detailed quantitative data is more complicated, despite the agreement for many components, because available reference components have not been specifically identified (*13*). Recently, the synthesis of the octa- and nonachlorobiphenyls and their quantitation in Aroclors was reported (*23*). Agreement for the components available to us is reasonable; quantitative data for six additional components contributing about 6% (*23*) cannot be confirmed by us because of lack of reference compounds.

Conclusions

As on other capillary columns, several PCB components remain unresolved on the present SE-54 fused silica column. The application of both electron capture and mass spectrometric techniques for the detection of components present in Clophen A30, A40, A50, and A60 and the availability of 102 individual components as pure reference compounds have revealed many previously unobserved details regarding the qualitative and quantitative composition of chromatographic peaks in these formulations. It was found that the contribution and composition of any given chromatographic peak may vary considerably within the Clophen series. Assignments were made for most major peaks and many of the smaller peaks. For some peaks, ambiguities in the assignments still remain, in particular with respect to coeluting components with equal chlorine numbers. The separation of some pairs can be improved by selection of other operational conditions such as preseparation by solid–liquid chromatography (*3, 16*) or by using a number of columns with different selectivities, either in parallel or in series (*6, 13, 18*). Until all individual components are available, we cannot be sure that for each peak or component, no other coeluting component(s) exist. The GC–MS results show that this is not likely to be a major problem for most peaks, at least not for those components having different chlorine numbers.

Registry No. 1, 2051-60-7; **2**, 2051-61-8; **3**, 2051-62-9; **4**, 13029-08-8; **5**, 16605-91-7; **7**, 33284-50-3; **8**, 34883-43-7; **9**, 34883-39-1; **10**, 33146-45-1; **11**, 2050-67-1; **12**, 2974-92-7; **14**, 34883-41-5; **15**, 2050-68-2; 18, 37680-65-2; **19**, 38444-73-4; **21**, 55702-46-0; **24**, 55702-45-9; **26**, 38444-81-4; **28**, 7012-37-5; **29**, 15862-07-4; **30**, 35693-92-6; **31**, 16606-02-3; **33**, 38444-86-9; **37**, 38444-90-5; **40**, 38444-93-8; **41**, 52663-59-9; **42**, 36559-22-5; **44**, 41464-39-5; **46**, 41464-47-5; **47**, 2437-79-8; **49**, 41464-40-8; **50**, 62796-65-0; **52**, 35693-99-3; **53**, 41464-41-9; **58**, 41464-49-7; **60**, 33025-41-1; **61**, 33284-53-6; **62**, 54230-22-7; **65**, 33284-54-7; **66**, 32598-10-0; **67**, 73575-53-8; **69**, 60233-24-1; **70**, 32598-11-1; **71**, 41464-46-4; **72**, 41464-42-0; **75**, 32598-12-2; **77**, 32598-13-3; **80**, 33284-52-5; **82**, 52663-62-4; **83**, 60145-20-2; **84**, 52663-60-2; **86**, 55312-69-1; **87**, 38380-02-8; **88**, 55215-17-3; **90**, 68194-07-0; **92**, 52663-61-3; **95**, 38379-99-6; **97**, 41464-51-1; **98**, 60233-25-2; **99**, 38380-01-7; **101**, 37680-73-2; **105**, 32598-14-4; **107**, 70424-68-9; **110**, 38380-03-9; **116**, 18259-05-7; **118**, 31508-00-6; **120**, 68194-12-7; **123**, 65510-44-3; **128**, 38380-07-3; **129**, 55215-18-4; **132**, 38380-05-1; **138**, 35065-28-2; **141**, 52712-04-6; **149**, 38380-04-0; **151**, 52663-63-5; **153**, 35065-27-1; **155**, 33979-03-2; **156**, 38380-08-4; **167**, 52663-72-6; **170**, 35065-30-6; **171**, 52663-71-5; **172**, 52663-74-8; **174**, 38411-25-5; **176**, 52663-65-7; **177**, 52663-70-4; **179**, 52663-64-6; **180**, 35065-29-3; **183**, 52663-69-1; **187**, 52663-68-0; **189**, 39635-31-9; **193**, 69782-91-8; **194**, 35694-08-7; **196**, 42740-50-1; **197**, 33091-17-7; **200**, 40186-71-8; **201**, 52663-75-9; **202**, 2136-99-4; **206**, 40186-72-9; **207**, 52663-79-3; **209**, 2051-24-3; Clophen A30, 55600-34-5; Clophen A40, 52306-32-8; Clophen A50, 8068-44-8; Clophen A60, 11096-99-4.

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Laser Microprobe Mass Analysis (LAMMA) as a Tool for Particle Characterization: A Study of Coal Fly Ash

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■ Laser microprobe mass analysis (LAMMA) is used for the characterization of a fly ash derived from a conventional coal-fired electrical generating plant. The mass spectra provide data on the chemical composition including speciation data on the matrix and minor constituents and organic constituents present at the surface. It appears that LAMMA constitutes a fast and probably cost-effective tool for qualitative screening and for establishment of some physical and chemical characteristics of fly ash. However, at present the quality of the information is insufficiently high to warrant its use as a screening tool for particle characterization.

Introduction

Assessment of the potential environmental and toxicological effects of particulate material emitted to the atmosphere, together with design of emission-control strategies, required detailed physical and chemical characterization of the particles. A large number of such studies dealing with a variety of particle types has been reported in the literature (*1–8*).

The information that is most frequently required includes particle morphology, particle size distributions of number, mass for elemental and organic species, identity of inorganic compounds and minerals, and surface-enrichment and solubility characteristics. Determination of such a body of information is time consuming and costly and requires deployment of instrumentation and methodology that is not usually present in a single laboratory.

In fact, full and detailed physical and chemical characterization of particulate matter is not really required in most cases, and a more qualitative investigation, such as oultined in the level I Source Assessment Protocol developed by the United States Environmental Protection Agency (*9*), is often sufficient. Consequently, it is desirable to develop a methodology that is capable of providing a sufficient amount of information in a short time with minimal sample handling, preferably utilizing a single instrument.

To this end we have investigated the utility of laser microprobe mass analysis (LAMMA) for studying environmental particles. The LAMMA technique, which is described in detail elsewhere (*10–12*), utilizes a focused laser beam to vaporize and partially ionize the sample material. The ions produced are then extracted into a time-of-flight mass spectrometer for mass analysis in either positive or negative ion modes. Sample observation is achieved with a high-resolution optical microscope, so in principle LAMMA is capable of providing information about the morphology, size distribution, chemical composition, and possibly even the surface composition of individual particles. Furthermore, the time required for a single analysis is short, and sample preparation is relatively simple. The use of LAMMA in aerosol research has been demonstrated previously (*5*, *13–15*).

In order to establish the degree to which LAMMA is useful for particle characterization, the technique has been applied to a sample of fly ash derived from a conventional coal-fired electrical generating plant. This fly ash has previously been extensively characterized, and a large body of information is available against which to judge that provided by LAMMA. It is the objective of this paper to report the results of these studies and to assess the extent to which either existing or new physical and chemical data are provided.

Experimental Section

Materials. Coal fly ash was collected in bulk from the electrostatic precipitation of the Corrette plant in Billings, MT.

Instrumentation. For a full description of the LAMMA-500 instrument (Leybold-Heraeus, GmbH, Köln, FRG) we refer to other publications (*11*, *12*). A Q-switched Nd:YAG laser is used to generate intense light pulses with a duration of 15 ns. The radiation is quadrupled in frequency to 265 nm. A He–Ne laser continuously emitting in the red is aligned collinearly to the invisible UV light of the Nd:YAG laser. The He–Ne laser beam eases the alignment of the UV laser beam with respect to the axis of the microscope and serves for aiming at a selected area on the specimen. For mass spectrometric analysis the sample needs to be placed into the vacuum. It is transferred onto a coated electron-microscopic grid that fits into a *x*–*y* movable sample stage. A standard quartz cover slide serves as vacuum seal and optical window. The ions that are formed by laser irradiation of the selected sample area are accelerated into a time-of-flight mass spectrometer, which can be used for the analysis of positive or negative ions. An open secondary electron multiplier with 17 CuBe dynodes is used for ion detection and has a gain of 10^6 or higher. The analog signal of the detector is digitized with 8-bit resolution and stored in a transient recorder of 2048 channels. The recorded spectrum is displayed on a CRT screen. It can be plotted by a strip-chart recorder or transferred to a data system.

The most attractive features of the LAMMA instrument for particle analysis are spatial resolution down to 1 μm, high collection efficiencies (10–50%), mass resolution of about 700–800, and ease of operation, simplicity, and speed.

The laser energy on the sample can be varied with a set of attenuating filters and is monitored by an energy meter. It is either adjusted to provide complete vaporization of a micrometer-size sample of the fiber or else adjusted to the lowest energy that provides a mass spectrum. Adsorbed impurities onto the fiber surface can be detected in this laser desorption (LD) operation mode (*16*).

Procedures. Fly ash particles were mounted on a transmission electron microscopy grid coated with a thin Formvar film (thickness ~0.1 μm).

This was achieved simply by touching the coated grid to the bulk fly ash. The grid was then mounted directly in the sample chamber of the instrument.

Microscopic examination of samples to identify morphological characteristics was made by using both 400× and 1250× magnification. For particle analyses however,

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observation at 400× was used. The laser power, which varies by ±15% between pulses, was monitored for each pulse, and the power delivered to the sample was varied by means of transmission filters. For elemental analyses, the laser power was maintained at a high level to completely vaporize a particle and thereby maximize sensitivity. For analyses designed to identify molecular species, however, low laser powers were employed so as to promote desorption and minimize molecular fragmentation.

Because of poor spectral reproducibility, which was also noted in other work (*10*), spectral information was obtained for a number of visually identical particles of similar size which were averaged.

The protocol developed for investigation of a bulk particulate sample and employed in this study consists of several steps: (1) Between 100 and 1000 particles are examined microscopically and classified in terms of morphology and size by using conventional optical microscopic procedures (*3*). If appropriate, photomicrographs can be taken to provide a visual record. (2) Individual particles, representative of chosen size and morphological classifications, are analyzed under high laser power conditions in both positive and negative ion modes, to obtain data on elemental composition and some inorganic species. (3) The above procedure is repeated under low laser power conditions to obtain data on organic compounds that may be present. (4) Specifically designed studies are conducted to confirm previous findings. These could include analyses of authentic compounds for spectra calibration and, possibly, analyses of selected areas of apparently heterogeneous large particles. It has been reported that surface analytical information may be obtainable by deploying the laser beam at grazing incidence to a particle (*17*). Solubility behavior may be obtained by analyzing particles before and after leaching with water or a suitable organic solvent. Results obtained till now are not encouraging (see Results and Discussion).

One of the calibration experiments performed as part of this study involved analyses of particles that had been doped with polycyclic aromatic compounds. Two doping procedures were employed. In the first activated carbon (Norit, Jackson, FL) and Al_2O_3 were placed in individual chloroform solutions containing several different concentrations of coronene and 9,10-diphenylanthracene, respectively, in the range 100–1000 μg/mL. The solvent was removed by evaporation under a stream of nitrogen gas. The second procedure involved passing phenanthrene vapor through an expanded bed of fly ash. This method, which has been previously reported (*18*, *19*), achieved a level of 225 μg/g on the bulk fly ash.

Results and Discussion

Microscopic Examination. Use of the optical microscopic capability of the LAMMA instrument established conclusively that, with the aid of a calibrated graticle, the particle number distribution can be determined almost as effectively as with a free-standing microscope. It should be recorded, however, that the optical qualities of the LAMMA microscope have been degraded somewhat due to the need to remove the plane of focus beyond its optimum position in order to accommodate the sample in the vacuum system of the instrument. Some difficulty was encountered initially in achieving even distribution of particles on the Formvar mounting film and avoiding clumping; however, with practice samples suitable for counting can be prepared. Examination of several samples indicated that the sample mounting procedure was uniformly selective for all particle types and sizes present in the well-mixed bulk fly ash.

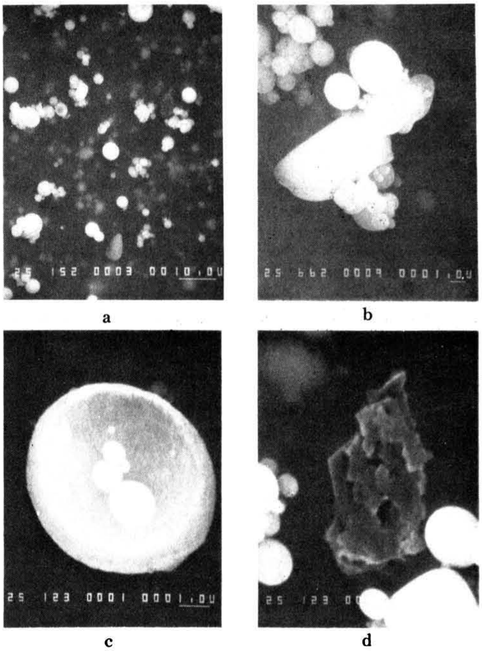

Figure 1. Secondary electron micrographs of the three morphological classes in the Corrette fly ash: (a) overall picture; (b) clear glassy particles, type A; (c) solid spheres, type B; (d) carbonaceous material, type C.

All of the morphological forms that have previously been reported for coal fly ash (*20*, *21*) could be observed and identified microscopically. For the purpose of the present investigation, however, only three classifications were employed. These consisted of the following: (1) Clear or white glassy particles whose morphology varies from a regular sphere to irregular rounded lumps. These particles, which previous work (*22*) has shown to have little or no ferromagnetic character, are classified as type A. (2) Solid black spheres that could be separated from the bulk fly ash magnetically (*22*, *23*). These are classified as type B. (3) Irregular black particles of apparently carbonaceous material, which were classified as type C.

Examples of each of these particle types are depicted in the electron microphotographs in Figure 1.

Elemental Composition. Analyses of individual coal fly ash particles under high laser irradiance conditions (~5 times the ionization threshold for the sample) enabled qualitative identification of more than 20 elements in the types A and B particles. Of these only six elements were systematically detected in all particles investigated (Figure 2). In general, the electronegative elements C, S, and Cl and clusters of Si, Fe, and Al were observed in the negative spectra. Very few elemental constituents except Na and K were detectable in the type C particles. In addition, H, Li, Be, B, and O atomic ions can be detected in spectra that include the mass range 0–23 amu.

These analyses showed that the heterogeneity between individual particles was significantly greater than the imprecision of the LAMMA method. Also, not all the elements listed for a particle type were observed in each particle. Such an observation, which supports the mechanisms of coal fly ash formation recently published by Natusch et al. (*21*), is a useful contribution of the LAMMA technique since electron microprobe analyses do not detect enough trace elements in coal fly ash to illustrate high

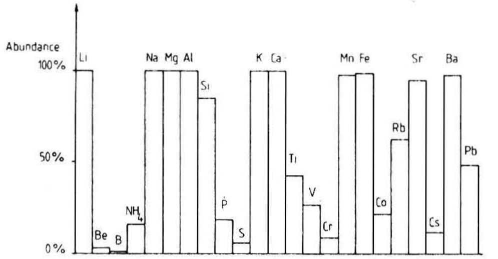

Figure 2. Frequency of detection of elemental constituents in type A particles.

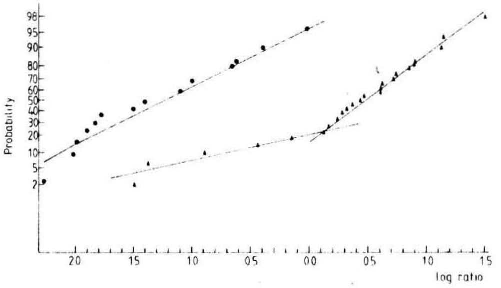

Figure 3. Cumulative probability as a function of intensity ratio of $^{54}Fe/^{44}Ca$ for type A particles (●) and type B particles (▲).

degree of heterogeneity that exists. Unfortunately, LAMMA does not enable definition of concentration dependences on particle size unless a sufficiently large number of particles are analyzed to account for both interparticle heterogeneity and the poor precision of the technique. It is considered that this is beyond the type of preliminary survey analysis being proposed.

Consideration of the mass spectra obtained from each morphological classification indicated that the carbonaceous type C particles are quite uniform in composition and consist primarily of elemental carbon. However, in a statistical evaluation of the $^{54}Fe/^{44}Ca$ peak height ratios for particle types A and B a discontinuity in the frequency distribution of the measured ratio for type B particles is observed at a value of 1.4, dividing the sampled population into two distinct subclasses. Thus, 76% of the type B particles analyzed have a composition in which the $^{54}Fe/^{44}Ca$ intensity ratio is >1.4% and 24% have this ratio <1.4 (Figure 3). On the 95% confidence level it is possible to make a distinction between type A particles and the iron-rich type B particles or between both classes of type B particles by using the $^{54}Fe/^{44}Ca$ ratio. No significant difference is detectable between type A and the low-iron-content type B particles.

These results illustrate the fact that, despite its poor precision, the LAMMA technique can be used to indicate quite small compositional differences in an ensemble of particles. The reasons for the distinct compositional distinctions among type B particles are not clear. One possible explanation, which receives some support from X-ray powder diffraction studies of coal fly ash (*25*), is that the 24% subfraction of the type B particles contains nonmagnetic γ-Fe_2O_3, whereas the 76% subfraction contains ferromagnetic Fe_3O_4. This would account for the similarity in $^{54}Fe/^{44}Ca$ ratios between type A and the 24% subfraction of the type B particles since type A particles have been shown conclusively to contain a nonmagnetic form of Fe_2O_3 (*2, 25*).

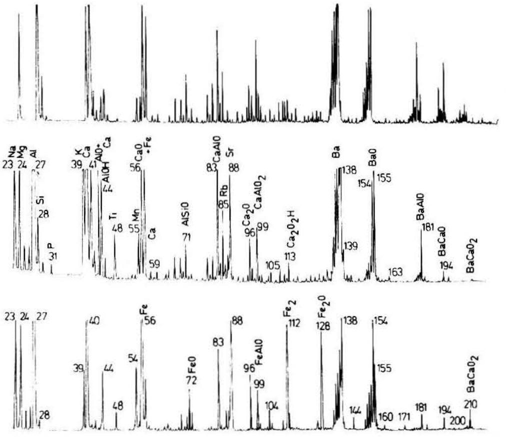

Figure 4. Positive LAMMA mass spectrum of NBS-309 glass research material (top), type A particles (middle), and type B particles (bottom).

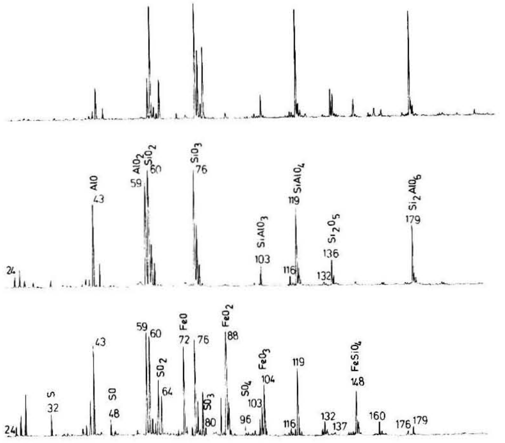

Figure 5. Negative mass spectrum of NBS-309 glass (top), type A particles (middle), and type B particles (bottom).

Quantitative analysis of the elemental composition of fly ash is not possible with an accuracy better than a factor of 5 (*24*), because of the heterogeneity of the chemical composition of individual particles but also because of inherent limitations of the method (spectral interferences, inaccuracies in the measurement).

Matrix Composition. The negative ion mass spectra of particle types A and B provide convincing evidence for the presence of an aluminosilicate matrix. Thus, extensive studies for a number of pure mineral forms having the formula $Al_xSi_yO_a$ have shown that quite typical LAMMA fingerprint spectra result. A comparison of spectra of NBS-309 glass with one derived from a type A or B coal fly ash particle is presented in Figures 4 and 5 in the positive and negative mode, respectively. The K-309 glass standard research material contains 7.9% Al, 18.7% Si, 10.7% Ca, 10.5% Fe, and 13.4% Ba. The low laser irradiance used provides cluster peaks in the spectra of both materials. However, the spectrum of the type A particles corresponds closely with that obtained for the NBS glass. The spectra of type B particles show intense iron- and oxygen-containing fragments. These iron oxide species are also present in the LAMMA spectra of hornblende, but with a lower intensity. The presence of iron oxides in coal

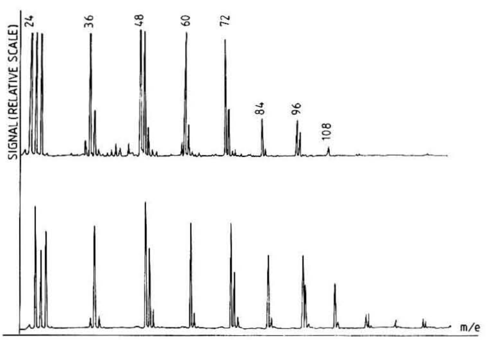

Figure 6. Negative LAMMA mass spectrum of carbonaceous (type C) particle (upper curve) and activated carbon (lower curve).

fly ash is consistent with results of X-ray diffraction studies that have identified Fe_2O_3 and Fe_3O_4 (*23*). As indicated above, LAMMA spectra of the type C particles show them to consist of a carbonaceous matrix. Comparison of these spectra with those obtained from studies of a variety of carbonaceous materials indicates that the type C particles resemble activated carbon (a partially oxidized carbon) rather than the fully dehydrogenated graphite (Figure 6) in whose negative spectrum the $^{12}C_xH$ are consistently of lower intensity. Positive mass spectra give further support to this. The high laser energy ($E > 1$–2 μJ) spectra contain peaks corresponding to $C_nH_m^+$ ions, which indicates carbonaceous material. These peaks are generally less intense than the series of peaks at *m/e* 53, 65, 77, 89, 101, 113, and 125, which can be assigned to C_nOH^+ cluster ions in the spectrum of activated carbon. This is consistent with suggestions (*20*) that the type C fraction of coal fly ash represents incompletely burned partly oxidized coal. This finding is in exact accord with that of solid nuclear magnetic resonance spectroscopy of isolated type C particles utilizing magic angle spinning (*22, 26*). Furthermore, it is a finding that would not normally be forthcoming from the types of analyses normally applied to the characterization of individual airborne particles.

Minor and Trace Level Speciation. Identification of inorganic compounds present in minor or trace amounts is not conclusive, but useful indicative information is provided by LAMMA. Thus, both the positive and negative ion spectra of type A and B particles contained a series of peaks assignable to Fe_xO_y ions and observed in the spectra of authentic Fe_2O_3 and Fe_3O_4. Unfortunately, it is not possible to distinguish between these two reference spectra (*10*), so more detailed assignment of the coal fly ash spectra is not possible.

Indications were also obtained for the presence of SO_x species in the negative ion spectra of all three particle types. The distribution of these species was highly inhomogeneous among particles of each type, and no correlations between particle type and the detection of SO_x species could be made. Extensive studies of pure compounds containing S^{2-}, S^0, $S_2O_3^{2-}$, and SO_4^{2-} have shown that, in the presence of other oxygen donor compounds, essentially indistinguishable spectra result. It is not possible, therefore, to identify the sulfur species present, but the results are supportive of previous identification of sulfate species in coal fly ash (*2, 26*) by other techniques at concentrations on the order of 0.1–2.2%.

The presence of oxides of phosphorus follows from peaks at *m/e* 63 and 79 in the negative spectra. These peaks are the sole feature of K_3PO_4. Phosphorus may be present in coal fly ash with a concentration of 0.1–1.0% as P_2O_5.

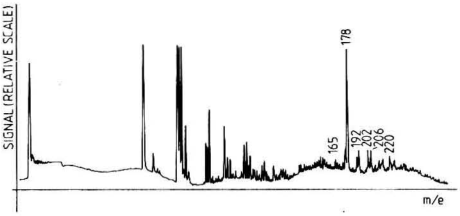

Figure 7. Positive LAMMA spectrum of carbonaceous particulate fraction at laser desorption conditions.

Table I. Probability of Detection of Coronene at the Surface of the Particles as a Function of Laser Pulse Energy

laser energy, μJ	probability of observation, %	laser energy, μJ	probability of observation, %
0.3–0.4	72	0.36–0.52	50
0.15–0.20	80	1.3–1.7	25

Table II. Polycyclic Organic Compounds Mass Spectra Obtained at Low Laser Energy

ion, *m/z*	identification	ion, *m/z*	identification
178	phenanthrene, anthracene	216	benzofluorene, methylpyrene
192	methylphenanthrene, methylanthracene	220	trimethylphenanthrene, trimethylanthracene
202	fluoranthene, pyrene	228	chrysene, benzo[*a*]anthracene
206	dimethylphenanthrene, dimethylanthracene	236	?
210	?		

Organic Constituents. Analyses of the carbonaceous type C fly ash under low laser irradiance resulted in the appearance of a number of negative ions having *m/e* >165. An example is shown in Figure 7. These ions are apparently due to polycyclic organic matter which is strongly adsorbed onto the carbonaceous (but not the mineral types A and B) fraction of the fly ash. The evidence in support of this contention is as follows: (1) Analyses for phenanthrene, 9,10-diphenylanthracene, and coronene adsorbed onto activated carbon and alumina showed that these compounds could be observed by LAMMA at low laser irradiance. The probability of detection was maximum below approximately 3 μJ. (2) The intensity and frequency of occurrence of spectra derived from adsorbed polycylic aromatic hydrocarbons (PAHs) reached a maximum at laser powers around 0.15 μJ (Table I), and the same behavior was observed for the spectral peaks >165 amu in undoped samples. In this regard it is noteworthy that only the alkali metals and carbon compounds are substantially ionized at such low laser irradiance, thereby suggesting the presence of organic rather than inorganic species at high mass (*m/e* >165). (3) Independent studies of PAH adsorption onto this coal fly ash sample have shown that most of the surface area available for adsorption is provided by the carbonaceous type C particles (*23*) and that adsorption onto type A and B particles does not occur substantially until the carbonaceous fraction approaches saturation. (4) Combined gas chromatographic–mass spectra analysis of Soxhlet extracts (in benzene) of coal fly ash have identified the presence of several of the same PAHs as tentatively assigned by LAMMA (Table II), namely, fluoranthene, pyrene, benz[*a*]anthracene, dimethylphenanthrene, and chrysene.

Several studies (*23, 26, 28*) have established that essentially no PAHs are extractable from coal fly ash that has been collected at elevated temperatures due to the fact that the adsorption process is highly temperature dependent (*19, 26, 29*), being less efficient at higher temperatures. Consequently, one would not expect PAHs to be observable by LAMMA. If this argument is accepted, then the higher molecular weight peaks observed should be assigned to $C_nH_m^-$ fragments that undoubtedly arose from adsorbed or substrate carbonaceous material. On the other hand it has recently been observed (*23*) that PAHs that have been adsorbed onto the carbonaceous type C fraction of several fly ashes (including Corrette) are only partially recoverable by conventional extraction methods. This is no doubt due to the fact that the average activation energy for PAH desorption lies in the range 9–11 kJ/mol (*26, 29*), thereby rendering it likely that some PAH adsorption onto carbonaceous fly ash does occur at elevated temperatures and that little, if any, adsorbed PAH is normally recovered by extraction.

Overall, therefore, we incline to the view that the stringent thermal conditions imposed by LAMMA do in fact enable observation of PAHs. If this view is correct, then LAMMA analyses offer a significant advantage for qualitative characterization of these compounds directly onto the microscopic particles as they are collected. A fuller account on the detection of PAHs and organic compounds will be published separately.

Surface Analysis and Solubility. Several studies were conducted in which the laser beam was direct tangentially at grazing incidence to the surface of the fly ash particles in an attempt to distinguish surface analytical features. The results provided no convincing evidence that the LAMMA-500 instrument is a useful tool for such surface analyses. This is due to the heterogeneity of the particles (even of a given type), to the poor reproducibility of the analyses, and to the inability to achieve a reproducible focus and depth of grazing.

Studies were also conducted to look for compositional changes that occurred as a result of leaching the fly ash particles with water. For this purpose gram amounts of the fly ash were leached by placing them on a Büchner filter and passing distilled water through for 8 h. Such treatment has previously been shown to remove or reduce a number of elements that are present in soluble form near the particle surface (*8*). With the exception of chlorine and sulfur species, which are quantitatively removed from all fly ash types, results for other elements were inconclusive. There was some evidence that the levels of Na, K, Ca, and Co were reduced, as was expected, but the experimental reproducibility was not great enough to confirm this result. Bulk analyses, e.g., by X-ray fluorescence does provide evidence for water leachability (*30*).

Conclusions

In conclusion it can be stated that LAMMA constitutes a fast and probably cost-effective tool for conducting qualitative screening to establish some of the physical and chemical characteristics of fly ash. This contention is supported by the fact that a surprisingly large amount of information that is corroborated by previous specific studies was obtained.

The real question, however, is whether the quality of the information obtained is sufficiently high to warrant serious consideration of the exclusive use of LAMMA as a screening tool for particle characterization. This question can be addressed at four levels: (1) For determination of particle morphology and size distribution the microscopic capability of LAMMA is considered to be almost as adequate for initial characterization as any other high-quality optical microscope. (2) For determination of particle matrix composition and, to a lesser extent, of elemental composition and minor trace-level speciation the technique is undoubtedly useful but probably marginally adequate for initial screening characterization except in the case of carbonaceous particles. (3) For determination of organic content and solubility characteristics of coal fly ash particles LAMMA provides some useful (and in the case of PAHs, possibly unique), information, which is, however, likely to be rather less than that desired for initial characterization. (4) For determination of surface chemical characteristics and of the size distributions of elements or chemical species the technique has, at present, no demonstrated value.

Overall, therefore, it is concluded that while LAMMA has considerable potential value for particle characterization, its widespread use in this mode must await further methodological developments and improvements in the technique. In these regards it is noted that direct sample collection on a transmission electron microscope grid have been reported (*14, 31*). The largest single factor requiring improvement is the poor reproducibility of LAMMA analyses of individual particles and the difficulties with obtaining quantitative analytical information.

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Influence of Algae on Photolysis Rates of Chemicals in Water

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■ Sunlight-induced algal transformations of 22 nonionic organic chemicals were studied in order to provide kinetic results and equations concerning the influence of algae on the behavior of pollutants in freshwater environments. Screening studies indicated that green and blue-green algae, at concentrations of 1–10 mg of chlorophyll *a*/L, accelerate photoreaction of certain polycylic aromatic hydrocarbons, organophosphorus compounds, and anilines in water. The rate of change in aniline concentration, [P], in the aniline–*Chlamydomonas* photoreaction can be described by the following expression: rate = $A(1 + B/[P])^{-1}$. At low substrate concentrations, the reaction rate is first order with respect to both algae and substrate concentration. Methyl parathion and parathion photoreacted 390 times more rapidly when sorbed by algae than in distilled water, and aniline and *m*-toluidine reacted over 12000 times faster, indicating that light-induced algal transformations of certain pollutants may be significant. Other results indicated that reaction rates are unaffected by heat-killing the algae.

Introduction

The role of sunlight in the transport and transformation of chemicals in natural waters is affected in various ways by suspended particles such as sediments or microorganisms. These particles may influence photolysis rates of chemicals in water bodies through attenuation of sunlight (*1–3*), through initiation of indirect photoprocesses (*4–6*), and through physical or chemical interactions that change the microenvironment or alter the speciation of a photoreactive chemical.

Several recent studies have focused on the influence of sediments (*1*, *2*) and algae (*3*) on the attenuation of solar radiation in natural waters. Other studies (*4–6*) have examined the photoreactivity of organic chemicals that are sorbed on suspended sediments.

The studies reported here concerning sunlight-induced transformation rates of nonionic organic chemicals involving algae were prompted by several considerations. First, bioaccumulation of a pollutant by algae is expected to be affected by the rate of degradation of the pollutant by the algae as well as by other factors such as the hydrophobicity of the pollutant (*7*, *8*). Moreover, because algae are the most important sunlight absorbers in many aquatic environments (*3*), the algae-mediated phototransformation of toxic chemicals may have a significant effect on concentrations in the water column. To assess the significance of this process by using deterministic computer models (*9*), rates of transformations involving algae are required. A number of studies have shown that visible light absorption by the photosynthetic apparatus of algae commonly results in the photometabolism of polar, ionic organic substrates such as carboxylic acids, carbohydrates, and amino acids (*10*). Other investigations demonstrated that nonionic organic compounds, including pesticides, photolyze more rapidly in the presence of photosynthetic microorganisms (*11*). Most of these studies, however, were conducted in culture media by using artificial light sources having spectral outputs that are dissimilar to sunlight, especially in the photochemically important ultraviolet region.

In this report experimental results are presented concerning transformation rates of a broad cross section of chemicals in the presence of living algae and sunlight. The chemicals include polycyclic aromatic hydrocarbons, organophosphorus insecticides, anilines, phenol, and various other organic chemicals with structural features commonly found in commercial synthetic chemicals. Kinetic data are analyzed to formulate a rate expression and a kinetic model for the light-induced transformations. Finally, results concerning possible mechanisms for indirect photoreactions involving algae are presented.

Experimental Section

Chemicals. Aromatic hydrocarbons were purified as described by Zepp and Schlotzhauer (*12*). γ-Methoxy-*m*-(trifluoromethyl)butyrophenone (MTB) was synthesized as described elsewhere (*5*). *cis*-1,3-Pentadiene was obtained commercially and purified by distillation. *p*-Nitroacetophenone and *p*-nitroanisole (PNA) were also obtained commercially and were purified by recrystallization from 95% ethanol. Commercially obtained refer-

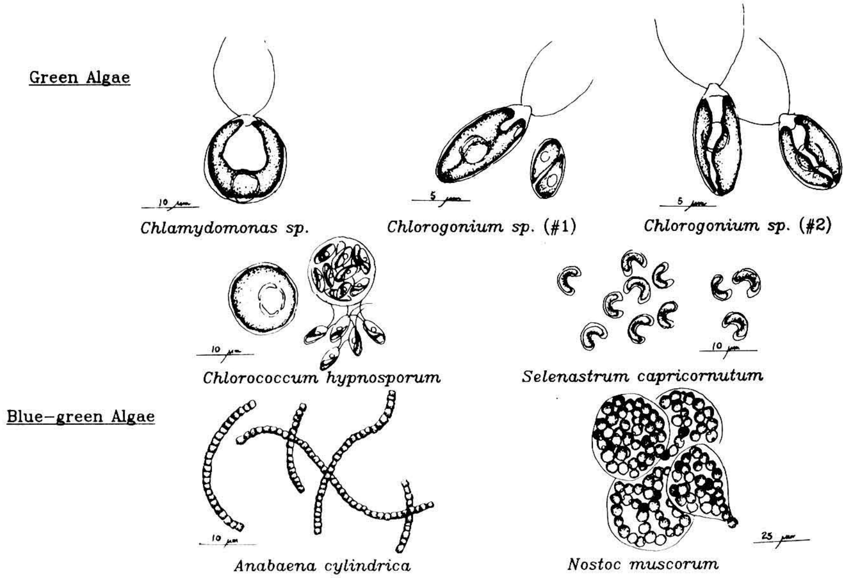


Figure 1. Algae used in the study.

ence standards of aniline, *m*-toluidine, *cis*-1,2-dichloroethylene, and nitrobenzene were used as received. The remaining chemicals were obtained from the U.S. Environmental Protection Agency, Research Triangle Park, NC, and were used as received.

Algae. Pure cultures of six algae commonly found in U.S. waters were obtained from the Starr collection at the University of Texas, Austin, TX, and from the Department of Botany, University of Georgia, Athens, GA (Figure 1). The identities of the algae were determined by microscopic examination. The algae were grown at 20 °C under Vitalites (TM) by using an 8:16 light–dark cycle. The growth medium (*13*) consisted of 0.005 M KNO_3, 0.0005 M K_2HPO_4, 0.0005 M KH_2PO_4, 0.002 M $MgSO_4$, 0.000 25 M $Ca(NO_3)_2$, 130 μM EDTA, 76 μM $ZnSO_4$, 180 μM H_3BO_3, 26 μM $MnCl_2$, 18 μM $FeSO_4$, 6.7 μM $CoCl_2$, 6.3 μM, $CuSO_4$, and 0.89 μM ammonium paramolybdate; the medium was adjusted to pH 5.5 by using hydrochloric acid. Algae used in most of the experiments were obtained from axenic cultures that were started every 10–14 days to keep the cells growing in log phase. For some experiments with aniline and methyl parathion, the algae were heat-killed by warming them to 50 °C for 30 min. To remove collodial ferric hydroxide particles that may have adsorbed on the cells, a modified version of the procedure described by Anderson and Morel (*14*) was used in some of the experiments with methyl parathion or aniline. This procedure involved washing the cells by gentle agitation for 30 min with 0.01 M aqueous ascorbic acid adjusted to pH 3.

General Procedures. With employment of centrifugation procedures that are discussed elsewhere (*5*), the majority of the chemicals that were studied were found to be sorbed less than 5% by the algae under the reaction conditions used. Analysis for these chemicals was accomplished by first centrifuging the algae suspensions (2500 rpm for 20 min) and then analyzing the supernatant with a Micromeritics high-pressure liquid chromatograph (HPLC) equipped with UV and fluorescence detectors. Direct aqueous injections were made onto an ODS-2 column, employing an acetonitrile–water mixture as mobile phase.

An alternative procedure was used in the case of the chemicals that were more strongly sorbed to the algae. These chemicals included pyrene, phenanthrene, fluoranthene, aldrin, Ronnel, and chlorpyrifos. This procedure involved exhaustive extraction of the algae suspension by an organic solvent after addition of 35% acetonitrile, by volume. The organic layer was analyzed by HPLC using a silica gel column with isooctane–isopropyl alcohol as mobile phase or by gas–liquid chromatography (GLC) employing a Tracor MT-222 gas chromatograph equipped with a linearized ^{63}Ni electron capture detector. The GLC columns were packed with 3% SE-30 or with 1.5% OV-17 and 1.95% OV-210 on 80/100 Gas Chrom Q. With methyl parathion and aniline, two compounds that were sorbed less than 5% on the algae, equivalent results were obtained when this extraction procedure was compared to the usual procedure involving direct analysis of the supernatant.

The volatile chemicals pentadiene and dichloroethylene were studied in air-saturated algae suspensions contained in gas-tight reaction cells that were filled to eliminate head space. After light exposure, a portion of the reaction-cell contents were removed, and the head space was analyzed by GLC employing a 6-m long by 2-mm i.d. column packed with 20% 1,2,3-tris(2-cyanoethoxy)propane on Gas Chrom RA (*15*).

Chlorophyll *a* concentrations were determined as described elsewhere (*16*), and the procedure of Houle et al. (*17*) was used to analyze for formaldehyde.

Screening Procedures. After washing the algae three times with distilled water, the cells were suspended in an aqueous solution having a substrate concentration that was lower than 2.0×10^{-5} M and lower than the solubility limit of the substrate. The resulting algae suspensions along with solutions of the substrate in distilled water were exposed to sunlight in test tubes that were mounted on a rotating, tilted turntable (a Cole-Palmer Roto-Torque heavy duty rotator) to provide the mixing necessary to maintain uniform suspensions. Solutions of PNA (1.0×10^{-5} M) were also exposed to sunlight on the turntable along with the algae suspensions and the distilled water solutions. After exposure for time *t* (usually 3–4 h), rate

Table I. Effects of Several Algae (1–10 mg/L Chlorophyll *a*) on Sunlight-Induced Transformation Rate Constants, $(k_p)_p/(k_p)_{act}$, of Selected Organic Chemicals[a]

compound	distilled water	*Chlamydomonas* sp.	*Chlorogonium* sp. (1)	*Chlorogonium* sp. (2)	*Chlorococcum hypnosporum*	*Selenastrum capricornutum*	*Anabaena cylindrica*
pyrene	5.4	9.5 (1.8)	6.3 (1.2)		12 (2.2)	6.0 (1.1)	4.6 (0.84)
phenanthrene	0.67	0.38 (0.57)	0.21 (0.31)	0.16 (0.24)	0.52 (0.77)	1.6 (2.4)	0.13 (0.19)
fluoranthene	0.14	0.92 (6.6)	1.5 (10)	1.0 (7.3)	1.1 (7.9)		1.6 (11)
naphthalene	0.055	0.15 (2.7)	0.11 (2.0)		0.12 (2.2)	0.12 (2.2)	0.07 (1.3)
aniline	0.04	2.0 (50)	0.41 (10)	0.28 (7)	0.31 (8)	0.15 (4)	0.86 (20)
phenol	<0.02	0.11	0.04			<0.04	0.04
aldrin		1.8	1.0	0.855	0.41	0.30	2.1
cis-1,2-dichloroethylene		<0.05	<0.05				
cis-1,3-pentadiene		<0.05	<0.05				
methyl parathion	0.060	0.15 (2)	0.58 (10)		1.04 (17)	0.56 (10)	0.15 (2)
p-nitroacetophenone		<0.05	<0.05				
p-nitroanisole	1.0	1.2 (1.2)	1.3 (1.3)				1.1 (1.1)
nitrobenzene	<0.1	<0.1	<0.1				
MTB	8.8	7.9 (0.90)	7.0 (0.79)			5.4 (0.62)	2.2 (0.25)

[a] Ratio of algae to distilled water results in parentheses. [b] Mean of three determinations is reported; standard deviation is typically < + 20% of mean value.

constants, $(k_p)_p$, were computed from the initial, $[P]_0$, and final concentrations, [P], of substrate in the algae suspensions and in distilled water, assuming that the reactions were described by the following first-order rate expression:

$$\ln [P]_0/[P] = (k_p)_p t \qquad (1)$$

First-order rate constants, $(k_p)_{act}$, were similarily computed for the PNA photoreactions.

Dark controls showed no transformations during the period of time used for the sunlight exposures.

Kinetic Studies Involving Anilines and Parathions. A series of aniline solutions ranging in concentration from 6.0×10^{-6} to 8.0×10^{-4} M were prepared. Each of these solutions was mixed with an equal portion of a suspension of *Chlamydomonas* sp. that had been washed with distilled water. The resulting suspensions were added to reaction cells that were irradiated in parallel in a photochemical merry-go-round (*18*) with light from a mercury lamp that was filtered through Corning 0-52 glass filters to block wavelengths less than 340 nm. Periodically, the reaction cells were removed and centrifuged, and the supernatants were analyzed for aniline by HPLC. Studies using the same aniline–*Chlamydomonas* suspensions were also conducted in sunlight for comparison, as described in the Screening Procedures section. Additional experiments were carried out by employing a constant aniline or methyl parathion concentration but with a varying concentration of algae. Other experiments involving algae treated by washing with ascorbic acid or by heat-killing were performed by simultaneously exposing to sunlight equivalent concentrations of the treated and the untreated algae suspended in aqueous solutions of aniline or methyl parathion.

Results and Discussion

Screening Studies. To determine the susceptibility of a variety of chemicals to algal transformation, screening studies were conducted by exposing aqueous suspensions of living algae containing chemicals at trace concentrations (less than 20 μM) to sunlight. Most of the chemicals selected for these screening studies had been shown to be reactive in the presence of algae (*11*) or were known to be susceptible to photosensitized reactions in natural waters (*16*). Preliminary studies showed that the components of commonly used culture media were effective photosensitizers, so the screening studies were conducted with washed algae suspended in distilled water or phosphate buffers. The algae did not metabolize the chemicals in the dark during the period of light exposure, which was usually less than 4 h, indicating that rate constants for dark metabolism of the substrates were no larger than about 0.03 h^{-1}.

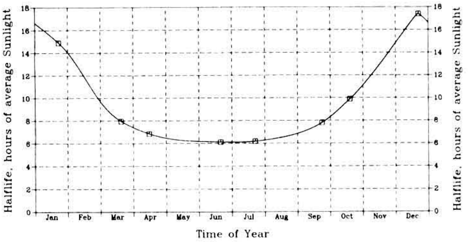


Figure 2. Half-lives computed for the direct photoreaction of *p*-nitroanisole in water exposed to sunlight at latitude 40° N (*19*, *20*).

Outdoor actinometers developed by Dulin and Mill (*19*) consisting of PNA in water were exposed to sunlight along with the algal suspensions. The rate constants for the algae-mediated photoreactions were ratioed to the first-order constants for the actinometer to correct for the variations in sunlight intensity (Table I). Whenever possible, rate constants were also obtained for competing photoreactions involving direct absorption of light. Rate constants for these direct photoreactions, also shown in Table I, are assumed to equal rate constants for photolysis of the chemicals in air-saturated, distilled water (*20*). Approximate half-lives for the algae-mediated and direct photoreactions can be computed by dividing the PNA half-lives shown in Figure 2 by the ratios in Table I. A representative value of $(k_p)_{act}$ for near the surface of a water body during summer in the U.S. is 0.11 h^{-1}.

Results, as shown in Table I, indicated that (1) most of the aromatic hydrocarbons examined reacted faster with algae present than in distilled water, (2) simple olefins were unreactive—isomerization and other reactions did not occur, (3) nitroaromatic compounds were not susceptible to algal phototransformation, with the exception of the organophosphorus insecticide methyl parathion, (4) the chlorinated cyclodiene insecticide aldrin was readily transformed by all the algae included in the study, (5) aniline was found to be the most reactive chemical with algae present, although its reactivity varied considerably from one alga to another, but phenol, another electron-rich benzene derivative, was at least an order of magnitude less reactive than aniline, (6) the direct photoreaction of MTB, a UV-absorbing compound that we previously used to quantitate light attenuation by sediments (*1*), was retarded

Table II. Kinetic Parameters for Transformation of Selected Organophosphorus Compounds in Suspensions of *Chlorogonium* sp. Exposed to Sunlight

compound	$(k_p)_p/(k_p)_{act}$[a]	chl *a* concn mg/L	ratio of algae to distilled H_2O	K_{ow}[b]
methyl parathion	0.58	6.8	10	2100
	0.53	6.8	8.8	
	0.39	6.3	6.5	
	0.16	1.8	2.7	
	0.10	0.68	1.7	
	0.06	0.0068	1.0	
	0.06[c]	0[c]		
parathion	1.6	6.8	27	6500
	0.06	0		
fenitrothion	1.38	1.7	1.0	2400
	1.33	0		
Ronnel	0.66	2.9	22	76000
	0.03	0		
chlorpyrifos	<0.1	2.2	<2	130000
	0.04	0		
diazinon	<0.1	2.4		
	<0.1	0		
malathion	0.5	7.8	>25	
	<0.02	0		
MTB	7.4	8.4	0.8[d]	
	9.2	0		

[a] Mean of three determinations is reported; standard deviation is typically ±15% of mean value. [b] Octanol–water partition coefficients (*23*): the methyl parathion value was determined by Lu and Metcalf (*27*). [c] Same value observed in distilled water and supernatant of centrifuged algal suspension. [d] Assumed to involve light attenuation only.

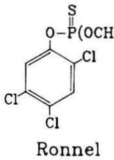
Table III. Influence of *Chlamydomonas* sp. on Rate Constants for Sunlight-Induced Reactions of Anilines (8.0×10^{-6} M)

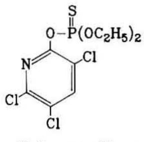
substrate	medium	condition of algae	algae concn, mg/L Chl *a*	$(k_p)_p/(k_p)_{act}$[a]	K_{ow}[b]
aniline	algae suspension	growing in log phase	6.6	5.0	9.5
			0.65	0.55	
			0.06	0.089	
	supernatant from centrifuged, living algae suspension	not applicable	0	0.1	
	supernatant from centrifuged, heat-killed algae suspension	not applicable	0	1.2	
	distilled water	not applicable	0	0.04	
m-toluidine	algae suspension	growing in log phase	6.6	11	25
	distilled water	not applicable	0	<0.1	
p-chloraniline	algae suspension	growing in log phase	14	14	
	distilled water	not applicable	0	16	

[a] Mean of three determinations is reported; standard deviation is typically ±15% of mean value. [b] Octanol–water partition coefficients from ref 21.

only slightly with the algae present, indicating that light attenuation did not have a major effect on the rates of the other reactions that were considered in Tables I and II.

Prompted by the methyl parathion results in Table I, additional organophosphorus chemicals were studied in the presence of *Chlorogonium* sp., a green alga (Table II). Several of the compounds exhibited enhanced reaction rates in the presence of the algae, although the aza aromatics were notably unreactive. For example, Ronnel and Chlorpyrifos have similar structures with the exception of a nitrogen atom in the aromatic ring of the latter, but chlorpyrifos was much less reactive.


Ronnel


Chlorpyrifos

The combined results in Tables I and II indicate that the algae considered here do enhance the photolysis rates of organic chemicals, but in a very selective manner. These results prompted additional experiments that were designed to provide a better understanding of the algal-induced photoreactions.

Kinetic Model. The reactions of anilines and parathions were studied in some detail to obtain the data necessary to develop a kinetic model. The kinetic data for the *Chlamydomonas*-induced reaction of aniline could be described by a hyperbolic relation. (*A* and *B* are constants in the equation on Figure 3). At the low concentrations used in the screening studies reported in Tables I and II, the rate becomes approximately proportional to substrate concentration, and the kinetic data are described by a first-order rate expression. Other studies indicated that the rate constants for the algal-induced photoreactions of methyl parathion (Table II) and aniline (Table III) in sunlight are proportional to the algae concentration. The dependence of the rate constants on algal concentration could be described by eq 2, where k_d is the first-order rate

$$(k_p)_p = k_d + k_{alg}C_a \tag{2}$$

constant for direct photolysis, k_{alg} is the second-order rate constant for the algal-induced photoreaction, and C_a is the algae concentration (mg of chlorophyll *a*/L). Applying a

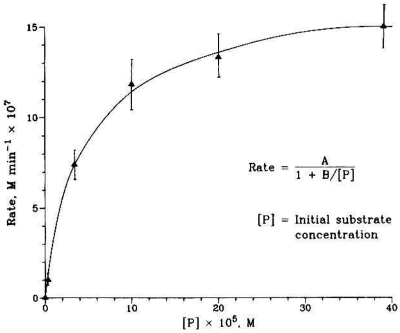


Figure 3. Dependence of initial rate for *Chlamydomonas*-induced photoreaction of aniline on substrate concentration; error bars denote the range of two replicate experiments.

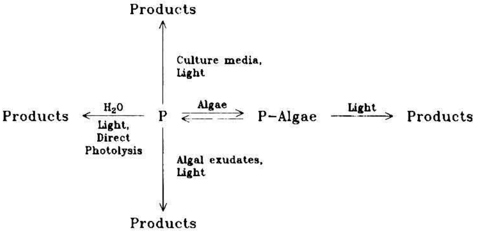


Figure 4. Kinetic model for light-induced transformation of substrate involving algae; P and P-algae represent substrate dissolved in bulk water and sorbed on the algae, respectively.

linear least-squares fit to the kinetic data, we compute that values of k_{alg}, ratioed to the actinometer rate constants, are 0.068 ± 0.007 L/(mg of chlorophyll *a*) for the methyl parathion–*Chlorogonium* photoreaction and 0.75 ± 0.002 L/(mg of chlorophyll *a*) for the aniline–*Chlamydomonas* reaction.

Although both aniline and methyl parathion were found to be over 95% dissolved in the bulk water under the conditions employed for these studies, several experiments indicated that the observed reactions mainly involve substrate sorbed on the algae. First, the hyperbolic rate expression found for the aniline reaction (Figure 3) is consistent with a mechanism involving photoreaction of a reversibly sorbed substrate. Second, removal of the suspended algae by centrifugation greatly reduced the photolysis rate constants (Tables II and III). These experiments, however, did not exclude the possibility that the reactions involve transient, reactive oxidizing species that were released by the algae into the bulk water upon irradiation. Finally, the ratio of the rate constants for algal-induced photoreaction of parathion to methyl parathion, 2.8, approximately equalled the ratio of their octanol–water partition coefficients, 3.1 (Table II). In comparison, direct photolysis rates of these chemicals were the same (Table II). Likewise, the ratio of rate constants for *m*-toluidine and aniline, 2.2, was close to the ratio of their K_{ow}'s, 2.6 (Table III). Recent studies by Geyer et al. (*22*) have indicated that sorption of nonionic, organic chemicals by algae is inversely correlated to their water solubilities. Because it is well established that water solubility is inversely correlated with K_{ow} (*23*), it follows that the results described above are also consistent with a kinetic model that includes sorption of the substrate on the algae prior to photoreaction.

Although the removal of the *Chlamydomonas* by centrifugation greatly decreased the photolysis rate of aniline, photolysis of the aniline in sunlight was still more rapid in the supernatant than in distilled water (Table III). When the *Chlamydomonas* cells were heat-killed, they released substances into the bulk water that caused rapid photolysis of the aniline in sunlight (Table III). These results are consistent with other recent studies by Momzikoff and co-workers (*24*) and by Matsumura and Esaac (*25*), who have shown that substances released by algae can photosensitize a variety of reactions in water.

A kinetic model that accounts for the results discussed above is shown in Figure 4. The algae–substrate reaction is proposed to involve reversible sorption of the substrate by the algae, where photosensitizing substances are present. As the substrate concentration is increased, the reactive sites on and/or in the algae become saturated, and the rate becomes independent of substrate concentration. The model is consistent with the general finding that the algae have the least effect on photolysis rates of chemicals that rapidly undergo direct photolysis, a competing process. For example, the photolysis rate constants of fenitrothion and *p*-chloraniline in sunlight are almost unaffected by the presence of algae (Tables II and III). Finally, the reaction scheme takes into account the findings that algal exudates or culture media photosensitize reactions. The effects of culture media may involve, in part, free-radical reactions that are initiated by photolysis of media constituents. For example, Skurlatov et al. (*26*) have found that the ferric–EDTA complex, a species commonly added to algal culture media (*13*), rapidly photosensitizes the reaction of methyl parathion in sunlight.

The kinetic model may be used in conjunction with the data in Tables II and III to estimate the photoreactivity of various substrates when sorbed by the algae. Assuming that the concentration ratio of sorbed to dissolved substrate is constant throughout the reaction, the rate constant for photoreaction of the sorbed substrate equals $(k_p)_p$ divided by the fraction of total substrate that is sorbed. For methyl parathion and parathion, the fractions sorbed at a *Chlorogonium* concentration of 6.8 mg of chlorophyll *a*/L were 0.023 and 0.071, respectively. Employing the kinetic data for this concentration (Table II) and assuming a value of 0.11 h^{-1} for $(k_p)_{\text{act}}$ (Figure 2), the rate constant for photoreaction of the sorbed parathions in sunlight was computed to be about 2.6 h^{-1}. This value is about 390 times larger than the rate constant for direct photolysis of these substrates in water. With aniline and *m*-toluidine the fraction sorbed was less than 1%, indicating that the rate constant for photoreaction of the sorbed anilines is greater than 55 h^{-1} based on kinetic data in Table III. Thus, the anilines are estimated to be over 12 000 times more reactive when sorbed to *Chlamydomonas* sp. than when dissolved in water.

Nature of Algal-Mediated Photoreactions. Experiments were conducted to elucidate the mechanisms of the algal transformations, thus providing some basis for generalizing the results of this study.

Several experiments indicated that the photosynthetic apparatus of two green algae did not play a role in the sunlight-induced transformations of aniline or methyl parathion. Prolonged irradiation of the algal suspensions using monochromatic light at a wavelength (665 nm) that corresponds to peak light absorption by the chlorophyll in the algae (*3*) resulted in no reaction of either substrate. Moreover, the rate constants for photoreaction of methyl parathion or aniline were unaffected by heat-killing (50 °C for 0.5 h) the algae (Table IV). The heat-killed algae were washed by distilled water prior to the irradiations to remove the sensitizing substances that were released into the bulk water. Similar results have also been reported

Table IV. Kinetic Parameters for Sunlight-Induced Photoreactions of Methyl Parathion and Aniline with Algae Present

substrate	algae	treatment	algae concn, mg/L[a]	$(k_p)_p/(k_p)_{act}$[b]
methyl parathion	*Chlorogonium* sp. (no. 1)	none	530	0.28 ± 0.03
		heat-killed	530	0.26 ± 0.02
		washed with ascorbic acid	530	0.26 ± 0.02
	none present			0.06
aniline	*Chlamydomonas* sp.	none	160	2.7 ± 0.2
		heat-killed	160	3.1 ± 0.1
		washed with ascorbic acid		
	none present			0.04

[a] Computed from chlorophyll *a* concentration of algae prior to treatment assuming algal dry weight is 67 times greater than chlorophyll weight (*16*). [b] Mean values of three experiments are reported.

by Matsumura and Esaac (*25*), who found blue-green algae photosensitized reactions of several pesticides more rapidly when the algae were denatured by boiling.

The stability of the algal-associated sensitizers to heat, coupled with the fact that hydrous iron oxides known to be photochemically active (*26*) adsorb on algal cells from growth media (*14*), prompted us to examine the possibility that ferric hydroxide sorbed to the algae was the sensitizing agent. Employing a procedure similar to one described by Anderson and Morel (*14*), we washed the algae with an acidic solution of ascorbic acid to remove cell-associated ferric hydroxide. As shown in Table IV, this washing procedure had no effect on the rate constants for the photoreactions, excluding the possible involvement of hydrous iron oxides.

Conclusions

The results of this study unequivocally demonstrate that a variety of algae can accelerate the sunlight-induced transformations of nonionic organic chemicals, although in a very selective fashion. Components of culture media as well as substances released by the algae into the bulk water are also capable of photosensitizing reactions. The effects of the latter were minimized in this study by washing the algae with distilled water prior to irradiation. Dark metabolism of the organic substrates by the algae studied here was found to make little or no contribution to the observed transformations.

Detailed kinetic and product studies of the reactions of the anilines and parathions lead to several conclusions. The algal-induced reactions involve the reversible sorption of the substrate by the algal cells, where photosensitizing substances are present. At low substrate concentrations the reaction rates are first order with respect to both algae and substrate concentrations. Employing the rate expression and typical algae concentrations that are found in natural freshwaters, which are several orders of magnitude lower than used in this study, we conclude that light-induced algal transformation of most of the 22 chemicals studied here would have very little effect on their concentrations in lakes and rivers. Competing processes such as direct photolysis are more rapid. On the other hand, the rates are subject to a hydrophobic effect, suggesting that algal-induced photoreactions of pollutants more hydrophobic than the ones included in this study may be much more rapid. Indeed, rate constants computed for sunlight-induced photoreaction of substrates sorbed by the algae were remarkably large, ranging from an estimated near-surface average of 2.6 h^{-1} for sorbed parathion to over 55 h^{-1} for sorbed aniline.

Elucidation of the identity of the algal-associated photosensitizers was beyond the scope of this study. It was shown, however, that the rate constants for reactions of anilines and parathions were unaffected by heat-killing the algae and that the use of 665-nm light to sensitize the reactions was very inefficient. These results indicate that the photosynthetic apparatus of the algae was probably not involved in the algal transformations studied here.

Acknowledgments

We acknowledge the assistance provided by Gary Kochert and Wren Howard, Botany Department, University of Georgia, and by the Bionetics Corp., especially Lita Proctor and Vince Howard. We express thanks to Proctor and Ronnie Moon for preparation of the algae sketches. Several helpful suggestions were provided by Francois Morel, Bill Sunda, and Richard Larson. We thank Morel for a prepublication copy of ref 14.

Supplementary Material Available

Molecular structures of the synthetic chemicals included in this study and a first-order kinetic plot of the data for the *Chlamydomonas*-induced photoreaction of aniline (4 pages) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper or microfiche (105 × 148 mm, 24× reduction, negatives) may be obtained from Distribution Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, DC 20036. Full bibliographic citation (journal, title of article, author, page number) and prepayment, check or money order for $7.50 for photocopy ($9.50 foreign) or $6.00 for microfiche ($7.00 foreign), are required.

Registry No. MTB, 79049-96-0; pyrene, 129-00-0; phenanthrene, 85-01-8; fluoranthene, 206-44-0; naphthalene, 91-20-3; aniline, 62-53-3; phenol, 108-95-2; aldrin, 309-00-2; *cis*-1,2-dichloroethylene, 156-59-2; *cis*-1,3-pentadiene, 1574-41-0; methyl parathion, 298-00-0; *p*-nitroacetophenone, 100-19-6; *p*-nitroanisole, 100-17-4; nitrobenzene, 98-95-3; parathion, 56-38-2; fenitrothion, 122-14-5; ronnel, 299-84-3; chlorpyrifos, 2921-88-2; diazinon, 333-41-5; malathion, 121-75-5; *m*-toluidine, 108-44-1; *p*-chloroaniline, 106-47-8.

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Stability of 2-Chloropropenal and Some Other Mutagens Formed in the Chlorination of Softwood Kraft Pulp

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■ It is shown that the mutagenicity of spent chlorination liquor from the bleaching of softwood kraft pulp will decrease to low levels within a matter of weeks or shorter periods of time when such liquors are stored under neutral or weakly alkaline conditions. The results further show that 2-chloropropenal, known as a major contributor to overall mutagenicity (Ames test, *Salmonella typhimurium* TA 1535), is more stable than a number of previously identified mutagenic compounds such as trichloroethylene, monochloroacetaldehyde, and various chlorinated acetones. However, it is also apparent that spent chlorination liquors contain mutagens with a higher degree of stability than 2-chloropropenal.

Introduction

It is now clear that the spent chlorination liquors from the bleaching of most pulp types with chlorine exhibit mutagenic activity when tested according to the Ames test (*1–6*). To assess the risks involved in releasing such liquors into rivers, lakes, and oceans, information on the structures, quantities, and stabilities of the mutagenic compounds is required.

The identification of some of the mutagenic compounds in the spent liquor from the chlorination of softwood kraft pulp was recently described (*7–9*). Among the identified mutagens, three appear to be particularly strong. These are 1,3-dichloroacetone (*7, 10*), 2-chloropropenal (*7, 10*), and a furanone derivative tentatively identified as 3-chloro-4-(dichloromethyl)-5-hydroxy-2(5*H*)-furanone (*8*). The two former compounds were also recently identified as reaction products in the chlorination of humic acid (*11*).

Previous investigations have furthermore shown that the Ames test mutagenicity of spent chlorination liquors from the bleaching of pulp decreases upon storage of the liquors (*1–3, 5, 12–14*). Under acidic conditions the rate of the decrease is very low, and under alkaline conditions the mutagenicity may be eliminated in a short period of time. In this paper we describe studies on the storage stabilities of some of the identified mutagens. Special attention was given to 2-chloropropenal, since previous results suggest that this compound makes a major contribution to the mutagenicity of spent softwood kraft pulp chlorination liquor (*10*). The studies were primarily carried out to obtain a better understanding of the behavior of these compounds under conditions similar to those prevailing in receiving waters.

Experimental Section

Spent Chlorination Liquors. A spent chlorination liquor was prepared in the laboratory by chlorinating an industrially produced unbleached softwood kraft pulp with a Kappa number of 33 (corresponding to a lignin content of 5.1%). The chlorination was carried out by using 3.5% pulp consistency, a charge of 6.5% Cl_2, a temperature of 20 °C, and a reaction time of 60 min. The spent liquor (pH 2.0; in total corresponding to 27 m^3/ton of pulp) was separated from the pulp by filtration and any residual chlorine present removed by purging with N_2. The liquor was stored at 4 °C until further use.

For some experiments an industrially produced spent chlorination liquor was used. This had been produced in the bleaching of a softwood kraft pulp with a Kappa number of 36 (corresponding to a lignin content of 5.6%). The pH of the spent liquor was 1.8, and the total effluent volume corresponded to 40 m^3/ton of pulp.

Storage and Workup Procedures. Samples of spent chlorination liquors were adjusted to pH 6, 7, or 8 by adding 1 M NaOH under vigorous stirring. Subsequently, phosphate buffer of the respective pH was also added to

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ensure that the pH remained constant during the total period of storage. The volume of buffer added corresponded to about 13% of the volume of the neutralized spent chlorination liquor. Storage of the neutralized and buffered liquors took place at 4, 6, or 18 °C.

Samples were withdrawn from the stored liquors at different time intervals. One part of the sample was used in testing for mutegenicity according to the Ames test as described below. The major part (laboratory-prepared liquor), 400 mL, was adjusted to pH 2.2 by adding 4 M HCl and thereafter extracted with 150 mL of ether [May and Baker Ltd. (pro analysis)] in a liquid–liquid extractor for 48 h. The extract was dried with anhydrous Na_2SO_4 and thereafter concentrated in a rotary evaporator (at a temperature of about 25 °C) to a volume of 18 mL. The mutagenicity of the extracted sample and the concentrated ether extract (18 mL) was also tested according to the Ames test as described below. In addition, the concentrated ether extract was analyzed by the GC–MS (MID) technique after further evaporation to about 5 mL.

Mutagenicity Tests. Spent chlorination liquors prior to and after storage, ether extracted liquors, ether extracts of the liquors, or solutions of single model compounds were tested according to the Ames test as described previously *(1, 7)*. As a test organism, *Salmonella typhimurium* TA 1535 was used without metabolic activation. The toxicity of all samples toward the *Salmonella typhimurium* TA 1535 strain was determined after appropriate dilution of the bacteria and plating onto nutrient broth agar (3×10^2 cells/plate). The surviving bacteria were estimated by visual comparison of the plates with 100% representing the number of bacteria per unit area in the blank with no test solution (no toxicity) and 0% representing death of all bacteria.

Samples for the Ames test were withdrawn from the stored industrially prepared spent chlorination liquor every fourth hour during the first 2 days and then daily for about 3 weeks.

Samples for the Ames test were withdrawn from the laboratory prepared spent chlorination liquor after 6, 10, 18, 20, and 25 days.

The differently stored liquor and ether-extracted liquor samples were tested by adding 0.45 mL/plate. Samples of 0.45 mL (instead of 0.40 mL) were used here in order to compensate for the dilution of the original spent chlorination liquor due to the addition of phosphate buffer. The ether extracts of the stored liquors (which had been concentrated to 18 mL) were tested by adding 20 μL/plate corresponding to 0.45 mL/plate of the stored liquor.

For two stored spent chlorination liquors (pH 6.0, 6 °C, 25 days and pH 8.0, 18 °C, 10 days) dose response tests were carried out by adding 0.2, 0.4, 0.45, 0.6, and 0.8 mL of the liquor respectively per plate. For the ether-extracted liquor an identical procedure was used. The ether extract of the stored liquor was evaporated to a final volume of 9 mL. Of this solution, 20 μL (corresponding to 0.9 mL/plate of the stored liquor) was added per plate. The ether extract was thereafter diluted with ether such that 20 μL corresponded to 0.675, 0.45, and 0.225 mL respectively per plate of the stored liquor.

Dose response curves for 2-chloropropenal and 2,3-dichloropropanal were obtained by adding 20 μL of differently concentrated ether solutions of the respective compound to the plates.

All reported mutation test values are mean values obtained from assays that were carried out at least two times each involving 5 plates/sample. The ether and sodium chloride controls gave in all cases 18–24 revertants/plate.

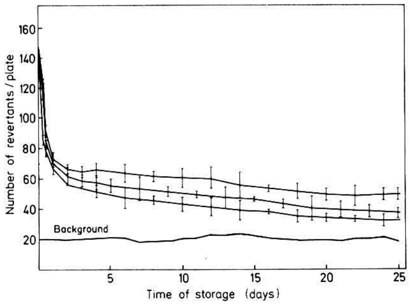

Figure 1. Changes in mutagenicity (Ames test, *Salmonella typhimurium* TA 1535 without metabolic activation) upon storage of an industrially produced spent chlorination liquor (softwood kraft pulp) at three different pH levels and 18 °C; upper curve, pH 6; middle curve; pH 7; lower curve, pH 8. Background number of revertants: sodium chloride, 19–24.

All results presented herein are based upon tests giving 70–100 % survival of the test bacteria. A sample was listed as mutagenic when the following three criteria were fulfilled: (a) a 2-fold increase in the number of revertants over the background level (ether or NaCl control), and/or (b) a dose-related increase over the background level, and (c) reproducibility of test results.

Gas Chromatography and Mass Spectrometry. The ether extracts were analyzed by the GC–MS (MID) technique as described previously *(10)*.

Model Compounds. The origin of all model compounds used, with the exception of 2,3-dichloropropanal, was described previously *(7)*. 2,3-Dichloropropanal was synthesized as described previously *(15, 16)*. The structure of the compound was confirmed by ^{1}H NMR, ^{13}C NMR, and mass spectrometry. ^{1}H NMR ($CDCl_3$) δ 3.90 (H-3, dd, 2 H, $J_{2,3app} = 6.2$ Hz), 4.39 (H-2, dt, H, $J_{2,3app} = 6.2$ Hz, $J_{1,2} = 1.7$ Hz), 9.46 (H-1, d, H, $J_{1,2} = 1.7$ Hz); ^{13}C NMR ($CDCl_3$) δ 42.46 (C_3), 61.24 (C_2), 192.11 (C_1). The ^{1}H NMR and the ^{13}C NMR spectra were run on a Varian CFT-20 spectrometer. Mass spectra, m/e (relative intensity) 62 (100), 29 (71), 90 (70), 61 (48), 64 (32), 92 (21), 63 (19).

Results and Discussion

Figure 1 shows the changes that occur in the mutagenicity of an industrially produced spent chlorination liquor when stored at pH 6, 7, and 8 at 18 °C. Initially, the number of revertants per plate decreases rather drastically at all three pH levels. However, after 3 or 4 days, the curves gradually level out. The pH 6 liquor is still mutagenic after 3 weeks of storage. In other experiments, not presented here, it was found that when stored at 4 °C, the liquor was mutagenic at all three pH levels after 3 weeks.

With the aim of correlating the decrease in mutagenicity resulting from storage with changes in the content of 2-chloropropenal and of some of the other mutagens identified so far, a spent softwood kraft pulp chlorination liquor was prepared in the laboratory and stored at pH 6 or 8 and a temperature of 6 or 18 °C. After 6, 10, 18, 20, and 25 days samples were withdrawn and worked up and analyzed as described in the experimental section. Table I shows the mutagenicities of the starting and the stored liquor samples before and after ether extraction and of the corresponding obtained ether extracts. Ether extraction was primarily carried out to work up mutagens for quantitative analysis. Table I also shows the contents of 2-chloropropenal found in the samples as well as some data on the stability of 2-chloropropenal when stored as a "single" organic compound in pH 6 buffered water.

Table I. Mutagenicity (Ames Test, *Salmonella typhimurium* TA 1535 without Metabolic Activation) and Content of 2-Chloropropenal in Laboratory Spent Chlorination Liquor (Softwood Kraft Pulp) before and after Storage at Two Different pH and Temperature Levels[a]

type of liquor			no. of revertants[b]			
pH of storage	temp of storage, °C	time of storage, days	before ether extraction	after ether extraction	ether extract	2-chloropropenal,[b] µg/L
2[c]	6		149 ± 7.5	52 ± 4.7 [21][d]	130 ± 5.3 [22][d]	46 ± 3.5
6	6	6	76 ± 6.4	40 ± 1.9 [19]	76 ± 8.6 [21]	31 ± 2.1
6	6	18	69 ± 6.8	41 ± 3.2 [22]	69 ± 5.0 [24]	23 ± 2.6
6	6	25	58 ± 5.2	39 ± 0.7 [20]	61 ± 5.0 [22]	18 ± 2.4
6	18	10	62 ± 3.5	38 ± 2.9 [21]	59 ± 3.5 [21]	32 ± 3.3
6	18	20	52 ± 3.1	32 ± 3.7 [20]	58 ± 5.5 [22]	20 ± 1.4
8	6	6	51 ± 5.5	36 ± 5.1 [19]	59 ± 4.4 [21]	24 ± 1.7
8	6	18	45 ± 3.0	39 ± 5.1 [22]	55 ± 6.5 [24]	17 ± 1.2
8	6	25	37 ± 3.1	34 ± 4.3 [20]	48 ± 3.5 [22]	14 ± 1.4
8	18	10	43 ± 2.4	39 ± 4.6 [21]	48 ± 5.1 [21]	16 ± 1.6
8	18	20	34 ± 4.2	28 ± 3.8 [20]	46 ± 4.6 [22]	11 ± 1.6
6	6	6				16 ± 2.4
6	6	25				4 ± 1.8

[a] Ames test carried out before and after ether extraction. Two lower lines: content of 2-chloropropenal stored as a single organic compound in pH 6 buffered water solution. Content at start of storage: 48.0 ± 4.1 µg/L. [b] Standard deviation ($n = 5$). [c] Starting liquor. [d] Background number of revertants, sodium chloride and ether.

A general inspection of the data in Table I allows some unexpected observations to be made. First, a consideration of the mutagenicities of the starting and the stored liquor samples reveals—as in the experiment described above—that a significant reduction in mutagenicity occurs as a result of storage. From an extrapolation of the numbers of revertants found per plate it can be concluded that the mutagenicity reaches levels below twice the background level after approximately 5 weeks at 6 °C and 4 weeks at 18 °C. The corresponding periods for the liquors stored at pH 8 are approximately 3 weeks (6 °C) and 1 week (18 °C). However, there is a lack in agreement between the number of revertants per plate found for the various liquor samples on one hand and combined number of revertants per plate for the corresponding ether-extracted liquor samples and ether extracts on the other. The discrepancy, which is further clearly illustrated in Figure 2, varies between 13 and 25 revertants/plate. The reason for the lack in agreement is not known. Possible explanations may be that a toxic or an antagonistic mutagenic effect is active in the complex mixture of the chemical compounds present in these liquor types. A corresponding extrapolation, as above, but this time based on the "combined" number of revertants per plate for the ether-extracted liquor samples and ether extracts reveals that to reach low levels of mutagenicity, a longer storage time is required. The eventual toxic and/or antagonistic effect present thus covers the mutagenicity of well stored liquors.

A second unexpected aspect comes to light when inspecting the contents of 2-chloropropenal found after storage. As can be clearly seen from Table I, 2-chloropropenal is not stable under these storage conditions. However, the compound appears to decompose considerably faster when stored as a single organic compound in buffered water solution than as a constituent of the spent chlorination liquor. The reason for this is also unknown. It is possible that spent chlorination liquor contains compounds that protect 2-chloropropenal from decomposition or that compounds may be present from which additional quantities of 2-chloropropenal may form during storage. In a recent investigation it was shown that 2,3-dichloropropanal will easily dehydrohalogenate under neutral conditions to give 2-chloropropenal in high yields (*17*). We synthesized 2,3-dichloropropanal and found after ether extraction and GC–MS (MID) analysis, using this compound as reference, that a freshly prepared spent softwood kraft pulp chlorination liquor indeed contains about 15 µg/L 2,3-dichloropropanal. At this point it should be noted that we found in accordance with previous results (*17*) that 2,3-dichloropropanal is itself a rather strong direct acting mutagen. As can be seen in Figure 3 a dose of 20 ng/plate yields about 25 revertants, corresponding to an Ames mutagenicity for the TA 1535 tester strain of some 1.5×10^2 revertants/nmol. This is about half the Ames mutagenicity of 2-chloropropenal for the same strain (*10*). Furthermore, at a content of about 15 µg/L a rough estimate suggests that 2,3-dichloropropanal may be responsible for some 10% of the mutagenicity of spent softwood kraft pulp chlorination liquor.

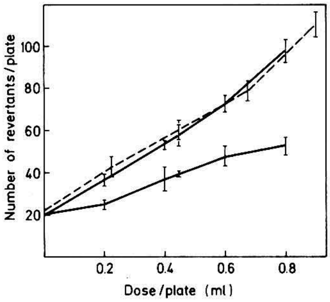

Figure 2. Dose response curves (Ames test, *Salmonella typhimurium* TA 1535 without metabolic activation) for spent chlorination liquor, stored for 25 days at pH 6 and 6 °C before (upper drawn curve) and after (lower drawn curve) ether extraction and for the corresponding ether extract (upper dotted curve). Background number of revertants; sodium chloride, 20; ether, 22.

However, we were only able to find a very modest increase in the content of 2-chloropropenal in a spent chlorination liquor that had been stored for 6 days at pH 6 at a temperature of 6 °C to which had been added 37 µg/L 2,3-dichloropropanal prior to storage; the 2,3-dichloropropanal was no longer detectable after the 6 days of storage. Of course, this result does not rule out the possibilty that other compounds in the spent chlorination liquor may form 2-chloropropenal upon storage.

As discussed in the Introduction, previous results suggested that 2-chloropropenal makes a major contribution (about 45–55%) to the mutagenicity of spent softwood kraft pulp chlorination liquor when tested according to the

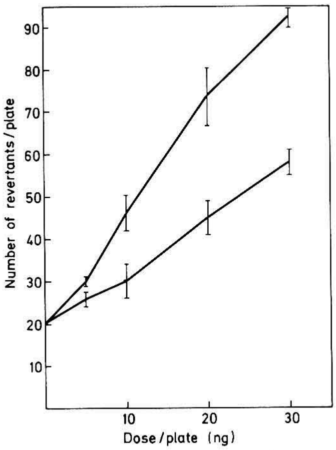

Figure 3. Dose response curves (Ames test, *Salmonella typhimurium* TA 1535 without metabolic activation) for 2-chloropropenal (upper) and 2,3-dichloropropanal (lower). Background number of revertants: ether, 21.

Table II. Content of 1,1,3,3-Tetrachloroacetone in Laboratory Spent Chlorination Liquor (Softwood Kraft Pulp) before and after Storage at Two Different pH and Temperature Levels

type of liquor			
pH of storage	temp of storage °C	time of storage, days	1,1,3,3-tetrachloroacetone, µg/L[a]
2[b]	6		319 ± 19.9
6	6	6	65.6 ± 7.1
6	6	18	5.8 ± 1.2
6	6	25	c
8	6	6	5.4 ± 0.9
8	6	18	c

[a] Standard deviation (n = 5). [b] Starting liquor. [c] Not detectable.

Ames test (*Salmonella typhimurium* TA 1535 without metabolic activation) (*10*). This conclusion had been reached after examining (a) the Ames mutagenicity of pure 2-chloropropenal (found to be about 3 × 10^2 revertants/nmol, (b) the quantity of the compound present in the spent liquor, and (c) the mutagenicity of the spent liquor. Experiments were carried out that showed no presence of synergistic or antagonistic mutagenic effects.

As discussed above, the data in Table I show that 2-chloropropenal decomposes during storage under the conditions of the experiment. At the beginning of the storage period, the rate of reduction is considerably lower than the rate of reduction in the mutagenicity of the liquor as such (or of the "combined" mutagenicity). This suggests that in the initial stages of storage, the relative importance of 2-chloropropenal as contributing mutagen increases. In accordance with this, it was found by GC–MS analysis of the ether extracts from the fresh and the stored liquor samples, that trichloroethylene, monochloroacetaldehyde, 1,3-dichloroacetone, pentachloroacetone, and hexachloroacetone—which are some other previously identified mutagens in such liquors—were no longer detectable after storage at pH 6 (or 8) for 6 days at 6 °C. Of the previously identified mutagens only 1,1,3,3-tetrachloroacetone was found. However, as shown in Table II, this compound also disappears quickly upon further storage. The strong mutagenic furanone derivative described in the introduction was not available as reference compound and therefore could not be analyzed. On long-term storage, the rate of reduction in the content of 2-chloropropenal increases relative to the reduction in mutagenicity of the liquor. This suggests that other, more stable mutagens than 2-chloropropenal must be present in the spent chlorination liquor or that new mutagens are formed upon storage. Investigations to elucidate the structure and properties of these are underway at this laboratory.

Acknowledgments

Thanks are due to Dr. U. Rannug, Department of toxicological genetics, Wallenberg Laboratory, Stockholm, for valuable discussions and criticism of the paper.

Registry No. 2-Chloropropenal, 683-51-2; 2,3-dichloropropanal, 616-23-9; 1,1,3,3-tetrachloroacetone, 632-21-3.

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Behavior of Organic Compounds during Infiltration of River Water to Groundwater. Field Studies

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■ The behavior of organic micropollutants during infiltration of river water to groundwater has been studied at two field sites in Switzerland. In agreement with predictions from model calculations, persistent organic chemicals exhibiting octanol/water partition coefficients smaller than about 5000 moved rapidly with the infiltrating river water to the groundwater. The biological processes responsible for the "elimination" of various micropollutants (e.g., alkylated and chlorinated benzenes) occurred predominantly within the first few meters of infiltration. Alkylated benzenes were "eliminated" at faster rates than 1,4-dichlorobenzene. Anaerobic conditions in the aquifer near the river hindered the biological transformation of 1,4-dichlorobenzene. Among the compounds that were found to be persistent under any conditions were chloroform, 1,1,1-trichloroethane, trichloroethylene, and tetrachloroethylene. With respect to such chemicals, bank filtration is ineffective as a first step in the treatment of river water for water supplies.

Since in many European countries a significant fraction of the groundwater is recharged through infiltration of river water (*1, 2*), the impact of river pollution on groundwater quality is of major concern. In addition, many waterworks use natural or artificial bank filtration as a first step in the treatment of river water for water supplies (*3, 4*). Therefore, the behavior of organic pollutants during infiltration is of great interest.

The transport and fate of organic pollutants in a river water–groundwater infiltration system is determined by several interacting processes, including advection, dispersion, (ad)sorption/desorption, hydrolysis, redox reactions, and biological transformations. In laboratory experiments, individual processes may be studied under controlled conditions (*5, 6*), and mathematical models may be developed to predict the effect of a particular process on the transport and fate of a compound in the environment (*7, 8*). However, comprehensive field investigations are needed to evaluate the applicability of laboratory studies and model calculations to natural systems.

To date, most of the field studies on natural river water–groundwater infiltration systems have been conducted with respect to the use of bank filtrate for public water supplies (e.g., ref 3). These studies have usually been confined to monitoring selected water constituents in the river and in groundwater wells near the region of infiltration. The temporal and spatial variations in concentration of organic compounds along the infiltration path have not been thoroughly investigated. Consequently, the results of such investigations provide only very limited insights into the behavior of individual compounds during infiltration.

In this paper, we report the results of two field studies aimed at investigating the transport and fate of organic micropollutants, including chlorinated hydrocarbons, alkylated benzenes, and chlorinated phenols during natural infiltration of river water to groundwater. In the near fields of two rivers, a network of observation wells was installed that allowed the contaminants in the infiltrating water to be traced from the river to the groundwater. The results of this 2-year field study contribute significantly to the limited field data on the behavior of trace organics in the groundwater environment (*9–11*).

Theoretical Section

Prediction of Retardation Factors for Hydrophobic Organic Compounds in the Ground. A rough estimate of the retention behavior of a given hydrophobic organic compound during infiltration may be obtained by treating transport through the river bed and in the aquifer in a first approximation as a one-dimensional process with constant flow in a homogeneous porous medium. Assuming that only the fine fraction of the aquifer material is relevant for sorption (*5, 12*) and assuming a linear sorption isotherm, an average retardation factor (R_f^z = ratio of the residence time τ_z of the solute to the residence time τ_w of the water) can then be calculated for compound z for a given segment of the aquifer (e.g., ref 8):

$$R_f^z = \tau_z/\tau_w = 1 + fK_p^z\rho(1 - \epsilon)/\epsilon \qquad (1)$$

where f = fraction of the aquifer material responsible for sorption (e.g., grain size range $\phi < 125$ μm; assumption: homogeneous distribution), K_p^z = equilibrium partition coefficient of the compound z between water and the fine fraction of the aquifer material at a given location in the ground (cm^3/g), ρ = density of the aquifer material (g/cm^3), and ϵ = total porosity. As we have shown in a previous study (*5*), for the compounds reported here, the equilibrium partition coefficient, K_p^z, may be estimated from the organic carbon content of the fine fraction of the aquifer material, f_{oc}, and from the octanol/water partition coefficient of the compound, K_{ow}^z:

$$K_p^z = 3.2f_{oc}(K_{ow}^z)^{0.72} \qquad (2)$$

Similar relationships have been found for other types of compounds and natural sorbents (*12, 13*). Note that eq 2 is valid only for sorbents exhibiting organic carbon contents of greater than about 0.1% ($f_{oc} > 0.001$). For organic-poor sorbents, interactions of the chemical with the inorganic matrix of the sorbent may become important (*5*). Combining eq 1 and 2 yields

$$R_f^z = 1 + 3.2ff_{oc}(K_{ow}^z)^{0.72}\rho(1 - \epsilon)/\epsilon \qquad (3)$$

Retardation factors calculated from eq 3 are valid only at sorption equilibria. At high groundwater-flow velocities, e.g., such as those encountered in the near field of a river during stormwater events (0.5 m/h; see ref 14), due to slow sorption kinetics, the compounds may be transported even faster than would be assumed from equilibrium considerations (*5, 15*). However, relationships such as eq 3 are very valuable for predicting the magnitude of the velocity at which a specific hydrophobic organic compound is transported in a given aquifer.

Experimental Section

Description of the Field Sites. The main field site of this investigation (field site I) is located in the lower

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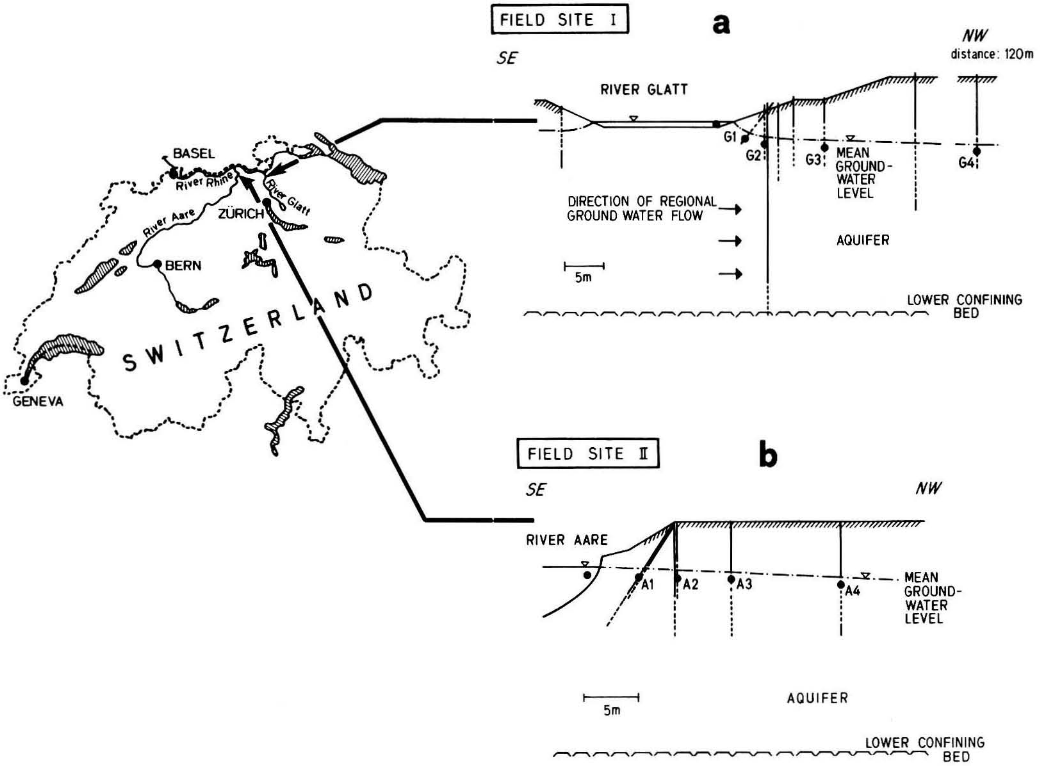

Figure 1. Locations and layouts of the two field study sites: (a) lower Glatt Valley, Switzerland (field site I); (b) lower Aare Valley, Switzerland (field site II); (● = sampling locations).

Glatt Valley, Switzerland (see Figure 1). In this region, the River Glatt infiltrates over a distance of about 5 km into a quaternary fluvioglacial valley fill aquifer composed of layers of gravel and sand containing very little organic carbon (<0.1%). The River Glatt is a small, rather heavily polluted perialpine river which has been studied extensively (*16, 17*). The average discharge of the river is approximately 8 m^3/s, of which 15–20% is effluent from a number of mechanical–biological sewage treatment plants. These treatment plants are the major source for organic micropollutants in the river. At the study site, permanent infiltration of the River Glatt through a saturated zone can be assumed.

Figure 1a gives a cross-sectional view of the study site on the right bank of the River Glatt. The groundwater flows beneath the river at an angle between 60 and 90° to the flow of the river. The results presented in this paper have been obtained primarily from measurements in wells G1–G4 (see Figure 1a). These wells gave access to freshly infiltrated water that stratified in the top layers of the aquifer. Some data from observation well G15, which is screened throughout the saturated thickness of the aquifer, will also be discussed. G15 is located in the center of the valley about 60 m downstream from G4. A detailed description of this field site is presented elsewhere (*18*).

To check the general validity of conclusions drawn from results obtained from the main field site, a second study was conducted on a different type of river system: River Aare in the lower Aare Valley (field site II; see Figure 1b). River Aare is a moderately polluted alpine river with an average flow of 550 m^3/s in the study area. The aquifer into which the river loses water is of the same geological formation as the one in the lower Glatt Valley (*19*). At the study site, the River Aare infiltrates through a saturated zone. Figure 1b shows the network of observation wells that were installed on the left bank of the river. At this location the regional groundwater flows beneath the River Aare at an angle of between 45 and 90° to the flow direction of the river.

Groundwater Observation Wells. All wells were lined with hard PVC tubes. In laboratory experiments, the PVC material was found neither to contaminate the samples nor to (ad)sorb the organic water constituents of interest. For technical details, see Hoehn et al. (*18*).

Sample Collection and Analytical Program. Between May 1979 and Apr 1980 (field site I) and between Nov 1980 and Oct 1981 (field site II), a program was conducted to determine temporal and spatial variations in the water composition of the rivers and of the groundwater in the observation wells shown in Figure 1. Samples were collected at approximately monthly intervals. In addition to the trace organic compounds, a variety of other chemical parameters were determined, mainly to characterize the river water and the groundwater, as well as to study the biogeochemical processes occurring during infiltration. Results of these measurements are discussed elsewhere (*20*).

The groundwater was sampled by using a small underwater plunger pump as described by Käss (*21*). The small discharge rate of this pump, typically between 0.5 and 1 L/min, allowed sampling of the groundwater without causing a measurable drawdown of the groundwater level. For sampling the upper layer of the groundwater, the pump was usually placed 0.5 m below the groundwater

Table I. Ranges of Retardation Factors (Lower Limit-Upper Limit) Calculated for Some Hydrophobic Organic Compounds Detected in the River Glatt

compound	octanol/water partition coeff (log K_{OW})	calcd retardation factors $(R_f)^{a,b}$		
		river sediment^{c} (~0.1 m)	aquifer close to river bed^{d} (<5 m)	aquifer far from river bed^{e} (>5 m)
chloroform	1.97^{f}	2.7-8	1.2-4	1-1.2
1,1,1-trichloroethane	2.17^{g}	3.4-11	1.2-6	1-1.2
trichloroethylene	2.29^{f}	4-13	1.3-7	1-1.3
toluene	2.69^{f}	7-23	1.6-12	1-1.6
tetrachloroethylene	2.88^{h}	9-31	1.8-16	1-1.8
1,3-dimethylbenzene	3.15^{f}	13-48	2.2-24	1-2.2
naphthalene	3.30^{i}	16-62	2.5-31	1-2.5
1,4-dichlorobenzene	3.38^{f}	18-70	2.7-35	1-2.7
α-hexachlorocyclohexane	3.72^{k}	32-123	4-62	1-4
hexachlorobenzene	6.06^{f}	1500-6000	150-3000	~10-150

[a] Equation 3; $\rho = 2.5$ g cm^{-3}, $\epsilon = 0.2$. [b] Ranges in values for f and f_{oc} are based on experimental data (see ref 5 and 18). [c] $f_{oc} = 0.01$-0.02, $f = 0.2$-0.4. [d] $f_{oc} = 0.001$-0.01, $f = 0.2$-0.4. [e] $f_{oc} \leqslant 0.001$, $f \leqslant 0.2$. [f] Reference 39. [g] Reference 40. [h] Reference 41. [i] Reference 26. [k] Reference 42.

table. The water was pumped through stainless steel tubing (5 mm i.d.) into 1-L glass bottles. The bottles were filled completely and closed without headspace. The samples were stored at 4 °C within 6 h of collection and analyzed within 48 h.

Analytical Methods. Volatile organic compounds were concentrated from the water samples by the closed-loop gaseous stripping/adsorption/elution procedure developed by Grob (*22, 23*). The water samples (typically 1 L) were stripped for 90 min at 30 °C, and the organic compounds were trapped by adsorption on a filter of 1.5 mg of activated charcoal. The filter was then extracted with 20 μL of carbon disulfide (CS_2) and the extract analyzed by high-resolution glass capillary gas chromatography and, when necessary, by gas chromatography/mass spectrometry. The gas chromatographic equipment and parameters used have been described elsewhere (*24*).

Purgeable organochlorine compounds (POCl) were determined by the method described by Zürcher (*25*). The compounds were purged with oxygen from 1-L water samples for 30 min at 60 °C. The purged compounds were continuously combusted at 950 °C, and the resultant chloride was trapped and quantified by ion chromatography.

Pentachlorophenol was determined by a method based on the procedure described by Renberg and Lindström (*26*). The lipophilic phenols were extracted by percolating 0.5 L of the acidified water sample (pH 2) through a SepPak C_{18} cartridge (Waters Inc., Milford, MA). The adsorbed phenols were eluted with 1.5 mL of acetone and acetylated by adding 50 μL of acetic anhydride. The excess anhydride was then destroyed by adding 3 mL of 0.1 M aqueous K_2CO_3, and the acetylated phenols were extracted with 2 mL of pentane. The pentane extract was analyzed by glass capillary gas chromatography using electron capture detection. 2,4,6-Tribromophenol was used as internal standard.

α- and γ-hexachlorocyclohexane and hexachlorobenzene were determined by the method of Müller (*27*). For all three compounds, the detection limit of the method used was 0.02 ng/L.

Dissolved Organic Carbon (DOC). Fractionation of the DOC was carried out with the method described by Schneider et al. (*28*). The DOC is operationally separated into three fractions: a "hydrophilic" fraction, an "acidic" fraction, and a "hydrophobic" fraction (see Figure 2). The fractionation is based on the retention of the organic constituents on a column (50 mm × 4 mm) packed with octadecylsilica (LiChrosorb RP 18) and connected to an on-line DOC detector (*29*). The "hydrophilic" fraction 1 is not retained on the column at pH 2 (peak 1 in Figure 2). The "acidic" fraction 2 is retained at pH 2 but is eluted from the column at pH 8 (peak 2 in Figure 2). This fraction includes all fulvic acid type materials (*28*). The "lipophilic" fraction cannot be eluted from the column with water at any pH. Its concentration is calculated by subtracting fraction 1 and 2 from the total DOC, which is determined by passing the adsorption column (see peak T in Figure 2).

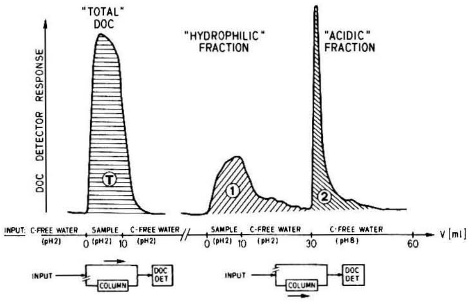

Figure 2. DOC fractionation by the method of Schneider et al. (*28*).

Results and Discussion

Field Site I. The names and octanol/water partition coefficients of some of the hydrophobic organic compounds found in the River Glatt are given in Table I. A more comprehensive inventory of the trace organics detected in this river has been published previously (*17*). The concentrations of individual compounds were usually between 0.01 and 2 μg/L.

Figure 3 depicts the temperature values, the concentrations of two representative volatile organic compounds, and the concentrations of oxygen, ammonium, and dissolved organic carbon determined over the course of 1 year in the River Glatt and in the wells G2 and G3, located 5 and 14 m, respectively, from the river. The average concentrations of some water constituents in the River Glatt and in wells G1-G4 are presented in Table II and Figure 4.

On the basis of the results of tracer experiments (*18*) and from the temperature data presented in Figure 3a, it can be assumed that the residence time of the water between the river and the two wells G2 and G3 was usually in the order of hours to a few days (well G2) and days to a few weeks (well G3). Figure 3b shows that for tetrachloroethylene, large fluctuations in concentration were observed

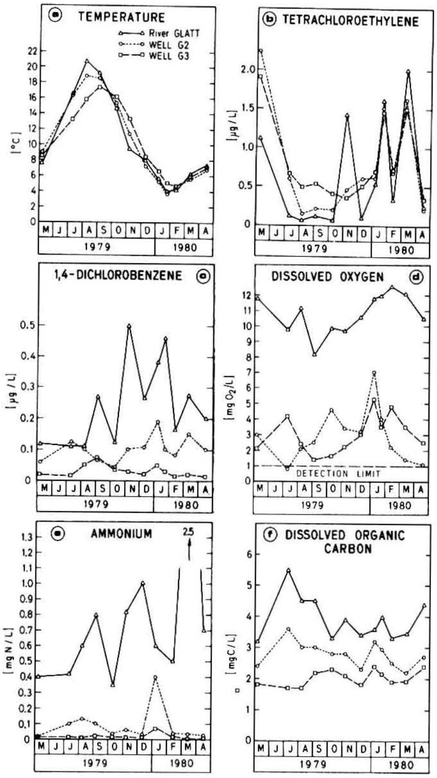

Figure 3. Field site I: monthly determined values for temperature, tetrachloroethylene, 1,4-dichlorobenzene, dissolved oxygen (detection limit = 1 mg of O_2/L), ammonium, and DOC, in the River Glatt and in observation wells G2 and G3.

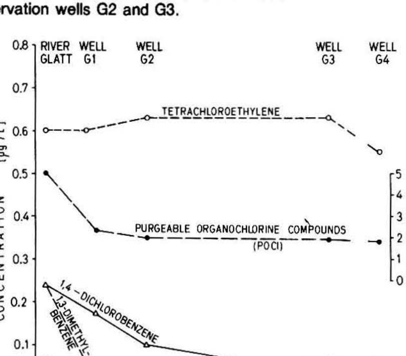

Figure 4. Field site I: average concentrations of selected organic micropollutants in the River Glatt and in the upper layers of the groundwater at various distances from the river (DL = detection limit).

in the River Glatt and in both observation wells, indicating a rapid response in the groundwater to concentration changes in the river. From the very similar average concentrations found for this compound in the river and in the groundwater in the top layers of the aquifer at different distances to the river (see Figure 4), one can conclude that tetrachloroethylene was not significantly affected by any elimination processes. The effect of the sorptive and dispersive processes, i.e., the attenuation of concentration

Table II. Yearly Average Concentrations and Standard Deviations of DOC, POCl, and Four Individual Organic Micropollutants in the River and in the Upper Layers of the Groundwater at Different Distances from the River

sampling location[a]	dist from river, m	DOC, mg/L	POCl,[b] µg of Cl/L	tetrachloroethylene,[c] µg/L	1,4-dichlorobenzene,[d] µg/L	1,3-dimethylbenzene,[e] µg/L	pentachlorophenol,[f] µg/L
field site I							
River Glatt	0	3.9 ± 0.7 {16}[g]	5.0 ± 4.2 {7}	0.60 ± 0.70 {16}	0.23 ± 0.13 {16}	0.23 ± 0.25 {16}	0.08 ± 0.005 {4}
well G1	2.5	3.0 ± 0.7 {9}	2.3 ± 1.8 {7}	0.60 ± 0.59 {9}	0.17 ± 0.07 {9}	<0.02 {9}	0.08 ± 0.02 {4}
well G2	5	2.8 ± 0.6 {16}	2.0 ± 1.0 {7}	0.63 ± 0.57 {16}	0.10 ± 0.04 {16}	<0.02 {16}	0.05 ± 0.04 {4}
well G3	14	2.1 ± 0.4 {16}	1.9 ± 0.9 {7}	0.63 ± 0.47 {16}	0.03 ± 0.02 {16}	<0.02 {16}	<0.02 {4}
well G4	120	1.5 ± 0.4 {9}	1.8 ± 0.9 {7}	0.55 ± 0.14 {9}	<0.005 {9}	<0.02 {9}	<0.02 {4}
field site II							
River Aare	0	2.3 ± 0.5 {12}	1.6 ± 0.9 {7}	0.24 ± 0.12 {12}	0.035 ± 0.015 {12}	0.05 ± 0.03 {12}	nd
well A1	4	1.0 ± 0.4 {12}	0.9 ± 0.6 {7}	0.25 ± 0.09 {12}	<0.01 {12}	<0.02 {12}	nd
well A2	7.5	0.8 ± 0.4 {12}	0.8 ± 0.5 {7}	0.24 ± 0.10 {12}	<0.005 {12}	<0.02 {12}	nd
well A3	13	0.7 ± 0.4 {12}	0.7 ± 0.3 {7}	0.20 ± 0.08 {12}	<0.005 {12}	<0.02 {12}	nd
well A4	23	0.7 ± 0.3 {12}	0.7 ± 0.3 {7}	0.20 ± 0.07 {12}	<0.005 {12}	<0.02 {12}	nd

[a] See Figure 1. [b] Purgeable organochlorine compounds (group parameter), detection limit 0.1 µg of Cl/L. [c] Detection limit 0.01 µg/L. [d] Detection limit 0.005 µg/L. [e] Detection limit 0.02 µg/L. [f] Detection limit 0.02 µg/L; nd = not determined. [g] The number of measurements is given in brackets.

fluctuations (see, e.g., ref 8), are reflected in the decreasing standard deviations observed with increasing flow distance (see Table II). Very similar results were found for chloroform, trichloroethylene (see Figure 4), and 1,1,1-trichloroethane.

The strong response in the groundwater to concentration changes in tetrachloroethylene in the River Glatt (Figure 3b) suggets that during infiltration this compound was not strongly retained in the ground. This finding is in agreement with the rather small average retardation factor predicted for tetrachloroethylene from eq 3 for this field site (see Table I and footnotes in Table I). It should be noted that for the aquifer in the near field of the River Glatt (<5 m; see Table I), the average retardation factors for the various compounds must be assumed to be closer to the indicated lower limits, since a sharp drop in the organic carbon content of the aquifer material occurs within a few meters distance from the river (*18*). Thus, at this field site, rapid transport in the ground can be expected for persistent organic compounds exhibiting octanol/water partition coefficients of smaller than about 5000 (see Table I). Unfortunately, because of the short residence time of the water between the river and the observation wells G2 and G3, no quantitative information on the actual retardation of the various compounds can be obtained from our data, since samples were taken only at monthly intervals.

Among the volatile organic compounds that were always present in the River Glatt but were almost never detected in any of the groundwater observation wells, were the aromatic hydrocarbons including toluene, various C_2- and C_3-benzene isomers (e.g., 1,3-dimethylbenzene; see Table II and Figure 4), and naphthalene. Since under the conditions typical for the groundwater environment these aromatic hydrocarbons, as well as all other volatile organic compounds listed in Table I (e.g., 1,4-dichlorobenzene), do not undergo chemical reactions at significant rates, and since these compounds are also only weakly sorbed, any observed "elimination" during infiltration must be attributed to biological transformation and/or mineralization. Parts d–f of Figure 3 indicate that the major biologically mediated processes, i.e., aerobic respiration and nitrification, occurred predominantly within the first few meters of infiltration. Therefore, it could be expected that the biological "elimination" of xenobiotic compounds would also take place primarily in the near field of the river.

Although the volatile aromatic hydrocarbons are biodegradable under simulated groundwater conditions (*30*), it is interesting to note that they were always eliminated between the river and well G1. Thus, considering the short residence time of the water between the river and this well and the small retardation factors of the compounds, the biological processes responsible for their removal were quite efficient, even at temperatures as low as 5 °C.

The observed significant decrease in concentration of 1,4-dichlorobenzene with increasing distance to the river (see Figures 3b and 4, Table II) indicates that this compound was also affected by biological processes. However, compared with the aromatic hydrocarbons, 1,4-dichlorobenzene was "eliminated" at a much slower rate, such that it was still detected in well G3. In addition, in July and Aug 1979 (Figure 3c) and during several short-term investigations in July and Aug 1980 and 1981 (*31*), no decrease in the concentration of 1,4-dichlorobenzene was found between the River Glatt and well G2. These findings suggest that, considering the steep concentration gradients usually detected between the river and G2, 1,4-dichlorobenzene was not significantly eliminated during parts of the summer. Since denitrification and manganese reduction were also observed during this time of the year (*20*, *31*), the persistence of 1,4-dichlorobenzene may be explained by the anoxic conditions that prevailed in parts of the aquifer near the river. This hypothesis is corroborated by other field observations (*32*) and by the results of laboratory experiments that suggest that halogenated benzenes are not biotransformed under anaerobic conditions (*33*). Whether, under aerobic conditions, 1,4-dichlorobenzene is completely mineralized or only transformed to products not detected by the analytical techniques used (e.g., to dichlorophenol and dichlorocatechol; see ref 34) is presently under investigation.

The results of the measurements of the group parameter "purgeable organochlorine compounds" (POCl; Table II, and Figure 4), which includes substances such as tetrachloroethylene and 1,4-dichlorobenzene, showed the same picture as the results of the single-component measurements: (i) the major "elimination" of volatile organochlorine compounds occurred predominantly within the first few meters of infiltration; (ii) for compounds not affected by any transformation processes, similar average concentrations were found throughout the upper layers of the aquifer.

From the few data obtained for pentachlorophenol (Table II), no final conclusions can be drawn as to whether or not this compound was "eliminated" during infiltration. At a pH of between 7.4 and 8, pentachlorophenol is present predominantly as phenolate anion ($pK_a = 4.75$). Thus, retardation factors of smaller than 50 in the near field of the river and smaller than 10 in the actual aquifer would be expected for this compound (*35*). The fact that the concentration of pentachlorophenol in well G3 was always below the detection limit could be an indication that this compound underwent some chemical and/or biological transformation reactions.

To date, only two sets of measurements have been conducted for α- and γ-hexachlorocyclohexane and for the highly lipophilic compound hexachlorobenzene. Although detected at very low concentrations, these compounds were found in the River Glatt and in all of the observation wells. The concentrations determined for α- and γ-hexachlorocyclohexane were 4 ng/L in the river, about 2 ng/L in the near field of the river (G2, G3), and less than 1 ng/L in G4. For hexachlorobenzene, very similar concentrations (between 0.1 and 0.2 ng/L) were found in the River Glatt and in all observation wells including G4. These findings demonstrate that, especially in aquifers composed of materials of low organic carbon content, even highly lipophilic compounds may be transported over long distances.

Field Site II. Compared to the River Glatt, the River Aare is a large river exhibiting much smaller short-term fluctuations in water composition (*31*). Also, in contrast to the field site in the lower Glatt Valley, the residence time of the water in the ground between the river and the observation wells (see Figure 1b) is generally much longer (in the order of weeks). This is evident from the temperature data shown in Figure 5a. Figure 5a also shows that very similar residence times can be assumed between the river and the two wells A1 and A3. Since a detailed investigation of the flow directions and velocities of the groundwater in the near field of the River Aare has not been conducted, it is not possible to give exact values for linear flow distances of the infiltrating water between the river and the wells. However, the results of the year-round study at this field site (see Figure 5 and Table II) can be qualitatively compared to those obtained in the lower Glatt Valley.

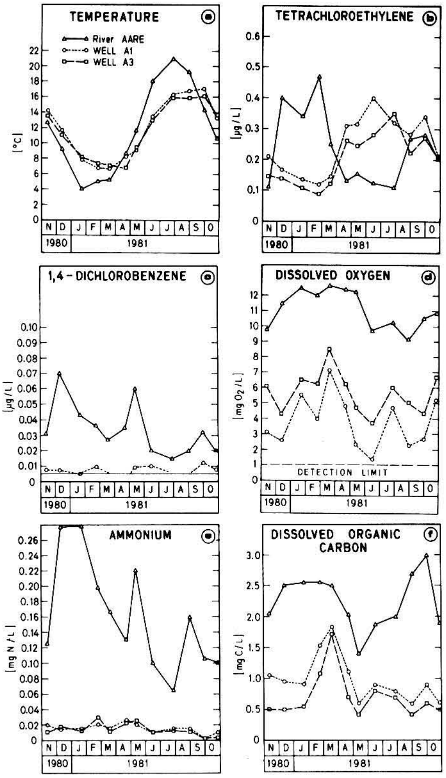

Figure 5. Field site II: monthly determined values for temperature, tetrachloroethylene, 1,4-dichlorobenzene, dissolved oxygen (detection limit = 1 mg of O_2/L), ammonium, and DOC, in the River Aare and in observation wells A1 and A3.

The data presented in Figure 5d–e show that the biologically mediated processes respiration and nitrification always occurred between the river and the wells A1 and A3. Reducing conditions were never observed in the groundwater at this field site. With respect to the organic micropollutants, all compounds exhibited behaviors similar to those observed at the Glatt site; that is, no elimination of tri- and tetrachloroethylene during infiltration, and degradation and/or transformation of the alkylbenzenes and 1,4-dichlorobenzene (see Figure 5b,c; Table II). It should be noted that the slightly lower average concentrations of tetrachloroethylene in A3 and A4 (see Table II) may be attributed to dilution of the infiltrated water with less polluted groundwater from other sources.

From the data shown in Figure 5b, it is possible to determine an average retardation factor for tetrachloroethylene. Figure 5b shows that significantly higher concentrations of this compound were observed in the river between Dec 1980 and Mar 1981. The response in the groundwater (i.e., in wells A1 and A3) to the high concentrations in the river was observed about 4 months later (τ_{tetra}). Thus, when an average residence time (τ_w) of the water between the River Aare and A1 and A3 of approximately 3 weeks to 1 month is assumed (see Figure 5a), an average retardation factor (τ_{tetra}/τ_w) of about 5 is obtained. This value is rather low when compared to the retardation factors determined by Roberts et al. (*11*) for compounds of similar lipophilicity in an aquifer in the Palo Alto Baylands (e.g., R_f = 33 for chlorobenzene). The result is, however, not surprising considering the much lower organic carbon content of the aquifer materials at this field site as compared to the Palo Alto site, and it is consistent with predictions from model calculations for the very similar type of aquifer at the study site in the Glatt Valley (see Table I).

Table III. Average Concentrations of Total DOC and of the Three DOC Fractions Determined by the Method of Schneider et al. (*28*)

sampling location[a]	dist from river, m	dissolved organic carbon,[b] mg of C/L: total	fraction 1[c]	fraction 2[d]	fraction 3[e]
River Glatt	0	4.0	1.5	1.0	1.5
well G1	2.5	2.7	1.0	0.9	0.8
well G2	5	2.6	1.0	0.9	0.7
well G3	14	2.0	0.8	0.8	0.4
well G4	120	1.5	0.9	0.5	0.1

[a] See Figure 1. [b] Average values from four measurements conducted between Sept 1979 and Dec 1979. [c] Hydrophilic at pH 2. [d] "Acidic" fraction: hydrophobic at pH 2, hydrophilic at pH 8. [e] Hydrophobic at pH 2 and pH 8.

Behavior of Dissolved Organic Carbon (DOC) during Infiltration. Although this study focused on the behavior of individual organic micropollutants, a few remarks may be made on compositional changes in the bulk DOC during infiltration. Table III contains the average values for DOC and the three DOC fractions determined in the River Glatt and in wells G1–G4. During the first few meters of infiltration, the concentrations of the hydrophilic (fraction 1) and the hydrophobic fraction (fraction 3) of the DOC were significantly reduced. These reductions may be primarily attributed to microbial mineralization (*20*). The "acidic" fraction 2, which includes all fulvic acid type materials (*28*), was not significantly affected by these processes. With increasing distance from the river (G1 → G4), the decrease in concentration of the "acidic" fraction might have been caused by the formation of insoluble complexes with metal ions (e.g., Ca^{2+}) and/or by adsorption onto clay minerals (*36–38*). Between G1 and G4, no significant changes in concentrations were observed in the hydrophilic fraction, whereas the lipophilic fraction was, to a great extent, removed and/or transformed into compounds appearing in one of the other fractions. It is not possible to identify the processes responsible for the removal of the lipophilic fraction of DOC from the available data.

Long-Range Effects of River Water Infiltration. Figure 6 shows the vertical concentration profiles of oxygen, DOC, and two persistent volatile organic compounds determined in well G15, which provides a representative picture of the water composition at various depths in the aquifer in the lower Glatt Valley (*20*). From the data in Figure 6 and from the results of the measurements of other parameters (*20*), it can be assumed that the upper half of the aquifer contained water that had predominantly been infiltrated from the River Glatt, whereas the water in the bottom half of the aquifer originated mostly from less polluted sources.

It is interesting to note that throughout the upper half of the aquifer, the concentrations of tri- and tetrachloroethylene were very similar to the average concentrations detected in the River Glatt (see Figure 4). Thus, when considering that the deeper layers of the upper half of the aquifer contained water that had been infiltrated from the river at distances of up to several kilometers from this well

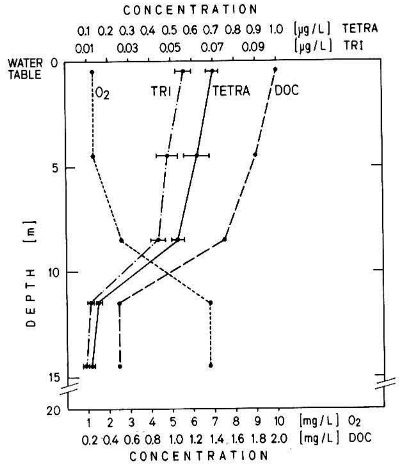

Figure 6. Field site I: vertical concentration profiles of selected parameters in well G15: (---) = dissolved oxygen (O_2); (– – –) dissolved organic carbon (DOC); (–··–) trichloroethylene (tri); (—) tetrachloroethylene (tetra).

(*18*), these findings again clearly demonstrate the great mobility of such persistent compounds in these types of aquifers and hence their potential to contaminate large groundwater areas.

Summary and Conclusions

The transport and fate of organic pollutants, including various volatile organic compounds, during infiltration of river water to groundwater has been studied in year-round investigations at two different field sites in Switzerland. The most important results and conclusions of this field investigation follow.

(1) As predicted by model calculations, volatile organic compounds move rapidly with infiltrating water from rivers to groundwaters. If a river is permanently charged with such chemicals, large groundwater areas may be contaminated, unless the compounds are eliminated during infiltration by biological processes.

(2) Among the volatile organic compounds for which no evidence of biological transformation under any conditions was found were chloroform, 1,1,1-trichloroethane, trichloroethylene, and tetrachloroethylene. With respect to such persistent chemicals, bank filtration is ineffective as a first step in the treatment of river water for water supplies.

(3) The compounds for which biotransformation was observed (e.g., all alkylated C_1–C_4-benzenes, naphthalene, the methylnaphthalenes, and 1,4-dichlorobenzene) were "eliminated" during infiltration to concentrations below their detection limits. Alkylated benzenes were always "eliminated" within the first few meters of infiltration, even at temperatures below 5 °C. The biotransformation of 1,4-dichlorobenzene occurred at a slower rate.

(4) There is strong evidence that certain organic micropollutants (e.g., 1,4-dichlorobenzene) were only biotransformed under aerobic conditions. The elimination of such compounds may therefore be hindered if anaerobic conditions prevail in the aquifer in the near field of a river.

(5) The retention of even highly lipophilic compounds such as hexachlorobenzene is rather small in aquifers composed of materials of low organic carbon content (i.e., $f_{oc} < 0.001$).

The results of this study show that long-term field measurements are useful (i) to gain relevant insights into the behavior of organic micropollutants in a natural river water–groundwater infiltration system and (ii) to check the general validity of conclusions drawn from laboratory investigations.

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Registry No. 1,4-Dichlorobenzene, 106-46-7; toluene, 108-88-3; 1,3-dimethylbenzene, 108-38-3; naphthalene, 91-20-3; hexachlorobenzene, 118-74-1; chloroform, 67-66-3; 1,1,1-trichloroethane, 71-55-6; trichloroethylene, 79-01-6; tetrachloroethylene, 127-18-4.

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OH Radical Rate Constants and Photolysis Rates of α-Dicarbonyls

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■ Photolysis rates of glyoxal, methylglyoxal, and biacetyl and OH radical reaction rate constants for glyoxal and methylglyoxal have been determined at 298 ± 2 K in an environmental chamber, by using the photolysis of CH_3ONO–air mixtures to generate OH radicals. The OH radical rate constants obtained were $(1.15 \pm 0.04) \times 10^{-11}$ and $(1.73 \pm 0.13) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} for glyoxal and methylglyoxal, respectively. The photolysis rates of glyoxal, methylglyoxal, and biacetyl increased throughout this series, and average quantum yields for the wavelength region $\geq$290 nm of 0.029 ± 0.018, 0.107 ± 0.030, and 0.158 ± 0.024 were derived for glyoxal, methylglyoxal, and biacetyl, respectively. In addition, upper limits to the rate constants for the reaction of O_3 with glyoxal and methylglyoxal of $<3 \times 10^{-21}$ and $<6 \times 10^{-21}$ cm^3 $molecule^{-1}$ s^{-1}, respectively, were obtained at 298 ± 2 K. These data will serve as needed input to chemical kinetic computer modeling studies of the aromatic hydrocarbons.

Introduction

The α-dicarbonyls glyoxal, methylglyoxal, and biacetyl are important ring-cleavage products in the NO_x–air photooxidations of the aromatic hydrocarbons (*1–6*), and the photolysis of methylglyoxal to radical species is postulated to lead to the observed photochemical reactivity of toluene and the higher aromatics (*4, 6*). In addition, methylglyoxal is postulated to be an intermediate product in the NO_x–air photooxidation of the naturally emitted hydrocarbon isoprene (*7, 8*). Under atmospheric conditions, these α-dicarbonyls, besides photolyzing, may also react with OH radicals or with O_3. On the basis of the data for methylglyoxal (*9, 10*), their reactions with O_3 are expected to be negligible, as is the reaction of OH radicals with biacetyl (*2*). However, both glyoxal and methylglyoxal are expected to react rapidly with OH radicals with rate constants of $\sim(1-2) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K (*4*), although the only OH radical rate constant available for glyoxal or methylglyoxal is a recent value of $(7.1 \pm 1.6) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at 297 K for methylglyoxal (*11*). In addition, the rates and products of the photolysis of these α-dicarbonyls under atmospheric conditions are not well-known (*4, 6, 12*), and hence there is clearly a need to investigate the atmospheric loss processes of these α-dicarbonyls in more detail.

In this work, rate constants for the reactions of OH radicals with glyoxal have been determined at 298 ± 2 K, relative to the rate constant for the reaction of OH radicals with cyclohexane, and the photolysis rates of glyoxal, methylglyoxal, and biacetyl have been determined in 1 atm of air in an environmental chamber. In addition, upper limits to the rate constants for the reaction of O_3 with glyoxal and methylglyoxal have been determined at 298 ± 2 K.

Experimental Section

Photolysis and OH Radical Reactions. The technique for the determination of relative OH radical rate constants and of photolysis rates was essentially identical with those described previously (*13, 14*). Hydroxyl radicals were generated by the photolysis of methyl nitrite in air at $\gtrsim$290 nm, at part-per-million concentrations:

$$CH_3ONO + h\nu \rightarrow CH_3O + NO$$

$$CH_3O + O_2 \rightarrow HCHO + HO_2$$

$$HO_2 + NO \rightarrow OH + NO_2$$

In order to minimize the formation of O_3 during these irradiations, NO was included in the reaction mixtures. In the presence of an α-dicarbonyl and a reference organic (cyclohexane), the OH radicals can, besides reacting with CH_3ONO, NO, NO_2, and the organic reaction products, react with these organics:

$$OH + \text{dicarbonyls} \rightarrow \text{products} \quad (1)$$

$$OH + \text{cyclohexane} \rightarrow \text{products} \quad (2)$$

Additionally, the α-dicarbonyls also photolyze:

$$\text{dicarbonyl} + h\nu \rightarrow \text{products} \quad (3)$$

Under the experimental conditions employed, reactions of the dicarbonyls and cyclohexane with $O(^3P)$ atoms and O_3 were negligible, and since dilution due to sampling was also negligible (<0.2%), then

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$$-\mathrm{d}[\text{dicarbonyl}]/\mathrm{d}t = k_1[\text{OH}][\text{dicarbonyl}] + k_3[\text{dicarbonyl}] \qquad \text{(I)}$$

$$-\mathrm{d}[\text{cyclohexane}]/\mathrm{d}t = k_2[\text{OH}][\text{cyclohexane}] \qquad \text{(II)}$$

and hence

$$\ln\left(\frac{[\text{dicarbonyl}]_{t_0}}{[\text{dicarbonyl}]_t}\right) = k_1\int_{t_0}^{t}[\text{OH}]\,\mathrm{d}t + k_3(t - t_0) \qquad \text{(III)}$$

and

$$\ln\left(\frac{[\text{cyclohexane}]_{t_0}}{[\text{cyclohexane}]_t}\right) = k_2\int_{t_0}^{t}[\text{OH}]\,\mathrm{d}t \qquad \text{(IV)}$$

where k_1, k_2, and k_3 are the rate constants for reactions 1–3, respectively, $[\text{dicarbonyl}]_{t_0}$ and $[\text{cyclohexane}]_{t_0}$ are the concentrations of the α-dicarbonyl and cyclohexane, respectively, at time t_0, and $[\text{dicarbonyl}]_t$ and $[\text{cyclohexane}]_t$ are the corresponding concentrations at time t. Eliminating the integrated OH radical concentrations from III and IV yields

$$\frac{1}{t - t_0}\ln\left(\frac{[\text{dicarbonyl}]_{t_0}}{[\text{dicarbonyl}]_t}\right) = k_3 + \frac{k_1}{k_2(t - t_0)}\ln\left(\frac{[\text{cyclohexane}]_{t_0}}{[\text{cyclohexane}]_t}\right) \qquad \text{(V)}$$

Hence plots of $(t - t_0)^{-1}\ln([\text{dicarbonyl}]_{t_0}/[\text{dicarbonyl}]_t)$ vs. $(t - t_0)^{-1}\ln([\text{cyclohexane}]_{t_0}/[\text{cyclohexane}]_t)$ should yield straight lines of slope k_1/k_2 and intercept k_3. The OH radical concentrations during the irradiations were varied by varying the initial CH_3ONO concentrations, and irradiations were also carried out in the absence of CH_3ONO to minimize OH radical concentrations.

Irradiations of CH_3ONO–dicarbonyl–cyclohexane–NO–air and dicarbonyl–cyclohexane–air (which contained traces of NO_x from previous runs) mixtures were carried out in a 5800-L Teflon-coated, evacuable, thermostated environmental chamber, equipped with a 25-kW xenon arc solar simulator *(15)*. The radiation from this solar simulator, which approximates that of the deep-space solar spectrum in the ultraviolet and visible regions *(15)*, was filtered by passage through a 0.64-cm Pyrex pane in order to eliminate radiation below ~300 nm. The resulting spectral distribution, which approximates that of the lower tropospheric solar spectrum, measured at the time of the present experiments is shown in Figure 1. The absolute light intensity, monitored as the photolysis rate of NO_2 in N_2 *(15)*, was 1.40×10^{-3} s^{-1}, with an estimated uncertainty of $\sim\pm 10\%$. A light intensity of this magnitude was used to decrease the rates of consumption of the α-dicarbonyls and cyclohexane, hence allowing several data points to be obtained during each irradiation.

Cyclohexane was quantitatively monitored prior to and during the irradiations by gas chromatography with flame ionization detection using a 20 ft × $^1/_8$ in. stainless steel column with 5% DC703/C20M on 100–120 mesh AW, DMCS Chromosorb G, operated at 333 K. The α-dicarbonyls were monitored prior to and during the irradiations by differential optical absorption spectroscopy (DOAS) *(16)* with a multipass optical system (3.77-m focal length White system) arranged along the longitudinal axis of the chamber using typically 32 passes, corresponding to a 120.6-m pathlength. The wavelength regions used to monitor these α-decarbonyls were from 430 to 460 nm *(17)*.

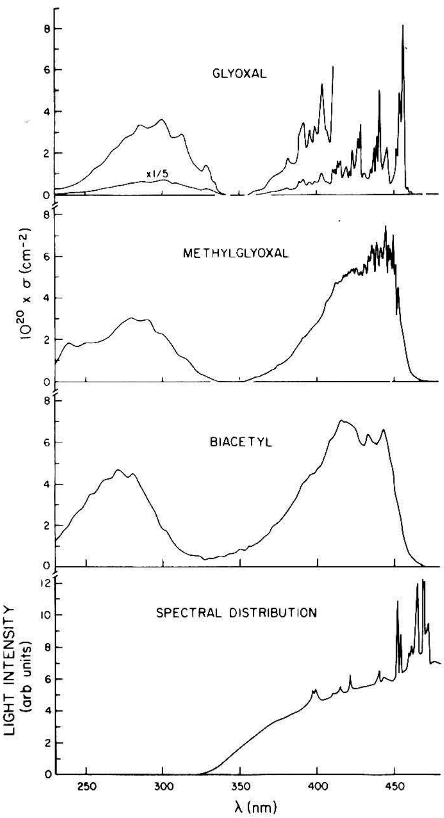

Figure 1. Gas-phase absorption spectra determined for glyoxal, methylglyoxal, and biacetyl, together with the relative spectral distribution used in this study.

For glyoxal and methylglyoxal, irradiations of α-dicarbonyl–air and of α-dicarbonyl–CH_3ONO–NO–air mixtures were carried out. The initial concentrations were as follows (molecules cm^{-3}): glyoxal, $\sim 1.2 \times 10^{14}$, or methylglyoxal, $\sim 2.4 \times 10^{14}$; CH_3ONO (when present $\sim$(3–20) $\times 10^{13}$; NO (when present) $\sim$(2–3) $\times 10^{13}$; cyclohexane, $\sim 2.4 \times 10^{13}$. It should be noted that since photolysis of these α-dicarbonyls can, in the presence of NO, yield OH radicals and since glyoxal and methylglyoxal react rapidly with OH radicals, the observed glyoxal and methylglyoxal decay rates in the α-dicarbonyl–air irradiations are expected to be higher than the actual photolysis rates. For biacetyl, only a biacetyl–air–photolysis was carried out at an initial concentration of biacetyl of $\sim 2.7 \times 10^{14}$ molecule cm^{-3}, since the reaction of OH radicals with biacetyl is very slow *(2)* and the observed biacetyl decay rate corresponds to its photolysis rate.

Ozone Reactions. The technique used for the determination of the ozone reaction rate constants *(10, 18)* was based on observing the rate of ozone decay in the presence of a known excess of a reactive compound. In the presence of such a reactant, the processes removing O_3 are

$$O_3 + \text{wall} \rightarrow \text{loss of } O_3 \qquad (4)$$

$$O_3 + \text{dicarbonyl} \rightarrow \text{products} \qquad (5)$$

and hence

$$-\mathrm{d}[O_3]/\mathrm{d}t = (k_4 + k_5[\text{dicarbonyl}])[O_3] \qquad \text{(VI)}$$

where k_4 and k_5 are the rate constants for reactions 4 and 5. With the dicarbonyl concentration being in large excess over the initial O_3 concentration ($[\text{dicarbonyl}]/[O_3]_{\text{intl}} \geq$

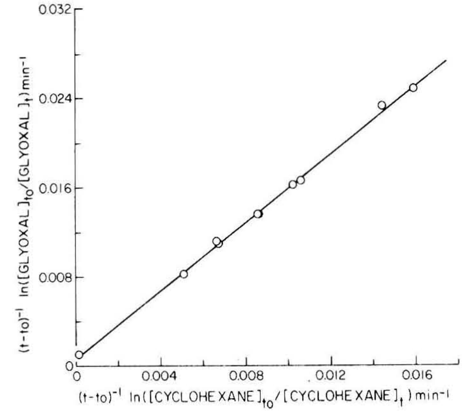

Figure 2. Plot of eq V for glyoxal.

100), the dicarbonyl concentration remained essentially constant throughout the reaction, and equation VI may be rearranged to yield

$$-\mathrm{d}\ln[O_3]/\mathrm{d}t = k_4 + k_5[\text{dicarbonyl}] \qquad \text{(VII)}$$

Thus with a knowledge of k_4, the background ozone decay rate, the rate constant k_5, or an upper limit thereof, can be readily obtained.

As described previously (*10, 18*), reactions were carried out in a ~175-L Teflon bag, constructed out of a 2 mil thick, 180 × 140 cm FEP Teflon sheet, heat-sealed around the edges, and fitted with Teflon injection and sampling ports at each end of the bag. The reaction bag was initially divided into two subchambers, with O_3 being injected into one subchamber and the dicarbonyl into the other. The reactions were initiated by removing the bag divider and rapidly mixing the contents of the bag by pushing down on alternate sides of the entire bag for ~1 min. Initial O_3 concentrations after mixing were ~2×10^{13} molecule cm^{-3}, and after mixing of the reactants, the O_3 concentrations were monitored as a function of time by a Monitor Labs Model 8410 chemiluminescence ozone analyzer.

Absorption Cross Sections. For the purpose of calculating effective quantum yields (see below) the absorption cross sections for glyoxal, methylglyoxal, and biacetyl were determined by using a Cary 17-D spectrophotometer and known pressures (~3–13 torr as measured with an MKS Baratron capacitance manometer) of the α-dicarbonyls.

Materials. Glyoxal and methylglyoxal were prepared by first evaporating a commercially available glyoxal–water or methylglyoxal–water solution to dryness under vacuum. Then, after adding and mixing P_2O_5 to the resulting crystalline- or polymer-like material, the α-dicarbonyl was distilled off under vacuum and collected at 77 K. Biacetyl and cyclohexane were obtained from the Aldrich Chemical Co. The α-dicarbonyls were flushed into the reaction chambers by a stream of N_2 from calibrated ~5-L Pyrex bulbs containing known pressures (as measured by an MKS Baratron capacitance manometer) of the α-dicarbonyls.

Results

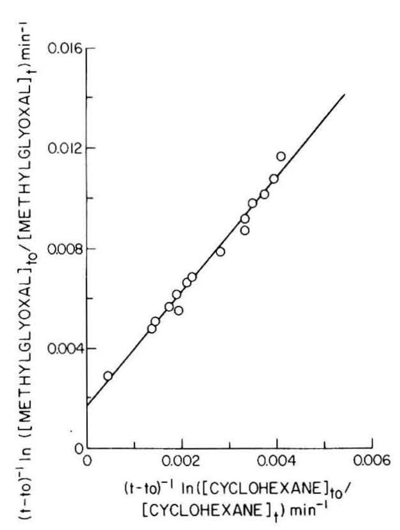

Figure 3. Plot of eq V for methylglyoxal.

Table I. Photolysis Rates k_3 and OH Radical Reaction Rate Constant Ratios k_1/k_2 and Rate Constants k_1 for the α-Dicarbonyls Studied

α-dicarbonyl	k_1/k_2 [a]	$10^{11}k_1$, cm^3 molecule^{-1} s^{-1} [a,b]	10^5k_3, s^{-1} [a,c]
glyoxal	1.52 ± 0.05	1.15 ± 0.04	1.1 ± 0.7
methylglyoxal	2.29 ± 0.16	1.73 ± 0.13	2.7 ± 0.7
biacetyl			5.0 ± 0.3

[a] Indicated error limits are 2 least-squares standard deviations. [b] Placed on an absolute basis by using a rate constant of $k_2 = (7.57 \pm 0.05) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (*13*), which in turn is based on a rate constant for the reaction of OH radicals with *n*-butane of 2.58×10^{-12} cm^3 molecule^{-1} s^{-1} (*13*). [c] At an NO_2 photolysis rate constant of 1.4×10^{-3} s^{-1}.

Photolysis and OH Radical Reactions. Glyoxal and Methylglyoxal. Irradiations of glyoxal or methylglyoxal–cyclohexane–air and glyoxal or methylglyoxal–CH_3ONO–NO–cyclohexane–air mixtures were carried out, with cyclohexane serving as the reference organic. The data from these irradiations, plotted in the form of eq V, are shown in Figures 2 and 3 for glyoxal and methylglyoxal, respectively. It can be seen from these figures that the data yield good straight-line plots, in accordance with eq V, and the slopes (yielding the rate constant ratios k_1/k_2) and the intercepts (the glyoxal or methylglyoxal photolysis rates k_3) are given in Table I. The OH radical concentrations, as derived from the cyclohexane decay rates via eq II, were higher by a factor of ~30–100 and 3–9 for the glyoxal and methylglyoxal systems, respectively, when CH_3ONO was included in the initial reactant mixture, compared to when CH_3ONO was absent. No dark decay of these α-dicarbonyls, within the experimental uncertainties of ~4%, was observed over periods of ~1 h.

During the irradiation of the glyoxal–cyclohexane–air mixture, formaldehyde, a potential photolysis product (*19*), was detected by DOAS at the end of the irradiation at a concentration of 9.0×10^{11} molecule cm^{-3}.

Biacetyl. Since reaction of biacetyl with OH radicals is slow ($k_2 = (2.4^{+0.8}_{-0.6}) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} (*2*)), the photolysis rate for biacetyl was obtained directly from the exponential biacetyl disappearance in an irradiated biacetyl–air mixture. This photolysis rate is also given in Table I.

Ozone Reactions. The O_3 decay rates obtained in the presence of ~3×10^{15} molecule cm^{-3} of glyoxal and me-

Table II. Observed and Calculated Photolysis Rate Ratios k_3/k_{NO_2} for Glyoxal, Methylglyoxal, and Biacetyl and Calculated α-Dicarbonyls Effective Quantum Yields

	k_3/k_{NO_2}			
		calcd		
α-dicarbonyl	obsd[a]	$\phi_\lambda = 1$	$\phi_\lambda = 1, \lambda \leq 340$ nm $\phi_\lambda = 0, \lambda > 340$ nm	eff quantum yield ϕ[b]
glyoxal	0.008 ± 0.005	0.29	0.000 38	0.029 ± 0.018
methylglyoxal	0.019 ± 0.005	0.18	0.000 03	0.107 ± 0.030
biacetyl	0.036 ± 0.004	0.23	0.000 07	0.158 ± 0.024

[a] The indicated error limits include 2 standard deviations of the α-dicarbonyl photolysis rates (Table I) together with a 10% uncertainty in k_{NO_2}. [b] Effective quantum yield = $[k_3/k_{NO_2}(\text{calcd}, \phi_\lambda = 1)]$.

thylglyoxal were 7×10^{-6} and 1.8×10^{-5} s^{-1}, respectively. These ozone decay rates in the presence of added glyoxal or methylglyoxal were indistinguishable from the background O_3 decay rates observed in the absence of reactants, which typically are in the range $\sim(5\text{–}30) \times 10^{-6}$ s^{-1} in this system. Thus from these data, upper limits to the rate constants k_5 of

$$k_5(\text{glyoxal}) < 3 \times 10^{-21} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

and

$$k_5(\text{methylglyoxal}) < 6 \times 10^{-21} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

can be derived.

Discussion

Reaction with OH Radicals and O_3. The rate constant ratios k_1/k_2 may be placed on an absolute basis by using a rate constant k_2 of $(7.57 \pm 0.05) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (*13*), which in turn is based on a rate constant for the reaction of OH radicals with *n*-butane of 2.58×10^{-12} cm^3 molecule^{-1} s^{-1} (*13*). The rate constants k_1 so derived are also given in Table I. The present rate constant for reaction of OH radicals with methylglyoxal of $k_1 = (1.73 \pm 0.13) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 ± 2 K is a factor of 2.4 higher than the recent absolute value obtained by using the flash photolysis–resonance fluorescence technique (*11*). The reason for this discrepancy is not known at the present time, but the rate constants k_1 for glyoxal and methylglyoxal determined here are very similar to these at room temperature for formaldehyde ($k_1 = 1.0 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (*20, 21*)) and acetaldehyde ($k_1 = 1.6 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (*20*)), respectively, indicating that the extra $>C{=}O$ group has little effect on these reactions. These OH radical rate constants are probably essentially independent of temperature over a small temperature range centered at ~300 K and lead to $1/e$ atmospheric lifetimes due to reaction with OH radicals of ~24 and ~16 h for glyoxal and methylglyoxal, respectively, when an OH radical concentration of 1×10^6 cm^{-3} is assumed.

The upper limits for the rate constant for reaction of O_3 with methylglyoxal of $k_5 < 6 \times 10^{21}$ cm^3 molecule^{-1} s^{-1} determined in this work is totally consistent with the previous room-temperature data from these laboratories (*9, 10*), which yielded values of $k_5 = (1.1 \pm 0.5) \times 10^{-21}$ (*9*) and $k_5 < 7 \times 10^{-20}$ cm^3 molecule^{-1} s^{-1} (*10*). Thus, these data show that, as expected, reaction with O_3 is negligible for these α-dicarbonyls under atmospheric conditions.

Photolysis. The photolysis rates for the α-dicarbonyls given in Table I are only strictly applicable for the light intensity and spectral distribution employed in these irradiations. However, these data can be normalized for differences in the light intensity by dividing the observed α-dicarbonyl photolysis rates by the observed NO_2 photodissociation rate constant of 1.4×10^{-3} s^{-1} measured under the same experimental conditions, and the resulting photolysis rate ratios are given in Table II. The present ratio of the biacetyl and NO_2 photolysis rates of 0.036 ± 0.004 is in excellent agreement with the ratio of 0.032–0.040 obtained previously by Darnall et al. (*2*) in the same environmental chamber at a higher light intensity.

The ratio of the rate constants for the photolysis of the α-dicarbonyls, k_3, relative to that for NO_2, k_{NO_2}, can be related to the absorption cross sections, σ_λ, of the α-dicarbonyls and the relative spectral distribution, J_λ^{rel}, of the radiation according to the expression

$$\frac{k_3}{k_{NO_2}} = \frac{\int_{\lambda_{\min}}^{\lambda_{\max}} J_\lambda^{\text{rel}} \sigma_\lambda \phi_\lambda \, d\lambda}{\int_{\lambda_{\min}}^{\lambda_{\max}} J_\lambda^{\text{rel}} \sigma_\lambda^{NO_2} \phi_\lambda^{NO_2} \, d\lambda} \qquad \text{(VIII)}$$

where ϕ_λ is the quantum yield for photodissociation of the α-dicarbonyl, $\sigma_\lambda^{NO_2}$ and $\phi_\lambda^{NO_2}$ are the known (*22, 23*) NO_2 absorption cross sections and photodissociation quantum yields, respectively, and $\lambda_{\min}$ and $\lambda_{\max}$ are the minimum (~290 nm) and maximum (~470 nm for the α-dicarbonyls, 420 nm for NO_2) wavelengths for which photodissociation occurs in the present experimental system. The measured absorption cross sections for glyoxal, methylglyoxal, and biacetyl are given in Table A (available as supplementary material; see paragraph at end of text) and are plotted as a function of wavelength in Figure 1, which also shows the relative spectral distribution used in this study. The absorption cross sections determined in this work for biacetyl are in excellent agreement with those presented by Calvert and Pitts (*24*).

Thus the only unknown quantities in eq VIII are the quantum yields for the photodissociation of the α-dicarbonyls. However, since these quantum yields cannot exceed unity, eq VIII allows the maximum photolysis rate ratios k_3/k_{NO_2} to be calculated by setting $\phi_\lambda = 1$ at all wavelengths, and these calculated maximum photolysis rate ratios are given in Table II, along with the experimentally determined ratios. Also given in Table II are the photolysis rate ratios calculated on the assumption that photodissociation only occurs from the lower wavelength absorption band, i.e.

$$\phi_\lambda = 1 \text{ for } \lambda \leq 340 \text{ nm} \qquad \phi_\lambda = 0 \text{ for } \lambda > 340 \text{ nm}$$

It can be seen from Table II that the observed photolysis rate ratios are significantly less than the calculated maximum values. However, it is also clear from Table II that the α-dicarbonyl photodissociation quantum yields at $\lambda > 340$ nm must be nonnegligible, since the use of $\phi_\lambda = 1$ ($\lambda \leq 340$ nm) and $\phi_\lambda = 0$ ($\lambda > 340$ nm) leads to calculated photolysis rate ratios much lower than the observed values. Thus these data show that for glyoxal ≳95% and for methylglyoxal and biacetyl >99% of the presently observed α-dicarbonyl photodissociation occurs from the

Table III. Atmospheric Lifetimes of Glyoxal, Methylglyoxal, and Biacetyl due to Photolysis, Reaction with OH Radicals, and Reaction with O_3

α-dicarbonyl	τ_{photol}, h[a]	τ_{OH}, h[b]	τ_{O_3}, h[c]
glyoxal	5	24	$>9 \times 10^4$
methylglyoxal	2	16	$>4 \times 10^4$
biacetyl	1	$\gtrsim 900$	$\gtrsim 4 \times 10^4$ [d]

[a] At a zenith angle of 0°. [b] At an OH radical concentration of 1×10^6 cm^{-3}. [c] At an O_3 concentration of 1×10^{12} cm^{-3} (40 ppb). [d] Estimated by analogy with glyoxal and methylglyoxal.

340–470-nm absorption band and that relaxation processes such as fluorescence or relaxation to the ground state compete significantly with photodecomposition in this wavelength region.

The "effective" quantum yields for the photodissociation of the α-dicarbonyls studied here, obtained by dividing the observed photolysis rate ratios by those calculated assuming $\phi_\lambda = 1$, are given in Table II and are 0.03 for glyoxal, 0.11 for methylglyoxal, and 0.16 for biacetyl. Since in general it is expected that ϕ_λ will vary with wavelength, these "effective" quantum yields are valid only for the particular spectral distribution used in this study. However, since the spectral distribution of the filtered solar simulator used is similar to that of sunlight in the lower troposphere (*15*), then the photolysis rate ratios k_3/k_{NO_2} observed here can be used with the NO_2 photodissociation rate constants k_{NO_2} to estimate the atmospheric α-dicarbonyl photolysis rates k_3.

The estimated atmospheric photodecomposition lifetimes for glyoxal, methylglyoxal, and biacetyl are compared in Table III with the estimated lifetimes for removal of these species by reaction with OH radicals and with O_3. It can be seen that, despite the relatively low "effective" photodissociation quantum yields, the photodissociation lifetimes are appreciably shorter than the lifetimes due to reaction with OH radicals or O_3 (the latter reaction being essentially negligible). Photolysis of these α-dicarbonyls is thus clearly their major tropospheric loss process.

The formation of peroxyacetyl nitrate (PAN) was observed during the irradiation of methylglyoxal–NO_x–air and biacetyl–NO_x–air mixtures, showing that in both cases, photodissociation yields, at least partially, CH_3CO radicals:

$$CH_3COCHO + h\nu \rightarrow CH_3CO + CHO$$

$$CH_3COCOCH_3 + h\nu \rightarrow 2\ CH_3CO$$

followed by

$$CH_3CO + O_2 \rightarrow CH_3CO_3$$

$$CH_3CO_3 + NO_2 \rightleftarrows \underset{\text{PAN}}{CH_3C(O)OONO_2}$$

However, the magnitude of these and other photodissociation pathways were not determined in this work.

For glyoxal, the observation of formaldehyde shows that the process

$$(CHO)_2 + h\nu \rightarrow HCHO + CO$$

occurs, with the formaldehyde yield corresponding to approximately 13% of the glyoxal photolyzing via this pathway. (Loss of formaldehyde by photolysis and reaction with OH radicals were minor under the irradiation conditions employed.) Hence the major photodissociation pathway of glyoxal is probably

$$(CHO)_2 + h\nu \rightarrow 2CO + H_2$$

as has been discussed recently (*19*).

While obviously further work is needed concerning the photodissociation pathways and wavelength-dependent quantum yields for the region >290 nm, the present data concerning the photodissociation rates and OH radical rate constants are important and necessary inputs to chemical kinetic computer modeling studies of the aromatic hydrocarbons and of isoprene. In particular, this work indicates that the photolysis rate of methylglyoxal, a critical parameter in NO_x–air photooxidation chemical computer models for toluene and other aromatics (*4*, *6*) is significantly lower than has been previously assumed (thus the present photolysis rate ratio of $k_3/k_{NO_2} = 0.019 \pm 0.005$ can be compared to the previously assumed ratios of ~0.045 (*6*) and 0.15 (*4*)). Thus it is obvious that all present chemical computer models of the aromatic–NO_x–air systems need to be reevaluated in the light of these present data.

Acknowledgments

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Supplementary Material Available

Table A, listing the absorption cross sections for glyoxal, methylglyoxal and biacetyl (3 pages) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper or microfiche (105 × 148 mm, 24× reduction, negatives) may be obtained from Distribution Office, Books and Journals Division, American Chemical Society, 1155 16th St., NW., Washington, DC 20036. Full bibliographic citation (journal, title of article, author, page number) and prepayment, check or money order for \$6.00 for photocopy (\$8.00 foreign) or \$6.00 for microfiche (\$7.00 foreign), are required.

Registry No. O_3, 10028-15-6; OH radical, 3352-57-6; glyoxal, 107-22-2; methylglyoxal, 78-98-8; biacetyl, 431-03-8.

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Mass Transfer of Volatile Organic Contaminants from Aqueous Solution to the Atmosphere during Surface Aeration

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■ The transfer of six organic compounds and of oxygen from aqueous solution to the atmosphere was studied by using an agitated vessel contactor. The transfer rate constants were measured under conditions of controlled energy input in the range $P/V = 0.8$ to 320 W/m^3. The data were interpreted on the basis of the assumption of liquid-phase control. The transfer rate constants, K_La, were proportional to power input in the turbulent regime. Transfer rate constants for the organic compounds were approximately 60% as great as that of oxygen, independent of power input. The ratio of the individual phase-transfer coefficients was inferred to be $k_G/k_L \simeq 25$ in the turbulent regime. Under the conditions of these experiments, the customary criterion for neglecting the gas-phase resistance must be reassessed.

Introduction

Contamination of water supplies by synthetic organic chemicals is a problem of increasing concern in water supply. Particularly, halogenated organic substances are recognized as a threat to public health that in some instances must be dealt with by removing the chemicals from water supplies through suitable treatment. Many of the halogenated compounds of health concern are known to partition from water to air, owing to their hydrophobic behavior in aqueous solution (*1–3*). Hence, transfer to the atmosphere by air–water contact represents a convenient and possibly cost-effective treatment method for removing volatile compounds (*4–7*). Numerous previous studies have shown that the equilibrium is favorable for transfer of halogenated organics to the atmosphere (*1–3*) and that the transfer proceeds at an appreciable rate (*2, 3, 5, 8–10*). Moreover, it has been observed that volatile organic contaminants are transferred to the atmosphere from natural water bodies at substantial rates (*11*).

In this paper a methodology is demonstrated that is useful for quantifying the transfer rates of volatile organic contaminants from an agitated tank to the atmosphere. The methodology consists of comparing the overall liquid-phase transfer rate constants (K_La) of the individual compounds with one another and with that of oxygen, under conditions of controlled energy input.

Methods

The aeration device (Figure 1) consisted of a cylindrical glass vessel open to the atmosphere. The stirrer speed was adjusted by means of a voltage regulator and monitored by means of an electronic counter. The impeller was a compound device comprised of a ring-guarded turbine with three upward-curved blades (75-mm diameter) positioned at the water surface and a flat-bladed paddle (90-mm diameter) positioned at the bottom of the vessel. This design manifested a practical compromise to achieve two objectives: intense disturbance of the air–water interface to promote mass transfer as is typical in water and wastewater treatment, and thorough mixing of the vessel contents to assure representative liquid samples.

The power input to the stirrer was measured with an in-line torque meter (Bex-O-Meter, Model 38) that was installed on the shaft between the motor and the stirrer. The torque was read from a calibrated scale, with a stroboscopic light, while the instrument was rotating. The power input P (W) was calculated from the measured torque τ (J) and the impeller speed N (s^{-1}) by using the relation

$$P = 2\pi\tau N \qquad (1)$$

It was observed that the torque depended strongly on the rotational speed, with the result that the calculated power input P increased approximately in proportion to $N^{3.15}$ ($r^2 = 0.99$), as shown in Figure 2.

The experiments were conducted within a forced-draft exhausting fume hood. The continuous removal of air (0.4 m^3/s) prevented accumulation of organic compounds in the air above the water surface. The air velocity in the vicinity of the aeration vessel was approximately 0.5 m/s.

Water for the mass-transfer experiments was purified by passing tap water through a Milli-Q reagent grade water system. The product water had the following characteristics: TOC, 0.25 mg/L; turbidity, 0.1 TU; electrical conductance, 0.8 μS. The volume of water was 7.3 L in all experiments reported here.

After the water had been equilibrated to a constant temperature of 20 ± 1 °C, the oxygen was purged from the system by bubbling nitrogen through the vessel. Thereafter the reactor was spiked with a solution of the following six compounds: Freon-12, CCl_2F_2; chloroform, $CHCl_3$; 1,1,1-trichloroethane, CH_3CCl_3; carbon tetrachloride, CCl_4; trichloroethylene, $CHCl{=}CCl_2$; tetrachloroethylene, $CCl_2{=}CCl_2$. Their properties are summarized in Table I. These six compounds were chosen because their Henry's constants cover a range of nearly 3 orders of magnitude,

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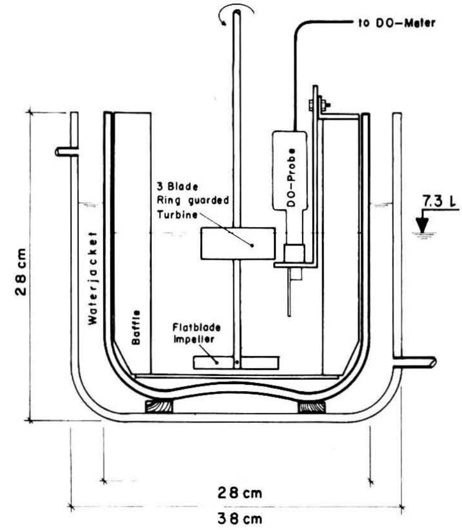

Figure 1. Surface aeration contactor.

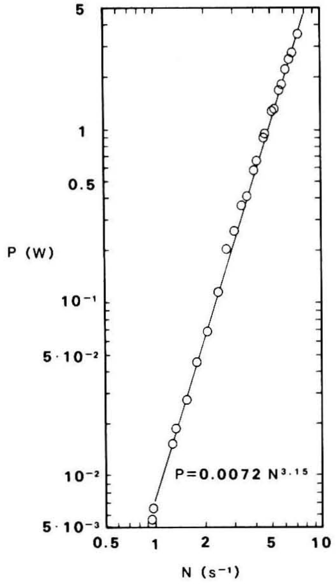

Figure 2. Power input.

from 5.3×10^{-3} to 1.5 atm·m^3·mol^{-1}.

The spiking solution was prepared by first bubbling CCl_2F_2 gas through 5 mL of methanol until approximately 100 mg of CCl_2F_2 had absorbed; then the remaining five compounds were added to the methanol with a syringe: chloroform, 45 μL; trichloroethane, 50 μL; carbon tetrachloride, 45 μL; trichloroethylene, 50 μL; tetrachloroethylene, 40 μL. Thereafter methanol was added to make up a total solution volume of 10 mL, resulting in concentrations on the order of 5 mg/L. This quantity of methanol was found not to affect mass transfer significantly (*15*).

After 1 min of mixing following introduction of the organic compounds, an initial sample was taken. Thereafter nine samples were taken at regular intervals. Concurrently, the oxygen concentration in the reactor was measured with a dissolved oxygen (DO) probe (YSI Model 5720A) and plotted on a chart recorder.

Table I. Properties of Compounds Studied

compd	mol wt, amu	Henry's const, atm·m^3·mol^{-1}	diffusivity[a] in water at inf dilut, 10^{-9} m^2·s^{-1}
CCl_2F_2	120.9	1.5[b]	1.02
CCl_4	153.8	2.4×10^{-2} [c]	0.85
$CCl_2{=}CCl_2$	165.8	1.5×10^{-2} [c]	0.79
CH_3CCl_3	133.4	1.5×10^{-2} [c]	0.83
$CHCl{=}CCl_2$	131.4	9.9×10^{-3} [c]	0.86
$CHCl_3$	119.4	5.3×10^{-3} [c]	0.94
O_2	32.0	0.73[d]	1.88[e]

[a] Estimated by using the Wilke–Chang correlation (*12*), with the molar volume estimated by means of Schroeder increments (*13*) and the association parameter $\phi = 2.26$ according to the recommendation of Hayduk and Laudie (*14*). [b] Estimated from vapor pressure and solubility data, as proposed by Mackay and Wolkoff (*1*). [c] Measured (*15*, p 69). [d] Measured (*16*). [e] Calculated as in *a*, but by using measured value of the molar volume (*14*).

The range of stirrer speeds was chosen in view of the following constraints: Below 65 rpm, complete mixing could not be guaranteed, whereas above 375 rpm appreciable amounts of air bubbles began to be entrained beneath the water surface. Appreciable surface waves were observed even at the lowest stirrer speeds. A spray of droplets was formed at speeds in excess of 150 rpm, increasing with increasing speed to form a virtually continuous sheet of spray emanating from the surface impeller at the highest speeds.

The sample intervals ranged from 1 h for the slowest stirrer speed (65 rpm) to 1 min for the highest stirrer speed (375 rpm). The first and last samples typically differed by an order of magnitude in concentration. The sample was drawn from the vessel with a large Mohr pipet under a slight vacuum, transferred into a 15-mL hypovial sealed with a Teflon-faced rubber septum, and stored at 4 °C prior to analysis. Analysis generally was performed within 1 day.

The six halogenated organics were analyzed quantitatively by a procedure of direct pentane extraction (*17, 18*) in the sealed vial in which the sample was stored, followed by injection of an aliquot of the pentane layer into a gas chromatograph (2-m packed column, 10% squalane on chromosorb W(AW)) fitted with an electron capture detector (ECD). Quantitation was achieved by comparison of the peak area to that of a known quantity of the internal standard, 1,2-dibromoethane. The ECD peak areas were converted to concentrations by multiplying by response factors previously determined for the corresponding compounds.

Mass Transfer Theory

Under the conditions of the experiments in this work, the mass-transfer rate expression can be written as in the customary fashion:

$$dC_L/dt = K_L a C_L \qquad (2)$$

where C_L = bulk average solute concentration in the liquid (g/m^3), K_L = overall mass-transfer rate coefficient based on the liquid-phase resistance (m/s), and a = specific surface area (m^2/m^3). The accumulation of organic compounds in the air above the water surface is implicitly ignored in eq 2, owing to the rapid replenishment of air

Table II. Results of Mass-Transfer Experiments

stirrer speed, s^{-1}	power, W	mass transfer rate const, K_La, s^{-1}						
		O_2	CCl_2F_2	CCl_4	$CCl_2{=}CCl_2$	CH_3CCl_3	$CHCl{=}CCl_2$	$CHCl_3$
6.3	2.34	5.8×10^{-3}	4.1×10^{-3}	3.8×10^{-3}	3.7×10^{-3}	3.7×10^{-3}	3.6×10^{-3}	3.2×10^{-3}
1.3	0.018	1.4×10^{-4}	9.0×10^{-5}	8.6×10^{-5}	8.7×10^{-5}	8.6×10^{-5}	9.1×10^{-5}	8.9×10^{-5}
4.1	0.60	2.1×10^{-3}	1.5×10^{-3}	1.4×10^{-3}	1.4×10^{-3}	1.4×10^{-3}	1.4×10^{-3}	1.2×10^{-3}
0.95	0.0061	1.3×10^{-4}	7.8×10^{-5}	7.5×10^{-5}	7.7×10^{-5}	7.5×10^{-5}	8.0×10^{-5}	7.8×10^{-5}
6.0	2.01	5.7×10^{-3}	4.0×10^{-3}	3.7×10^{-3}	3.7×10^{-3}	3.6×10^{-3}	3.5×10^{-3}	3.1×10^{-3}
4.5	0.85	3.3×10^{-3}	2.2×10^{-3}	2.1×10^{-3}	2.0×10^{-3}	2.0×10^{-3}	2.0×10^{-3}	1.8×10^{-3}
2.2	0.084	2.9×10^{-4}	1.8×10^{-4}	1.8×10^{-4}	1.7×10^{-4}	1.7×10^{-4}	1.8×10^{-4}	1.7×10^{-4}
2.9	0.20	6.2×10^{-4}	3.5×10^{-4}	3.3×10^{-4}	3.2×10^{-4}	3.2×10^{-4}	3.4×10^{-4}	3.1×10^{-4}
6.2	2.28	6.5×10^{-3}	4.5×10^{-3}	4.1×10^{-3}	3.9×10^{-3}	3.9×10^{-3}	3.9×10^{-3}	3.4×10^{-3}
5.2	1.27	4.2×10^{-3}	2.9×10^{-3}	2.7×10^{-3}	2.5×10^{-3}	2.6×10^{-3}	2.6×10^{-3}	2.3×10^{-3}
4.2	0.68	2.5×10^{-3}	1.7×10^{-3}	1.6×10^{-3}	1.5×10^{-3}	1.5×10^{-3}	1.5×10^{-3}	1.4×10^{-3}
3.3	0.31	8.8×10^{-4}	5.8×10^{-4}	5.5×10^{-4}	5.4×10^{-4}	5.4×10^{-4}	5.6×10^{-4}	5.2×10^{-4}
5.4	1.46	5.1×10^{-3}	3.5×10^{-3}	3.2×10^{-3}	3.1×10^{-3}	3.2×10^{-3}	3.1×10^{-3}	2.7×10^{-3}
2.4	0.12	4.2×10^{-4}	2.5×10^{-4}	2.3×10^{-3}	2.3×10^{-3}	2.3×10^{-3}	2.4×10^{-3}	2.3×10^{-3}
4.7	0.96	3.5×10^{-3}	2.4×10^{-3}	2.2×10^{-3}	2.2×10^{-3}	2.2×10^{-3}	2.2×10^{-3}	1.9×10^{-3}
5.7	1.75	5.1×10^{-3}	3.5×10^{-3}	3.2×10^{-3}	3.2×10^{-3}	3.2×10^{-3}	3.2×10^{-3}	2.9×10^{-3}

by the exhausting fume hood in which the experiments were conducted.

The overall mass-transfer coefficient K_L in eq 2 may be influenced by both the liquid- and gas-phase resistances, but for very volatile substances such as those studied in this work the liquid-phase resistance is expected to dominate (*8–10*), according to

$$R_T = R_L + R_G \tag{3}$$

$$1/K_La = 1/k_La + (RT/H)1/k_Ga \tag{4}$$

where R_T, R_L, and R_G = total, liquid-phase, and gas-phase mass-transfer resistances, respectively, K_L = overall mass-transfer coefficient (m/s), k_L and k_G = liquid- and gas-phase transfer coefficients (m/s), respectively, R = universal gas constant = 82.06×10^{-6} atm·m^3·mol^{-1}·K^{-1}, T = absolute temperature (K), and H = Henry's constant (atm·m^3·mol^{-1}). The relative importance of the liquid- and gas-phase resistances can be assessed using eq 5. Clearly,

$$R_L/R_G = (H/RT)k_G/k_L \tag{5}$$

the liquid-phase resistance dominates for large values of the Henry's constant and large values of the ratio k_G/k_L. Mackay and co-workers (*19, 20*) state that the ratio k_G/k_L typically is on the order of 100 for conditions of surface aeration, based largely on interpretation of mass-transfer rates at the air-sea interface. This approach generally has been accepted by subsequent workers (*8, 10, 21*) in defining the criterion for liquid-resistance control.

Following Mackay and Leinonen's recommendations (*19*), it was estimated from eq 5 that the liquid-phase resistance dominates [$(R_L/R_G) \geq 20$] for all compounds having $H > 4.8 \times 10^{-3}$ [atm·m^3·mol^{-1}]. All of the compounds studied in this work satisfy this definition of liquid-phase control (Table I). This assumption regarding the relative magnitudes of the individual phase resistances is reexamined below.

Results

Values of the mass-transfer rate constant, K_La, were determined in 16 experiments. A typical data set is shown in Figure 3. The data were correlated as $-\ln [C_L(t)/C_L(0)]$ vs. t, in accordance with the integrated form of eq 2, namely

$$-\ln [C_L(t)/C_L(0)] = K_La(t - t_0) \tag{6}$$

where $C_L(t)$ and $C_L(0)$ are the solute concentrations in samples taken at times t and t_0, respectively. The linearity of the typical data set (Figure 3) attests to the goodness of fit of the mass-transfer model. The value of r^2, the square of the correlation coefficient, generally exceeded 0.99 and in no case was less than 0.98 for oxygen or for any of the six organic compounds. The experimental data are summarized in Table II. Additional details are available elsewhere (*22*).

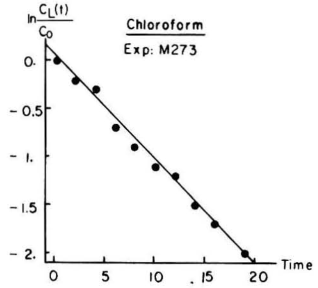

Figure 3. Example data plot: stripping of $CHCl_3$ from Milli-Q water at an agitator speed of 273 rpm.

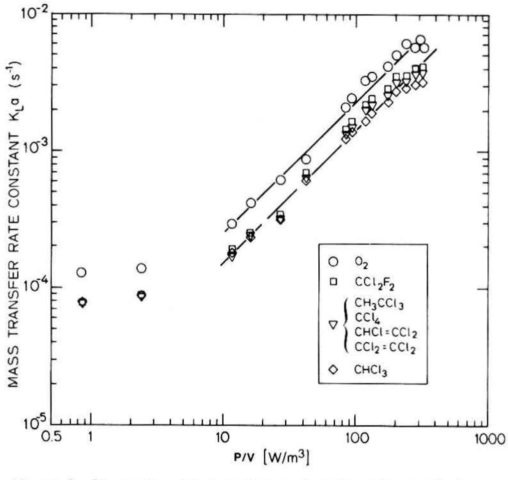

Figure 4. Power dependence of mass-transfer rate constants.

Discussion

Dependence on Power Input. The mass-transfer rate constant K_La depended significantly upon the power input, as shown in Figure 4. Values of K_La (s^{-1}) are shown as a function of the specific power input (W/m^3). For power

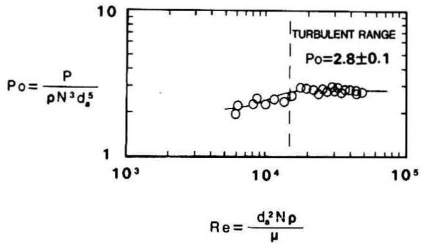

Figure 5. Power curve for the agitated vessel.

inputs greater than 10 W/m^3, the value of K_La increased nearly linearly with power input, as indicated by the slopes of the regression lines in Figure 4. The relation for oxygen obtained from linear regression of log K_La on log (P/V) is

$$(K_La)_{O_2} = 2.9 \times 10^{-5}(P/V)^{0.95} \qquad (7)$$

with $r^2 = 0.99$, whereas that for the organic compounds is

$$(K_La)_{org} \simeq 1.6 \times 10^{-5}(P/V)^{0.98} \qquad (8)$$

with $r^2 = 0.98$. According to eq 7 and 8, the mass-transfer rate constant is nearly proportional to the power input. (The amount of water was not varied in the experiments.) The exponent of the power dependence was significantly different ($\alpha = 0.05$) from unity for oxygen, but not for the organic compounds. Nevertheless, for practical purposes the transfer rate constant for oxygen as well as the organic compounds can be considered approximately proportional to the power input, e.g., for oxygen $(K_La)_{O_2} \simeq 2.5 \times 10^{-5}(P/V)$ with $r^2 = 0.99$, in the range $10 < P/V < 200$ W/m^3.

The relatively weak dependence of K_La on the power input in the range below $P/V = 10$ W/m^3 is attributed to deviation from turbulent mixing at low levels of energy input. It is customary (*23, 24*) to characterize hydrodynamic conditions in an agitated vessel in terms of the relation between two dimensionless groups: the Power number, $Po = P/\rho N^3 d_a^5$, and the impeller Reynolds number, $Re = \rho N d_a^2/\mu$. The Power number is a measure of the impeller drag coefficient (*24*, p 124) and for baffled tanks in the turbulent range is independent of the Reynolds number (*25*, p 125). The relationship between the Power and Reynolds numbers for the impeller and vessel configuration in this work, calculated by assuming an effective impeller diameter of $d_a = 0.08$ m, is shown in Figure 5. The Power number increased gradually with increasing Reynolds number up to $Re = 15000$, reaching a plateau of $Po = 2.79 \pm 0.10$ in the range $15000 < Re < 45000$. This is in accord with the general observation that most impellers reach the turbulent regime at values of Re slightly greater than 10000 (*24*, pp 132–133) and confirms that turbulent conditions prevailed in this work where $Re \geq 15000$ ($P/V \geq 15$ W/m^3).

Hence, the proportionality between K_La and P/V appears to be limited to the turbulent region. Fortunately, mixing conditions usually assure turbulence in large-scale surface aerators, as well as in most major natural water bodies.

Table III. Experimental Values of the Mass-Transfer Proportionality Coefficient, ψ

compd	$\psi_i = (K_La)_i/(K_La)_{O_2}$ av ± std dev (n = 16)	regression eq^a	r^2
CCl_2F_2	0.66 ± 0.04	$0.626 + 12.4(K_La)_{O_2}$	0.51
CCl_4	0.62 ± 0.03	$0.593 + 8.2(K_La)_{O_2}$	0.27
$CCl_2{=}CCl_2$	0.61 ± 0.03	$0.590 + 8.4(K_La)_{O_2}$	0.12
CH_3CCl_3	0.61 ± 0.03	$0.590 + 5.9(K_La)_{O_2}$	0.15
$CHCl{=}CCl_2$	0.62 ± 0.03	$0.616 - 0.3(K_La)_{O_2}$	0.07
$CHCl_3$	0.56 ± 0.04	$0.587 - 9.2(K_La)_{O_2}$	0.34

^{a} Valid in the range $1.3 \times 10^{-4} < (K_La)_{O_2} < 6.5 \times 10^{-3}$ s^{-1}. The coefficients of $(K_La)_{O_2}$ are significantly different from zero at the $\alpha = 0.05$ level for the following compounds: CCl_2F_2, $CHCl_3$, and CCl_4.

Oxygen as a Reference Compound. It follows from the comparison in Figure 4 that the transfer rate constants for the organic solutes are approximately proportional to that of oxygen, an observation consistent with the findings of previous investigators (*8, 10*). This proportionality is expressed as

$$(K_La)_i = \psi_i(K_La)_{O_2} \qquad (9)$$

where $(K_La)_i$ and $(K_La)_{O_2}$ are the mass-transfer rate constants for compound i and oxygen, respectively, and ψ_i is the coefficient of proportionality for compound i (*5, 10*). The values of the proportionality coefficient are summarized in Table III. The average values of ψ are tightly grouped in the range from 0.56 ($CHCl_3$) to 0.66 (CCl_2F_2), with four compounds (CH_3CCl_3, CCl_4, $CHC{=}CCl_2$, and $CCl_2{=}CCl_2$) exhibiting virtually identical values of 0.61–0.62. The value of ψ was found to be statistically independent of the magnitude of $(K_La)_{O_2}$ for three compounds ($CHCl{=}CCl_2$, $CCl_2{=}CCl_2$, and CH_3CCl_3). Of the three compounds for which a significant dependence was observed, two of the ψ values appeared to increase with $(K_La)_{O_2}$, whereas one of the ψ values varied inversely with $(K_La)_{O_2}$. None of the ψ values changed by more than 15% over the range of $(K_La)_{O_2}$ values measured. Recalling that K_La is proportional to the specific power input, we can state that the proportionality between the mass-transfer coefficients of volatile organic solutes and that of oxygen is for practical purposes independent of the mixing intensity under the conditions of this work.

Dependence on Diffusivity. It is not surprising that the values of K_La for the organic compounds agree closely with one another and that K_La is consistently smaller for the organic compounds studied than for oxygen. These similarities and differences could be predicted from the relative magnitudes of the diffusivities in water (Table I); the diffusivities of the organic compounds studied range from 42% to 54% as great as that of oxygen.

In this work it was found that the value of K_La was proportional to the diffusivity to the 0.66 power:

$$\frac{(K_La)_i}{(K_La)_{O_2}} = \left(\frac{D_i}{D_{O_2}}\right)^{\Omega} = \left(\frac{D_i}{D_{O_2}}\right)^{0.66} \qquad (10)$$

on the average, where D = diffusivity in water at infinite dilution, estimated by using generalized correlations (*12–14*) (Table I). The accuracy of the diffusivity estimates is believed to be approximately ±10% (*12*). The average values of the diffusivity exponent Ω (eq 10) for the individual compounds are given in Table IV, calculated by using the diffusivities in Table I. The Ω value for chloroform was significantly higher than that of the other compounds; omitting the $CHCl_3$ data reduces the overall average value of Ω from 0.66 to 0.62. The 95% confidence interval for Ω for the five most volatile organic compounds studied (CCl_2F_2, CCl_4, $CCl_2{=}CCl_2$, CH_3CCl_3, and $CHCl{=}CCl_2$) was $0.61 < \Omega < 0.63$ (n = 80 observations).

These results agree closely with Smith et al. (*8*), who found K_La to depend on the diffusivity to an exponent 0.61. Skelland (*25*, pp 101–102) noted that the diffusivity exponent in eq 10 frequently is found to lie in the range

Table IV. Estimated Values of the Diffusivity Exponent and the Resistance Ratio

compd	diffusivity exp, Ω, mean ± std dev[a]	resistance ratio, R_L/R_T
CCl_2F_2	0.65 ± 0.09	1.000
CCl_4	0.63 ± 0.07	0.96
$CCl_2{=}CCl_2$	0.57 ± 0.07	0.94
CH_3CCl_3	0.62 ± 0.06	0.94
$CHCl{=}CCl_2$	0.63 ± 0.06	0.91
$CHCl_3$	0.84 ± 0.09	0.85
O_2		0.999

[a] $n = 16$ observations.

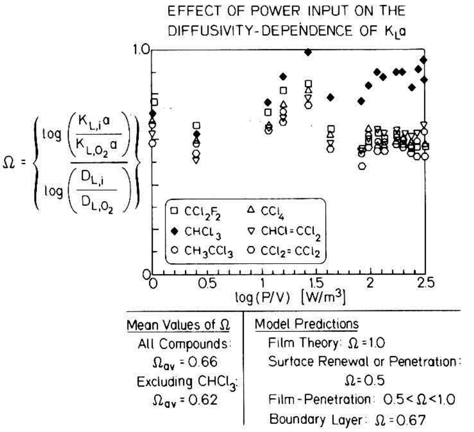

Figure 6. Diffusivity-dependence exponents for overall liquid-phase transfer rate constants.

0.5–0.67. On the other hand, some investigators (*5, 10, 26*) perceive their results as confirming the validity of the film theory, according to which K_La is proportional to the diffusivity to the first power.

The film-penetration theory (*27*) predicts that the diffusivity exponent Ω may vary in the range 0.5–1.0 with changing intensity of turbulence, from a maximum of unity corresponding to film diffusion under laminar conditions to a minimum of 0.5 corresponding to a surface renewal mechanism under conditions of extreme turbulence. To test the applicability of the film-penetration hypothesis to our data, the diffusivity exponent is shown as a function of specific power input in Figure 6. The value of the diffusivity exponent was calculated for each organic solute at each experimental condition by using the relation

$$\Omega_i = \log((K_La)_i/(K_La)_{O_2})/\log(D_i/D_{O_2}) \qquad (11)$$

where Ω = diffusivity exponent in eq 10. The values of Ω in the turbulent range were for the most part closely grouped around Ω = 0.6, especially for $P/V > 30$ W/m³, although $CHCl_3$ appeared to behave as an exception. Except for $CHCl_3$, there is no clear trend in Ω as P/V increases. Even at the low extreme, $P/V \simeq 1$, the values of Ω are clustered around Ω = 0.6, although three somewhat higher sets of Ω values were found at intermediate P/V values in the range $10 < P/V < 30$. In general, the prediction of the film-penetration theory, that Ω should decrease from unity toward 0.5 with increasing energy input, is not borne out by these data. Indeed, the value of Ω for $CHCl_3$ tends in the opposite direction, increasing with increasing P/V.

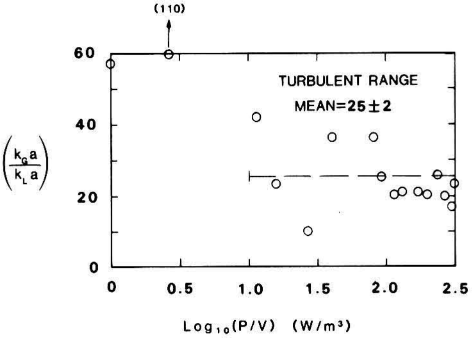

Figure 7. Estimated ratio of gas-phase to liquid-phase transfer rate constants.

Gas-Phase Resistance. The apparent anomalous behavior of chloroform may be caused by the influence of the gas-phase resistance. The gas-phase resistance has been ignored in the data analysis up to this point, based on the assumption of liquid-phase control, justified as described above. If the gas-phase resistance were in fact significant, the overall transfer rate constant would be diminished according to eq 3 and 4. To assess this possibility, the gas-phase resistance was estimated for $CHCl_3$ by subtracting from the total resistance the value of the liquid-phase resistance calculated by assuming that the true K_La value was consistent with Ω = 0.62 as was the case for the other compounds. The result of this calculation is shown in Figure 7 as the ratio k_Ga/k_La; the mean value of that ratio was 25 ± 2 for the experiments in the turbulent range, $P/V > 15$ W/m³. Hence, the estimated value of k_Ga/k_La for $CHCl_3$ in our experiments was substantially smaller than is customarily assumed (*8, 10, 19–21*) for purposes of assessing the potential significance of the gas-phase resistance, i.e., $k_Ga/k_La \simeq 100$.

This conclusion must be considered speculative, however, because of the indirect method used to calculate the ratio k_Ga/k_La and the considerable uncertainty in data and, to a lesser extent, because of possible inaccuracies in the diffusivity estimates. Especially in the region $P/V < 10$ W/m³, the estimation of k_Ga/k_La entailed calculating the difference between large positive values, a procedure that inherently is prone to large relative error. Also, the estimate of k_Ga/k_La may be biased by our neglect of potentially significant changes in the bulk gas-phase concentration; however, the fractional saturation of the bulk gas phase is believed to have been less than 5% in all of our experiments, which would justify neglecting the change in the concentration driving force.

Assumption of Liquid-Phase Control. These uncertainties notwithstanding, the assumption of liquid-phase control was reevaluated for the compounds studied in this work by computing the resistance ratios using eq 3 with a ratio $k_G/k_L = 25$ and the Henry's constants given in Table I. The resulting resistance ratios are summarized in Table IV as the fraction (R_L/R_T) of the total resistance represented by the liquid-phase resistance. The computed resistance fraction was greater than 0.90 for oxygen and the five most volatile compounds but not for the least volatile compound, $CHCl_3$.

The quantitative estimation of the resistance ratio as described here is subject to considerable uncertainty but serves to caution us that the assumption of liquid-phase control needs to be examined more carefully from the outset in studies such as this one. It may be misleading to extrapolate values of k_G/k_L from large natural systems to estimate the resistance ratio in laboratory experiments conducted under vastly different hydrodynamic conditions and vice versa. Also, it is reasonable to expect that the gas-phase resistance is less important at the air-sea interface than with mechanical surface aeration, where deliberate agitation of the aqueous phase may preferentially enhance the liquid-phase coefficient relative to that of the gas phase.

Conclusions

The mass transfer of all of the solutes studied in this work could be interpreted satisfactorily by using a model based on liquid-resistance control without substantial accumulation of the diffusing substance in the surrounding air. However, the data suggest that the gas-phase resistance may have been more significant than was predicted by using the usual criterion for the ratio of the individual transfer coefficients. Further work is necessary to assess the possible influence of the gas-phase resistance on the transfer of volatile organic solutes in practical applications.

The rate of mass transfer of volatile organic contaminants was shown to be proportional to that of oxygen, with a proportionality coefficient of approximately 0.6 for the compounds studied. This proportionality was essentially independent of the mixing intensity. It appears that the mass-transfer rate constant is dependent on the solute's diffusivity in water raised to a power approximately equal to 0.62.

In the turbulent region, the transfer rate constants of chlorinated organic solutes as well as oxygen were proportional to the power input. There are indications that the model is relevant to understanding transfer of organic contaminants to the atmosphere from natural waters, as well as to interpreting the effects of surface aeration during water and wastewater treatment.

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Christine Matter-Müller and Christoph Munz participated in a preliminary phase of this research. James Westrick and Paul Warner made helpful suggestions.

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U.S. "Mussel Watch" 1976–1978: An Overview of the Trace-Metal, DDE, PCB, Hydrocarbon, and Artificial Radionuclide Data†

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■ Data are presented for trace metals, polychlorinated biphenyls (PCBs), aromatic hydrocarbons and ^{239,240}Pu in *Mytilus edulis*, *M. californianus*, and *Crassostrea* sp. colected in the U.S. Mussel Watch program in 1976–1978 from 62 locations on the U.S. east and west coasts. General similarities in geographical distributions of concentrations were present in all 3 years with at least an order of magnitude elevation of concentrations of Pb, PCBs, and fossil fuel hydrocarbons in bivalves sampled near the larger urban areas. Elevated Cd and ^{239,240}Pu concentrations in bivalves from the central California coast are apparently related to enrichments of Cd and nuclear weapons testing fallout ^{239,240}Pu in intermediate depth water of the North Pacific and upwelling of this water associated with the California Current system. Our data have revealed no evidence of local or regional systematic elevations of environmental concentrations of ^{239,240}Pu as a result of effluent releases from nuclear power reactors.

Introduction

The real and perceived problems with the disposal of chemical wastes on land have once again focused attention on the disposal of industrial and domestic wastes, sewage sludge, and dredge spoils in the ocean (*1–4*). Herein, the relative merits of ocean disposal, land disposal, incineration, or technological innovation and their respective costs to society in terms of economics and quality of life are not assessed. Rather, we submit that these concerns emphasize the need for improved knowledge of the current state of chemical pollution in U.S. coastal waters and the processes controlling the input, fate, and effects of the pollutants. The sentinel organism or "Mussel Watch" concept (*5–9*) is one approach to assess the present status of chemical pollution in U.S. coastal waters and to identify geographic areas of concern and topics for new or renewed scientific research.

The rational for the sentinel organism approach using the common mussels (*Mytilus* spp.), various oysters (*Crassostrea* and *Ostrea*) species, and other bivalves are as follows (*5–9*):

1. Bivalves are cosmopolitan (widely distributed geographically). This characteristic minimizes the problems inherent in comparing data for markedly different species with different life histories and relationships with their habitat.
2. They are sedentary and are thus better than mobile species as integrators of chemical pollution status for a given area.
3. They concentrate many chemicals by factors of 10^2–10^5 compared to seawater in their habitat. This makes trace constituent measurements often easier to accomplish in their tissues than in seawater.
4. Inasmuch as the chemicals are measured in the bivalves, an assessment of biological availability of chemicals is obtained.
5. In comparison to fish and crustacea, bivalves exhibit low or undetectable activity of those enzyme systems that metabolize many xenobiotics such as aromatic hydrocarbons and polychlorinated biphenyls (PCBs). Thus a more accurate assessment of the magnitude of xenobiotic contamination in the habitat of the bivalves can be made.
6. They have many relatively stable local populations extensive enough to be sampled repeatedly, providing data on short- and long-term temporal changes in concentrations of pollutant chemicals.
7. They survive under conditions of pollution that often severely reduce or eliminate other species.
8. They can be successfully transplanted and maintained on subtidal moorings or on intertidal shore areas where normal populations do not grow—most often due to lack of suitable substrate—thereby allowing expansion of areas to be investigated.
9. They are commercially valuable seafood species on a worldwide basis. Therefore, measurement of chemical contamination is of interest for public health considerations.

We herein provide an overview of the results of selected U.S. Mussel Watch measurements of trace metals, artificial radionuclides, PCBs, 1,1′-(2,2-dichlorethenylidene)bis(4-chlorobenzene) (DDE), and fossil fuel hydrocarbons for samples collected along the U.S. coast in 1976–1978. The initial results for the 1976 and some 1977 samples have already been reported (*5–8*). More complete data sets and extensive interpretations are being reported elsewhere for the 1976–1978 collections (*10–13*).

Methods

The sampling locations for the 1976 collections are given in Figure 1. Some changes in station locations during 1977 and 1978 were dictated by changes in population densities, accessibility to collection sites, or the need to add stations in areas of particular concern.

Station locations were generally on the outer coast, at mouths of estuaries, or in a few selected harbor areas, e.g., San Diego, Los Angeles, San Francisco, Boston. No attempt was made to sample extensively in those large estuaries such as Chesapeake Bay or Narragansett Bay where chemical pollutant research programs are ongoing (*14–18*). In general, the sampling was designed to support an assessment of regional or temporal trends of chemical pollution at the interface between the outer coast and the ocean.

Detailed descriptions of sampling locations, collection procedures, and analytical methodology are available (*5, 9, 20*), and only information needed for the purposes of clarity will be summarized here. Organisms were collected with care to avoid contamination during sampling. Polyethylene gloves were used, and the bivalves were carefully placed in polyethylene bags (trace-metal and transuranic analyses samples) or aluminum foil bags (PCB, DDE,

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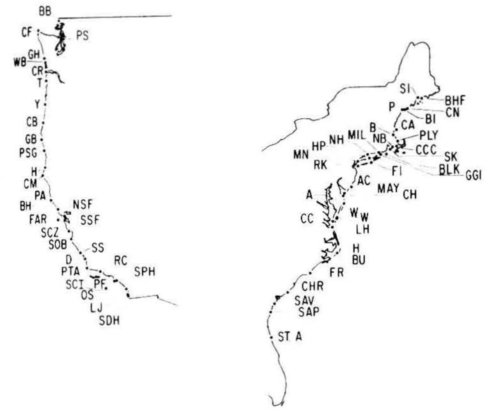

Figure 1. Locations of U.S. Mussel Watch sampling locations for the east and west coasts. Data for several Gulf coast locations are not complete, and thus that region is not included in this overview. Detailed sample locations and descriptions are available from the authors and in ref 8, 11, and 19.

hydrocarbon analyses samples). Samples were kept frozen at -10 to -20 °C and air shipped frozen periodically to the laboratories where they were kept frozen at these temperatures until analysis—usually within a year. Combined tissues of between 5 and 250 bivalves were homogenized depending on the constituents to be measured. Trace-metal analyses were accomplished by drying aliquots of the homogenate and digesting with nitric acid and then perchloric acid or charring and treating with hydrogen peroxide. Metals were measured by analysis of solutions of the digestate by flame and/or flameless atomic absorption spectrometry.

Plutonium, americium, and, in some cases, cesium were isolated from much larger sample aliquots by drying, oxidative acid digestion, and a series of coprecipitations and ion-exchange column separations, using appropriate carrier elements and isotopic yield monitors. Radiocesium was finally measured by low-level β-particle counting of thin layers of precipitated cesium chloroplatinate. Plutonium or americium plus curium were finally measured by α-particle spectrometry on the elements electroplated on polished stainless steel or platinum disks. Brief descriptions of the methods and of their performance in intercomparisons are to be published (*20*); details, and other references, can be obtained from individual authors.

Hydrocarbons and chlorinated hydrocarbons were extracted from aliquots of homogenized tissue samples by alkaline digestion or solvent extraction. The compounds of interest were isolated from other lipids in the extract by column chromatography using silica gel or alumina over silica gel. The isolated compounds were analyzed by gas chromatography using packed columns and glass capillary columns in gas chromatographs equipped with flame ionization detectors and/or ^{63}Ni electron capture detectors. Compounds were tentatively identified by Kovat's retention indices (*11*) with confirmation for representative samples by glass capillary gas chromatography–mass spectrometry. Aromatic hydrocarbons were quantitatively measured by glass capillary gas chromatography–mass spectrometry.

Most of these measurements for trace constituents require caution when comparing data between two laboratories or attempting to establish temporal or geographical differences between stations. An intercalibration/intercomparison program with measurements of split samples or aliquots of specially prepared homogenates has been part of the Mussel Watch program and continues. Results of the initial stages have already been reported (*11, 20*) and provide us with a basis for interpretations of data sets from two or three laboratories.

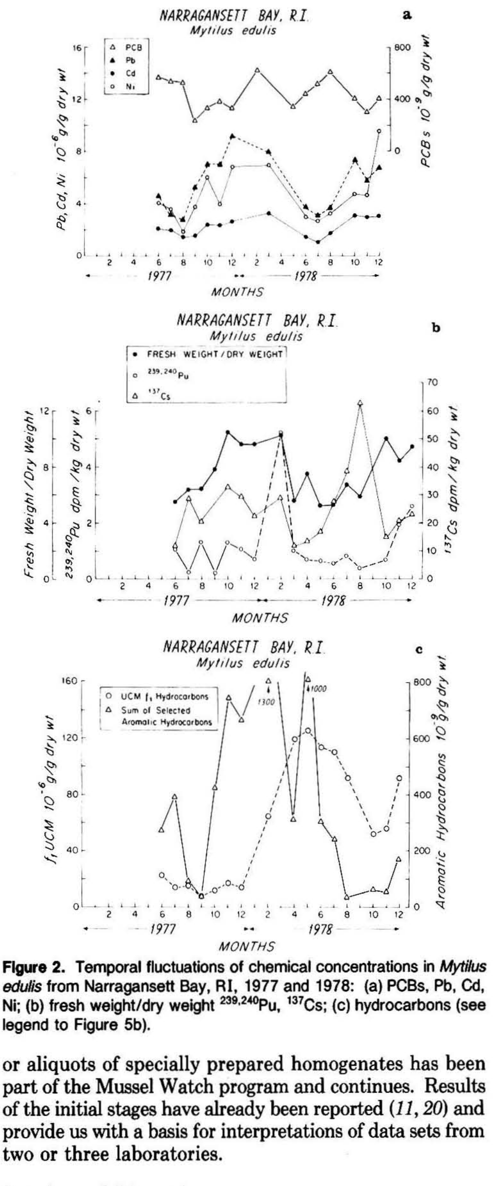

Figure 2. Temporal fluctuations of chemical concentrations in *Mytilus edulis* from Narragansett Bay, RI, 1977 and 1978: (a) PCBs, Pb, Cd, Ni; (b) fresh weight/dry weight ^{239,240}Pu, ^{137}Cs; (c) hydrocarbons (see legend to Figure 5b).

Results and Discussion

Monthly Collections and Temporal Variability. Temporal variability of concentrations of chemicals on the scale of months was investigated by analyses of collections from Narragansett Bay, RI (*Mytilus edulis*), and Bodega Head, CA (*Mytilus californianus*). Ice cover prevented sampling in several winter months at Narragansett Bay, and ice scouring, very low temperatures, or some unknown event decimated the 1976 sampling station mussels, causing a relocation of the station during 1977 and 1978. Nevertheless, sufficient data were obtained to demonstrate temporal fluctuations of metals, PCBs, and hydrocarbons at this station. These data are presented in Figure 2. Data for *Mytilus californianus* sampled at Bodega Head, CA, are presented in Figure 3.

The data for temporal variability as reported in Figures

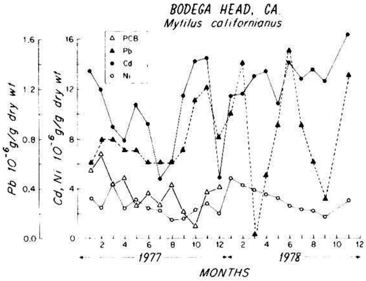

Figure 3. Temporal fluctuations of PCBs, Pb, Cd, and Ni in *Mytilus californianus* from Bodega Head, CA, 1977 and 1978.

2 and 3 are from analyses of individual chemicals by a single laboratory. It should be noted that at low concentrations of DDE and PCBs (10–50 × 10^{-9} g/g dry weight), the between laboratory variability for analyses of splits of collections of whole mussels from Bodega Head was as large as a factor of 2 in some cases (*11*). The scale of this between laboratory variability constrains assessment of temporal fluctuations of low concentrations of organic pollutants if data sets are combined from several laboratories.

There are several possible reasons for temporal fluctuations in concentrations of the chemicals in these bivalves: changes in biological or biochemical activity of the mussels, e.g., filtration rate or spawning activity; changes in biological or biochemical activity of other organisms commonly associated with bivalves, e.g., microbial activity or phytoplankton uptake of the chemicals in question; changes in the environmental concentrations, forms (solid, adsorbed, colloidal), or species of the chemicals in question.

We will not treat this question further except to state that our data and those of others (*6*, *21*) show that temporal fluctuations can be complicated and are not ascribable to a single factor. The fluctuations of the organic pollutants are obviously not all in synchrony even though many of them such as PCBs and aromatic hydrocarbons might be expected to behave similarly due to their limited water solubility and similar lipophilicity.

A comparison of the data for a few trace metals and PCBs from the Bodega Head time series samples (Figure 3) with data from Narragansett Bay samples shows that not all bivalve populations have temporal variability of the same magnitude nor are the variations necessarily in synchrony. This is similar to conclusions of Boyden and Phillips (*21*) investigating trace-metal variability in oysters.

We have presented these data on temporal variability to provide a framework within which we can interpret data from stations sampled once a year on the U.S. coast. We are continuing to investigate temporal variability and its causative factors so that comparisons between stations, or for the same station a few years apart, can be interpreted with greater certainty. The ability to determine subtle concentration gradients on geographical or temporal scales can be important in providing an early indication of significant changes in pollutant levels.

Geographical Results. A detailed presentation and discussion of the Mussel Watch data from the point of view of natural and anthropogenic sources are presented elsewhere (*8*, *10–13*). We will present and discuss the Pb, Cd, PCB, and selected hydrocarbon and transuranic radionuclide data as examples and, as it proves valuable, to compare these sets of data. We do not imply our other data are less important. Rather, the entire data set for trace metals, radionuclides, and organic pollutants is too large to treat extensively in an overview.

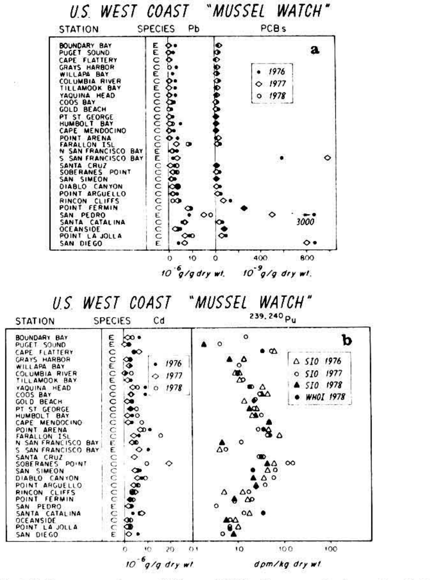

Figure 4. (a) Concentrations of Pb and PCBs in mussels from the U.S. west coast 1976–1978. Species: E = *Mytilus edulis*, C = *Mytilus californianus*. (b) Concentrations of Cd and ^{239,240}Pu in mussels from the U.S. west coast 1976–1978. SIO, Scripps Institution of Oceanography; WHOI, Woods Hole Oceanographic Institution.

The distributional pattern of concentrations of the trace metals Pb, Cd, Ag, Zn, Cu, and Ni in mussels and oysters for both the coasts repeats each year 1976, 1977, and 1978 within the uncertainty of a factor of 2–4-fold introduced by the temporal variability expected at each station. The uncertainty might be less than 2–4-fold for comparisons of some individual stations where samples were collected each year within a week or two of the same date.

Some of the first year lead analyses involved flame atomic absorption. This method is less sensitive than the graphite furnace technique used for all the other samples. This complicates comparison of the 1976 results with those of 1977 and 1978. However, the same geographical trends are clearly evident from all these data sets. Lead data for all 3 years are presented in Figures 4a and 5a.

Lead concentrations in mussels from Washington, Oregon, and northern California were consistently low (less than 1.6 × 10^{-6} g of Pb/g dry weight) for 1977 and 1978 collections. With few exceptions, mussels from central California coastal areas (San Simeon to San Francisco) had low lead concentrations. In 1976 and 1978, mussels from the Farallon Islands were an exception, with lead concentrations of almost 10 × 10^{-6} g/g dry weight. Mussels from the same location in 1977 had lead concentrations of 3 × 10^{-6} g/g dry weight, much the same as in other years at Soberanes Point, Santa Cruz, and other central California sites. This pattern, both geographical and temporal, was also recently reported by the California State Mussel Watch Program (*22*). High lead concentrations (greater than 2.5 × 10^{-6} g of Pb/g dry weight) were found in mussels from the southern California coast with the exception of Point Arguello and Rincon Cliffs. Notably high concentrations were found for Point La Jolla (6.5 × 10^{-6} and 10.0 × 10^{-6} g/g dry weight), Point Fermin (7.9 × 10^{-6} g/g dry weight), Santa Catalina (6.2 × 10^{-6} and 6.4 × 10^{-6} g/g dry weight), and San Pedro Harbor (14 × 10^{-6} and 18 × 10^{-6} g/g dry weight).

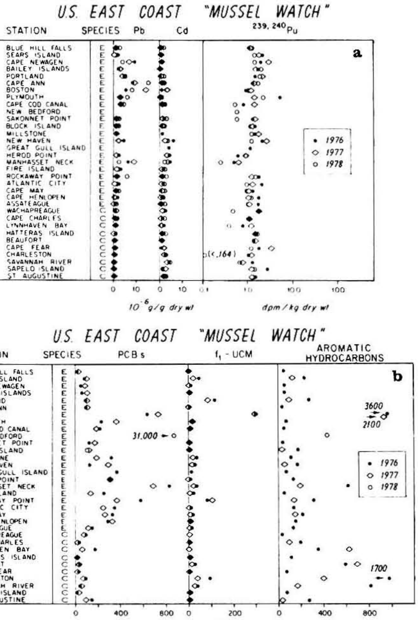

Figure 5. (a) Concentrations of Pb, Cd, and $^{239,240}Pu$ in mussels and oysters from the U.S. east coast 1976–1978. Species: E = *Mytilus edulis*, C = *Crassostrea virginica*. (b) Concentrations of PCBs and hydrocarbons in mussels and oysters from the U.S. east coast 1976–1978. F_1-UCM is an unresolved complex mixture of alkanes and cycloalkanes in gas chromatograms. Aromatic hydrocarbons are the sum of the following naphthalene; C_1-, C_2-naphthalene; phenanthrene; C_1-, C_2-phenanthrene; fluoranthene, pyrene; aromatic hydrocarbons with molecular weight 228 (e.g., chrysene), 252 (e.g., benzopyrene); dibenzothiopene and C_1-dibenzothiophene.

East coast mussels had lead concentrations greater than 2×10^{-6} g/g dry weight (Figure 5a) for stations from Cape Newagen, ME, south to the Cape Cod Canal, MA; New Haven, CT; Manhasset Neck and Rockaway Point, NY. Highest concentrations occurred at Cape Ann and Boston, MA. There were no apparent trends in the lead concentrations in oysters collected along the southeast coast of the U.S. (*10*). The 1977 and 1978 oyster collections had lead concentrations ranging from less than 0.1×10^{-6} to 1.6×10^{-6} g/g dry weight. Unlike mussels on the east and west coasts, oysters sampled near urban areas did not have appreciably higher lead concentrations than oysters sampled near remote areas. Whether this reflects a different biogeochemistry of Pb in the oyster habitat or insensitivity of oysters to elevated Pb concentrations in their habitat can only be discerned from further research.

The high lead concentrations in mussels near urban areas of the U.S. east and west coasts are clearly demonstrated in the data sets (Figures 4a and 5a). Direct atmospheric input as well as sewage, storm, and river and coastal runoff contribute anthropogenic lead from the combustion of lead alkyls in gasolines (*23*) to coastal areas. The exact mechanisms of transport and their relative importance for various areas are usually not known. A mass balance has been made for the west coast Los Angeles area (*24*). The phase-out of lead alkyls in gasolines should eventually result in decreasing lead concentrations in mussels. The lag time between phase-out and lower concentrations in mussels may be on the order of years due to the large amounts of anthropogenic lead in soil and sediment reservoirs. Knowledge of the details of the relationship between the phase-out and the time response of the mussel populations in the various coastal areas will be valuable in understanding how anthropogenic perturbations of natural element cycles proceed from the perturbation phase through the control phase toward restoration of the natural conditions. Since the scale of change over a period of years may be subtle, this exemplifies our previous discussion of the need to understand the causative factors of short-term temporal variability.

Mussels and oysters of the east coast had similar cadmium concentrations with the exception of somewhat elevated concentrations at Boston, MA, New Haven, CT, Manhasset Neck, NY, and Herod Point and Savannah River, GA (*10*). There is a site specificity for cadmium concentrations in Gulf coast oysters. Whether these are natural or anthropogenic phenomena we cannot discern from the available data (*10*). West coast mussels have cadmium concentrations (Figure 4b) similar to east coast mussels except for markedly elevated concentrations in a few areas especially between Point Arena and Diablo Canyon, where values exceed 6×10^{-6} g of Cd/g dry weight. Plutonium and americium concentrations (not shown) in west coast mussels show the same general distribution as do the cadmium concentrations (Figure 4b).

The elevated cadmium, plutonium, and americium concentration in organisms from the central California coast are apparently related to upwelling of middepth water in this area associated in general with the California Current. These elements exhibit marked surface water depletions and intermediate depth enrichments in the oceans (*25, 26*). Thus, upwelling of deeper water to the surface exposes organisms in the region to higher concentrations than are normally found in contiguous areas not experiencing upwelling events. Cesium-137, for which the upwelling mechanism would not provide higher concentrations, does not show elevations parallel to those of Cd, Pu, or Am.

It is important to point out that systematic national and regional surveys were needed to establish clearly the elevated concentrations of cadmium and plutonium in mussels of the central California coasts. Then, interpretation of these data required knowledge of biogeochemical cycles in the marine environment. Simple measurements without proper interpretations could have been misleading and led to the misconception that the elevated values were due to local or regional releases. This would have been a potentially severe error in the case of the elevated plutonium levels as several of these sites represent waters contiguous to a radioactive waste disposal site off the west coast (*27*).

Our data have revealed no evidence of local or regional systematic elevation of environmental concentrations of transuranic radionuclides or radiocesium released in effluent from nuclear power reactors. A slight elevation of plutonium concentration was observed in mussel tissues at our Plymouth, MA, station in 1976 (Figure 5a); a similar elevation was observed at about the same time in mussels from another station only a few miles way, and both samples were indicated by their isotope and nuclide ratios to represent freshly produced waste material, undoubtedly from the nearby Pilgrim reactor at Plymouth. Later sampling in 1977 and 1978, and in subsequent years, showed this was a nearly isolated event (*28*).

The vast majority of our east coast and all of our Gulf and west coast data are clearly explainable in terms of worldwide fallout from nuclear weapons testing. Concentrations of plutonium, americium, and ^{137}Cs in oysters and in mussels sampled at our various stations were several orders of magnitude lower than those found in similar species on the coast of the Irish Sea near the Windscale Nuclear Fuel Reprocessing Plant (*28*).

PCB (polychlorinated biphenyl) concentrations in mussels and oysters from all coasts were low in areas remote from urban centers while highest concentrations were found in organisms living near urban centers (Figures 4a and 5b). In particular, there is a northeast megalopolis effect with elevated PCB concentrations frequently in samples from the Chesapeake Bay area to Cape Ann, MA. Presumably the elevated PCB concentrations near urban areas are due to the PCB release to the environment by a myriad of intentional and unintentional activities now and in the past (*29*). Where our data are relevant, we see no evidence that PCBs have yet decreased in east coast mussels because of recent restrictions on PCB production and use. This may be due to the fact that these coastal areas are now in the slowly changing part of the exponential type decrease curve noted for DDT and PCB concentrations in mussels between 1971 and 1978 near the Los Angeles County Sanitation District Joint Water Pollution Control Plant when open uses of PCBs and DDT manufacturing waste discharges were curtailed (*30*). An alternative explanation is that the primary sources of PCBs to the areas we sampled are only gradually responding to the cessation of manufacture of PCBs in the U.S. Only future measurements will show clearly the time constraints involved for decreasing PCB concentrations in the environment, and as in the case of lead, these changes may prove to be subtle long-term decreases requiring very careful sampling and analyses to define accurately the processes involved.

During the course of the Mussel Watch program it became apparent from other research and environmental measurements (*28*) that we should focus attention on the New Bedford harbor area of Buzzards Bay. We established a station there in 1978 to check PCB contamination levels and measured the very high value of 17 × 10^{-6} g of PCB (1254 mixture/g dry weight and an equal amount of the 1242 or 1016 mixture PCBs. This concentration was more than an order of magnitude higher than other east coast samples, e.g., the 0.93 × 10^{-6} g/g dry weight in the mussels from Manhassett Neck, NY, 1977, and a factor of 4 higher than mussels from San Pedro Harbor, Los Angeles, CA, the highest on the U.S. west coast. Risebrough et al. (unpublished) measured 110 × 10^{-6} g of PCBs/g dry weight in *Mytilus edulis* sampled in 1976 near the 1978 New Bedford sampling location.

The data for PCB concentrations in mussels from the New Bedford harbor when compared to other data on the U.S. coast clearly established this harbor area as a "hot spot" of PCB pollution. An in-depth investigation is now in progress via an expanded set of mussel sampling locations, transplanted mussels on moorings, sediment, water, fish, lobster, and other bivalve sampling and analyses (e.g., ref 31 and 32).

Fossil fuel hydrocarbon concentrations exhibited geographical patterns similar to but not exactly overlapping with PCB concentrations (Figure 5b). This is demonstrated by the east coast data, which comprise the more extensive data set at this time due to unforeseen analytical instrument difficulties with analyses of several Gulf Coast and most west coast samples (*11*). The measurement of the unresolved complex mixture (UCM) gas chromatogram signal of alkanes and cycloalkanes indicative of fossil fuel hydrocarbon contamination shows a geographical distribution similar to that for the total of individual aromatic hydrocarbons measured. The aromatic hydrocarbons are another indicator of fossil fuel hydrocarbon pollution in coastal areas. There is not a strong covariance of the UCM of alkanes and cycloalkanes with the aromatic hydrocarbon concentrations ($R = 0.65$). This is not surprising since there are marked differences in the relative abundances of these two groups of compounds in petroleum and fossil fuel combustion products (*33*). Biogeochemical processes acting on the mixture of alkanes, cycloalkanes, and aromatic hydrocarbons also result in their exhibiting varying rates of degradation, metabolism, and movement through coastal ecosystems (*34*).

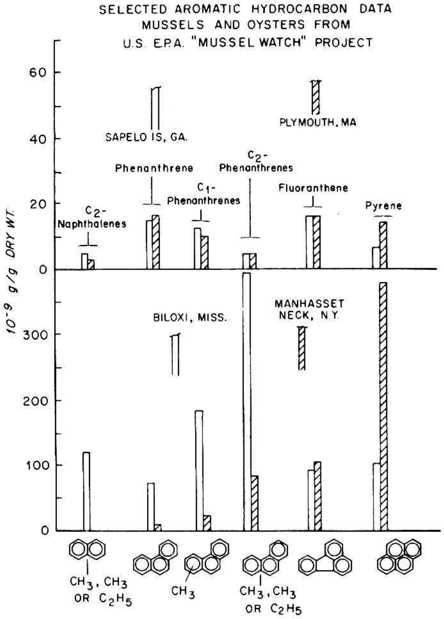

Figure 6. Selected aromatic hydrocarbon data from mussels and oysters.

The relative abundances of the individual or groups of aromatic hydrocarbons are of interest as a means of providing insight to probable major sources of aromatic hydrocarbons in the bivalves. Examples of the types of relative abundance distributions encountered are given in Figure 6. The key features are the relative abundances of phenanthrene, methylphenanthrenes (C_1-phenanthrenes), and dimethyl- or ethylphenanthrenes (C_2-phenanthrenes). In petroleum the alkylphenanthrenes (C_1 and C_2) are more abundant than the parent phenanthrene (*31*). In contrast, phenanthrene is more abundant than C_1-phenanthrene, which is more abundant than C_2-phenanthrene, in pyrogenic sources.

In most cases where lower concentrations of aromatic hydrocarbons were present in bivalves, the distribution of phenanthrenes plus fluoranthrene and pyrene indicates a pyrogenic source for many of the aromatic hydrocarbons. The amounts of these compounds in samples remote from urban areas could be a consequence of (i) long-range transport of fossil fuel combustion products via a combination of aeolian and fluvial transport processes, (ii) the leaching of aromatic hydrocarbons from creosoted pilings near the sampling sites (*35*)—none of the samples reported here were obtained directly from wood pilings although a few San Francisco Bay samples in 1976 and 1977 were from wood pilings (*5*), (iii) small boat exhausts in coastal areas, and (iv) long-range aeolian/fluvial transport of forest and grass fire products (*11*).

Bivalves from sampling locations near urban areas had elevated concentrations of aromatic hydrocarbons with phenanthrene distributions indicative of a petroleum source, e.g., crude oil or fuel oil spills and waste oil inputs in effluents. The elevated levels of fluoranthrene and pyrene in these samples probably have a mixed origin in pyrogenic sources (fossil fuel combustion) and petroleum inputs. Bivalves with intermediate concentrations had relative abundances of phenanthrenes indicative of mixed pyrogenic and petroleum sources. The state of the art of analytical measurements and our present understanding of biogeochemistry of PAH in coastal areas limit our ability to make a qualitative distinction among sources of PAH in the samples.

We have discussed in detail elsewhere (*36*) the interesting contrast between the relative abundances of phenanthrenes in surface sediments and in mussels from the same general locations in the northeast U.S. coast. Near urban areas the surface sediments have higher concentrations of PAH compared to surface sediments in more remote coastal locations. The predominant source of PAH in sediments appears to be pyrogenic. In contrast, near urban areas mussels have phenanthrene distributions indicative of mainly petroleum sources for these compounds. We have advanced the hypothesis (*11*, *36*) that petroleum hydrocarbons discharged to coastal areas are available for biological uptake to a greater extent than pyrogenic source hydrocarbons. Petroleum compound inputs would be dissolved, colloidal, or associated with particles in the water or sediments. As such they would be available for uptake across gill surfaces or during filter feeding or particulates by bivalves. Pyrogenic hydrocarbons would probably be more strongly absorbed to, or incorporated into, particulates from pyrogenic sources and less readily available for biological uptake. Chemical extraction methods used for sediment analyses release these compounds. The consideration of biological availability is important in assessing the relative importance of the various types of inputs of fossil fuel compounds to the oceans and the coastal areas in particular.

As a hypothetical example, even if there is a significantly larger amount of pyrogenic fossil fuel compounds entering the coastal area compared to petroleum spill and effluent inputs, only a small amount of the pyrogenic inputs would be biologically available, thereby making the two sources of comparable importance. There is a need for research in this general area in order to properly assess the relative importance, i.e., costs and benefits, of controlling pyrogenic and petroleum inputs.

General Discussion

There is a general similarity in geographical distributions of stations with elevated levels of Pb, PCBs and fossil fuel compounds near urban centers (Figures 4 and 5). However, if we plot any of these data sets one against the other, we do not find significant linear correlations. There are several reasons for this: (i) in the case of Pb we are measuring the perturbation of the biogeochemical cycle of Pb caused by man's activities; (ii) the modes of entry of the chemicals into the coastal environment are diverse; (iii) the biogeochemistry of each chemical or group of chemicals can be quite different once they enter coastal waters. Pb primarily comes from combustion of lead alkyls in automobiles and subsequent entry of the atmosphere followed by either deposition on land and fluvial transport to the coast via runoff or sewers or aeolian transport and fallout or rainout directly to coastal waters. Local sources of Pb input, e.g., smelting or fossil fuel combustion, might be important in some of the coastal areas. In comparison, PCBs are released by vaporization from leaking containers and (in the past) from dispersive usages: combustion of PCB containing materials in low-temperature incinerators and leakage from landfills that contain PCB-contaminated material. The PCBs released to the atmosphere are subject to transport processes similar to those described for Pb. Fossil fuel compounds enter the environment via a wide range of activities: accidental and normal operations from ships and coastal drilling and production operations, refinery and other industrial effluent, natural seeps, municipal effluents and storm sewer runoff, and atmospheric transport of combustion product fossil fuel compounds. Lead is probably primarily associated with particulates from internal combustion engines while PCBs are considered to be mobilized primarily in a vapor phase. Pyrogenic fossil fuel compounds are probably associated with a variety of particulates produced in the many different types of fossil fuel combustion, e.g., coal-fired power plants, oil-fired power plants, home heating furnaces. Each physical–chemical form is probably subject to different atmospheric behaviors, different atmospheric transport modes, and interaction with land and coastal waters. Once they enter coastal waters, the physical–chemical behaviors of these chemicals can be governed by differences in solubilities, particle/solution partitioning, biological uptake/release, metabolism, and microbial transformation.

Thus, while there is a general association with man's activities as a first-order governing factor in geographical distributions of elevated concentrations of some chemicals in bivalves of the U.S. coast, some or all of the factors discussed above (i–iii) provide a second- or third-order influence on the route between input and occurrence in the mussels or oysters.

We have presented data for a limited number of the many pollutant organic compounds known or suspected to be in the marine environment (*2*, *5*, *30*). Our gas chromatograms obtained via electron capture detectors, flame ionization detectors, and GC–MS reveal many other halogenated compounds in addition to DDT family compounds and PCBs. Some of these peaks may represent naturally occurring compounds (*37*). However, further analyses of a few samples (*30*) clearly identify other chlorinated pesticides and industrial compounds. One goal for continuing Mussel Watch activities is to provide a means for rapidly searching existing GC and GC–MS data files to identify widely distributed anthropogenic compounds and to indicate areas with anomalously high concentrations of a given compound. We seek to maximize the detection of kepone-type incidents (*17*) in the early stages and think that the Mussel Watch concept offers promise in that regard.

A comparison of our data with national and regional data sets for trace metals, organochlorines, and hydrocarbons in bivalves sampled in other coastal areas of the world is now in progress. Strict intercomparability may not have been achieved because of differences in methodology or a lack of intercalibration between laboratories. Broad comparisons may, however, reveal trends in differences in concentrations between urban and remote areas and the presence or absence of covariability for different types of chemicals. The sentinel organism approach can assist in making an assessment of the status of chemical pollution in coastal areas. However, it must not be viewed as a panacea for understanding all important aspects of the biogeochemistry of pollutant chemicals in coastal areas. It is a prototype of one type of monitoring system that yields data usefully interpretable within the context of knowledge of biogeochemical processes gained from research.

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Registry No. Pb, 7439-92-1; Cd, 7440-43-9; Ni, 7440-02-0; ^{239}Pu, 15117-48-3; ^{240}Pu, 14119-33-6.

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NOTES

Organic Compounds in the Rainwater of Los Angeles[†]

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■ Solvent-extractable and purgeable (volatile) organic matter was studied by using a capillary GC–MS in rainwater from a station in West Los Angeles on the UCLA campus. More than 600 peaks were obtained on gas chromatograms, and approximately 300 compounds have so far been either identified or tentatively identified in the neutral, acidic, and basic fractions of solvent extracts, including aliphatic and aromatic hydrocarbons, phthalates, benzaldehydes, phenols, aliphatic and aromatic ketones, mono- and dicarboxylic acids, amines, azaarenes, etc. The most abundant components were an unresolved mixture of hydrocarbons (ranging from 25 to 56 μg/L) and a homologous series of aliphatic monocarboxylic acids, which show a strong even-carbon-numbered predominance in the C_{10}–C_{30} range (7–16 μg/L), with a maximum at C_{16}. Smaller amounts of normal hydrocarbons (0.6–2 μg/L), nitrogen- and oxygen-containing polycyclic aromatics such as fluoren-9-one, phenanthrene-9,10-dione, and isoquinoline, and polycyclic aromatic hydrocarbons (0.05–0.1 μg/L) were also identified. Helium stripping and direct injection of volatiles into GC–MS showed ten identifiable compounds, including hydrocarbons and halocarbons, as relatively minor components (ca. 0.7 μg/L) compared to the solvent-extractable compounds.

Introduction

During precipitation, rainwater dissolves and scavenges from the atmosphere gases as well as aerosols that contain a large array of inorganic and organic materials. Although numerous studies have recently been conducted on the inorganic chemistry of rainwater, little attention has so far been paid to the organic compounds. As certain polynuclear aromatic hydrocarbons, phenols, aldehydes, and organic nitrogen-containing compounds, among others, are considered hazardous to health, an effort was initiated to evaluate their distribution in rainwater.

Lunde et al. (*1*) have provided the most detailed report on aliphatic and aromatic hydrocarbons, ketones, aldehydes, phthalates, fatty acid ethyl esters, free fatty acids, and other acids in rain and snow samples in Norway and discussed their origin and transport through the atmosphere. Matsumoto and Hanya (*2*) reported nonvolatile organic constituents in atmospheric fallout (dry fallout plus rain) in the Tokyo area and discussed the fluxes of *n*-alkanes, fatty acids, phenolic acids, and bisphenol A. Hydrocarbons were, on the average, twice as abundant as fatty acids and 12–130 times as abundant as phenolic acids. Semenov et al. (*3*) have reported data for the USSR, while other miscellaneous reports have appeared on specific organic compounds in rain in the U.S. (*4–8*).

This paper is a preliminary report on the identification and distribution of organic compounds in rainwater from a station on the roof of the Geology building at UCLA in West Los Angeles collected during the 1981–1982 winter season from Dec 1981 to Mar 1982 (see Table I).

Experimental Section

Rainwater was collected in samplers (the interception area was ca. 2800 cm^2) constructed from a galvanized iron standard trash can (~1 m high × 60-cm diameter). The cover was inverted, the handle removed, the center of the cover drilled, and a 20 cm × 2 cm stainless steel tube soldered in. The lid was then pressed into the top of the trash can with the lip of the cover overhanging the can. The cover thus acts as a funnel for collection of rainwater. The stainless steel tube fits into the entrance of a 20-L glass carboy inside the trash can that collects the rainwater. This apparatus is carefully washed by scrubbing with soap and water, followed by a dilute hydrogen peroxide wash, and finally with methylene chloride. Repeated tests of the blank following washing demonstrated only trace organic components in the extractables, usually phthalates. The collector is covered with a weight-loaded stainless steel lid (also washed as above) and held in place with polyvinyl alcohol paper. This paper dissolved quickly in rainwater, allowing the lid to spring open and expose the collector. Two such collectors were deployed side by side on a roof of the Geology Building, ca. 30 m above the ground. Figure 1 shows the sampling location at the UCLA campus relative to the major freeway arteries of Los Angeles. The campus is located near the San Diego Freeway, 8 km from Santa Monica Bay and 20 km from central Los Angeles. The rain samples were brought into the laboratory soon after the rain stopped and spiked with 50 mg of $HgCl_2$ as preservative and then stored at ca. 4 °C. Two liters each of three samples (Dec 30, 1981; Feb 10, 1982; Mar 26, 1982) were used for analysis of solvent-extractable organic compounds.

To each sample was first added 30 mL of a 1 N Na_2CO_3 solution, and the sample was next extracted three times with methylene chloride. Each sample was then acidified with 30 mL of 6 N HCl. Samples from Dec 30, 1981 (sample 1) and from Feb 10, 1982 (sample 2), were then further extracted with three 50-mL portions of chloroform and finally with three 100-mL portions of ethyl acetate. The other sample (Jan 5, 1982; sample 3) was extracted successively with several portions of a 1:1 ethyl acetate/methylene chloride mixture. To increase the efficiency of fractionation, the extracts were combined, concentrated, and then transferred into a 125-mL separatory funnel. The acidic and neutral fraction was then extracted with CH_2Cl_2

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Table I. Some Atmospheric Conditions Prevailing during the Rainstorms Described from the Winter Season in Los Angeles (1981-1982)[a]

	12/30/81	01/05/82	02/10/82	03/26/82
precipitation, cm	1.8	1.5	1.1	0.8
ozone, pphm[a]	0.4	0.5	0.1	1.0
carbon monoxide, ppm[a]	2.9	2.5	3.3	2.8
wind	subtropical	subtropical	subtropical	subtropical
temp range, °C	10-14	6-14	8-12	9-14

[a] These data were obtained at station 086 located at 5.5 km ESE from the sampling location at UCLA. [b] The concentrations of ozone and carbon monoxide are averaged. They were measured hourly. [c] Subtropical means a wind from ocean to land (from west to east).

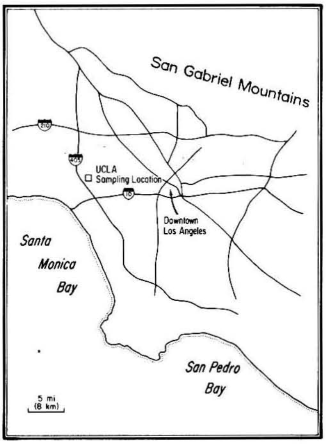

Figure 1. Map of sampling location (Los Angeles, CA). Major highways and freeways are shown.

(3 × 10 mL) under acidic conditions (10 mL of 1 N HCl was added). The remaining basic compounds were then extracted with CH_2Cl_2 (3 × 10 mL) from the residual solution (at pH ≥10) after adding 20 mL of 1 N Na_2CO_3.

The acidic/neutral fraction was then further separated into five subfractions (hydrocarbons, esters and ketones, aldehydes, alcohols, and free acids) on a 0.25-mm silica gel G thin-layer plate. The free acid fraction was methylated with BF_3/MeOH and fractionated on TLC into three subfractions. Each fraction was analyzed on 0.25 mm × 30 m SE54 fused silica capillary columns installed in a Hewlett-Packard Model 5840 gas chromatograph with a flame ionization detector and a Finnigan Model 4000 GC–MS system with an INCOS 2300 data acquisition and interpretation system. Identification of fatty acids, aliphatic hydrocarbons, and polynuclear aromatic hydrocarbons were made by comparing the elution retention time and mass spectra with those of authentic standards. Other compounds described in this paper were tentatively identified on the basis of library searches and comparison of fragmentation patterns using mass spectral information stored in the INCOS data system (EPA/NIH mass spectral data base). Recovery tests were performed by using authentic standards of several of the compound types identified, as shown in Table II.

Rainwater (500 mL) collected on Mar 26, 1982, was analyzed for volatile organics by using a Tekman LSC-2 liquid sample concentrator (purging) system combined with a Finnigan 4000 GC–MS computer system. Identification of the volatile compounds was made by using authentic standards.

The blanks for extractable and volatile organic analyses were run on GC and GC–MS. The results showed no serious contamination during the procedures, with the exception of octyl phthalates.

Table II. Recoveries of Authentic Standards[a] during Extraction and Identification Procedures

		recovery, %		
compounds	amt, μg	sample 1	sample 2	mean
aliphatic hydrocarbons (n-C_{15}–n-C_{36})	1.21-1.96	79.6	85.9	82.3
polynuclear aromatic hydrocarbons (PAHs)	1.00	75.9	83.6	80.0
fatty acids (C_{12}, C_{16}, C_{18})	1.05-1.20	86.7	70.6	78.7
phthalates	1.30-1.51	86.5	82.1	84.3
fluoren-9-one	1.53	72.9	62.4	67.7
quinoline	2.13	47.6		47.6
benzaldehyde	1.0	14.0		14.0
phenol	1.0	6.0		6.0

[a] The authentic standards were added to 1.5 L of preextracted distilled water and treated by the procedure described in the text. Recoveries for aliphatic hydrocarbons, PAHs, fatty acids, and phthalates were averaged. PAHs include fluorene, phenanthrene, fluoranthene, and pyrene. Phthalates include dimethyl, diethyl, di-n-butyl, benzyl butyl, di-n-octyl, and bis(2-ethylhexyl) phthalates.

Results and Discussion

Over 300 individual organic compounds (neutrals, acids, and basics) have presently been detected in the rainwater samples from Los Angeles. Table III shows selected extractable organic compounds and their approximate concentrations.

The concentrations were gas chromatographically determined by using the following authentic standards: n-C_6 to n-C_{30}, fatty acid methyl esters; n-C_{10} to n-C_{36}, hydrocarbons and polynuclear aromatic hydrocarbon mixture (containing 36 components). The concentration of the unresolved hydrocarbon mixture was determined by measuring the peak areas of the hump on the gas chromatogram and comparing with the response of a n-C_{20} hydrocarbon standard (the n-C_{20} peak is located around the center of the hump). The concentrations of other compounds were tentatively calculated by comparing the peak area on the gas chromatogram with that of palmitate. The concentrations for phthalates, benzaldehydes, phenols, polycyclic aromatic ketones, phenyl ketones, and basic compounds (quinoline and isoquinoline) were recalculated later by obtaining relative FID response factors of the following compounds to palmitate: phthalates (average 0.73), benzaldehyde (0.73), phenols (average 0.95), acetophenone (0.63), quinoline (0.88), and fluoren-9- and phenanthrenequinone (average 0.82), respectively.

Hydrocarbons. Normal C_{13}–C_{35} aliphatic hydrocarbons with a maximum at C_{29} were identified. n-C_{13}–n-C_{23} hydrocarbons showed almost no odd/even predominance,

Table III. Selected Extractable Organic Compounds in Los Angeles Rainwater and Their Approximate Concentrations ($\mu g/L$)

	rain samples					
	12/30/81		2/10/82		1/5/82	
classes of org compd	uncorr	corr[a]	uncorr	corr	uncorr	corr
saturated fatty acids	13	17	15	19	7	9
unsaturated fatty acids	3		1		tr	
α,ω-dicarboxylic acids	3		3		3	
benzoic acids	tr[b]		0.8		0.8	
p-coumaric acid	tr		0.4		0.3	
phthalates	3	4	8	9	3	3
benzaldehydes	1	7	3	21	1	7
phenols	0.5	8	0.5	8	0.1	2
isoprenoid ketone (C_{18})	0.1		0.2		0.1	
polycyclic aromatic ketones	0.3	5	0.4	7	0.3	5
2,3-dihydro-1*H*-inden-1-one	0.5		0.8		0.5	
phenyl ketones	2		3		1	
alkylfuranones	0.5		4		0.3	
isobenzofuranones	4		6		1	
oxiranes	2		0.7		0.3	
n-hydrocarbons	2	2	0.9	1	0.6	0.7
unresolved hydrocarbons (hump)	56		25		32	
polycyclic aromatic hydrocarbons	0.1	0.1	0.1	0.1	0.05	0.06
quinoline and isoquinoline and their substituted compounds	0.7	1	2	4	2	4
4-methyl-1(2*H*)-phthalazinones	0.2		1		1	
major unknown peaks	5		15		5	

[a] Corrected data are based on recoveries on Table II. [b] Trace.

suggesting that these hydrocarbons are of petroleum origin, whereas n-C_{25}–n-C_{33} hydrocarbons showed a strong odd/even predominance, suggesting that higher plant waxes contribute to the organic matter in rainwater (*9*). Unresolved hydrocarbons (hump) showed a bimodal distribution at ranges of n-C_{15}–n-C_{20} (with a peak near n-C_{18}) and of n-C_{20}–n-C_{33} (with a peak near n-C_{27}). A similar pattern was observed during the initial stages of storm runoff from the Los Angeles River (*10*). The presence of a hump in the rain, which is probably a mixture of alkyl-substituted aliphatic and aromatic hydrocarbons because the hump was recognized on the mass chromatograms (m/z 57, 91, 105, 119), may be associated with fuel combustion and automobile exhaust (*11*). Fifteen di- and triterpenoids such as ($17\alpha H,21\beta H$)-hopanes (C_{29} and C_{30}) were tentatively identified on the basis of their mass spectral fragmentation patterns at m/z 191. These hopanes have been proposed as sensitive molecular markers of petroleum pollution in California (*12*). Sixteen polycyclic aromatic hydrocarbons (PAHs) were identified in the rainwater. The major PAHs are phenanthrene, fluoranthene, and pyrene.

Esters. Seven phthalic acid esters were detected and found to be the most abundant esters. Dibutyl, butyl phenyl, and dioctyl phthalates were major components. These compounds, which are commonly used plasticizers, have been reported by Lunde et al. (*1*) in rain in Norway. Ethyl esters of C_{14}, C_{16}, and C_{18} fatty acids were tentatively identified, although their concentrations were very low. Two kinds of phosphoric acid esters (triphenyl and tributyl), which have not been reported in rain, were detected. 2-Methylphenyl benzoate and methyl 3-phenyl-2-propenoate were also detected.

Ketones. Six aliphatic ketones (C_6, C_7, C_8, C_{18}), three phenyl ketones, and eight polycyclic aromatic ketones were tentatively identified. Phenyl ketones were most abundant (1–3 $\mu g/L$) in this group. It is of interest to note that 9*H*-fluoren-9-one and phenanthren-9,10-dione, which are major polycyclic aromatic ketones, were more abundant (0.3–0.4 $\mu g/L$) than PAHs (0.05–0.1 $\mu g/L$). These polycyclic aromatic ketones are probably of anthropogenic origin and have been reported in diesel emission particulates (*13*). Cyclohexanone and *p*-benzoquinone were also tentatively identified. A series of alkylfuranones (R = C_2–C_{12}, γ-lactones), benzofuranone, isobenzofuranone, and their alkyl-substituted compounds were detected. Isobenzofuranones were major components (1–6 $\mu g/L$). The origin of these furanones is presently obscure. The following pyran-type ketones were detected: 1*H*,3*H*-naphtho[1,8-*cd*]pyran-1-one, 1*H*,3*H*-naphtho[1,8-*cd*]-pyran-1,3-dione, and 3-phenyl-2*H*-benzopyran-2-one; however, their origin is also not clear.

Aldehydes. Aliphatic aldehydes (C_6, C_7, C_{14}, C_{16}, C_{18}, C_{20}, C_{22}, C_{24}, C_{26}, C_{28}, C_{30}, and C_{32}) were tentatively identified on the basis of characteristic peaks at m/z 69, 82, 96, and 111. However, they were present in very low abundance. Major aldehydes were aromatic aldehydes (benzaldehyde, 1,4-benzenedicarboxaldehyde, and their alkyl-substituted forms). Their concentrations were in a range of 1–3 $\mu g/L$. They probably arise from combustion of fuels, as benzaldehyde was detected in auto exhausts (*14*). 9-Anthracenecarboxaldehyde and (1,1′-biphenyl)-4-carboxaldehyde were also detected.

Alcohols. The following alcohols were detected: dihydro-3-hydroxy-4,4-dimethyl-2(3*H*)-furanone; 1-hexen-3-ol; 4-methyl-3-hexanol; 3-methoxy-2-butanol; 3,7-dimethyl-6-octen-ol; cyclodecanol; 2-methyl-1-dodecanol; phenylmethanol; 2,3-dihydro-1*H*-inden-1-ol; 3-chlorobenzeneethanol; 2-hydroxy-3-(2-propenyl)benzaldehyde; nonadecanol; 1-phenanthrenol. These alcohols are generally not present in organisms and probably represent either an anthropogenic origin or photochemical reaction products in the atmosphere. The following phenols were detected: phenol; 2-nitrophenol; 4-bromophenol; 3,4,5-trimethylphenol; 2-(1,1-dimethylethyl)-6-methylphenol. Phenol is the most abundant component. Phenols have been shown to be common constituents in air particles (*15*, *16*).

Others. The following compounds were also detected in the neutral fraction: dibenzo[*b*,*e*][1,4]dioxin; 9*H*-xanthene; 9*H*-xanthen-9-one; phenanthridione 5-oxide; 4-methyl-1(2*H*)-phthalazinone; 5-methyl-5-phenylimidazolidine-2,4-dione; *N*-(3-nitrophenyl)-3-phenyl-2-propenamide; *N*,*N*,4-trimethylbenzosulfonamide; etc.

Although several large peaks appeared on the gas chromatogram from the polar regions of the TLC fractions, we have not yet been able to identify them.

Acids. A series of aliphatic saturated monocarboxylic acids (C_6–C_{30}) were the most abundant group identified in this fraction. Their concentrations (7–16 μg/L) are approximately 10 times more abundant than normal hydrocarbons (0.6–1.6 μg/L). Normal C_{12}, C_{14}, C_{16}, and C_{18} acids are predominant, whereas the n-C_{20}–n-C_{30} acids were minor components. Their distribution is characterized by a strong even/odd ratio with a maximum at n-C_{16}. A similar pattern was reported in the fallout in the Tokyo area (*2*). Since their distribution is similar to that for algae and plants, they probably originate from biogenic sources. Although iso and anteiso branched C_{15}, C_{16}, and C_{17} acids, which are characteristic constituents of bacteria, were detected in the samples, they represent trace amounts in comparison to straight-chain compounds. On the other hand, the C_6–C_9 acids displayed a different distribution. They showed not an even/odd predominance but relatively high uniform concentrations in the range of C_6 and C_9 acids, suggesting that their origin is different from that of the C_{12}–C_{30} acids.

Mono- and diunsaturated fatty acids ($C_{16:1}$, $C_{18:1}$, and $C_{18:2}$) were also identified, indicating a short residence time for those compounds in the atmosphere, due to their reactive nature under oxidizing conditions.

A series of aliphatic α,ω-dicarboxylic acids (C_4–C_{12}) was detected. Their concentration was lower than that of fatty acids. Dicarboxylic acids in atmospheric particulates have been reported to result from photochemical oxidation of olefins (*17*). In our samples, the C_9 diacid was the most abundant. It may be derived by oxidation of the Δ^9 double bond of unsaturated fatty acids in the atmosphere. This interpretation seems reasonable as the normal C_6 and C_9 monocarboxylic acids, which may comprise the other part of degraded unsaturated acids, were detected in all samples in relatively high abundance.

Other minor carboxylic acids were tentatively identified. These include β-hydroxy acids (C_6–C_{26}), 9,10-dihydrooctadecanoic acid, dehydroabietic acid, benzoic acids, phthalic acids, aliphatic and aromatic keto acids, *p*-coumaric acid, 2-naphthalenecarboxylic acid, benzo[*c*]cinnoline-2-carboxylic acid, etc. The presence of β-hydroxy acids, which are characteristic constituents of bacterial cell walls (*18*), may indicate bacterial contribution to rainwater. Dehydroabietic acid may be derived from resinous plants (*19*). *p*-Coumaric acid probably also comes from vascular plants (*2*). Phthalic acids may be produced by hydrolysis of phthalates in the atmosphere (common plasticizers and ubiquitous contaminants).

Basics. The following nitrogen-containing compounds were tentatively identified: quinoline and isoquinoline and their alkyl-substituted compounds, 1,2,4-triazolo[1,5-*a*]pyrazine; 8-methyltriazolo[4,3-*a*]pyrazine; 3-pyrazinecarboxylic acid hydrazine; 1-(3-aminophenyl)ethanone; benzo[*c*]cinnoline and its methyl form; 2-aminonaphthalene. Isoquinoline is the most abundant basic compound in every sample. The nitrogen-containing aromatics such as isoquinoline and quinoline are more abundant than PAHs and oxygen-containing aromatics. The quinolines were reported in a California crude oil (*20*) and in the atmosphere (*21*) and may be derived from industrial and diesel exhausts. Evidence that other nitrogen-containing polycyclic aromatics exist in the neutral fraction is suggested by intesne molecular ion peaks at m/z 265, 279, 391.

Table IV. Volatile Organic Compounds in Rainwater Collected on Mar 26, 1982

compounds	formula	concn, ng/L
Halocarbons		
1,2-dichloroethene	CHClCHCl	230
chloroform	$CHCl_3$	250
1,1,1-trichloroethane	CH_3CCl_3	69
tetrachloroethene	CCl_2CCl_2	21
Hydrocarbons		
toluene	C_7H_8	76
ethylbenzene	C_8H_{10}	9
m-xylene	C_8H_{10}	2
p-xylene	C_8H_{10}	9
propylbenzene	C_9H_{12}	tr

As seen in Table III, the most abundant group is the unresolved hydrocarbon mixture probably originating from fuel combustion and motor exhausts, suggesting that anthropogenic sources are the most important factor in controlling the distribution of organic matter in the atmosphere of Los Angeles. The next most abundant group is carboxylic acids (mainly fatty acids), probably biogenic in origin, suggesting that natural sources are also important factors in controlling the atmospheric organic matter. Although phenols and benzaldehydes were detected in the extractable fraction as minor components only (Table III), the corrected amounts for these compounds in rainwater, based on recoveries (Table II), suggest that they are significantly large. We believe that those volatile polar compounds are not effectively extracted from rainwater and/or are lost during TLC procedures, drying, etc. In fact, we found recently (by using continuous extractive steam distillation methods) that phenols, benzoic acids, and lower molecular weight fatty acids (C_5–C_{10}) represent a major fraction of the organic constituents in Los Angeles rainwater. Their amounts are in the same concentration range as that of high molecular weight fatty (carboxylic) acids.

Volatiles. Halocarbons and hydrocarbons were identified by the helium purging method, in the amounts shown in Table IV. The concentrations were determined by comparing peak height of the compounds on the reconstructed ion chromatogram with that of authentic standards. These volatiles are probably of anthropogenic origin, since they are used as solvents and found in motor exhausts (*22*). The concentrations of the volatiles identified are relatively low compared to solvent extractable compounds. Other hydrocarbons (n-hexane, cyclohexane, n-heptane and methylfuran, 2,5-dimethylfuran, 2,5-diethyltetrahydrofuran, dihydro-2-methyl-2(*H*)furanone, and 1-(2-furanyl)ethanone were tentatively identified. Although the origin of furans detected in the rainwater is not clear, an earlier report (*23*) on the presence of 3-methylfuran in rainwater from Washington, DC, suggests that this compound may originate from the photochemical oxidation of plant-derived triterpenoids.

This study represents the first reported attempt to characterize the organic components in rainwater in the western U.S. The data contain a wide variety of recognized individual compounds; many others have not yet been identified. The mixture contains compounds that have previously been reported to arise from biogenic or anthropogenic sources as well as from in situ photochemical reactions. Although we believe that specific anthropogenic compounds are formed from either mobile (auto exhaust) or stationary (refineries, chemical plants, etc.) sources, we have not yet been able to assign a specific (unique) source to many compounds. Continuing study will focus on temporal variation and source apportionment of the organic compounds in rainwater.

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Registry No. 1,2-Dichloroethene, 540-59-0; chloroform, 67-66-3; 1,1,1-trichloroethane, 71-55-6; tetrachloroethane, 127-18-4; toluene, 108-88-3; ethylbenzene, 100-41-4; *m*-xylene, 108-38-3; *p*-xylene, 106-42-3; propylbenzene, 103-65-1; *p*-coumaric acid, 7400-08-0; 2,3-dihydro-1*H*-inden-1-one, 83-33-0; quinoline, 91-22-5; isoquinoline, 119-65-3.

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Corrected Fluorescence Spectra of Fulvic Acids Isolated from Soil and Water

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■ The fluorescence of humic matter is a ubiquitous phenomenon that occurs for isolated soil and aquatic matter and for natural water samples. This property is used to compare humic substances, but uncorrected emission spectra can be especially misleading for spectra taken on different instruments. This paper details the corrections of emission fluorescence spectra of well-characterized fulvic acids isolated from soil and a fresh-water river. The corrections significantly modify the uncorrected spectra. This effect demonstrates the need for emission spectra corrections before comparing the fluorescence properties of diverse humic matter samples.

Introduction

The fluorescence of humic matter is a general phenomenon, and there have been several publications on the fluorescence spectra of isolated humic matter (*1–6*) and of natural water samples (*7–12*). Comparison of these samples is difficult or impossible with uncorrected spectra. However, to our knowledge, there are no examples of corrections for comparison of various samples measured in different laboratories.

The purpose of this paper is to demonstrate the necessity of correcting fluorescence emission spectra of humic substances and explain how to make the corrections. We illustrate the procedure with the emission spectra of well-characterized fulvic acid (FA) samples isolated from soil (SFA) and water (WFA) (*6*). The fluorescence emission spectra of both FA samples are significantly changed by the corrections. Thus the corrections are crucial for comparison of humic matter measured by different laboratories on materials from different sources. No quantitative comparison of samples is possible in the absence of corrections.

Generally the needed corrections are of two types (*13, 14*). Type 1 correction is for background scattered light which is recorded simultaneously with the fluorescence of humic substances. This scattered light includes, in addition to the classical Raman band of water, a background of white stray light coming from the excitation monochromator which is scattered by the examined solution. Because humic acids cause Tyndall scattering and it is possible that inorganic substances exhibiting this property may be present in natural water samples, the level of scattered light by water (Rayleigh effect) could be greatly enhanced (*10, 11*). Type 2 correction takes account of the variation of instrumental sensitivity with wavelength.

Experimental Section

Materials. Quinine sulfate dihydrate (QS) was purchased from the U.S. National Bureau of Standards

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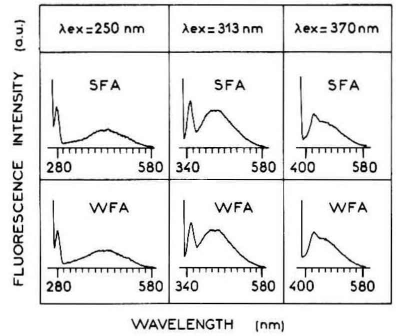

Figure 1. Effect of excitation wavelength on the uncorrected fluorescence emission spectra of 2 mg of C/L SFA and WFA at pH 2 and 25 °C. Arbitrary units are au.

(standard reference material 936), and "oyster" glycogen from Sigma Ltd. The isolation and characterization of SFA and WFA have been described (*6*). Both samples were freeze-dried before weighing. We prepared stock solutions of about 20 mg of C/L in Milli-Q (Millipore Ltd) water, adjusted them to pH 2 with HCl, and filtered them through glass-fiber 0.45-μm GF/C filters from Whatman that were pyrolyzed at 450 °C overnight. Stock solutions were stored at 5 °C in the dark.

Apparatus and Measurements. A Hitachi Perkin-Elmer MPF-3 spectrofluorimeter with an R106 photomultiplier tube was used for fluorescence measurements. Correction for the variation of instrumental sensitivity with wavelength was done by an external computer (Hewlett-Packard 9821A) after introduction into memory of the correction factors as a function of wavelength. The correction factors originate from comparison of fluorescence spectra of noncorrected 1.28×10^{-6} M NBS QS reference solution in 0.105 M $HClO_4$ and of that corrected by NBS researchers (*15*). The correction method is detailed below.

FA solutions of approximately 2 mg of C/L were studied because this concentration is appropriate for many natural waters and also prevents inner filter effects (*11, 13, 14*). All samples were maintained at 25 °C by a Haake cryothermostat and thermostated cell compartment. Excitation wavelengths were 250, 313, and 370 nm; the band widths were 16 nm for excitation and 4 nm for emission. Scattering corrections were made by using aqueous glycogen solutions that have the same Rayleigh scattering as FA samples under the same conditions. The glycogen solutions were prepared by trial and error.

Results and Discussion

Effect of Excitation Wavelength on FA Spectra. Figure 1 shows qualitative, uncorrected emission spectra for SFA and WFA when λ_{ex} = 250, 313, and 370 nm. At the same excitation wavelength, emission spectra for SFA and WFA are similar. These qualitative, uncorrected spectra show that the fluorescence of FA is wavelength dependent. The difference in uncorrected emission spectra as a function of excitation wavelength reflects the complexity of the SFA and WFA mixtures. We do not know what fraction of the FA molecules actually fluoresce (*3*), but it is not surprising that different groups of molecules are excited at each of the three excitation wavelengths. Close inspection of Figure 1 clearly signifies the necessity of emission spectra corrections. All spectra show the superimposition of the relatively sharp Raman scattering band that causes considerable distortion.

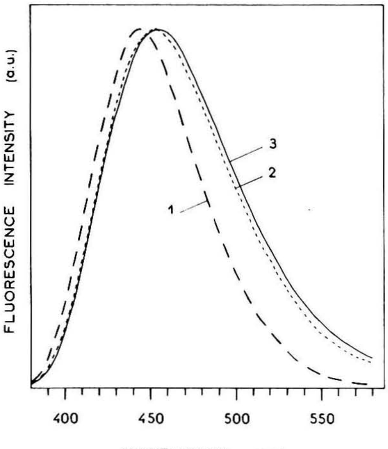

Figure 2. Fluorescence emission spectra of 1.88×10^{-5} M NBS standard reference material quinine sulfate dihydrate in 0.105 M perchloric acid at 25 °C and λ_{ex} = 347.5 nm: (1) fluorescence spectrum without correction; (2) fluorescence spectrum corrected to Perkin-Elmer specifications; (3) NBS corrected reference spectrum (*15*). Arbitrary units are au.

We chose a 370-nm excitation for further study for several reasons, including closeness to the commonly used 366-nm mercury line. Second, FA emission spectra from 370-nm excitation are less broad and of higher intensity relative to the available excitation light flux than those obtained from lower wavelength excitation. The increased light flux at 370 nm is due to the output of the xenon source and the monochromatic distribution as a function of wavelength. Third, since the UV–vis absorption of FA decreases from 250 to 370 nm, absorption of 370-nm excitation energy is lower than that of 350- or 313-nm energy. Thus λ_{ex} = 370 nm decreases inner filter effects (*11, 13, 14*).

Nature of Corrections to Observed Spectra. First, we correct the observed spectra for type 1 effects of Raman, Rayleigh, and Tyndall scattering of SFA and WFA solutions. Spectra obtained with nonfluorescent aqueous glycogen solutions that have the same Rayleigh and Tyndall scattering as the FA samples at 370 nm make possible corrections for Raman, Rayleigh, and Tyndall effects at all wavelengths. The corrections include those for scattered stray light from the exciting monochromator, which occurs at all wavelengths, especially those of the emission spectra of FA. The corrected FA fluorescence spectra are obtained by point-by-point subtraction of the glycogen spectra from the observed FA fluorescence spectra. Tyndall scattering of SFA and WFA solutions is very low due to the absence of large macromolecules, but it can be very important in natural water samples which contain larger macromolecules. Correction for Tyndall scattering is very important for examination of natural water samples.

After the type 1 scattering correction, we do the type 2 correction of the fluorescence spectrum for variation of instrumental sensitivity with wavelength. As a first step (Figure 2) we measure the emission spectrum of standard reference material QS (spectrum 1) and correct the spectrum using the rhodamine B method in the Perkin-Elmer instrument manual (spectrum 2). Comparison of spectra 1 and 2 of Figure 2 shows that the correction is significant but that the corrected spectrum 2 is not identical with NBS spectrum 3 (*15*). Therefore wer normalized point-

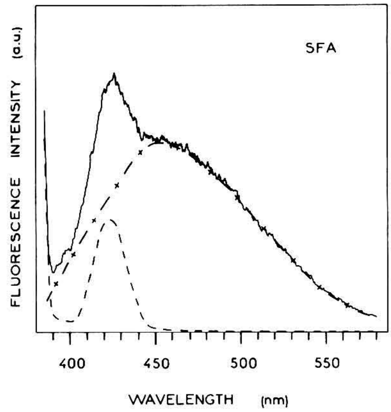

Figure 3. Fluorescence emission spectra of 2 mg of C/L SFA at pH 2, 25 °C, and $\lambda_{ex} = 370$ nm: directly recorded SFA spectrum (—); spectrum of water containing glycogen of similar scattering intensity at 370 nm as the SFA solution (- - -); type 1 corrected spectrum (– + –). Arbitrary units are au.

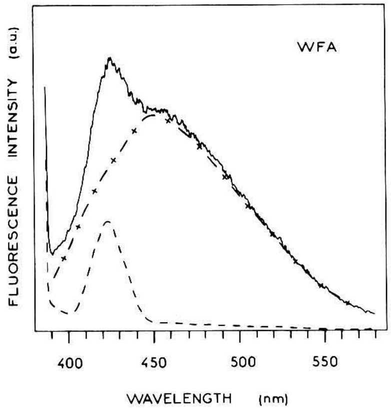

Figure 4. Fluorescence emission spectra of 2 mg of C/L WFA at pH 2, 25 °C, and $\lambda_{ex} = 370$ nm: directly recorded WFA spectrum (—); spectrum of water containing glycogen of similar scattering intensity at 370 nm as the WFA solution (- - -); type 1 corrected spectrum (– + –). Arbitrary units are au.

by-point our QS spectrum to that obtained by NBS by a series of correction factors Q_λ, which become more important at higher wavelengths. The factor Q_λ is used in the following equation in which $I_F(\lambda)$ is fluorescence intensity:

$$[I_F(\lambda)]_{\text{corrected}} = Q_\lambda[I_F(\lambda)]_{\text{apparent}} \qquad (1)$$

Corrections to FA Emission Spectra. Figures 3 and 4 show the observed spectra and the effect of the type 1 correction, which is mainly the Raman band of water at 423 nm. Figure 5 also shows the results of type 1 and type 2 corrections to SFA (solid line) and WFA (dashed line). Consider first type 1 corrections to observed SFA spectra (solid line 1) and type 2 corrections (solid line 2) due to variation of instrumental sensitivity. The final spectrum shows a great modification due to the type 2 correction including the maximum shift from ca. 455 to 495 nm. The quality of the correction is a determining factor in comparison of corrected fluorescence spectra of FA from different sources, and not even wavelength maxima can be compared with uncorrected spectra. We made no correction above 580 nm, where the photomultiplier response is very low and which is the limit for normalization with NBS QS (*15*). Correction beyond 580 nm would require a new fluorescence standard, which to our knowledge is not available. Similar corrections for WFA are shown in Figure 5 (dashed line 1 and 2).

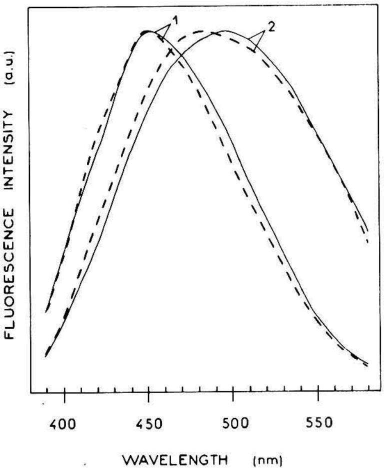

Figure 5. Fluorescence emission spectra of SFA (—) and WFA (- - -) ($\lambda_{ex} = 370$ nm) with type 1 corrections (1) and type 1 and type 2 corrections (2). Arbitrary units are au.

Conclusions

This work demonstrates that observed fluorescence emission spectra of humic matter change considerably due to corrections discussed in this paper. Corrections are necessary to compare humic matter from different sources, whose emission spectra are measured on a variety of spectrofluorometers. With corrected spectra researchers should be able to compare and contrast a variety of isolated and in situ humic matter samples.

Acknowledgments

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CORRESPONDENCE

Comment on "Chlorobenzenes in Sediments, Water, and Selected Fish from Lakes Superior, Huron, Erie, and Ontario"

SIR: The survey of chlorobenzenes (CBs) in the Great Lakes by Oliver and Nicol (*1*) provides a valuable picture of their present distribution. However, I disagree with their perpetuation of the myth that all CBs are resistant to microbiological oxidation. The lower CBs containing 1–3 chlorines have been shown to be biodegradable under aerobic conditions by many researchers using a variety of laboratory systems. Laboratory tests show biodegradation for monochlorobenzene (MCB) (*2–6*), 1,2-dichlorobenzene (1,2-DCB), 1,4-dichlorobenzene (1,4-DCB) (*2b,4*), and 1,2,4-trichlorobenzene (1,2,4-TCB) (*2, 6–9*). Their biodegradation is also demonstrated in the dilution bottle biochemical oxygen demand (BOD) test (Table I).

Those studies that found the lower CBs to be toxic or not biodegraded generally employed environmentally unrealistic concentrations of the CBs, 5 mg/L or more (*2b, 11, 12*). The toxicity of the CBs at these high concentrations to microorganisms may have led to their apparent recalcitrance (*13*).

One of the most interesting pieces of data in this paper is the distribution of the different CB congeners in the sediment core (Table IV, ref 1). In the older layers, the ratio of DCBs and TCBs to hexachlorobenzene (HCB) and pentachlorobenzene (QCB) increases dramatically. For example, the ratios of 1,4-DCB to HCB in the core slices are 0.41, 0.26, 0.40, 1.44, 1.16, 1.81, and 20 as the depth increases from 0–1 to 6–7. This is consistent with a slow dehalogenation process of HCB in the anaerobic sediment or a much different release pattern in the past. This change in CB congener distribution does not appear for 30–40 years, a long time to wait for laboratory experiments. Study of additional sediment cores might reveal more precisely the rate of change in distribution and those conditions that cause this change.

Table I

	BOD, % of theor		
compound	5 days	10 days	20 days
MCB (*10*)	26	29	45
1,2-DCB (*10*)	0	41	51
1,4-DCB (*10*)	65	77	77
1,2,4-TCB (*9*)	11	52	76

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SIR: Generally speaking, within a family of related compounds (e.g., CBs), the more highly chlorinated substances are more recalcitrant and resistant to microbiological oxidation (*1–4*). If signification CB biodegradation was occurring in the Lake Ontario sediments, the lower di- and trichloro congeners should become less predominant than the more highly chlorinated CBs in deeper, older sediments (assuming similar loading patterns over time).

Table I. Proportions of Di-, Tri-, Tetra-, Penta-, and Hexachlorobenzenes in Lake Ontario Sediments

sediment interval, cm	% di-	% tri-	% tetra-	% penta-	% hexa-
	Core No. 1 (Western Basin)[a]				
0-1	25	35	17	5	18
1-2	24	31	15	6	24
2-3	28	30	15	6	21
3-4	41	24	9	4	22
4-5	38	30	10	3	19
5-6	39	38	10	3	10
	Core No. 2 (Eastern Basin)				
0-1	10	30	21	11	28
1-2	16	29	19	10	26
2-3	13	34	20	7	26
3-4	12	32	21	11	24
4-5	10	36	20	11	23
5-6	8	38	18	11	25

[a] Western basin (Oliver, Barry G.; Nicol, Karen D. *Environ. Sci. Technol.* **1982**, *16*, 532).

From Table I it can be seen that the relative proportion of the lower CBs stays about the same or increases in deeper sediments. While biodegradation may effect the concentrations of CBs reaching the sediments, our results would indicate that microbiological oxidation is not an important process in Lake Ontario sediments. In our opinion, from the core data in our paper and from other cores we have analyzed, there is insufficient evidence to show the occurrence of anaerobic dehalogenation of CBs in these sediments.

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ADDITIONS AND CORRECTIONS

1981, Volume 16, Page 671

Arthur W. Stelson and John H. Seinfeld:* Chemical Mass Accounting of Urban Aerosol.

Recently, Dr. James J. Morgan of the California Institute of Technology pointed out an error in this paper. The error occurs in the [H], [OH], [H]′, and [OH]′ concentrations calculated on the basis of electroneutrality. The original manuscript assumed the sodium is ionic and neglected that the sodium could be present as oxides in solid solutions. In revising the manuscript, the electroneutrality balance was incorrectly adjusted. The correct values are listed in the table below. By reviewing the revised values, one can see that the statement on page 677, "Samples TC and TD were the only ones that were definitely acidic, whereas WK, WL, VJ, and TE could be basic or acidic", is incorrect. The change from an acidic to basic prediction based on the electroneutrality balance method indicates the desirability of measuring the hydroxyl or hydrogen ion concentration and the sensitivity of the electroneutrality balance method to the individual ion measurements. Although this error appears in the calculations in Tables II, VI, VII, and VIII and Figure 6, the general conclusions are not affected since the numerical values only change slightly.

Table I. Hydroxyl and Hydrogen Ion Concentration Based on Electroneutrality Balance

	hydroxyl and hydrogen ion concn, $\mu g\ m^{-3}$			
sample	[H]	[OH]	[H]′	[OH]′
WK	0.3			1.5
WL	0.1			4.1
VJ		0.1		5.7
TC	0.2			5.1
TD	0.1			4.1
TE	0.1			3.7

Corrected
A.J.
26/013.

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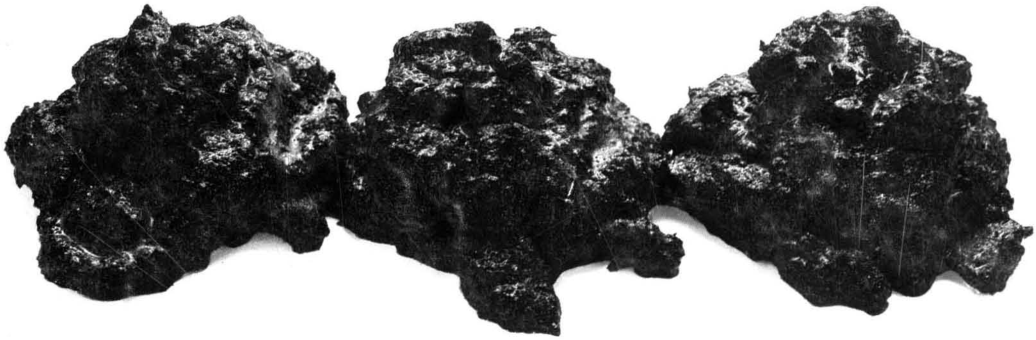

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