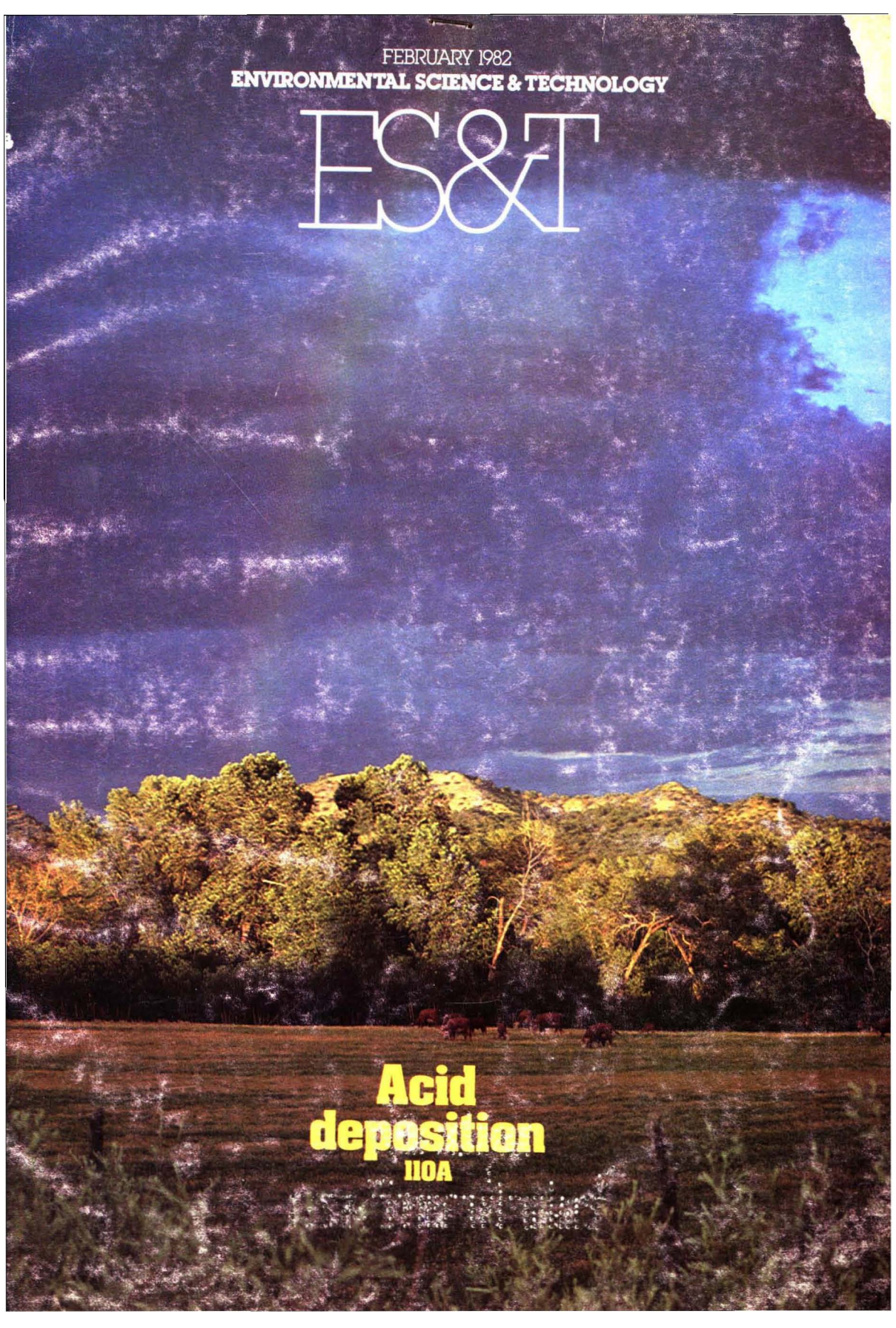


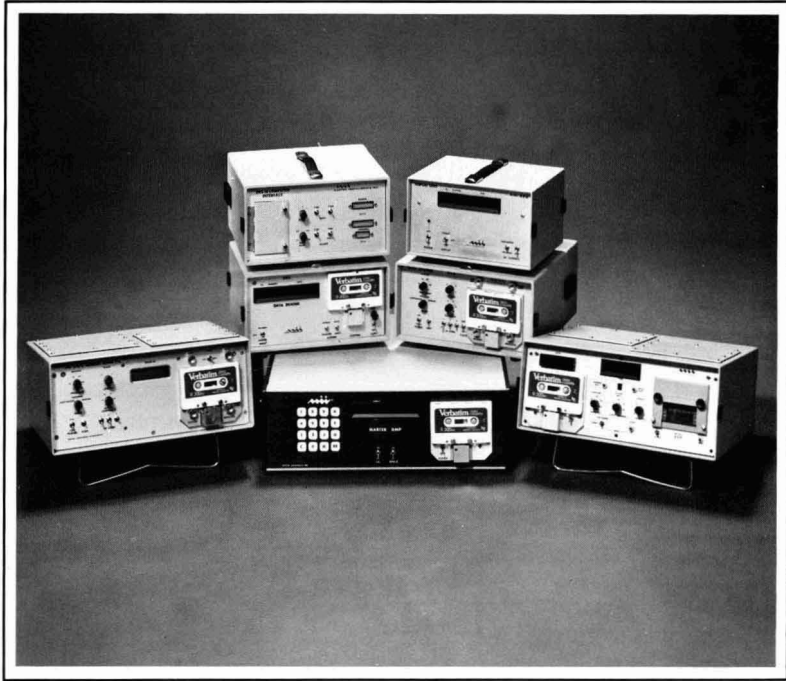
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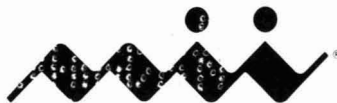
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CIRCLE 9 ON READER SERVICE CARD

Minamata disease

Dear Sir: I noted with interest the correspondence in your October issue between Messrs. Kurzel and Cetrulo and Mr. Laubusch concerning the potential teratogenic effects of mercury. While I do not wish to become involved in the main argument, some of the statements made by Kurzel and Cetrulo about the cause of Minamata disease shouldn't be allowed to go unchallenged.

It is now firmly established that the initial outbreak of Minamata disease in Japan in 1956 was caused by the consumption of fish and shellfish containing substantial quantities of organic mercury compounds. Minamata Bay received effluent discharges containing both inorganic and organic mercury compounds; however, the evidence suggests that the transformation of inorganic mercury to organic mercury in the environment did not make a significant contribution to the concentration of organic mercury in the fish and shellfish.

The Chisso production plant at Minamata City manufactured fertilizers, plastics, fibers, and a range of general chemicals such as acetic and nitric acids. Mercury was used as a catalyst in two processes: for the manufacture of acetaldehyde from 1932-1968 and for the production of vinyl chloride from 1941-1971. Irukayama et al. (1) report estimates by the factory management that the total losses of mercury to the aquatic environment from these operations were 81.3 tons and 0.2 tons respectively.

Organic mercury compounds were formed as byproducts in both plants. It is difficult to assess accurately how much of the mercury was discharged in an organic form since the first measurements of organic mercury in the works effluent were not made until 1962 (Irukayama et al. (2)). However, the data obtained between 1966-1969 (Irukayama et al. (3)) indicates that about 20-40% of the mercury discharged was probably in an organic form, i.e., Minamata Bay would have received about 30 tons of organic mercury by direct discharge.

According to Jernelov (Lindberg et al. (4)) sedimentary transformation of inorganic to organic mercury occurs at annual rates of 0.01-10%. The rate of transformation in the sediments of Minamata Bay is not known. However, it must be considerably less than 10% since according to Fujiki and Tajima (5) the total mercury content of the bay sediments did not change significantly between 1963 and 1971.

In addition, there is evidence from prolonged laboratory experiments to show that organic mercury could not be produced in detectable amounts from the bay sediments (Irukayama et al. (6)). Even if 10% of the inorganic mercury discharged was transformed in the environment, about 86% of the organic mercury present in the fish and shellfish would still be accounted for by the direct effluent discharge.

Data on the mercury content of fish in Minamata Bay (Fujiki and Tajima (5)) provides further confirmation of the view that environmental transformation was insignificant in this situation. In 1966, the Chisso factory ceased the discharge of effluents from their acetaldehyde plant into Minamata Bay. Prior to this date the organic mercury content of fish in the bay was in the range of 10-20 mg/Kg. Since the total mercury content of the sediments, and presumably the environmental transformation rate, did not change, the only explanation for this reduction is that the high levels of organic mercury in fish were the direct result of the organic mercury content of the effluent discharge.

In addition, the Japanese Ministry of Public Health and Welfare announced officially on Sept. 26, 1968, that the causative agent of Minamata disease was the methyl mercury compound contained in the waste from the acetaldehyde plant of the Minamata factory.

Kurzel and Cetrulo also quote the work of Uchida et al. (7), which identified the toxic compound in the shellfish in Minamata Bay as methyl mercuric sulfide $(\text{CH}_3)_2\text{HgS}$. However, this identification was shown in

1964 by Kondo (8) to be incorrect and it is now generally agreed (Irukayama et al. (1)) that the toxic compound was a lower alkyl mercury halide of the form RHgX ($\text{R} = \text{CH}_3$ or C_2H_5 ; $\text{X} = \text{Cl, I, Br}$).

I have not been able to check the statements with respect to the speciation of mercury in the water of Minamata Bay since neither of the references cited by the authors refers to this work.

In conclusion, and at a variance with the statements made by Kurzel and Cetrulo, all the evidence now available points to the direct discharge of alkyl mercury halides from the Chisso factory being the causative agent of Minamata disease.

D. Taylor

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References

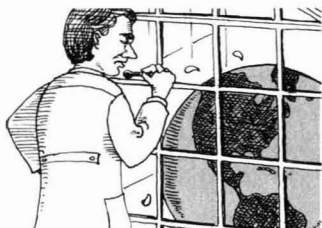
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- (8) Kondo, T. *Yakugaku Zasshi*, **1964**, *84*, 137.

Analytical method validation study

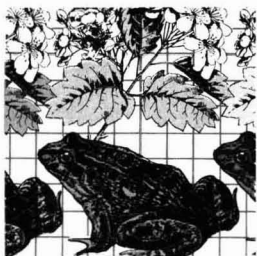
Volunteer (unpaid) and subcontracting (paid) participants are needed to perform GC/MS analyses on priority pollutants as part of a validation study on EPA Methods 624 and 625. Method 624 is for 32 purgeable, organic priority pollutants; Method 625 is for 82 acid and base neutral organic priority pollutants. Interested parties should contact Mr. J. E. Henderson or Mr. D. H. Rodgers, Radian Corporation, P.O. Box 9948, Austin, Tex. 78766, (512) 454-4797, ext. 5402 or 5251.

ES&T CONTENTS

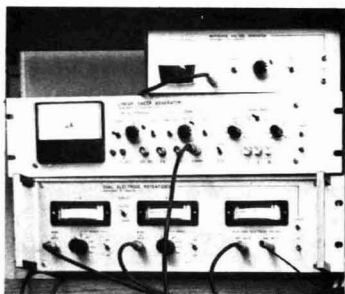
Volume 16, Number 2, February 1982



90A



94A



104A

OUTLOOK

90A

Carbon dioxide buildup. Climate changes are forecast in our most fascinating global experiment.

94A

Biological diversity. What is it? Why the new concern? How important is the concept? What is the outcome?

98A

Persistent PCBs. Half of all polychlorinated biphenyls ever made are still in use in the environment.

100A

Instrumentation meeting program. Pittsburgh Conference attendees will hear this environmental program in Atlantic City, N.J., next month.

REGULATORY ALERT

103A

Hazardous wastes. ERT legal counsel Michael Deland explains delays in implementation of the Resources Conservation and Recovery Act (RCRA).

FEATURES

104A

Environmental analyses. Anodic stripping voltammetry as an analytical tool, especially for heavy metal concentrations. Joseph Wang, New Mexico State University, Las Cruces, N.M.

110A

Acid precipitation: A historical perspective, including details of the national research program. Ellis B. Cowling, North Carolina State University, Raleigh, N.C.

RESEARCH

67

Subsurface distributions of petroleum from an offshore well blowout. The Ixtoc I Blowout, Bay of Campeche. Paul D. Boehm* and David L. Fiest

Seawater samples in the vicinity of an underwater well blowout were analyzed for petroleum hydrocarbon concentrations.

75

Isosteric heats of adsorption of selected compounds on diesel particulate matter. Mark M. Ross, Terence H. Risby*, Samuel S. Lestz, and Ronald E. Yasbin

This study represents the initial step in the determination of the physical characteristics of diesel particulate matter.

79

Identification of atmospheric particulate sources in Washington, D.C., using chemical element balances. Gregory S. Kowalczyk, Glen E. Gordon*, and Scott W. Rheingrover

This study tests whether a linear combination of the compositions of particles from major sources can accurately account for compositions of ambient particles.

Environmental Science & Technology

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Cover: Lester Tinker, UNIPHOTO

90

Method for detecting trace-element contamination of fish samples from handling. James G. Wiener

A statistical method to detect surface contamination of fish tissue and whole fish samples with trace elements is presented.

93

Sorption of amino- and carboxy-substituted polynuclear aromatic hydrocarbons by sediments and soils. Jay C. Means*, Susanne G. Wood, John J. Hassett, and Wayne L. Banwart

An investigation of the sorptive behaviors of three substituted PAH compounds on 14 sediments and soils is reported.

98

Optimal emission control strategies for photochemical smog. Vicente Costanza and John H. Seinfeld*

Qualitative features of optimal RHC and NO_x emission reduction paths for photochemical smog control are presented.

102

Characterization of polycyclic ketones and quinones in diesel emission particulates by gas chromatography/mass spectrometry. Dilip R. Choudhury

The chemical composition of two neutral, mutagenic subfractions of a diesel particulate extract sample are examined using GC/MS.

106

Formation of methyl nitrite in engines fueled with gasoline/methanol and methanol/diesel. Anders Jonsson* and Britt Marie Bertilsson

The concentration of methyl nitrate in vehicle exhaust emissions is determined for methanol/gasoline and methanol/diesel fuels.

110

Gas chromatographic speciation of methylstannanes in the Chesapeake Bay using purge and trap sampling with a tin-selective detector. Jo-Anne A. Jackson*, William R. Blair, Frederick E. Brinckman and Warren P. Iverson

The development and application of a method for the detection and speciation of organotin compounds in aqueous media is described.

NOTES

119

Effect of pipetting on mineral flocs. Ronald J. Gibbs* and Lohit N. Konwar

A procedure is presented for minimizing floc breakage when using pipettes in the handling of suspended material samples.

121

Improved method for polychlorinated biphenyl determination in complex matrices. Gail B. Copland and C. Steven Gohmann*

A fast, accurate, inexpensive procedure for PCB determination using GC is described.

124 ■

Atmospheric trace gases over China. R. A. Rasmussen, M. A. K. Khalil* and J. S. Chang

Results show that China may have significant anthropogenic sources of CH₄, N₂O and CCl₄, all of which are increasing in the atmosphere.

127

Mean residence time of plutonium in the troposphere. Robert W. Holloway* and David W. Hayes

A newly calculated mean residence time for Pu is presented and is compared with residence times obtained by other methods.

CORRESPONDENCE

130

Correspondence on: Anaerobic degradation of halogenated 1- and 2-carbon organic compounds. Paul E. Flathman* and James R. Dahlgren; Edward J. Bouwer*, Bruce E. Rittmann, and Perry L. McCarty.

* To whom correspondence should be addressed.

■ This article contains supplementary material in microform. See ordering instructions at end of paper.

DEPARTMENTS

81A Letters

85A Editorial

87A Currents

124A Products

127A Literature

129A Books

132A Meetings

133A Classified

134A Consulting services

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CIRCLE 11 ON READER SERVICE CARD

The spawning of the “gray” literature

A few years ago (1976–1978), several editorials appeared in *Science* warning of the socioeconomic penalties incurred when decisions are based on conclusions from scientific investigations that are not warranted by the data or in which the data are misapplied. The tradition of peer review and editorial responsibility in the acceptance of published articles has been an obvious control mechanism. Those professional controls have relaxed because of information pressures on agencies dealing with problems such as risks from environmental contaminants.

Scientific findings are increasingly appearing as reports, memoranda, hearing records, and as documents independently published by agencies, consultants and contractors, largely without outside review. This nonrefereed literature has been called the “gray” literature to characterize its elusive nature, although the term may be more disparaging than necessary. The work described in the gray literature is usually done in response to specific requests, under deadlines, and designed to fit some immediate needs of the decision maker.

The traditional review process may not be possible or appropriate where laws, regulations, budgets, standards and procedures are linked to information needs. Therefore, not all agency documents need an external review. However, the interpretation of scientific findings, in whatever source, are subject to some rules of the game. At the very least, the scientific ethos of the agency members should prevail over views of advancement of the agency mission. The agency mission is only as secure as the scientific foundations on which the program rests. One “rule of the game” is for agencies to act with fairness in their interpretation and dissemination of data for which they are acting as caretaker.

Recently I was a party to a conflict that may serve as a case study for the misuse of the gray literature. A long-term study was conducted by a federal agency to determine the extent of health and economic benefits derived from environmental improvement in a rural village within a developing country. The project investigators concluded that the benefits expected from the intervention did not occur. More importantly,

they noted that the methods available currently for such intervention studies were inherently incapable of answering the questions that had been asked.

The investigators’ report to the agency was neither reviewed by experts external to the agency nor distributed to the scientific community, since the findings were considered to be inimical to the agency mission. However, a revised interpretation of the study appeared in a house publication of the agency, claiming that the original findings were in error and concluding that there was indeed a health benefit connected with the intervention.

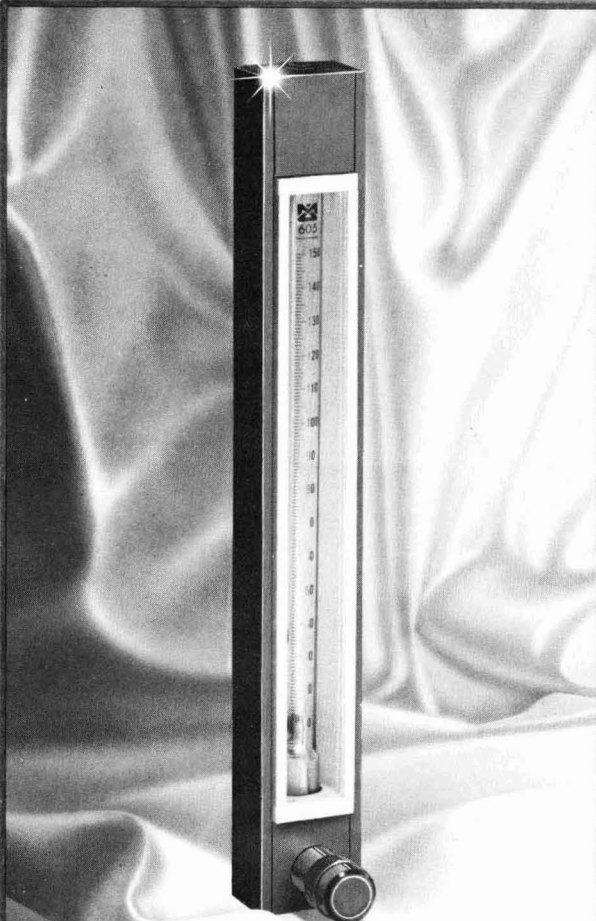
Next, underground reports were heard of agency people presenting the revised findings at meetings far distant from Washington, D.C. A summary of the revised findings was presented in an abstract journal with some connections to the agency. However, the process had some salutary consequences because of the conflict generated by the publication of the revised findings. The agency requested that the disagreement be resolved by an external review panel.

There is a lesson in this relatively minor issue for major public policy decisions involving radiation, occupational, and other environmental exposure limits. Governmental agencies are not disinterested parties to conflicts over interpretations of data and should, whenever possible, open up the data for peer review. Where such traditional approaches are not feasible, the agencies should encourage open publication and discussion. Beyond this, scientific conscience should guide their use of the gray literature.

Morris A. Shiffman



Morris A. Shiffman is professor of environmental health in the Department of Environmental Sciences and Engineering, School of Public Health, at the University of North Carolina at Chapel Hill. His experience ranges from the direction of local health department programs to consultant positions with international agencies.



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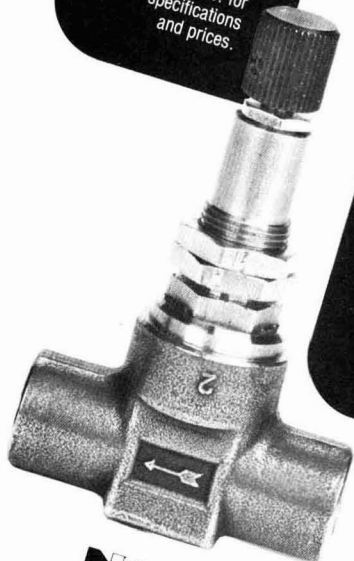
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CIRCLE 7 ON READER SERVICE CARD

ES&T CURRENTS

INTERNATIONAL

For directing toxic substances activities of Great Lakes Basin jurisdictions, no comprehensive management strategy exists, according to the International Joint Commission (IJC, a U.S.-Canadian body). Coordinated assessment processes useful for designing plans of action or control measures are "lacking," the IJC says. "There is no basin-wide system for setting priorities among substances which could adversely affect human or environmental health," the commission added. The IJC's Water Quality Board presented 16 recommendations for reducing environmental and health threats and making better use of limited staff and funds. It also listed 39 local areas of special concern.

Deadly pesticides such as DDT, aldrin, and parathion, which are tightly regulated in the U.S., are sold by American companies to Third World countries where environmental laws are almost nonexistent. These dangerous pesticides harm not only the developing nations but also the industrialized countries that import food from them because some imported foods are sprayed with pesticides that are banned at home. Farm workers in Third World nations often find it impossible to avoid dangerous pesticides; they eat, drink, and smoke in sprayed fields and bathe in contaminated drainage ditches. Few Third World governments warn farmers about the health hazards of pesticides. An executive order regulating the export of hazardous substances was revoked by President Reagan. He argued that "the imposition of export controls results in cumbersome regulatory prices, costly to both the public and private sectors."

WASHINGTON

President Reagan restored most of the drastic 1983 budget cuts the Office of Management and Budget had planned for EPA. However,

the funding is still down sharply from 1981 levels and below the greatly reduced level proposed to OMB by EPA administrator Anne M. Gorsuch. She proposed a budget of \$975 million, down from \$1.35 billion in 1981. The budget approved by OMB at the request of Reagan would reduce the funding to about \$916 million. This is a reduction of more than 40% from the original 1982 budget proposed by former President Carter. Many environmentalists and former agency staff members argue that these cuts will be great enough to virtually dismantle the agency. According to EPA officials, between 800 and 1500 headquarters staff will be fired beginning in March despite the fact that there is no budgetary need to do so this year.



Boesch: leasing schedule problems

The Interior Department may not have the resources to make adequate environmental studies before off-shore tracts are leased for oil and gas exploration, according to witnesses at a House subcommittee hearing. Interior Secretary James G. Watt has proposed eliminating site-specific studies in favor of area-wide studies that cover large portions of the outer continental shelf. Donald F. Boesch, executive director of the Louisiana Universities Marine Consortium, said the accelerated leasing schedule "is of questionable wisdom" and asked whether the information could be gathered quickly enough to lease large areas on an accelerated schedule.

Donald C. Malins of the Northwest and Alaska fisheries center

told the subcommittee that there are many gaps in knowledge about the effects of petroleum on the marine biota and that findings of no major environmental hazard are due to insufficient studies of the long-term effects of drilling discharges.

The EPA will soon expand the "bubble" program of air pollution tradeoffs and shift the responsibility for regulating this program to the states. Under the new policy, a company can calculate together emissions from all smokestacks, leaky doors, dirt roads, etc., at all its plants in a state to see whether the company meets clean air standards as set by the state. About 90 bubble applications are already pending and most will be approved, EPA officials have said. Current rules restrict bubbles to one plant that is already in compliance with the law and to areas where state implementation plans have been approved. Now bubbles will be allowed at any plant in any area, whether clean or dirty. The new concept will enable companies that have less pollution than is allowed to sell their pollution allotments to another firm at an emissions bank.

The hazards of past dumping of low-level radioactive wastes into the ocean have been exaggerated, according to a GAO report. The U.S. disposed of low-level radioactive waste by dumping it into the ocean from 1946 to 1970. Because detailed records were not required, the government has no complete or accurate catalogue of how much, what kind, or where nuclear waste was dumped. However, the overwhelming body of scientific research and opinion shows no evidence that this past dumping poses dangers to the environment.

The EPA is beginning a new program to curtail the illegal dumping of hazardous wastes. A newly established office of criminal enforcement will deter polluters with the threat of a jail sentence. In the past, EPA has used information

from state and local law enforcement agencies, postal inspectors, and the FBI. Now EPA will have a staff of prosecutors with criminal prosecution experience and trained investigators to help them. Under this new system, the agency expects to be able to develop stronger cases to send to the Justice Department for prosecution. The office will investigate industrial violations as well as "midnight dumpers," those haulers of waste who dispose of it wherever they can.

The Office of Management and Budget has proposed cutting the DOE funds for conservation programs and solar research sharply in the next fiscal year. Last year the conservation programs were funded at \$712 million. For next year the proposed funds are \$19 million. Solar research programs that were funded at \$500 million in 1981 will get only \$70 million in 1983. In addition, OMB wants the utilities to bear much of the cost of research on nuclear waste storage. The total budget cuts at DOE, if passed by Congress, would mean a loss of about 4000 jobs.

STATE

A decision to open five national recreation areas run by the National Park Service to mine for minerals and drill for oil and gas has been made by the Interior Department. The areas are Lake Meade in Arizona and Nevada, Glen Canyon in Utah and Arizona, Whiskeytown in California, and Ross Lake and Lake Chelan in Washington. The Interior Department has sent proposed regulations for mining and energy leasing to OMB, which is expected to approve them. The Carter administration proposed that energy leases be sold in the five areas; the Reagan administration is going further by allowing mining for such minerals as copper, gold, and silver.

A receiver has been appointed to displace the corporate management and clean up a hazardous waste storage facility at the Chem-Dyne Corporation in Ohio. In the first appellate decision of this kind, the Court of Appeals for Ohio's Twelfth Appellate District upheld the appointment of a receiver to perform the cleanup. The court decided that the corporation's failure to remove drums of flammable substances, pesticide residues, and

PCBs from its storage site made it necessary to use a receiver.

Each day up to 400 000 cubic feet of New York City sludge is dumped into a square mile of ocean water 12 miles from the New York and New Jersey coasts. A 1977 amendment to the Federal Marine Protection Sanctuaries Act banned ocean dumping after Dec. 31, 1981. However, in April 1981 New York City won a court case challenging the amendment, and ocean dumping continues in this area, where the water is only 78 feet deep. A recent study conducted by the National Advisory Committee on Oceans and Atmospheres said that more research was needed on the long-term effects of ocean dumping in contrast to those of land disposal.

AWARDS

His research on chromatographic separation and analysis of environmental pollutants brought Robert Sievers of the University of Colorado the Tswett Chromatography Medal. The prize, recognizing



Sievers: chromatography prize winner "outstanding research in chromatography," was given at Barcelona, Spain, and shared with Arnaldo Liberti of the University of Rome, Italy.

SCIENCE

Mixtures of pollutants can cause greater reductions in crop yields than ozone alone, according to preliminary results of experiments carried on at the Plant Physiology Institute in Beltsville, Md. When sulfur dioxide was added to ambient air already containing ozone, snap bean and tomato yields decreased as the sulfur dioxide concentration increased. Open-top chambers were used for the experiments. Artificial atmospheres, pumped into the bottom of the chambers, escaped through the top, keeping the sur-



Open-top chambers

rounding air out during fumigation. In snap beans, the two pollutants combined caused more loss than the cumulative effect of each separately. Tomato yields dropped as if the effects of the pollutants had been added together. It was also found that doses of sulfur dioxide above 0.12 ppm increased soil acidity significantly.

Haloethers in water can be analyzed without gas chromatography/mass spectrometry (GC/MS), according to EPA's Environmental Monitoring and Support Laboratory (EMSL, Cincinnati, Ohio). Instead, one can employ liquid/liquid extraction with methylene chloride, an evaporation step, column chromatography cleanup with Florisil, another evaporation step, and GC analysis with an electrolytic conductivity detector. Under contract with Monsanto Research Corp., EMSL studied this analysis method with 2-chloroethyl vinyl ether; bis(2-chloroisopropyl) ether, and several other haloethers. Different methods of solvent extraction and sample preservation were evaluated.

To collect 20 "significant probable or possible atmospheric carcinogens" from ambient air, EPA's Environmental Sciences Research Laboratory (ESRL, Research Triangle Park, N.C.) developed a sampling system using solid sorbent materials. These comprised Tenax-GC, Porapak R, and Ambersorb XE-340 in series. Samples were drawn through a Nutech Model 221-1A pump. Most analyses of Los Angeles, Niagara Falls, and Houston air were done by capillary GC/MS, though some also used flame ionization detection and other methods. One recommendation was that the sampling technique should be mainly a "screen"

for identifying the presence or absence of specific compounds. ESRL did this work also under contract to Monsanto Research.

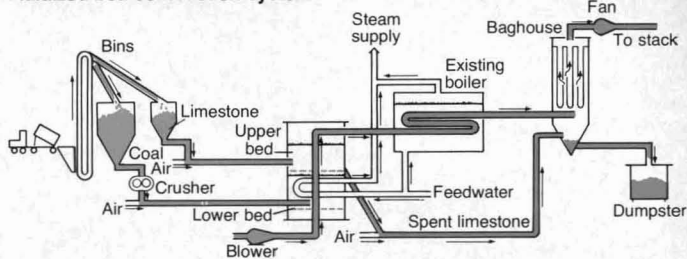
TECHNOLOGY

A wastewater treatment system also capable of conserving up to 92% of water used was announced by Eticam (Providence, R.I.). Principal application is in the jewelry and silversmithing plating industry. Eticam says that of the remaining 8% "work water," about 4.5% is treated and returned to "safe pH level" for further use. About 2.5% is rendered nontoxic and turned into a sludge that is disposable above ground at a public site. The aim of the technology is to prevent metals from reaching sewage plants and interfering with the plants' biological processes. Eticam says that another benefit is an "unconditional guarantee" of 99% recovery of all precious and nonferrous metals.

Integrated pest management (IPM) "is making good progress in America," says Lloyd Knutson, a leading U.S. Department of Agriculture (USDA) entomologist. He ascribes this success to entomologists who learn to use natural enemies of pests, such as parasites, predators, and diseases. Knutson told the First Japan-U.S. Symposium on IPM that "we are only beginning to build our natural enemy foundation. Yet IPM is already a 'proven technology' used in America to control pests of alfalfa, cotton, corn, apples, sorghum, and soybeans." Knutson is chairman of USDA's Insect Identification and Beneficial Insect Introduction Institute located in Beltsville, Md.

Some energy demands could be met with heat contained in magma (molten rock) within 10 km of the earth's surface, according to what was heard at the 1981 fall meeting of the American Geophysical Union. The U.S. Geological Survey estimates such energy at 800-8000 times the annual U.S. consumption. Sandia Laboratories in New Mexico has been investigating the tapping of magma energy since 1975. Energy extraction rates, drilling techniques, and heat exchangers have been among subjects studied. One possible future magma energy site is Valles Caldera, N.M., where two 4-km deep boreholes have already been drilled.

Fluidized-bed combustion system



Source: Wormser Engineering, Inc.

To burn inexpensive high-sulfur coal, a new fluidized-bed combustion (FBC) system will be provided by Wormser Engineering, Inc. (Middleton, Mass.) under two commercial contracts. One will go to the University of Lowell (Mass.); the other to Iowa Beef Processing Co. (Dakota City, Neb.). The system separates desulfurizing and combustion into two vertically-displaced fluidized beds. Also, the beds are shallow, allowing space requirements and attendant cost to be reduced. The company says that this feature will also permit retrofit to gas- and oil-fired burners "which is not possible with any other coal-burning technology."

INDUSTRY

To meet needs of private companies transporting liquid wastes and sludges, the National Solid Wastes Management Association (NSWMA) has formed the Liquid Waste and Sludge Transporters Council. This council will represent firms that haul liquid industrial wastes, chemical wastes, industrial and municipal sludges, and the like, and those that provide septic, sewer, and special cleaning services. The council will address Interstate Commerce Commission and Department of Transportation requirements, employee protection and safety, disposal options, spillage and cleanup procedures, and other such matters.

Remember the oil "shocks" of 1973-1974 and 1979-1980? Another crisis waiting in the wings could be that of nonfuel substances—particularly strategic minerals, the American Maritime Officers Service warns. For instance, chromium is vital for many industries in the U.S. Yet more than 91% of this metal is imported.

Other examples are manganese (nearly 100% is imported, some from unreliable sources), cobalt (100% imported), platinum (88% is imported), and bauxite (94% is imported). Of 36 strategic minerals for U.S. industry, 22, or more than 60%, are imported. The service warns of very serious economic displacements if imports are seriously disrupted, and for which little provision has been made.

A \$500,000 expansion of its environmental sciences laboratory, with emphasis on occupational health, has been completed by the Hartford Insurance Group (Hartford, Conn.). The idea is "to enhance our clients' ability to reduce occupational health hazards and employee injuries before they happen," said William Nebraska, Hartford's vice president for loss control. The lab is one of about a dozen accredited insurance company-operated industrial hygiene labs in the U.S., Nebraska pointed out. It is directed by certified industrial hygienist Darrell Smith. Among its missions are identifying and measuring chemicals affecting health and safety, emergency monitoring services, and general loss control support.

The solar energy industry could be "devastated" if tax credits are removed, William Bergman of the Solar Energy Industries Association (Washington, D.C.) warned. He attributed the "big leap" in solar sales in 1979 to the credits, and an additional 21% increase in sales after Congress further liberalized the credits in 1980. Loss of credits, he said, could delay the date by which solar could compete effectively with other fuel. Bergman also observed that cutting out the tax advantages could hamper efforts to reduce dependence on foreign oil, and to stimulate investments that could lead to new jobs.

The greenhouse effect

The climate change induced by man-made releases of carbon dioxide and other trace gases is likely to be our most fascinating global experiment

Many uncertainties surround the subject, but more and more scientists are coming to believe that accumulations of man-made carbon dioxide in the atmosphere will, through the so-called greenhouse effect, cause a significantly warmer planet. Recent evidence indicates that it is not only increased levels of carbon dioxide that may warm the planet, but other trace gases as well, such as methane and chlorofluorocarbons. There are several studies that suggest the warming has already begun, although they do not establish a definite cause and effect relationship between global temperatures and increased levels of carbon dioxide and other trace gases.

Since time immemorial, carbon dioxide has had a warming effect on the atmosphere. It absorbs much of the infrared radiation emitted from the earth's surface and then radiates some of the energy back to the surface. Without carbon dioxide, the earth would be several degrees cooler.

In the last century, the level of carbon dioxide increased from an estimated 293 parts per million in 1880 to 335 ppm in 1980, due mainly to the increased use of fossil fuel. That number is expected to double in the next century, even with slow growth in fossil fuel consumption. Carbon dioxide levels have been more accurately monitored since 1957 and it is known that they rose 12 ± 1 ppm in the decade from 1970 to 1980. There are presently 19 stations in remote sites to determine global background concentrations and another eight will be added shortly.

Some investigators believe that now



and in the future other trace gases will contribute an additional warming equal to 50–100% of the warming caused by carbon dioxide alone. From negligible amounts, CCl_2F_2 has apparently increased to 0.3 ppb and CCl_3F to 0.2 ppb. The methane level rose 1–3% per year from 1965 to 1980 and it has been estimated that nitrous oxide has risen from 295 ppb to 301 ppb during the last decade. These gases have been monitored precisely only in the past few years.

One-dimensional models

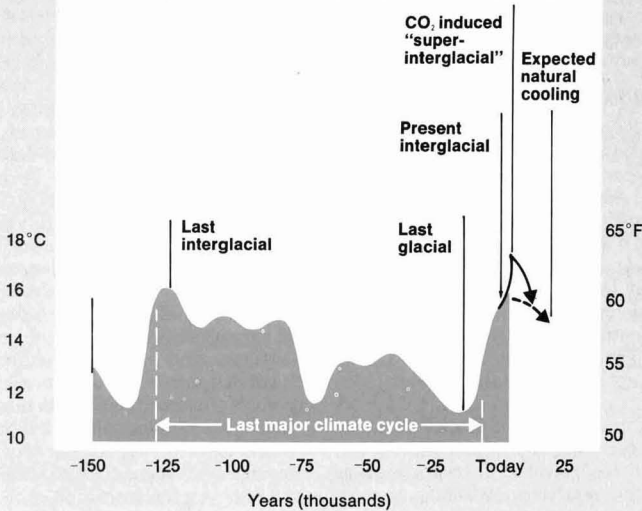
Several models have been devised to predict the warming that might be caused by increased levels of CO_2 and other gases, and they project a global warming of almost unprecedented magnitude. A paper recently published in *Science* by James Hansen and colleagues of the New York office of the Goddard Space Flight Center describes six one-dimensional radiative-convective models. Each model is based on the assumption that 50% of the man-made carbon dioxide will re-

main in the air and each differs slightly by taking different variables into account. The model in which they have the most confidence forecasts a temperature change of 2.8 °C for doubled carbon dioxide. It is not the only gas included in the model; there are other gases that are computed to contribute additional warming equal to 70% of that caused by carbon dioxide alone.

From this model, Hansen et al. predict that by the end of the next century, the global temperature will rise 3–4.5 °C with fast growth in the use of fossil fuels, 2.5 °C with slow growth, and only slightly more than 1 °C for no growth. But some might argue that natural processes are also responsible for changes in the earth's temperature balance. However, Hansen calculates that extreme variations in measured solar radiation could at most cause only a 0.7 °C global temperature change over this time period, while the aerosols resulting from exceptionally large volcanic eruptions would reduce the warming by about 1 °C. Because these two factors are what appear to have the greatest effect on climate over a century or less, it seems that global temperatures will rise no matter what—unless these large volcanic and luminosity changes are present along with constant levels in the global use of fossil fuel during the next hundred years, a highly unlikely situation.

The 2.5 °C rise in global temperatures predicted for slow growth in fossil fuel consumption does not sound very great, but it would cause the average global temperature to exceed that thought to have existed during the al-

Long-term trends in average global temperatures^a



^aCO₂-induced warming may cause higher temperatures than those during the last interglacial period.

Source: Technology Review

tithermal (6000 years ago) and the previous interglacial period (125 000 years ago) and to approach the warmth of the Mesozoic, the age of the dinosaurs. In other words, such an elevation in global temperatures would make the earth warmer than it has been at any time since human beings appeared on this planet.

The most sophisticated of Hansen's models is also used to predict the expected warming that may be caused by carbon dioxide and other trace gases in the 1970s and 1980s. This model forecasts a rise of 0.1–0.2 °C for the 1970s and a rise of 0.2–0.3 °C for the 1980s. Judging from temperatures during the past century, the natural variability, or standard deviation, in global temperatures is 0.1 °C for 10-year intervals. Therefore, unless there are very unusual changes in solar luminosity or in volcanic activity, this model predicts that gas-induced warming should exceed natural global temperature variability by the end of the 1980s; that is, the greenhouse effect should rise out of the noise level of natural temperature deviation less than 10 years from now.

What uncertainties surround these predictions? One difficulty is that the magnitude of the methane growth is not known very accurately. Another is that this model does not include variations in aerosols or solar luminosity when it is used to predict future warming because at present we have

no way of forecasting such variations. A third is that it does not take into account all predictable processes known to affect climate, but includes only three or four of the more important processes. Cloud feedbacks that occur in response to climate perturbations are not used as a factor because more reliable models need to be developed in this area. The most important source of error may be the assumption that 50% of the synthetic carbon dioxide will remain airborne. This hypothesis is somewhat uncertain

and can only be improved through a better understanding of the carbon cycle. There is also a lack of knowledge of ocean mixing processes. These do not affect the eventual temperature rise that would be caused by doubled carbon dioxide, since anthropogenic increases are expected to persist for centuries, but do affect the time at which the warming would occur. Ocean mixing could delay the warming by several decades, but it would happen eventually.

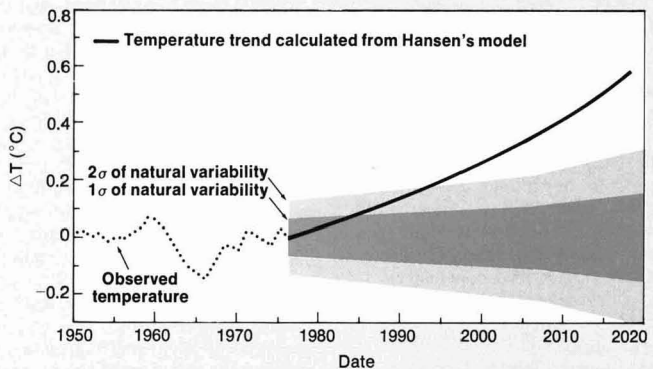
Global temperatures

What *did* happen to the average temperature of the earth during the last century and the previous decade? A temperature decrease in the northern hemisphere of about 0.5 °C from 1940 to 1970 has led people to believe the earth has been growing colder. However, northern latitudes warmed 0.8 °C between the 1880s and 1940 and by 0.1–0.2 °C in the 1970s.

Average global temperatures are the variable that should be used to assess the greenhouse effect because carbon dioxide is rapidly disseminated around the earth. The global mean temperature rose 0.5 °C between 1885 and 1940 with slight cooling thereafter, making a net rise of 0.4 °C in the past century. This is roughly consistent with the warming calculated from Hansen's model. The earth's mean temperature increased by 0.1–0.2 °C in the 1970s, which is also equivalent to the model's predictions for this decade.

When the model is applied to the last century and includes only variations in carbon dioxide, it shows the general trend in temperatures over the century, but does not show individual variations in temperatures over short

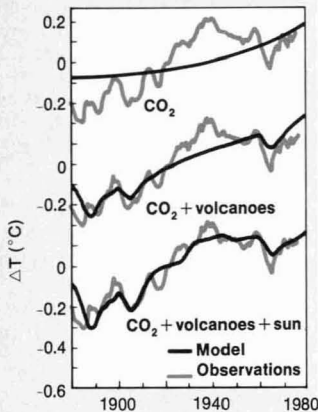
Predicted CO₂ warming versus natural climate variability^a



^aThe effect of other trace gases is not included.

Source: Science

A comparison between average global temperatures and those computed from Hansen's model^a



^aThe heat capacity component in the model is based on an ocean with a 100-m mixed layer and diffusion of heat into the thermocline to 1000 m. Source: Science

time periods. On the other hand, when the model includes changes in solar luminosity and volcanic aerosols as well as increasing levels of carbon dioxide, it gives a good match even over intervals as short as 10 years. Although it seems to explain past variations in global temperatures, further testing is needed to determine its predictive abilities. The agreement of the model's calculations and actual temperatures over the last hundred years, however, makes it seem that we may have identified the dominant processes affecting global temperature changes over time periods ranging from decades to centuries.

Declines in pack ice

More spectacular evidence for the effects of global warming is that, according to George Kukla and Joyce Gavin of Columbia University, the extent of pack ice around Antarctica during the summer decreased 2.5 million km² from 1973 to 1980, 35% of the average pack ice surrounding the continent in summer. Satellite observations since 1973 tell the area of ice much more accurately than it was known in previous years. The decrease cannot be ascribed conclusively to a rise in average global temperatures or in carbon dioxide levels. However, large atmospheric models of the climate developed by V. Ramanathan of the National Center for Atmospheric Research, Boulder, Colo., and M. S. Lai and R. D. Cess of the State

University of New York, Stony Brook, indicate that the greatest impact of global warming would be seen along the margins of the snow and ice fields during the spring and during late summer.

The carbon cycle

Behind any model that predicts warming caused by increased levels of carbon dioxide is an assumption about the percentage of man-made carbon dioxide that will remain airborne. In order to accurately predict this percentage, we need to understand and be able to model the carbon cycle—the sources and sinks of carbon dioxide and the fluxes between each.

The atmosphere, the ocean, and the biosphere are the three major reservoirs in the carbon cycle. Except for the atmosphere, the amount of carbon in each reservoir is somewhat uncertain; the individual fluxes between and within reservoirs are even more problematical. At present the atmosphere holds about 700×10^{15} g of carbon in the form of carbon dioxide. This is continuously being exchanged with the biota and with the surface waters of the ocean. The amount of carbon contained in the total worldwide biota is about 800×10^{15} g, somewhat more than is held in the atmosphere. The organic matter of the soil, mainly humus and peat, holds a still larger pool of carbon, estimated at $1000\text{--}3000 \times 10^{15}$ g. The oceans contain by far the largest amount of carbon: $40\,000 \times 10^{15}$ g in the form of dissolved carbon dioxide and 3000×10^{15} g as dissolved organic matter.

In contrast to these figures, the numbers relating to the combustion of fossil fuel sound very small. The worldwide use of fossil fuel releases about 5×10^{15} g of carbon per year, of which the atmosphere retains an increase of 2.3×10^{15} g. This means that about 2.7×10^{15} g of fossil fuel carbon are removed from the atmosphere by an uncertain combination of terrestrial and oceanic processes.

The largest ultimate sink for fossil fuel-produced carbon dioxide is the open ocean. It absorbs this gas in two ways. One is a simple equilibrium between carbon dioxide dissolved in the ocean water and that in the air. Another part of the carbon dioxide taken up by the ocean is used by organisms for photosynthesis and eventually sinks to the bottom as feces or dead organisms.

It is not clear whether inorganic carbon in the soil constitutes a source or sink for atmospheric carbon dioxide. The problem of estimating changes in soil carbon on a global basis is ex-

tremely difficult, even more so than for the living biomass.

Taken as a whole, the effect of the biomass on carbon dioxide levels is also extremely uncertain. Some evaluations of biomass data indicate that net biomass changes contribute amounts of carbon dioxide equal to or greater than the fossil fuel contribution itself, primarily because of the rapid deforestation that is taking place in many tropical areas. Currently $4\text{--}8 \times 10^{15}$ g of carbon dioxide and possibly more may be released each year through the destruction of forest and the accelerated oxidation of humus from the drainage of wetlands and the extension of agriculture into soil that contains large amounts of organic material. Increased levels of carbon dioxide probably induce accelerated rates of photosynthesis. But unless the biomass is able to store a net amount over several centuries, the accelerated rate will not remove a net amount from the atmosphere.

Effects of warming

If there is slow growth in the use of fossil fuels and the global temperatures increase by 2.5 °C in the next century, what effects will this have on climate and the living things of the earth? Actually we do not really know whether the net long-term effect would be beneficial or detrimental on a worldwide scale. To answer this question we need improved global climate models and reconstructions of past climate changes. The climate responses in individual regions are extremely difficult to quantify. For some areas, it is even a problem to know the sign of the temperature change, because the earth would not be warmed uniformly, nor indeed would all of it necessarily be warmed.

Paleoclimatic evidence suggests that the snow/albedo feedback would cause the surface warming at high latitudes to be two to five times the global mean warming. This would reduce the temperature gradient between the tropics and the poles, and change the energy and water vapor exchange between various parts of the earth, resulting in new circulation and precipitation patterns. Areas that are growing regions might become deserts and dry regions could become wet. Wetlands and tundra could change location. Some analyses predict that the Great Plains would turn into a desert; this would have global implications because it is such a large crop-growing region. There would probably be a poleward displacement of the natural range of tree species with a widening of the tropical zone. On a short-term

basis, this would be deleterious because tree species are generally best suited to the climate in which they are found.

Ice sheet disintegration

One of the most disturbing possible effects of a rise in global temperatures of 2.5 °C is the melting of the West Antarctic ice sheet. This may already have begun in the Amundsen Sea sector. During the last interglacial period (125 000 years ago) global sea levels were some 5–7 m higher, possibly due to a disintegration of this ice sheet. Because it lies primarily on bedrock below sea level, where the average summer temperature is –5 °C and because temperatures at high latitudes are predicted to rise 2–5 times the average global rise, a global rise of 2.5 °C could cause the ice sheet to melt rapidly and slump into the ocean over a few decades or a century. It seems that one ice sheet did melt almost this rapidly about 8000 years ago; the Hudson Bay ice dome apparently disappeared over a time period of about two centuries. If the West Antarctic ice sheet melts, this could cause a sea level rise of 5–6 m that would flood 25% of Louisiana and Florida and 10% of New Jersey and many other lowlands throughout the world. As mentioned earlier, the extent of pack ice around Antarctica has already diminished 35% of its summer average.

Another possible long-term effect of carbon dioxide warming would be a melting of the entire Antarctic ice sheet, which would raise sea levels by 60 m. This would take thousands of years, however, because much of it lies above sea level.

Food supply and the ocean

If a rise in levels of carbon dioxide does cause a substantial rise in global temperatures, it is not known whether this would enhance or decrease the world's potential food production. It would definitely lengthen the growing season in many parts of the world and alter the distribution and species composition of terrestrial ecosystems. Individual countries such as the U.S. might be adversely affected, but some parts of the world now too dry or too cold to grow crops might become productive regions. In addition, experiments indicate that a doubling of carbon dioxide levels would cause rates of photosynthesis to increase by about 20%. Nevertheless, there could develop a substantial reduction in world food supplies at a time when demand is at a maximum and shifts in crop-growing regions, even without decreased overall productivity, would cause social disruptions.

A potentially serious consequence is that if global temperatures rise substantially (e.g., by 2.5 °C), the higher latitudes would be warmed more, and the temperature difference between the latitudes would not be nearly so great. This would cause a general diminution in wind speeds. A 20% reduction in wind velocity would induce a 40% decrease in the wind-driven ocean circulation. Furthermore, melting of ice sheets would reduce the salinity of the surface layers at high latitudes. Taken together, these effects would lead to a slowdown in the circulation of ocean water and a consequent decrease in upwelling, which is the primary way aquatic life receives nutrients. As a result, fish production might well diminish substantially.

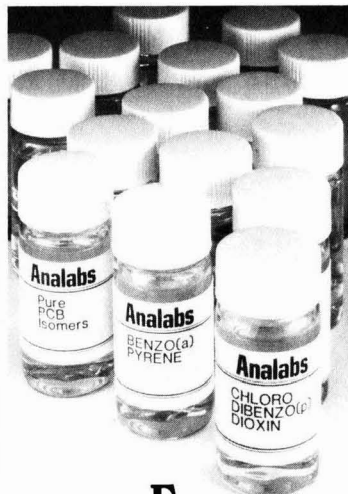
Research needs

There is a scientific consensus that increased levels of carbon dioxide would cause global warming. There is no consensus, however, about the degree of warming and no very good understanding of what the effects of warming might be. The rise in temperature will depend on the rate at which fossil fuels are used and the choice of fossil fuels. Not all fossil fuels give off the same amount of carbon dioxide per unit of heat. Natural gas, for example, produces a relatively large amount of heat for each ton of carbon dioxide put into the atmosphere. Synfuels lie at the other end of the spectrum. They produce carbon dioxide in their creation, processing, and even more when they are burned.

In order to understand the climate system well enough to accurately predict the effects of increased carbon dioxide concentrations, it is necessary to measure solar luminosity, cloud properties, ground albedo, and trace gases, and to study certain components of the climate system such as heat storage and transport by the oceans and ice sheet dynamics.

Even if the globe warmed up substantially, it might be possible for humans to adapt. The sea level, for example, would probably rise slowly enough to build sea walls around such cities as New York. But these accommodations might lead to catastrophes such as flooding from storms or earthquakes. In any event, all climate changes, even those that are beneficial in the long run, would impose stress, and there is the definite possibility of long-lasting detrimental effects. Adaptation may be possible, but adaptation may not be what is best for continued survival of the human race.

—Bette Hileman



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Why maintain biological diversity?

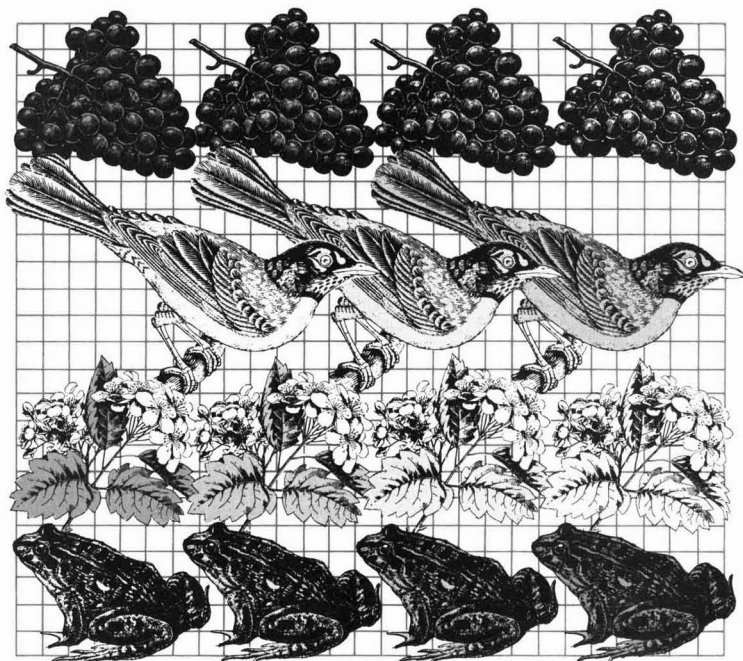
Not only for moral and aesthetic reasons, but also because experts believe that great scientific and economic benefits could be gained

Given the present state of knowledge, genes themselves cannot be manufactured by scientists; they can come only from nature. When a given species of plant or animal, from unicellular all the way up to the most complex organisms, becomes extinct, some of its genetic material is lost forever. And even if scientists learn how to make genes, there is little likelihood that an extinct species could be recreated, since knowledge of its genetic makeup would be lacking.

Conceivably, genes that are lost through species extinction may be those that could have conferred resistance to certain pests or diseases on a given food or fiber crop. Others might have contributed to industry, science, or even environmental cleanup. For these and many other reasons, scientists—especially biologists and biochemists—are beginning to look at the accelerating rate of species extinction as an environmental danger.

Biologist Paul Ehrlich of Stanford University concurs with this view. He warns that the threat of extinction is indeed global in scope, and that its materialization could lead not only to genetic resource losses, but to deleterious changes in weather patterns and soils, and to the loss of "other 'services' humanity can't do without." Among these "services" might be included the sustenance and improvement of agricultural, forestry, and fisheries production, and the usefulness of various species to act as a buffer against adverse environmental change.

For these and many other reasons, scientists are urging worldwide efforts to put a brake on the increasing rate of species extinction—at least, that portion attributable to human activity—and to encourage the preservation of biological diversity. "Biological diversity" can perhaps be defined in



terms of the total number of species in existence; the variations among individual species; and the relationships between them, sometimes very complex and unique, in different ecosystems.

An estimated 5–10 million microbial (both plant and animal) and higher plant and animal species inhabit the earth. Many of them have not yet been classified by science, especially in tropical areas. Scientists believe that between the years 1600 and 1900, about 75 mammal and bird species became extinct. Between 1900 and the present, this extinction rate is believed to have increased to one species a year.

Among human acts held responsible for species disappearances is habitat destruction for purposes of urbanization or agricultural development. Ehrlich believes, however, that if the development of virgin land were to end now, the extinction rate might be slowed somewhat, though not halted.

Presently, scientists forecast sharp increases in the extinction rate. For 1990, the rate is projected at 10 000 species/y; by the year 2000, perhaps 20% of *all* species presently extant will have disappeared, and possibly as many as 30–70% of the world's plant species. That is the view of botanist Billie Lee Turner of the University of Texas at Austin, who is generally

pessimistic that humanity will do much to try to reverse these projections.

A foreign policy interest

Concern with species extinction and consequent genetic resource loss was expressed at the Strategy Conference on Biological Diversity. Sponsored by the U.S. Departments of State, Interior, and Agriculture, and the Agency for International Development (AID), the conference was held in Washington in mid-November. Speakers and participants from the U.S. and several other countries considered "steps that the U.S. might pursue domestically and internationally, over the next three to five years, to maintain the earth's biological diversity in a manner that serves a range of economic, social, and ecological interests over the long term."

More specifically, aims of the conference were to:

- review the scope, magnitude, and sources of worldwide losses of plant and animal species
- assess the economic, social, ecological, political, and strategic implications of a continuing decline in species diversity, especially as it may relate to world food supply, energy demand, and commercial output
- identify and evaluate scientific knowledge, technologies, and institutions available for conserving biological diversity
- review the nature and effectiveness of U.S. government domestic and international programs
- recommend initiatives that the U.S. should undertake in order to stimulate and assist an expanded worldwide effort in this area.

The agenda covered crop and non-crop plants, including trees; domesticated and wild animals; microbes; aquatic resources; ecosystem maintenance;

and genetic engineering applications.

"Maintenance of world biological diversity has not been a traditional State Department concern; but, as you can see by our sponsoring this conference, our position in this regard is changing," said James Malone, Assistant Secretary of State for Oceans and International Environmental and Scientific Affairs. "Biological diversity has now become a U.S. foreign policy interest, in our view," he added.

That the narrowing of biological diversity through extinction is inherently an international problem, and hence, a U.S. foreign policy interest, was underscored by Undersecretary of State James Buckley. Noting that "future generations have a stake in stemming impoverishment of biological resources," he estimated that 40% of all prudent (ethical) drugs come from nature. Buckley also noted that biological resources most needing protection are more often found in less developed countries (LDCs).

Cataloging wild "relatives"

In tropical LDCs, up to 90% of the indigenous plant and animal species are as yet unclassified by biologists (although some scientists believe that for plants, the 90% figure is an overstatement). If habitat destruction through urbanization and expanded agriculture continues, these species may never be classified. Plants of concern comprise members of all phyla; with animals, although all are under consideration, emphasis is on invertebrates. The focus is on both terrestrial and aquatic environments.

Zoology professor Clark Hubbs, also of the University of Texas at Austin, observed that many of the species conservation efforts that have taken place dealt with colorful, conspicuous types of plants and animals, such as Saguaro cacti, or "big cats." Little or no attention has been paid to lower species such as fungi or insects, which might be of very great importance to an ecosystem, particularly in the tropics, he added.

As a first step toward slowing down the extinction rate, a systematic cataloging of species, with emphasis on those in tropical areas facing urban or agricultural development, was advocated by some conference speakers. Addressing plant species in particular, Quentin Jones of the U.S. Department of Agriculture (USDA) proposed establishing four categories:

- species, especially in tropical areas, for which no information as yet exists
- species of which ecological pa-

rameters and geographic distributions are generally known

- species that are not cultivars, but might be expected to be useful in the future as crops, or in some other capacity such as watershed stabilizers, revegetation plants, or the like
- cultivars grown in commerce for food, fiber, and other purposes, and—very important—their wild progenitors.

There was a strong recommendation that special attention be given to wild progenitors and relatives of many cultivars, such as cereal grains, legumes, and the like. For instance, these wild plants could provide genetic material that might furnish the cultivars with increased natural resistance to insects or diseases, the ability to withstand less favorable climatic conditions, or other such desirable traits. Without this diversity of material, the cultivars themselves could lose their adaptability to changes in their environments, perhaps with the consequence that they could become increasingly difficult or actually impossible to continue to cultivate to any large extent.

"No useless plant"

After species inventory the next step, which must probably be taken simultaneously, is establishing and maintaining genetic material "banks." Turner, of the University of Texas, who directs the University's Plant Resources Center, says that the best such bank for protecting an otherwise disappearing species would be a series of preserved actual habitats, perhaps 30–50 km² in area. Otherwise, genetic material banks might consist of specially constructed repositories properly maintained under carefully controlled environmental conditions, for both plant and animal species.

U.S. agencies and groups maintain such repositories, especially for cultivar varieties. For example, the USDA funds a National Germplasm System that has 450 000 accessions, and adds 7500/y from many different sources. The National Science Foundation sponsors biological diversity research, particularly for tropical areas.

AID contributes funds to sponsor germplasm systems at various international agricultural research institutes throughout the world. Also, the International Board for Plant Genetic Resources (IBPGR), a component of the U.N. Food and Agricultural Organization (Rome, Italy), has the task of preserving and expanding the world genetic resource inventory of crops. The IBPGR was founded in 1974, and is devoted to developing international

Some definitions

Biological diversity refers to the numbers of species and genetic types within species, plus maintenance of relationships among the species.

Ecological diversity refers to diversity exhibited by a species under different ecological conditions.

Genetic diversity refers to the existence of different genetic types of varieties within a given species.

A cultivar is an organism that exists or persists because it is cultivated. This term is most often applied to crop plants.

Biological diversity could protect crops

One possible illustration of the need to maintain biological diversity can be found in cereal grain growing. Corn (maize, *Zea mays*) for human and animal consumption is a prime example. Without genetic diversity, a given variety of maize could eventually be unable to adapt to changing conditions. For instance, its ability to "fend off" biotic threats, such as weeds, diseases, and insects, and abiotic threats, such as heat, cold, or drought, could be seriously impaired.

A source of genetic diversity for maize might be found in five of six teosinte grass species of Mexico and Guatemala, which, according to botany professor Hugh Illis of the University of Wisconsin (Madison), may be considered as subspecies, or ancestral forms of *Zea mays*, now known only as a cultivar. He adds that not only was teosinte an ancestor of maize 8000 years ago, "but it continues to play an important role in maize evolution today."

Until recently many in Mexico have regarded teosinte as a pesky field weed to be exterminated. However, on a parcel of land scheduled for development, a botanist found a species that "is resistant to more than half the viruses that plague domesticated maize types, is immune to a range of insects, and thrives in hostile areas where other varieties perish," according to UNEP. Possibly, these desirable traits could be transferred to certain domesticated maize varieties. UNEP notes that had the land parcel—the only known sanctuary of that wild maize species—been developed as scheduled, the plant would probably never have been known, and its genetic resource would most likely have been irretrievably lost.

Similarly, ancestral forms and older varieties of wheat grow in various parts of central Asia and Turkey. Stanford's Ehrlich warns that without such genetic renewal with material from the wild, many extensively cultivated wheat varieties (or substitute rye, millet, sorghum, and so on) could lose the genetic capability to adapt to a changing environment.



collaboration among its members in a global network of institutions active in the exploration, collection, conservation, documentation, and use of plant genetic resources.

Other international-level organizations working in species preservation include the U.N. Environment Program, and UNESCO's "Man in the Biosphere" program. On a nongovernmental level, there is the International Union for the Conservation of Nature and Natural Resources.

Recounting an ancient Indian proverb that "a useless plant has never been found," T. N. Khoshoo, director of the National Botanical Research Institute (Lucknow, India) said that his country has five national government agencies working to maintain and promote biological diversity. He added that India is establishing, or plans to establish "gene sanctuaries" and biosphere reserves. Khoshoo suggested that where habitat preservation is infeasible for some reason, tissue culture could be an "inexpensive" means of retaining a species' living material. He added that conservation of marine biota and microbe species "is of the utmost importance," perhaps because there are so many such species that have the potential of making important contributions to the world genetic resource base. One example of a benefit that can be derived is additional sources of enzymes for fermentation processes.

No bailout

The preservation of ecological and genetic diversity, then, transcends aesthetic, moral, or sentimental considerations. According to scientists at the State Department conference, and other experts in the field, it is a matter of absolute necessity for survival. As Stanford's Ehrlich put it, "In most cases, humanity does not know how to substitute for ecosystem services." And some of these may be biological and biochemical services without which human survival could become problematic.

Nevertheless, prospects for really large-scale global efforts toward species preservation and resultant ecological and genetic diversity retention are probably dim, especially in tropical areas where they are needed most. Urbanization and rural agricultural development continue; and, if anything, will probably accelerate further.

Botany professor Turner of the University of Texas takes the view that it is "probably too late anyway" for significant species preservation and biological diversity maintenance. He

Biological diversity could pay off

About 25% of the number of all prescription drugs in the U.S. are derived from higher plants, Norman Farnsworth of the University of Illinois Medical Center (Chicago) estimates. He pegs their total 1980 market value at \$8 billion. This does not take into account the value of pharmaceuticals derived from microorganisms and fungi, for instance.

Farnsworth, whose specialty is medicines derived from nature, told *ES&T* that about 10 prescription drugs used in the U.S., derived from plants, were discovered between 1950 and 1981. He believes that if the number of existing plant species remains constant, through the year 2000, 18 new prescription medicines might be found in the U.S. from plants that are presently predicted to become extinct. His analysis tells him that in rare and endangered plants in the U.S., pharmaceuticals may be found that could lead to an additional \$3.5 billion/y worth of business through the year 2000 (expressed in 1980 dollar values). Farnsworth acknowledged that his analysis, figures, and projections could be open to considerable controversy and debate.

One can readily imagine the economic possibilities that could be offered by plants in tropical areas, for example, where there still is great biological diversity, provided that the extinction rate is halted. This becomes even more the case when one considers the genetic resources available for bioengineering projects.

Among U.S. efforts to preserve plant biological diversity is a compilation by the California Gene Resource Program of a list of plants of real or potential economic importance to that state, and of steps recommended for preserving them. This program has been active since the early 1970s. Later in that decade, the New York Botanical Garden established an Institute of Economic Botany, as well as a Rare and Endangered Native Plant Exchange. Records of such plant and seed exchanges will be maintained by participating botanical gardens and societies, and in the computer facilities of the City University of New York. For further information, contact:

Plant Exchange
c/o New York Botanical Garden
Bronx, N.Y. 10458.

believes that "the psychological attitude of man is such that he is not likely to preserve any large number of tracts harboring plants and animals that may be on the verge of extinction." As for his suggestion concerning 30-50-km² species protection tracts, "I don't see the likelihood of this happening, since most people will ask, 'Why isn't this land under cultivation?'" Offering *ES&T* a contrasting view, Jones of the USDA said, "We also have the problem of feeding a burgeoning world population."

On balance, prospects for the maintenance of biological diversity must probably be characterized as bleak. However, that situation might be mitigated if it could be shown in clearly understandable terms how genetic material, which might otherwise be irretrievably lost, may have a tremendous potential economic value as new sources of food, fiber, fuel, medicines, and organic chemicals. In other words, genetic resources are a sort of biological "capital"; wisely invested, it could yield interest in the form of valuable goods and services, and perhaps a whole new genetic engineering and industrial base. By contrast, wholesale extinction of species would be tantamount to dissipating a family's capital fortune—only in this case, it may be all of humanity that could face economic and biological bankruptcy, with no one to turn to for a bailout.

—Julian Josephson

Additional reading

Ehrlich, P.; Ehrlich, A. "Extinction". Random House, 201 East 50th St., New York, N.Y. 10022. \$15.95.

Murray, J. R.; Hiam, A. "Biological Diversity and Genetic Engineering". Presented at the Strategy Conference on Biological Diversity, Washington, D.C., November 1981. Policy Research Corp., 738 North Wells St., Chicago, Ill. 60610

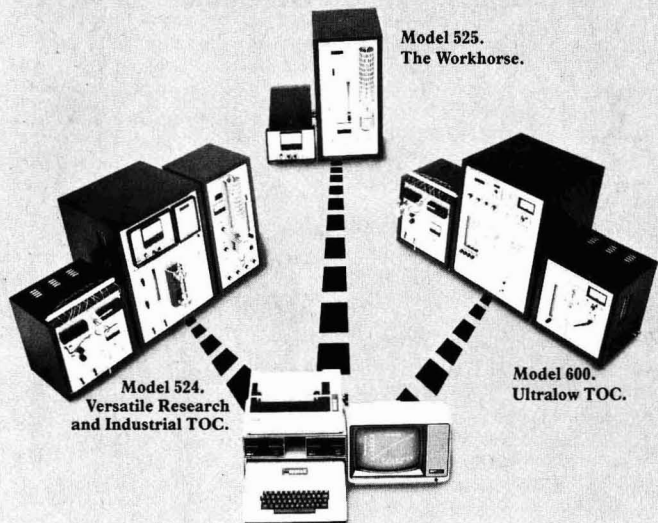
"Biological Diversity". Reprinted from the 11th Annual Report of the Council on Environmental Quality, Washington, D.C., December 1980.

"Genetic Resources, An Overview". UNEP Report No. 5 (1980). Na. 80-4559. United Nations Environmental Programme, Nairobi, Kenya.

"Crop Genetic Resources". AGP: IBPGR/81/67, September 1981. International Board for Plant Genetic Resources, Food and Agriculture Organization of the United Nations, Via delle Terme di Caracalla, 00100 Rome, Italy.

The Strategy Conference on Biological Diversity plans to publish a set of Proceedings, perhaps as early as this month, if possible. For more information, contact Ms. Anne Wickham, OES/ENR, Room 7819, U.S. Department of State, Washington, D.C. 20520.

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CIRCLE 14 ON READER SERVICE CARD

EPRI, the research arm of the electric utility industry, announced a \$7 million, five-year research program to find ways to manage . . .

The persistent PCB problem

On the one hand, PCBs are a very small segment of any hazardous waste management scheme. On the other hand, they are persistent environmental contaminants whose use has been controlled. They are the only group of chemicals specifically mentioned by the Toxic Substances Control Act, now five years old.

Between 1929 and 1977, about 1.4 billion lb of PCBs were produced in the U.S. Although its chemical manufacture has now ceased, 750 million lb are still in service, but only 162 million lb are associated with the electric utility industry.

PCBs are used in two types of sealed electric equipment:

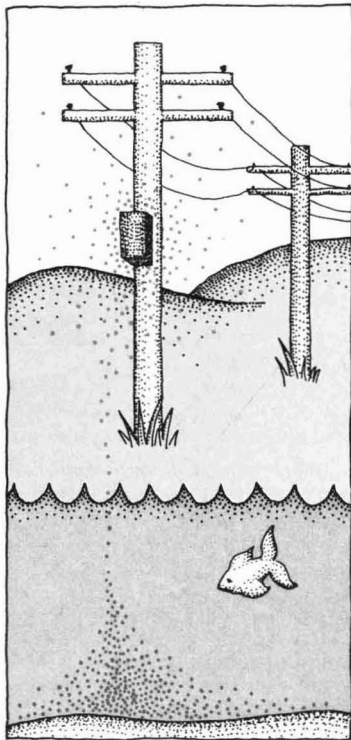
- transformers that raise or lower the voltage of a power line
- capacitors, the bread box-sized cans on utility poles that help maintain constant voltage in homes. Their good electrical properties (for capacitors) and low flammability (for transformers) make polychlorinated biphenyls especially suitable for these uses.

Of the other half of the PCBs, 3.6% have been destroyed; another 10.7% were exported. Some 21.4% are buried in landfills and 10.7% have escaped into the environment, much of that portion coming to rest at the bottom of the ocean.

The EPA regulations on PCBs have caused trouble for the electric utility industry. These regulations address two types of equipment: that containing PCB concentrations over 500 ppm, and so-called PCB-contaminated equipment containing 50–500 ppm PCBs. Concentrations below 50 ppm are not regulated.

Extent of the problem

The electric utilities estimate that fewer than 22% of the 750 million lb are the responsibility of their industry. According to estimates of the Edison Electric Institute, Askarel transform-



ers contain 75 million lb of PCBs and PCB capacitors another 87 million lb. Askarel contains PCBs with up to 50% trichlorobenzene. Together, the 162 million lb account for essentially all PCBs in the electric utility industry.

In addition, however, there are another 262 000 lb of PCBs in other transformers. These other transformers are filled with mineral oils. Approximately 10% of the utility transformers are contaminated with PCBs in the 50–500 ppm range. This includes 1.9 million distribution transformers and 25 000 power transformers. The remainder, below 50 ppm, are

considered free of contamination.

PCBs are an obvious problem for the electric utilities, though not exclusively, since fewer than 22% of the remaining PCBs still in use are found in their industry. Other industries are said to have a PCB problem; for example, the metal die-forming industry. Another use is in electrical equipment in high-rise buildings, industrial plants, and commercial operations. Here the equipment is not the responsibility of the electric utility industry per se, but rather that of other industry.

The regulations have caused such concern to the electric utility industry that the Electric Power Research Institute (EPRI) has launched its research effort to find ways to manage this PCB equipment. A recent three-day seminar in Dallas was devoted to the detection, extraction, destruction, and cleanup aspects of the problem. Now nine years old, EPRI operates on the premise that the research it conducts will save the utilities more money than the cost of the research.

A look at the statistics from another angle reveals that there are about 150 000 PCB transformers now in service. Some 40 000 are owned by utilities. Most are relatively small, and each contains about 200–600 gal of PCB liquids. Many are found in high-rise buildings where they were installed for fire safety reasons.

In practice, many are allowed to stay in service until they become faulty. Nevertheless, real problems exist. There is no reliable way to forewarn of incipient failure of transformers; however, there is partial discharge detection or measure of gas evolution. Using present methods, mainly incineration, disposal costs might be as much as \$2000 per unit, in which case the total cost to this industry might be \$300 million.

PCB-contaminated transformers, those with 50–500 ppm PCBs, repre-

sent a headache for the utilities. The location of these units is unknown. Finding faulty transformers is difficult and expensive. The most frequently used method of checking transformer oil is to take a sample, send it to the analytical laboratory, and have the analysis performed by gas chromatography with an electron capture detector. The cost of this analysis is \$50-100 per sample, so the total cost of testing 20 million transformers could reach \$1-2 billion. Eventually the contaminated oil must be drained, disposed of, or decontaminated. One of the goals of the research program is to find better and lower-cost ways of reducing PCB-contaminated transformer oil to acceptable (less than 50 ppm PCBs) levels while saving the oil.

The problem with capacitors differs. There are an estimated 2.8 million capacitors in use; about 2000 of them rupture each year, spilling PCBs into the environment. EPRI research goals in this area are to find a way to predict capacitor failure and to develop a mobile device for testing soil samples for PCB contamination. Unlike transformers, there are no valuable materials to be recovered from capacitors. In capacitors, PCBs are absorbed into paper insulation; at present this solid PCB-containing material must be shredded before it is fed into an incinerator.

Research on new capacitors is needed because exhaustive toxicological tests have not been made on the liquids now being used. Research is also needed for a mobile facility that could be used to destroy PCBs from the old capacitors. Most capacitors made before 1977 contained PCBs.

Detection and extraction

The electric utilities need a number of industry-specific detection and analytical devices. There is a need for a device to detect incipient failures in capacitors. Also needed is a portable device for testing transformer oil for PCB content in the 50-500-ppm range. Another device is needed to detect the PCB content of soils in the field so that cleanup completion could be declared when the level of PCBs is less than 50 ppm.

There are prototype instruments or ideas being developed in each of these problem areas, but they are just beginning to be tested in the field. Commercial instruments are not here today.

A portable X-ray fluorescence instrument for screening transformer oil for 50 ppm PCBs or less by measuring total chlorine content is being field-

tested by the Salt River Project, a utility in Arizona. Capacitors that are about to fail typically emit ultrasonic sounds. An acoustical detector (Dunnegan-Endevco) being field-tested alerts utility management to incipient capacitor failure. Another device, an infrared scanner, is being used to measure the temperature of operating capacitors. Capacitors that are about to fail may show a higher-than-normal operating temperature.

Spills

In the case of spills of either transformer oil after rupture or capacitor material after failure, it is necessary to



EPRI's Gil Addis: managing PCB destruction

take samples of the contaminated soil and send them to a laboratory for analysis. A more expedient approach would be to have a field instrument. EPRI is working with the Oak Ridge National Laboratory on a field device for on-the-spot analysis of PCB spills. A technique using a portable infrared spectrometer looks promising for Askarel spills from capacitors.

Destruction

Although there are several semi-commercial processes for destroying or removing PCBs in oil, none have been fully tested for treating transformer oil. A number of proposed processes use sodium in a reactive chemical to combine with the chlorine in the PCBs. A possible unknown in these latter processes is that the sodium treatment may also damage or remove some components of the mineral oil, making it unfit for continued use in transformers. Tests are under way to check this point.

Sunohio, based in Canton, Ohio, has constructed a mobile PCB chemical destruction unit (*ES&T*, November 1980, p. 1278) and has demonstrated that its system is capable of reducing the PCB concentration in contami-

nated mineral oil to a nondetectable level. Sunohio has received approvals for the unit in EPA Regions 1, 4, and 7. Acurex Corp. has also constructed a mobile PCB destruction system and demonstrated it for EPA.

Incineration on land and at sea seems to be the best option for disposal of Askarels (high-level PCB concentrations) at present. Two land-based incineration disposal sites are now licensed by the EPA—a Rollins incinerator in Texas and the EnSCO (Energy Systems Co.) incinerator in El Dorado, Ark.

The ocean incinerator ship, *Vulcanus*, is another option. The ocean incineration record with *Vulcanus* included EPA-approved test burns in 1974 and 1975 at designated sites in the Gulf of Mexico. In 1977, the *Vulcanus* incinerated the stockpile of Agent Orange, the defoliant used in Vietnam, in an area west of Johnston Island. More recently, an EPA permit, dated Oct. 23, 1981, granted permission for four separate burns in an area known as a near-biological desert, 200 miles south of Galveston, Tex. PCBs will be incinerated on *Vulcanus* for the first time. The *Vulcanus* can burn 4000 gal/h and has a holding capacity of 850 000 gal; the waste must be liquid and pumpable.

Other processes for removing PCBs from transformer oil are being investigated by EPRI in lab studies. These include solvent extraction, several additional alkali metal dechlorination processes (removing chlorine atoms from the PCB molecule), electron irradiation, and super critical fluid extraction.

Since a number of alkali metal processes are already under way, EPRI may sponsor scale-up of an extraction process, the most attractive of the alternative processes. Other destruction processes include Rockwell International's molten saltbath and the plasma arc process of Dr. Barton, Imperial College, Ontario, Canada.

Prognosis

The EPA regulations for PCBs are the classic example of a moving target. The EPA regulation has been challenged in a court case brought by the Environmental Defense Fund. The case has been remanded to the agency, which must now show cause for setting the 50 ppm cutoff. The preliminary agency response should appear in the *Federal Register* in March, but the final ruling is not expected until about September 1982. Originally, the cutoff value was made to distinguish between two disposal options—incineration or landfilling.

—Stanton Miller

Pittsburgh Conference: the environmental papers

We will see you at this year's conference in Atlantic City, N.J., at the Convention Hall on March 8-12. Plan to attend the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy. More than 840 technical papers reflecting research in 50 categories of analytical chemistry will be presented. More than 500 companies will exhibit instruments, services, and wares at the Exposition of Modern Laboratory Equipment.

Tuesday, March 9

Environmental Analysis Using Gas Chromatography

Room B Convention Hall

2:00-3:40 Compositing Acid and Base/Neutral Fractions for FSCC GC/MS Analysis of Priority Pollutants—*T. R. Smith, N. H. Mosesman* (Energy Resources)

2:15-3:41 Quantitative Determination of Formaldehyde at the TLV.—*F. J. Debrecht, J. D. Mitchell* (Analytical Instrument Development)

2:30-3:42 Factors Influencing Chromatographic Reproducibility of Priority Pollutant Determinations.—*M. R. Bogdan, L. J. Lynch, R. J. Bartram, W. R. Supina* (Supelco)

2:45-3:43 High-Resolution Quantitative Analysis of Polynuclear Aromatic Hydrocarbons—*M. P. Turner, R. R. Freeman, K. A. Knauss, J. Fullemann* (Hewlett-Packard)

3:00-3:44 Applications of Packed Columns and Fused Silica Capillary Columns for GC/MS Analysis of Environmental Samples—*J. Kinsinger* (Raltech Scientific Services)

3:15-3:45 Apparatus for Closed-Loop-Stripping Analysis of Environmental Water Samples—*R. G. Westendorf* (Tekmar)

3:30 Recess

3:45-3:46 Alternate Method to the GC/MS Analysis of Acid and Base/Neutral Priority Pollutants Using Two Capillary Columns—*J. R. Dahlgren, A. Palmer, D. Palmer* (O. H. Materials)

4:00-3:47 Comparison of Toxaphene Residues in Environmental Samples with Laboratory-Weathered Standards Using Capillary EC-GC and Computer-Assisted Pattern Recognition—*M. T. Zaranski, V. J. Homer, T. F. Bidleman* (U. of South Carolina)

4:15-3:48 Rapid High-Resolution Gas Chromatographic/High-Resolution Mass

Spectrometric Analysis of Transformer Soot Containing Dibenzo-p-dioxins and Dibenzofurans—*D. R. Hilker, R. M. Smith, B. Jelus-Tyror, K. M. Aldous, P. W. O'Keefe* (New York State Dept. of Health)

4:30-3:49 Microprocessor-Controlled Collection Techniques for Trace Organic Analysis—*A. G. Gargus, W. Bowe, R. Largione, S. A. Liebman, E. Levy, W. Dodson, G. Linwood* (Chemical Data Systems)

4:45-3:50 Analysis of Trace Sulfur Gases by Gas Chromatography Using Flame Photometric Detector—*M. Feeney, J. DeGood, E. Warren* (Hewlett-Packard)

Wednesday, March 10

Ambient Air Analysis

Room B Convention Hall

2:00-5:35 Continuous Hydrogen Sulfide Monitoring System for Coke Oven Gas Using Sulfide Selective Ion Electrode—*O. P. Bhargava, M. Gmitro* (Stelco)

2:15-5:36 Individual Microidentification of Atmosphere-Related Aerosols—*Y. Ueno* (Texas A&M), A. Williams

2:30-5:37 Simple Preconcentration Technique Allowing Ultratrace Determination of Gaseous Sulfur Compounds—*R. A. Kagel, S. O. Farwell* (U. of Idaho)

2:45-5:38 Determination of Ammonia in Air by Nondispersive Chemiluminescence—*R. M. Vasta, D. C. Thornton* (Drexel U.)

3:00-5:39 Long Optical Path NDIR for Measuring Trace Gases in Ambient Air—*M. Mamiya* (National Chemical Laboratory for Industry)

3:15-5:40 Application of Ion Chromatography in Air Pollution—*E. Cathers, A. W. Fitchett* (Dionex)

3:30 Recess

3:45-5:41 High-Temperature Incineration of PCBs—Viable Disposal Technol-

ogy—*G. T. Hunt, J. M. Hall, P. Wolf, P. F. Fennelly* (GCA/Technology)

4:00-5:42 Environmental Monitoring—Need for New Techniques—*J. Ramage, B. Scott, G. Gibson, T. Reynolds* (VG Instruments)

4:15-5:43 Determination of Arsenic by Hydride Generation Atomic Absorption in Ambient Air and in Stack Emissions; Effect of Different Collection Media and Different Digestion Techniques—*K. C. Li, C. Pupp* (Environmental Canada)

4:30-5:44 GC-IR Ambient Air Survey Technique—*K. W. Eastman, S. Day* (Foxboro)

4:45-5:45 Design and Development of a Sampling System for Trace-Level Organic Species in Ambient Air Using Multicomponent Sorbent Traps—*D. S. Lewis, R. D. Cox, K. W. Lee* (Radian)

Thursday, March 11

Symposium: Industrial Hygiene Monitoring of Chemical Hazards

Arranged by D. R. Balya and R. S. Danchik (Aluminum Co. of America)

Room A Playboy Ballroom

D. R. Balya, Presiding

9:00 Introductory Remarks—*R. S. Danchik*

9:05-5:90 Keynote Address: AIHA and Industrial Hygiene Biological Monitoring—*J. Long* (American Industrial Hygiene Association)

9:50-5:91 Past, Present, and Future Asbestos Monitoring—*G. L. Swallow* (Johns-Manville)

10:20 Recess

10:30-5:92 Evaluation of Diffusive Samplers for Industrial Hygiene Monitoring—*D. G. Taylor, R. D. Hull, M. E. Cassinelli* (National Institute for Occupational Safety and Health)

11:00-5:93 Determination of Occupational Exposure to Polycyclic Aromatic

Hydrocarbon by Analysis of Body Fluids—*A. Bjørseth, G. Becher* (Central Institute for Industrial Research)

11:30-594 Portable Gas Analysis System Using an Integrated Gas Chromatograph—*S. C. Terry, J. H. Jerman* (Microsensor Technology)

Thursday, March 11

Water Pollution Analysis

Room A Convention Hall

9:15-622 Direct Rapid Analysis of Water for Priority Pollutants Using Triple Quadrupole Mass Spectrometry—*J. Fulford, T. Sakuma, S. Tanner* (Scienc)

9:30-623 Application of Ion Chromatography in Water Pollution—*A. W. Fitchett, E. Cathers* (Dionex)

9:45-624 Improved Automated Procedure for Determination of Bromide and Iodide—*B. McClelland* (American Monitor)

10:00-625 Semiautomated Automated Method for Determination of COD—*G. Gorny* (American Monitor)

10:15-626 Determination of Toxic Metals in Waters and Wastes by Automated Furnace Atomic Absorption—*D. E. Shrader, L. M. Voth, L. A. Covick, W. B. Hobbins* (Varian Instrument)

10:30 Recess

10:45-627 Chemical Characterization of Retorted Oil Shale Leachates—*C. L. Grant, S. J. Endersen, M. Sullivan* (U. of New Hampshire), *T. R. Steinheimer*

11:00-628 Analysis of Organics in Leachates from Fossil Fuel Solid Wastes—Multilaboratory Investigation—*C. M. White* (U.S. Department of Energy)

11:15-629 Analytical Techniques Using the Batch Method to Study Attenuation of Dissolved Phenol and Trichloroethylene from Water by Area Soils—*J. D. Stuart, B. H. Heath, N. M. Nguyen, H. D. Luce, K. L. Hall* (U. of Connecticut), *R. W. Andrews*

11:30-630 Purification of Humic Acid for Use in Synthesis of Model Particulates—*G. A. Baur, C. L. Grant* (U. of New Hampshire)

11:45-631 Comparison of Three Extraction Techniques for the Determination of Polychlorinated Biphenyls in Waste Oils—*W. Ziegler, W. Hartman, J. Johnson* (Stablex-Reutter), *W. Howitz*

Thursday, March 11

Industrial Hygiene Monitoring

Room A Playboy Ballroom

2:00-694 Application of Ion Chromatography in Industrial Hygiene—*E. Johnson, K. Haak* (Dionex)

2:15-695 Application of Photoionization Organic Vapor Meter to Industrial Hygiene Problems—*J. O. Frohlinger, N. M. Kotsko* (Industrial Hygiene Associates)

2:30-696 Formaldehyde Emission from Pressed Wood Products—*T. G. Matthews, T. C. Howell* (Oak Ridge National Lab)

2:45-697 Simple Vapor Monitor for Detecting Quinoline, an Important Carcinogen—*T. Vo-Dinh, G. H. Miller* (Oak Ridge National Lab)

3:00-698 Adsorption of Vapors by Air Monitoring Sample Lines—*S. S. Cantor, T. M. Cardis* (Foxboro)

3:15-699 Design Concepts and Applications of Automated Thermal Desorption System for Environmental Sampling and GC Analysis—*C. Sadowski, R. A. Hurrell* (Perkin-Elmer)

3:30 Recess

3:45-700 Field Portable Auto Sampling Gas Chromatograph for Detection and Identification of Trace Air Contaminants—*R. C. Leveson, N. J. Barker, R. D. Young* (Photovac)

4:00-701 Use of Polyurethane Foam as Trapping Agent for Vapor-Phase Polycyclic Aromatic Hydrocarbons in Ambient Air—*C. K. Detmer, T. F. Bidleman* (U. of South Carolina)

4:15-702 Comparison of Two Solid Sorbents in Ambient Air Monitoring—*L. Horgan, J. W. Bozzelli, B. B. Keckebus* (New Jersey Institute of Technology)

4:30-703 Detection of Gas-Phase Polynuclear Aromatic Hydrocarbons by Laser-Induced Molecular Fluorescence—*L. Jandris, K. Force* (U. of Rhode Island)

Friday, March 12

Air Pollution Analysis

Room A Playboy Ballroom

9:00-782 Simultaneous Use of Photoionization (PID) and Flame Ionization (FID) Detection for Ambient Air Hydrocarbon Analysis—*R. D. Cox, K. W. Lee, R. Earp* (Radian)

9:15-783 Part-per-Billion Level Determination of C₂-C₁₀ Hydrocarbon Species in Ambient Air—*M. A. McDevitt, R. D. Cox, R. Earp* (Radian)

9:30-784 Identification of Air Pollutants from Landfill Sites: a Screening Method in Real Time—*N. H. Hijazi, S. Nacson* (Scienc)

10:00-785 Determination of Particulate and Vapor-Phase Polynuclear Aromatic Compounds in Air—*D. Karlesky, G. Ramelew, I. M. Warner* (Texas A&M)

10:15 Recess

10:30-786 Real-Time Qualitative and Quantitative Measurements of Fugitive Emissions—*N. H. Hijazi, S. Nacson, E. S. K. Quan* (Scienc)

10:45-787 Quantitative Evaluation of Gas Adsorption Efficiency of Solid Adsorbents for Air Sampling—*Y. Ueno, R. Evans, I. M. Warner* (Texas A&M)

11:00-788 Fluorescence Measurements of Isotherms for Adsorption of Organics on Model Particulates—*A. J. Lapen, F. W. Page, C. L. Grant, W. R. Seitz* (U. of New Hampshire)

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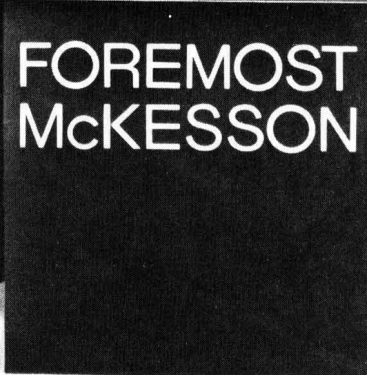
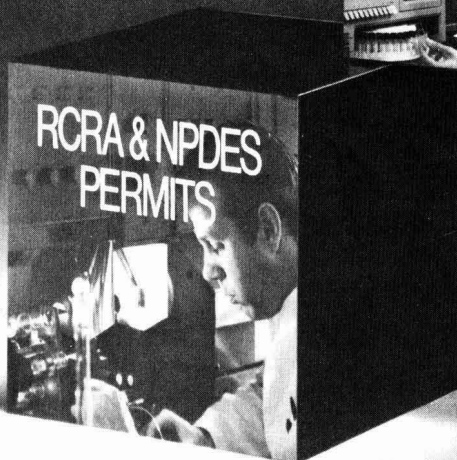
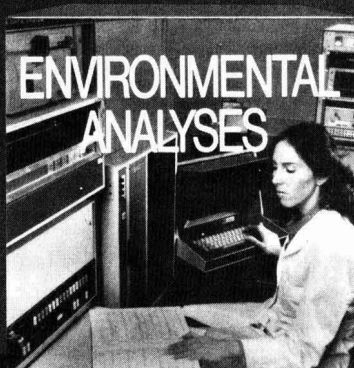
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CIRCLE 4 ON READER SERVICE CARD

Hazardous waste: the controversy continues



Michael R. Deland
ERT, Concord, MA

In the fall of 1976, Congress enacted the Resource Conservation and Recovery Act (RCRA) with the expectation that it would control safely from "cradle to grave" the enormous volume of hazardous waste generated in the U.S. EPA estimated that over 77.1 billion pounds of hazardous waste are produced annually and of that "only 10% are disposed of in an environmentally acceptable manner."

More than five years have elapsed since RCRA's passage and instead of the mature, "cradle to grave" control envisioned by Congress, chaos prevails. Part of the program is still in its infancy and suffering intense growing pains, while more substantial portions are yet to be conceived. The major problems predictably are pinpointed in three separate lawsuits, each involving multiple parties.

The deadline suit

When it became apparent in the fall of 1978 that EPA not only had missed the statutory deadline of April 1978 to issue RCRA's implementing regulations, but also that the delays would continue, the state of Illinois, the Environmental Defense Fund (EDF), Citizens for a Better Environment, and the National Solid Waste Management Association filed suit. This combined effort by states, environmentalists, and industry spurred the promulgation in May 1980 of the "most complex regulations EPA has ever gone forward with," which were accompanied by over 6000 pages of background documents. The agency admitted that this rulemaking was but

the "bare outline" of regulations to come. Both industry and environmental groups immediately challenged the regulations in court. Meanwhile, the deadline controversy continues.

This fall EPA requested a further extension until fall 1983 to promulgate the final standards for permitting hazardous waste land disposal facilities. In December 1981 the court denied this request and held firm to its previously imposed Feb. 1, 1982 deadline. By rushing to meet the deadline, the agency admitted that the regulations would be "inferior" by being less flexible and less tailored to site- and waste-specific conditions and would likely need to be amended. EPA's approach to establish a basic standard followed by two implementation "options" has been criticized in detail by EDF, thereby setting the stage for further litigation.

The consolidated permit suit

As part of its May 1980 rulemaking, EPA published the initial RCRA regulations and also sought to streamline the permitting process by consolidating five previously separate programs. The Natural Resources Defense Council (NRDC) and numerous industrial petitioners contested this approach on procedural grounds. In November 1981, EPA and the industry petitioners arrived at a "settlement agreement," which obligates EPA to promulgate as "expeditiously as possible" certain "technical" and "other" amendments and publish preamble language and a "Regulatory Interpretation Memorandum."

As a result of the agreement, the court deferred briefing of the issues and required EPA to file monthly status reports. The first one, submitted in January 1982, reveals that the agency has prepared *Federal Register* language for certain of the issues and has forwarded it to the Office of Management and Budget for review. Among the more significant and controversial issues agreed upon are to extend the life of a permit from the

current 10 years to the "designed operating life" of the facility, and to allow commencement of construction of a facility prior to receipt of a final permit. EDF has already indicated its intent to contest these and other parts of the settlement agreement once it is published in the *Federal Register*.

The substantive suit

The challenges to EPA's May 1980 regulations by over 40 industrial litigants and several trade associations were consolidated into one case, *Shell Oil vs. EPA*, in which EDF is again the sole representative of environmental interests. Twenty-seven separate issues were identified and according to industry counsel approximately 50% have been "negotiated away." However, among those remaining are such fundamental questions as the definition of hazardous waste as it pertains to recycled and reused materials and whether EPA in fact has the statutory authority to regulate such wastes. All parties admit that progress on resolving the substantive issues has recently languished while EPA and the courts have concentrated on the deadline suit, the promulgation of land disposal standards, and the "settlement agreement."

Five years after RCRA's passage, EPA's most ambitious regulatory program is still in its formative stages. Despite hundreds of pages of *Federal Register* notices, thousands of forms submitted to EPA, and numerous documents to the courts, industry and the states still have little concrete guidance on how to dispose of hazardous wastes. Unfortunately, more litigation, more years of uncertainty loom likely. Meanwhile, the waste continues to accumulate. This course will continue unless, starting now with EPA's Land Disposal proposal, industry environmental groups, local, state, and federal agencies, courts, scientists, and citizens recognize that a solution rests with their willingness to cooperatively seek a creative compromise.

Anodic stripping voltammetry as an analytical tool

Here is how it works and may be applied properly to environmental surveillance, especially where heavy metal contaminants are concerned

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Heavy metals are one class of contaminants that can produce undesirable effects even if they are present in extremely minute quantities. For instance, unlike many other pollutants, they are not biodegradable, and may persist for long time periods. Therefore, techniques are being devised to measure them at very low concentration levels. Anodic stripping voltammetry (ASV) is a sensitive, precise, and economical electroanalytical technique for detecting trace metals. Consequently, ASV has become one of the popular approaches to environmental analysis.

Electrochemical methods of analysis are generally applied to the qualitative and quantitative determination of electroactive species in solution. Anodic stripping voltammetry belongs to the voltammetric branch of electroanalytical techniques. Voltammetric techniques are those in which a current response is measured as a function of a potential waveform increasing in amplitude. In ASV, metals are concentrated by reduction into or onto a microelectrode, followed by anodically reoxidizing (stripping) them to produce a peak-shaped plot of

current as a function of potential. Although ASV cannot be regarded as a new analytical technique, new approaches and instruments have been introduced recently that have enhanced the technique's capabilities.

The increasing use of ASV is attributable to its ability to measure simultaneously several elements at concentration levels down to the fractional parts-per-billion (ppb) at a relatively modest cost. (A complete ASV system would cost \$4000-5000.) It is fair to say that there is no technique for trace metal analysis that can compete with ASV on the basis of sensitivity per dollar investment. Little expertise is required, and analysis time is on the order of a few minutes.

The inherently high degrees of accuracy and precision of ASV stem from its application of Faraday's law. Comparative studies with other analytical techniques, such as various atomic absorption procedures, have emphasized the particular reliability of ASV in trace metal analysis for all types of environmental matrices, especially in various types of natural

water. The technique has been applied to solving numerous trace metal analysis problems in a variety of other matrices such as food, blood, or fingernail, and has proved to be very sensitive. Moreover, the special property of ASV to be species-sensitive makes this technique an efficient tool in speciation studies of toxic trace metals dissolved in natural waters. Like atomic absorption spectroscopy, ASV is subject to various interferences when it is applied to real life samples; most of these interferences can be eliminated by proper selection of experimental conditions.

Water analysis

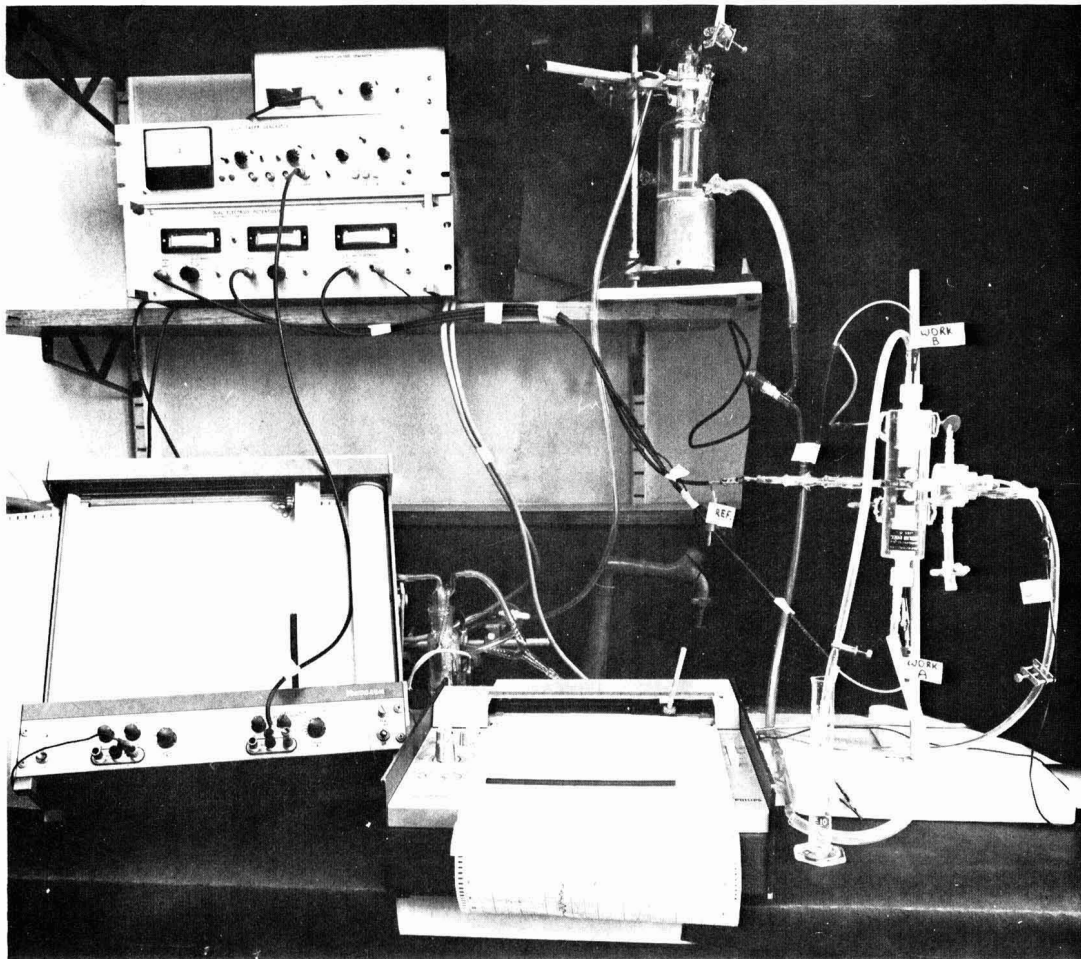
Anodic stripping voltammetry has been used extensively to analyze natural water samples. Ariel and Eisner used ASV, in one of its early (1963) environmental applications, to analyze zinc, cadmium, and copper in Dead Sea brine (1). The major ion content in the Dead Sea water did not interfere with the trace metal determination.

Much of the success in applying ASV for analyzing natural waters is attributed to Florence, who used ASV about 10 years ago to determine trace levels of lead, cadmium, zinc, copper, thallium, bismuth, indium, and antimony in seawater (Pacific Ocean), as well as in fish, seaweed, abalone, and oysters inhabiting the water (2, 3). Since then, and through the 1970s, ASV has been widely used for analyzing about 20 trace metals in different types of natural waters such as oceans, lakes, rivers, as well as in sewage or industrial effluents and tap waters. Waters analyzed came from Lake Superior (4), Oslofjord (5), the

Why anodic stripping voltammetry is successful

- Sensitivity: detection limits at the sub parts-per-billion level
- Multi-ion analysis per sample
- Precision and accuracy
- Powerful tool for determining the chemical nature of trace metal ions (speciation)
- Ability to perform on-line analysis
- Modest cost

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ASV: an actual working system in the laboratory

English Channel (6), the Arctic Ocean (7), Madison (Wis.) tap water (8), and sewage effluents from plants around San Francisco (9).

The more sensitive version of ASV, involving the sensitive differential pulse excitation ramp during the stripping step, is usually employed for measuring the ultratrace concentration level (0.001–1 ppb) of some toxic metals such as thallium, lead, and cadmium in seawater and inland waters. The advantage of using ASV for measuring trace metals in natural water is the direct analysis capability, that is, elimination of concentration steps, and minimum use of reagents (sample pretreatment). This is an important key to minimizing contamination possibilities and changes in the physiochemical nature of the species being measured.

Acidification (to pH 1 or 2) of natural water samples, upon their collection, is desirable to prevent loss of the

metals by adsorption on the container walls; an *ultrapure* acid should be used for this purpose. The added acid also serves as the supporting electrolyte in analyses of inland waters with low salt content. Depending upon the desired metal form, the sample may be filtered through an acid-washed filter.

Under the myriad of variances, such as surfactants, metals, and ligands, that are present in natural waters, ASV is subject to many potential interferences. Anamolous ASV response may be observed in natural waters containing considerable quantities of dissolved organic matter. Sorption of surface-active agents on the electrode surface can affect both diagnostic parameters (i_p and E_p) used in ASV. The sorbed organic layer may slow the rate of metal deposition or change the reversibility of the metal oxidation reaction, resulting in lower i_p , broader peak, or shift of E_p to more positive values.

These effects are greater in differential pulse ASV than in the linear scan data, because differential pulse peak currents are more sensitive to small changes in the rate of the electrode reaction. These sorption effects and their implications on the interpretation of ASV data have been discussed in detail by Brezonik et al. (10). For some types of organic rich waters (industrial effluents, marshes, and the like) destruction of the organic matter (by UV irradiation or ozone oxidation (9)) or its removal prior to ASV analysis is recommended.

In addition to sorption effects, stripping analysis of natural water samples is subject to interferences caused by intermetallic compound formation and overlapping stripping peaks. Table 1 lists some of the most common interferences to which ASV measurements in natural water samples may be subject, together with successful approaches to avoid them.

Flow-through ASV systems have been introduced in connection with *in situ* (real time) analysis (21, 22, 23). Such systems can provide adequate warning in cases of sudden contamination, and may be very useful for large-scale marine surveys. In addition, since sample handling is minimized and rapid analyses are performed (with no time delays as in laboratory-based analyses), these systems offer the most obvious way to minimize errors brought about by contamination or adsorption losses. An automated ASV flow system, based on a mercury-coated graphite tubular electrode, has been applied by Zirino and his coworkers for the continuous monitoring of copper and zinc in San Diego Bay (24). New designs and more applications of these flow-through ASV sensors should be forthcoming in the near future.

Speciation

An important feature of ASV is its capability to differentiate the various chemical forms of a given trace metal in solution in contrast to atomic absorption or neutron activation, which measure the total metal content. This feature makes ASV the technique of choice for speciation and physico-chemical characterization of dissolved trace metals in natural water.

Knowledge of the chemical state of trace metals in solution is important for understanding their transport, toxicity, and reactivity in natural waters. In this regard, emphasis has been placed on trace metal complexation because of the role it might play in

ASV—how it works

Anodic stripping measurements are usually done in an electrochemical cell, which is simply a container made of glass or quartz containing the sample solution and a three-electrode system. Sample volumes are usually between 5–50 mL; but smaller volumes, as low as few μL , can be analyzed with the aid of various microcells. The three-electrode system consists of a working reference electrode (such as the silver–silver chloride electrode), and an auxiliary electrode (for example, a platinum foil). The cell also contains a tube tipped with a glass frit for the deoxygenation gas.

Mercury electrodes of various forms are usually used as the working electrode, although carbon, gold, or platinum can also be employed. However, the most widely used form of stripping analysis involves a micromercury electrode; by reducing the volume of the mercury electrode, one can enhance the concentration of deposited metals.

The most popular working electrodes are the hanging mercury drop and the thin mercury film electrode. The hanging mercury drop is formed at the tip of a microsyringe or capillary, with a micrometer to control drop size. The thin mercury film is formed by electrolytically plating mercuric ions (added to the analyte solution) onto the surface of a carbon substrate. The resulting film is usually less than 100 Å thick. Measurements can be performed with any commercial polarograph for analytical application (see list of manufacturers); those containing the differential-pulse mode are preferable.

Essentially ASV is a two-step technique. The first, or deposition step, involves the electrolytic deposition of a small portion of the metal ions in solution into the mercury electrode to preconcentrate the metals. This is followed by the stripping step (the measurement step), which involves the dissolution (stripping) of the deposit. These steps are represented schematically in Figure 1.

Most frequently, the preconcentration is done by cathodic deposition at a controlled potential (more negative than the reduction potential of the element[s] to be measured) and time. The metal ions reach the electrode surface by diffusion and convection—forced by rotating the working electrode or stirring the solution—where they are reduced and concentrated as amalgams in the mercury.

The duration of the deposition step is selected according to the concentration level of the metal ions in question: from less than 1 min at the 0.1-ppm (0.1-mg/L) level to about 10 min at the 1-ppb (1- $\mu\text{g/L}$) level.

Following the preselected time of the deposition step, the potential is scanned anodically (toward more positive potentials), linearly, or in a more sensitive potential-time waveform (usually the differential pulse ramp in which a pulse is superimposed on a slow potential sweep, as shown in Figure 1). During this scan, the amalgamated metals are stripped out of the electrode in an order that is a function of each metal standard potential, are reoxidized, and give rise to anodic peak currents that are measured.

The resultant current-potential voltammogram (Figure 2) provides the analytical information of interest. The peak potential (position), E_p , of each metal is a characteristic of that metal and is related to the standard potential of its redox couple. Thus, it can be used for qualitative identification. The peak current (height), i_p , is proportional to the concentration of the corresponding metal ion in the test solution. The concentration is determined by a standard addition or a calibration curve.

Dissolved oxygen, which is electrolytically reduced at the mercury electrode with background current that covers most of the potential range of interest, is removed from the solution by bubbling high-purity nitrogen through the solution for about 10 minutes prior to the deposition step. The theoretical treatment for deriving the equations for the peak current demands that electrical migration of the metal ion caused by the electrical field be eliminated. To do so, one introduces into the sample solution a 100-fold excess of a supporting electrolyte that usually contains an inorganic salt, mineral acid, or base. Macro salt components in seawater can serve as natural supporting electrolytes, and thus do not create difficulties such as those which occur in atomic absorption spectroscopy.

Since ASV may be used only where the metal ion is readily reduced to the metallic state and reoxidized, the technique does not apply to as wide a range of metals as does atomic absorption. Nevertheless, about 20 amalgam-forming metals are measurable by ASV with mercury electrodes, including cadmium, lead, copper, zinc, bismuth, indium, thallium,

Diagnostic parameters used in anodic stripping voltammetry^a

Hanging mercury drop electrode:

$$i_p = k n^{3/2} D^{2/3} r v^{1/2} C_b t m$$

$$E_p = E_{1/2} - \frac{1.1 RT}{nF}$$

Thin mercury film electrode (<10 μ thick):

$$i_p = nFA v \phi e^{-1} D C_b t m$$

$$E_p = E^0 + \frac{2.3}{\phi} \log \frac{\delta i v \phi}{D}$$

^a k = Constant, n = number of electrons, D = diffusion coefficient, r = radius of the mercury drop, v = potential scan rate, C_b = concentration of the ion in the bulk solution, t = deposition time, m = mass-transport coefficient, $E_{1/2}$ = polarographic half-wave potential, R = gas constant, T = absolute temperature, F = Faraday's constant, $\phi = nF/RT$, $e =$ base of Napierian logarithm, E^0 = formal (standard) redox potential, δ = thickness of the diffusion layer.

FIGURE 1
Principle of ASV

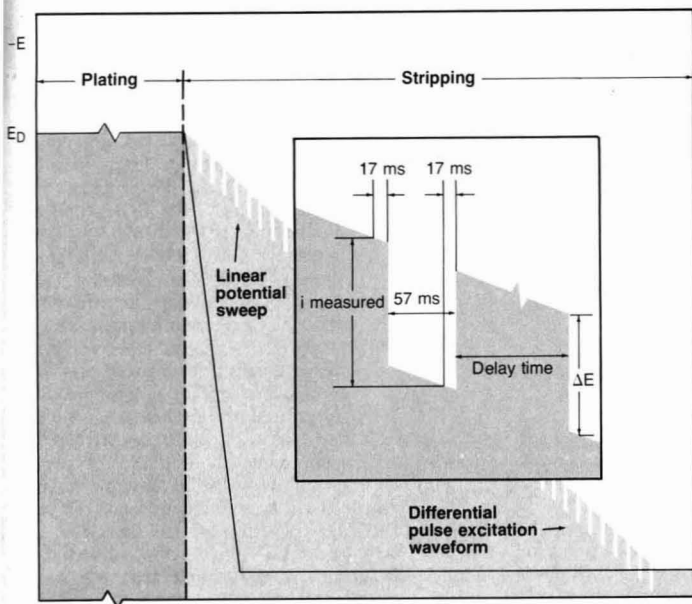
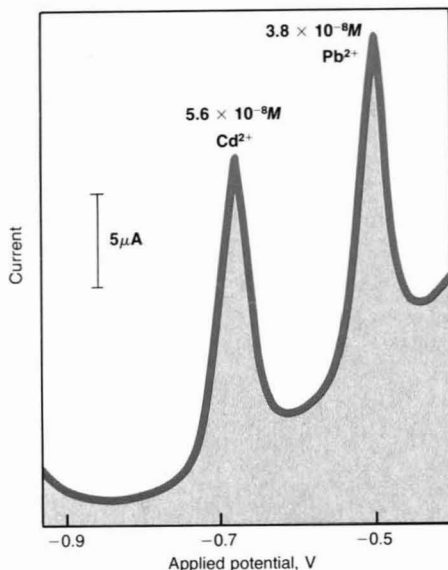


FIGURE 2
A typical voltammogram



Conditions:
 0.1 M KNO_3 (potassium nitrate)
 Rotating mercury-coated glassy carbon disc electrode
 1600 rpm
 3-min deposition at -1.0 V
 Differential pulse amplitude = 50 mV
 Scan rate = 2 mV/s

antimony, tin, nickel, cobalt, and gallium. In addition, metal ions such as arsenic, gold, mercury, selenium, or silver are determined on bare solid electrodes such as carbon or gold. In a single ASV cycle, four to six metal ions can be measured simultaneously (with clear separation between peaks), based upon the difference in the peak potentials of two successive peaks. Because of this multielement capability, in cases where this technique is to be used, ASV requires less time for the analysis than do sequential atomic absorption measurements.

The main types of interferences in ASV are overlapping stripping peaks and intermetallic compound formation. Overlapping peaks, caused by similarity in oxidation potentials, cause problems in simultaneous determination of lead with tin, thallium with cadmium, or bismuth with antimony. The use of selective complexation of one of the two metals or of different supporting electrolytes (so that peak potentials are altered) often minimizes this problem.

The formation of intermetallic compounds in or on the working electrode may affect the size or position of the peak current for a particular metal. For example, the deposition of zinc and copper in mercury results in such a mutual interference. This type of problem may be avoided or minimized by using the hanging mercury drop electrode rather than a thin mercury film electrode (in which this problem is more severe); by the addition of a third element that preferentially combines with one of the metals in question (for instance, gallium combines with copper so that zinc may be determined); or by using a deposition potential at which one of the ions is not plated.

To obtain accurate and reproducible results without difficulty, adequate attention must be paid to certain key operations. Analysts should be aware that they are working with extremely dilute solutions. All procedures of trace analysis practice, such as sample handling, preparation and storage of standards, glassware and reagent purity, clean bench working, and so on, must be observed to minimize systematic errors caused by contamination, adsorption losses, and alterations of the dissolved trace metal levels. The magnitude of these errors is further reduced by proper planning of the sampling and analytical procedures, including short time intervals between sampling and analysis, minimum of chemistry, and the like.

TABLE 1

Selected approaches for avoiding interferences in "real-life" samples^a

Element measured	Interference/problem	Solution	Refs.
Tl in the presence of Pb and Cd	Overlapping peaks	Addition of EDTA to mask Cd and Pb	11
Bi in the presence of Sb	Overlapping peaks	Adjustment of the deposition potential	12
Cu in the presence of Fe	Combined differential pulse ASV peak	Subtracting the iron peak (measured at zero deposition time) from the combined peak	13
Simultaneous measurement of Sn, Pb, and Tl	Overlapping peaks	Medium-exchange (after the deposition) to a proper complexing medium	14
Measurements in chloride media (i.e., seawater)	High background current because of calomel formation	Avoid anodic polarization of the electrode	15
Pb and Cd in sewage effluents	Irreproducible results due to sorption of organic matter on the electrode	Ozone oxidation for the destruction of organic matter	9
Zn in the presence of Cu	Cu-Zn intermetallic compound (poor precision and sensitivity)	Addition of Ga ions which combine with Cu, or electrolytic removal of Cu using a twin-working electrode cell	16, 17
Cu in seawater	Reduced sensitivity due to the formation of CuCl_2^- at the electrode	Acidifying the sample to prevent this deposit	18
Cu in the presence of Mn	Cu peak obscured by the Mn reduction current	Medium-exchange after the deposition step	19
Simultaneous determination of metals at widely varying concentrations	Changing the recorder scale during the analysis	Use of autoranging amplifier	20
Zn in the presence of Ni	Ni-Zn intermetallic compound (poor precision and sensitivity)	Use of citrate to complex Ni	16
Bi in the presence of Mo and W	Low sensitivity	Ion-exchange separation	3

^a Reagents used in these procedures should be as pure as possible.

trace metal distribution and availability. As a result of observing anomalous behavior in samples containing organic matter, Matson (1968) suggested the use of ASV as a tool of determining the chemical nature of trace metal ions (25). Since then, ASV has been employed in many studies of trace metal speciation (26, 27) Several approaches have been used in these studies, and can be classified as direct ASV measurements or titrimetric ASV procedures. One of the most widely used approaches is to apply two different sample pretreatment proce-

dures. The first procedure involves only filtration and addition of a supporting electrolyte. This treatment results in determination of the free hydrated metal ions and labile metal complexes, which are complexes that dissociate at a faster rate than the rate of plating the free metals. They can be inorganic complexes such as chloro, carbonato, and hydroxo, as well as various organic complexes. A second pretreatment includes acid digestion of the water sample (acidification to pH 0.7 and boiling gently for 10 min) or other vigorous treatment, such as

UV-photolyzed hydrogen peroxide. This treatment releases metals that are bound to soluble and colloidal material, and therefore permits measurement of the total metal.

By subtraction, the strongly bound or nonlabile fraction of the metal is determined. The differentiation between free (hydrated) metals and labile metal complexes can be made from the shift in the peak potential, E_p . These shifts are interpreted in the same way that half-wave potentials are interpreted in classical polarography, as an indication of the formation of reducible complexes in solution. Observations of E_p shifts as functions of ligand concentration or solution pH have been used for evaluating stability constants for various metal complexes or as evidence of the formation of different complexes. In another direct ASV approach, peak current variations with pH, organic chelate content, or carbonate alkalinity are observed and related to the formation or dissolution of nonreducible complexes, colloidal species, or solid phases.

In addition to the above direct procedures, ASV can be used to provide important information on metal-ligand interactions through titration techniques. This involves the addition of spikes of metal ion to solutions containing ligands that form nonreducible complexes. The end point of the resulting titration curve (i_p vs. added metal) is related to the solution concentration of these ligands. This titration provides a basis for defining complexation capacity of water samples, and has been further developed and applied to estimate conditional formation constants of metal-organic complexes.

An important and different approach has been proposed recently for the evaluation of stability constants and stoichiometry of metal complexes. It is based on plotting the peak current as a function of the deposition potential for different ligand concentrations. From the resulting wave-shaped curves, the stability constants and coordination numbers can be evaluated.

Recent papers describing one of the above ASV approaches have discussed the following aspects of metal speciation in natural waters: copper and cadmium associations with aquatic humic and fulvic acids (28, 29); the nature, concentration, and stability of Pb-carbonato complexes in seawater (26); speciation of dissolved zinc, cadmium, lead, and copper in Rhine River and North Sea water (30); cadmium-ethylenediamine complex formation in seawater (31); com-

plexing capacity of lake water (32); stoichiometry and stability constants of the chloro-complexes of cadmium in seawater (33); thallium speciation in seawater (34); as well as many other similar aspects (e.g., 35, 36). More researchers are being encouraged to apply these methodologies to the challenging field of applied physicochemistry. In the near future, more emphasis will be given to establishing the biological and chemical significance of the various metal fractions measured by ASV.

Other applications

Airborne particulate matter is analyzed for trace elements by collecting it on a suitable filter (such as Millipore) by using a filtration pump. Because of the complex nature of the airborne particulate matter, some additional steps are taken during the collection and preparation steps; these include destruction (by low temperature ashing) of the filter material, and the complete dissolution of the collected particulate matter. The high sensitivity of ASV permits the use of a relatively small sample, an advantage for size distribution studies. The results obtained by ASV are comparable with those of atomic absorption spectroscopy.

Other important environmental, clinical, and industrial applications of ASV have been reported recently. These include trace metal analyses of various rain and snow samples (37, 38); geological or soil samples (39, 40); clinical samples such as blood (41), urine (42), hair (43), teeth (44), or eye tissues (45); food samples such as rice, milk, juices, beer, or wine (46-48); as well as other matrices such as fertilizers (48), gasoline (48), alloys (49), or plating baths (50). More

comprehensive applications information has been given by Vydra, Štulík, and Julakova (see references).

Anodic stripping voltammetry has been shown to be a rapid, sensitive, reproducible, and inexpensive technique for measuring normal and pollution levels of heavy metals in natural waters, as well as for answering questions in connection with speciation and physicochemical properties of the metals. Full realization of these advantages is achieved by avoiding possible interferences that exist in real life samples. For these reasons, the technique has grown in acceptance among environmental scientists and will continue to do so in the future.

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Acid precipitation in historical perspective

*Awareness of the acid rain problem has developed
in many countries over more than a century*

Ellis B. Cowling

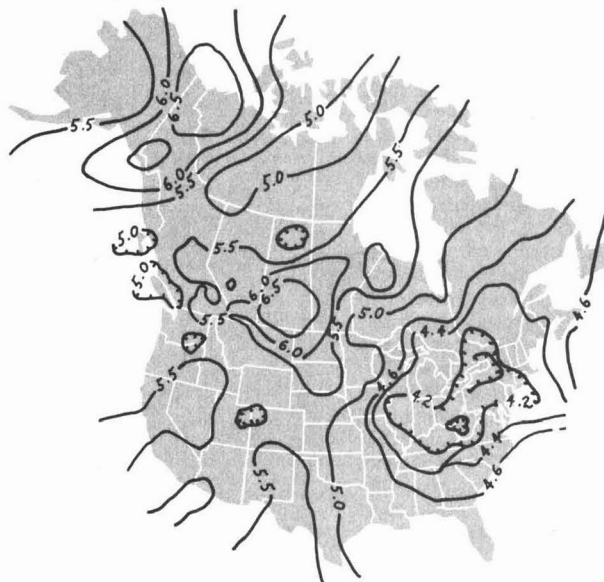
*Chairman, National Atmospheric
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Some years ago the terms "acid precipitation" and "acid rain" were bits of esoteric jargon used almost exclusively by scientists in certain specialized fields of ecology and atmospheric chemistry. Recently, these terms have become worrisome household words in many countries around the world. While they have inspired sensational and sometimes exaggerated headlines about "death from the sky," they also have prompted a more deliberate and careful examination of the role of humans in the biogeochemistry and chemical climatology of the earth. How did this transition come about? Who was responsible? Why did it take so long for acid precipitation to be recognized as an important environmental problem? What factors of scientific awareness and public perception have influenced the course of research on acid precipitation?

This brief article is an attempt to illuminate some of these questions. Our approach will be to review various steps in the transformation of the concepts of acid precipitation from the domain of scientific curiosity to the domain of public concern and debate.

Since the beginning of life on earth, plants have obtained an essential part of their nutrients from the atmosphere. From time to time, plants and animals have been injured by toxic substances dispersed in the atmosphere. When the industrial revolution started, people began to exert more and more influence on the biogeochemical circulation of the earth. We added progressively larger amounts of many kinds of sub-

FIGURE 1
About two-thirds of the total land area of North America receives acid precipitation^a



^aThis map prepared in Jan. 1982 shows average annual pH from Sept. 1979 to Oct. 1980. It is based on the data developed by the National Atmospheric Deposition Program (NADP/NC-141) in the U.S. and the Canadian Network for Sampling of Precipitation (CANSAP) in Canada. These two networks prepared the first continent-scale map of atmospheric deposition for North America in 1980.

stances to those that circulate naturally among the air, the water, the soil, and all living things. Some of these man-made materials were beneficial nutrients; some were inert; others were toxic or injurious depending upon their concentration or the nature of the organism receiving the deposition.

Because man now influences the chemical climate of the earth in so many important ways, it is essential that we understand the sources, transport, transformations, and chemistry of atmospheric deposition. We also must know the various effects that the deposited substances have on

forests, fish, crops, soils, surface waters, and buildings and other structures (Figure 1).

Table 1 contains a historical resumé of the progress that has been made toward understanding these phenomena and their biological consequences. Contributions are presented in the chronological order of their occurrence, whether or not the work was recognized or accepted at the time. The names of major scientists, the country in which the research was conducted, and the principal contribution to science or public affairs are presented with appropriate references

when that is possible.

Selecting particular accomplishments for inclusion in such a chronology is a hazardous undertaking because of the likelihood that some important contributions will not be given the credit or priority they deserve. I hope the table will serve a useful purpose, and look forward to receiving comments from anyone who may be interested in helping to describe the record more adequately.

Early awareness

Many features of the acid rain phenomenon were first discovered by an English chemist named Robert Angus Smith in the middle of the 19th century. In 1852, Smith published a detailed report on the chemistry of rain in and around the city of Manchester, England. In this remarkably early account, Smith called attention to the changes in precipitation chemistry as one moves from the middle of a polluted city to its surrounding countryside: "We may therefore find three kinds of air—that with carbonate of ammonia in the fields at a distance, that with sulphate of ammonia in the suburbs, and that with sulphuric acid, or acid sulphate, in town." Smith also pointed out that the sulfuric acid in city air caused the colors of textiles to fade and metals to corrode.

Twenty years later, in an extraordinary book entitled "Air and Rain: The Beginnings of a Chemical Climatology," Smith (1872) first used the term "acid rain" and enunciated many of the principal ideas that are part of our present understanding. On the basis of detailed studies in England, Scotland, and Germany, Smith demonstrated that precipitation chemistry is influenced by such factors as coal combustion, decomposition of organic matter, wind trajectories, proximity to the sea, and the amount and frequency of rain or snow. Smith proposed detailed procedures for the proper collection and chemical analysis of precipitation. He also noted damage by acid rain to plants and materials and commented on the atmospheric deposition of arsenic, copper, and other metals in industrial regions.

Unfortunately, however, Smith's pioneering and prophetic book apparently has been overlooked by essentially every subsequent investigator. Eville Gorham (1981) developed the first detailed analysis of Smith's early work for a report by the National Academy of Sciences.

Modern awareness

Contemporary concepts about acid precipitation and its environmental

TABLE 1
A historical resumé of progress toward understanding acid precipitation

Year(s)	Investigator and country	Principal contribution
1661–1662	Evelyn, Graunt, England	Noted the influence of industrial emissions on the health of plants and people, the transboundary exchange of pollutants between England and France; and suggested remedial measures including placement of industry outside of towns and use of taller chimneys to spread the "smoke" into "distant parts" (Evelyn, 1661; Graunt, 1662; see also Gorham, 1981)
1687	Hooke, England	On the basis of experiments by Brotherton, Hooke concluded that plants have "two-fold kind of roots, one that branches and spreads into the earth, and another that spreads and shoots into the air; both kinds of roots serve to receive and carry their proper nourishment to the body of the plant" (Hooke, 1687; see also Gorham, 1965; and Wittwer and Bukovac, 1969)
1727	Hales, England	Noted that dew and rain "contain salt, sulphur, etc. For the air is full of acid and sulphureous particles . . ." (Hales, 1727; see also Gorham, 1981)
1734	Linné, Sweden	Described a 500-year-old smelter at Falun, Sweden: ". . . we felt a strong smell of sulphur, . . . rising to the west of the city . . . a poisonous, pungent sulphur smoke, poisoning the air wide around . . . corrode(ing) the earth so that no herbs can grow around it" (Linné, 1734)
1852	Smith, England	Analyzed the chemistry of rain near Manchester, England and noted concentric zones with "three kinds of air—that with carbonate of ammonia in the fields at a distance, that with sulphate of ammonia in the suburbs, and that with sulphuric acid, or acid sulphate in the town." Smith also noted that sulfuric acid in town air caused fading in the color of textiles and corrosion of metals (Smith, 1852; see also Gorham, 1981, Austria)
1854–1856	Austria and Germany	Established "General Citizens Laws" prohibiting disposal of wastes by individuals on a neighbor's property. In the interest of encouraging industrialization, however, these same laws specifically excluded industries from legal liability when waste disposal caused pollution of water and air
1855–1856	Way, England	Completed a very detailed series of analyses of nutrient substances in precipitation at the Rothamsted Experiment Station and showed the value of these substances in crop production (Way, 1855)
1872	Smith, England	In a remarkable publication entitled "Air and Rain: The Beginnings of a Chemical Climatology," Smith first used the term "acid rain" and enunciated many of the ideas that we now consider part of the acid precipitation problem. These ideas included regional variation in precipitation chemistry as it is influenced by such factors as combustion of coal, decomposition of organic matter, wind direction, proximity to the sea, amount of rain, etc. After extensive field experiments, Smith proposed detailed procedures for the proper collection and chemical analysis of precipitation. He also noted acid rain damage to plants and materials and atmospheric deposition of arsenic, copper, and other metals in industrial regions (Smith, 1872; see Gorham, 1981)
1881	Brögger, Norway	Observed "smudsig snefeld" (dirty snowfall) in Norway and attributed it to either a large town or an industrial district in Great Britain (Brögger, 1881)
1909	Sørensen, Denmark	Developed the pH scale to describe the acidity of aqueous solutions (Sørensen, 1909)
1911	Crowther and Ruston, England	Demonstrated gradients in acidity of precipitation decreasing from the center of Leeds, England; associated the acidity with combustion of coal; and showed that both natural rain and dilute sulfuric acid inhibited plant growth and seed germination, as well as ammonification, nitrification, and nitrogen fixation in soil

Year(s)	Investigator and country	Principal contribution
		(Crowther and Ruston, 1911; see also Cohen and Ruston, 1912; and Gorham, 1981)
1919	Rusnov, Austria	Demonstrated that deposition of substances from the atmosphere accelerated the acidification of both poorly-buffered and well-buffered forest soils (Rusnov, 1919)
1921	Dahl, Norway	Recognized the relationship between acidity of surface water and trout production (Dahl, 1921, 1927)
1922	Atkins, England	Measured the alkalinity of surface waters and noted a relationship between alkalinity and biological productivity (Atkins, 1922)
1923	MacIntyre and Young, U.S.	Made the first detailed study of precipitation chemistry in the U.S. (MacIntyre and Young, 1923)
1925	Shutt and Hedley, Canada	Made very early measurements of the nitrogen compounds present in rain and snow and commented on the value of these compounds for crop growth (Shutt and Hedley, 1925)
1926	Sunde, Norway	Demonstrated the value of adding limestone to water in a fish hatchery (Sunde, 1926)
1939	Erichsen-Jones, Sweden	Demonstrated the relationship between acidity and the toxicity of aluminum to fish (Erichsen-Jones, 1939)
1939	Katz et al., Canada	Reported acidification and decreases in base saturation of soils caused by sulfur dioxide emissions from the lead-zinc smelter near Trail, British Columbia (Katz et al., 1939)
1939	Bottini, Italy	Detected hydrochloric acid in precipitation near the volcano on Mount Vesuvius, thus demonstrating that there are natural sources of strong acids in precipitation (Bottini, 1939)
1942	Conway, Ireland	Completed the first modern review of precipitation chemistry (Conway, 1942)
1948	Egnér, Sweden	Initiated the first large-scale precipitation chemistry network in Europe (Egnér et al., 1955; Rossby and Egnér, 1955)
1950–1955	Eriksson, Sweden	Enunciated a general theory of biogeochemical circulation of matter through the atmosphere (Eriksson, 1952, 1954, 1959, 1960) Expanded the regional network established by Egnér into the continent-wide European Air Chemistry Network, which has provided a continuing record of precipitation chemistry for three decades (Emanuelsson et al., 1954)
1953	Viro, Finland	Developed a regional chemical budget by comparing analytical data for precipitation and river waters in Finland (Viro, 1953)
1953–1958	Tamm, Sweden	Demonstrated the great dependence of mosses on atmospheric sources of nutrients, especially nitrogen (Tamm, 1953) and expanded this concept to include most forest plants (Tamm, 1958)
1953–1955	Various investigators in several countries	Simultaneously investigated precipitation chemistry data for evidence of atmospheric acidity (Barrett and Brodin, 1955, Sweden; Parker, 1955, and Gorham, 1955, England; Houghton, 1955, U.S.)
1954–1961	Gorham, England	Demonstrated that acidity in precipitation markedly influenced geological weathering processes and the chemistry of lake waters, bog waters, and soils (Gorham, 1955, 1958b, 1958c, 1961) Demonstrated that hydrochloric acid from combustion of coal rich in chlorine predominated in urban precipitation whereas sulfuric acid predominated in rural precipitation (Gorham, 1958a, 1958b) Established that acidity in precipitation affects the alkalinity and buffering capacity of lake and bog waters (Gorham, 1957, 1958b) Established that the incidence of bronchitis in humans can be correlated with the acidity of precipitation (Gorham, 1959)

effects originated in three seemingly unrelated fields of science: limnology (the study of lakes), agriculture, and atmospheric chemistry.

Progress in limnology. The relationship between rain or snow and the water in streams and lakes was obvious even to prehistoric man. But the connection between changes in the chemistry of rain and snow and alterations in the chemistry of lake waters remained obscure until the middle of the 20th century.

In a long series of papers beginning in 1955, Gorham (1955, 1957, 1958a–d, 1961, 1965), now professor of ecology at the University of Minnesota, built the major foundations for our present understanding of the causes of acid precipitation and its impact on aquatic ecosystems. On the basis of research both in England and in Canada, Gorham and his colleagues demonstrated the following principles:

- Much of the acidity in precipitation near industrial regions can be attributed to atmospheric emissions produced by the combustion of fossil fuels;
- Progressive losses of alkalinity in surface waters and increases in the acidity of bog waters can be traced to the atmospheric deposition of acidic substances by precipitation;
- The free acidity in soils receiving acid precipitation is due primarily to sulfuric acid;
- The incidence of bronchitis in humans can be correlated with the acidity of precipitation;
- Exposure to sulfur dioxide and the resultant acid rain contribute to the deterioration of vegetation, soils, and lake water quality around metal smelters.

Thus, by the mid 1950s and early 1960s, Gorham was the second scientist to establish a major part of our present understanding of the sources and environmental consequences of acid precipitation. But his pioneering research, like that of Smith a century before, was met by thundering silence from both the scientific community and the public at large. One plausible explanation is that Gorham's work, being highly interdisciplinary, was published in a diverse array of scientific journals. In any event, because Gorham's work was not recognized, there resulted a further lag in both the scientific and public awareness of acid precipitation.

Progress in the agricultural sciences. The importance of the atmosphere as a source of nutrients for the growth and development of plants was first recognized by Robert Hooke in 1687

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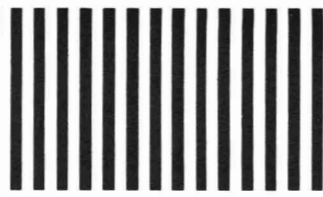
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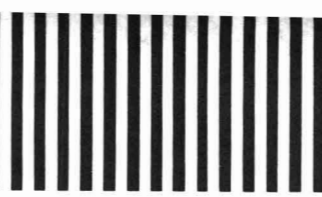
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(see also Gorham, 1965). From 1855 to 1916, scientists at the Rothamsted Experiment Station in England also demonstrated the relationship between nutrients in air and the growth of various crop plants (Way, 1855; Miller, 1905).

In the mid 1940s an imaginative Swedish soil scientist, Hans Egnér, developed a systematic way to look at the fertilization of crops by nutrients from the atmosphere. Working from his laboratory at the Agricultural College near Uppsala, Egnér created the first 20th-century network for the collection and chemical analysis of precipitation. A large number of sampling buckets were set out at experimental farms all over Sweden, and the major chemical constituents in what we now call bulk deposition (rain, snow, and dust fall) were measured on a regular monthly basis. The acidity of precipitation was one of several chemical parameters that were tested. Other agricultural scientists gradually expanded this network—first to Norway, Denmark, and Finland and later to most of western and central Europe. It came to be called the European Air Chemistry Network and it provided the first large-scale and long-term data on the changing chemistry of precipitation and its importance for agriculture and forestry (Emanuelsson et al. 1954; Egnér et al., 1955). In 1956, the International Meteorological Institute in Stockholm assumed responsibility for further coordination of the network. In 1957, as part of the International Geophysical Year, it spread eastward to include Poland and much of the Soviet Union. In marked contrast to monitoring efforts elsewhere in the world, the original European network with more than 100 collection stations has remained in continuous operation for nearly three decades.

Progress in the atmospheric sciences. Under the imaginative leadership of Carl Gustav Rossby and Erik Eriksson, the science of atmospheric chemistry began in Sweden and later spread across Europe and finally to North America (N.A.S., 1975). Rossby and Eriksson were convinced that atmospheric processes were efficient mechanisms for the long-distance as well as short-distance dispersal of many different substances. The data from Egnér's precipitation chemistry network provided the means to test various hypotheses about the trajectories of air masses, turbulent dispersal processes, and atmospheric scavenging and deposition processes (Rossby and Egnér, 1955). These observations led Eriksson to enunciate a general theory to describe the biogeochemical cir-

Year(s)	Investigator and country	Principal contribution
1957	Europe, U.S.S.R., and U.S.	During the International Geophysical Year, a one-year study of precipitation chemistry was made in Europe, the U.S.S.R., and the U.S.
1958–1959	Junge and Werby, Jordan et al., U.S.	Made the first regional studies of precipitation chemistry in the U.S. and noted the importance of atmospheric sulfur as a source of nutrients for crops (Junge and Werby, 1958; Jordan et al., 1959)
1959	Dannevig, Norway	Recognized the relationship between acid precipitation, acidity in surface waters, and disappearance of fish (Dannevig, 1959)
1960–1963	Gordon and Gorham, Canada	Established that exposure to sulfur dioxide and resultant acid rain contributed to the deterioration of lake quality, vegetation, and soils near metal smelters (Gorham and Gordon, 1960; Gordon and Gorham, 1963)
1960–1966	McCormick, U.S.	Operated the first continent-wide precipitation chemistry network in North America for six years (1960–66). Showed that precipitation is generally acidic east but alkaline west of the Mississippi River (Lodge et al., 1968)
1962	Carson, U.S.	Stimulated a global revolution in environmental awareness by publishing "Silent Spring" in which the term "poison rain" was used to describe concern about atmospheric transport and deposition of pollutants (Carson, 1962)
1967–1968	Odén, Sweden	<p>Outlined the changing acidity of precipitation as a regional and temporal phenomenon in Europe (Odén, 1968, 1976)</p> <p>Used trajectory analysis of air masses to demonstrate that acidity in precipitation in Scandinavia was attributable largely to emissions of sulfur in England and central Europe (Odén, 1968)</p> <p>Demonstrated temporal trends in acidity and in the concentrations of major cations and anions in precipitation over various parts of Europe (Odén, 1968)</p> <p>Demonstrated the increasing acidity of Scandinavian rivers (Odén, 1968)</p> <p>Described biological uptake and ion-exchange processes by which natural acidification of soils would be accelerated by atmospheric deposition of ammonia and other cations (Odén, 1968)</p> <p>Postulated that acid precipitation would lead to displacement of nutrient cations, reduction in nitrogen fixation, and release of heavy metals (especially Hg) which would damage surface waters and groundwaters (Odén, 1968, 1976)</p> <p>Postulated acidity in precipitation as a probable cause of decline in fish populations, impoverishment of forest soils, decreased forest growth, increased disease in plants, and accelerated corrosion and other damage to materials (Odén, 1967, 1968)</p>
1970	Odén and Ahl, Sweden	Discovered that soluble pollutants in snow accumulate in the snow pack and are released almost totally with the first meltwater in spring (Odén and Ahl, 1970)
1970	Hultberg, Sweden	Demonstrated the effect of acidity on fish populations in two Swedish lakes (Hultberg and Stenson, 1970)
1971–1972	Rodhe et al., Sweden	Developed the first quantitative analysis of long-distance transport of sulfur in Europe. Showed that distances of transport frequently exceed 1000 km, the residence time of sulfur in the air is 2–4 days, and fields of deposition are roughly symmetrical and slightly displaced to the northeast from sources of emission (Munn and Rodhe, 1971; Rodhe, 1972)
1972	Bolin et al., Sweden	Drafted Sweden's Case Study for the United Nations Conference on the Human Environment "Air Pollution Across National Boundaries: The Impact on the Environment of Sulfur in Air and Precipitation." Noted damage to materials as well as ecosystems by acid precipitation (Bolin et al., 1972)

Year(s)	Investigator and country	Principal contribution
1972	Hvatum, Norway	Demonstrated increasing content of lead near the surface of Norwegian peat bogs and postulated long-distance transport as the probable cause (Hvatum, 1972)
1972	Tyler, Sweden	Reported heavy metal accumulation in forest soils and speculated about their probable effects on forest productivity (Tyler, 1972)
1972	Granat, Sweden	Described the temporal and spatial deposition of sulfate and acid over northern Europe (Granat, 1972, 1978)
1972	Jonsson and Sundberg, Sweden	Established an experimental basis for the suspicion that acid precipitation had decreased the growth of forests in Sweden (Jonsson and Sundberg, 1972)
1972	Various agencies, Norway	Initiated the SNSF Project "Acid Precipitation: Effects on Forests and Fish (See <i>Ambio</i> , 1976, and Braekke, 1976)
1972-1980	Overrein, Norway	Demonstrated accelerated loss of calcium and other cations from soils receiving acid precipitation (Overrein, 1972)
		Provided leadership for the SNSF Project from its founding in 1972 until its completion in 1980 (<i>Ambio</i> , 1976; Overrein et al., 1980; Tollan, 1981)
1972	Likens et al., U.S.	Discussed the regional distribution of acid precipitation and its significance for aquatic and terrestrial ecosystems in North America (Likens et al., 1972)
		Indicated that nitric acid resulting from atmospheric transformation of NO _x adds to the acidity of precipitation in the eastern U.S. (Likens et al., 1972)
1972	Jensen and Snekvik, Norway	Showed that acidity in lakes and streams caused major decreases in salmon and trout populations in Norway (Jensen and Snekvik, 1972)
1972	Beamish and Harvey, Canada	Reported decline in fish populations due to acidification of lake waters in Canada (Beamish and Harvey, 1972)
1972-1980	Various investigators	Showed that mushrooms, mosses, and other vegetation in forests accumulate heavy metals, especially lead and cadmium. Found that wildlife feeding on these plants also accumulate the metals, sometimes making both the plants and the wildlife hazardous for human consumption (Munshower, 1972; Huckabee and Blaylock, 1974; Tyler, 1980)
1973	Malmer, Sweden	Summarized research on the ecological effects of increasing sulfur deposition, especially with reference to Swedish conditions (Malmer, 1973)
1973	Dickson et al., Sweden	Reported on the pH status of 314 lakes in western Sweden (Dickson et al., 1973)
1973	Wiklander, Sweden	Proposed a general theory to account for the effects of acid precipitation on soil chemical properties (Wiklander, 1973)
1973-1977	Ottar, Norway	Led the Organization for Economic Cooperation and Development in Europe in its continent-wide study of the long-range transport of air pollutants (Ottar, 1976; OECD, 1977)
1974	Almer et al., Sweden	Summarized the effects of changing lake water acidity on fish populations in Sweden (Almer et al., 1974)
1974	Grahn et al., Sweden	Discovered that <i>Sphagnum</i> (peat moss) invades acidified lakes and streams inducing a self-accelerating oligotrophication of the water body (Grahn et al., 1974)
1974	Cogbill and Likens, U.S.	Published maps showing changes in acidity of precipitation in the eastern U.S. between 1955-56 and 1972-73 (Cogbill and Likens, 1974)
1974	Hutchinson and Whitby, Canada	Established that strongly acid rain near Sudbury, Ontario is accompanied by deposition and/or mobilization of heavy metals (especially nickel, copper, cobalt, iron, aluminum, and manganese). Found toxicity of these metals sufficient to inhibit germination and establishment of many native and agricultural species of plants (Hutchinson and Whitby, 1974; Whitby and Hutchinson, 1974)

lation of matter on the earth (Eriksson, 1952, 1959, 1960).

The transport and deposition of water by atmospheric processes has been well known since the earliest observations of evaporation, cloud movement, and rain. But the notion that atmospheric transport and deposition were a major means for the dispersal and chemical transformation of many other substances was still only a working hypothesis in the early 1950s. Rossby and Eriksson championed these then-novel ideas and initiated various experimental tests of their hypotheses, using as a very powerful tool data from the European Air Chemistry Network. Rossby and Eriksson also sponsored a series of European conferences on atmospheric chemistry and dispersal processes, which attracted the interest of scientists in many other fields of inquiry including biology, forestry, agriculture, meteorology, and medicine (Eriksson, 1954). Both Gorham and Svante Odén were among the students at these conferences, but they never met personally until 1975.

Integration of knowledge

The first major unification of knowledge about acid precipitation in the fields of limnology, agriculture, and atmospheric chemistry was achieved by Odén, a soil scientist at the Agricultural College near Uppsala in Sweden. In 1961, as a young colleague of Egnér, Rossby, and Eriksson, Odén started a Scandinavian network to measure surface water chemistry. When data from this network were combined with those from the European Air Chemistry Network, a series of general trends and relationships began to emerge and were published by Odén in two different media—Stockholm's prestigious newspaper *Dagens Nyheter* (Odén, 1967) and in an Ecology Committee Bulletin (Odén, 1968). The newspaper report outlining Odén's audacious ideas about an insidious "chemical war" among the nations of Europe captured the attention of the press, who began the process of public education about acid precipitation in Europe. In much the same way, the Ecology Committee Bulletin stimulated scientific interest in acid precipitation and its ecological effects. Odén's analyses of air mass trajectories and temporal and geographical changes in precipitation chemistry clearly showed that:

- acid precipitation was a large-scale regional phenomenon in much of Europe with well-defined source and sink regions
- both precipitation and surface

waters were becoming more acidic

- long-distance (100–2000 km) transport of sulfur- and nitrogen-containing air pollutants was taking place among the various nations of Europe

- there were marked seasonal trends in deposition of major ions and acidity

- long-term trends in acidity could be detected in many countries of Europe.

Odén also hypothesized that the probable ecological consequences of acid precipitation would be changes in surface water chemistry, decline of fish populations, leaching of toxic metals from soils into surface waters, decreased forest growth, increased plant diseases, and accelerated damage to materials.

These conclusions and hypotheses led to a veritable storm of scientific and public concern about acid precipitation. Suddenly, limnological, agricultural, and atmospheric scientists began to argue and debate with each other about Odén's unconventional ideas and his general theory of atmospheric influences. Multidisciplinary discussions and international conferences ensued all over Europe and around the world as scientist after scientist was inspired (or provoked) into designing experimental tests to prove or to disprove Odén's ideas.

The Swedish government responded to the growing public and scientific controversies by initiating an inquiry that culminated in Sweden's Case Study for the U.N. Conference on the Human Environment: "Air Pollution Across National Boundaries: The Impact of Sulfur in Air and Precipitation" (Bolin et al., 1972).

The important ideas in both the Ecology Committee Bulletin and the Swedish Case Study were debated intensely all over Europe. Two major scientific initiatives followed in short order. The first took place in 1972 when three organizations in Norway joined together to establish the so-called SNSF Project: the Norwegian Interdisciplinary Research Programme "Acid Precipitation—Effects on Forest and Fish." These three organizations included the Norwegian Council for Scientific and Industrial Research, the Agricultural Research Council of Norway, and the Norwegian Ministry of Environment. The annual budget for the SNSF Project was about 10 million Norwegian kroner (\$2 million) per year for 1972–1980. This huge project had two comprehensive goals:

- to establish as precisely as possible the effects of acid precipitation on forests and freshwater fish

Year(s)	Investigator and country	Principal contribution
1974	Shriner, U.S.	Demonstrated that simulated rain acidified with sulfuric acid can accelerate erosion of protective waxes on leaves, inhibit nodulation of leguminous plants, and alter host–pathogen interactions of plants (Shriner, 1974, 1976, 1978)
1975	Brosset et al., Sweden	Described the chemical transformations and trajectories that lead to "white episodes" and "black episodes" of acid deposition in western Sweden. Showed that gaseous nitric acid increases acid deposition. Established a state-of-the-art titration method for the determination of acidity in precipitation (Brosset et al., 1975)
1975–1982	Cowling, U.S.	Testified in congressional hearings concerning the inadequacy of research in the U.S. on the ecological effects of acid precipitation (Cowling, 1976) Together with many other scientists in the U.S. and Canada, began the development of a permanent network to monitor chemical changes in wet and dry deposition and to study their biological effects in various regions of the U.S. (Galloway and Cowling, 1978)
1975	Cragin, Greenland	Determined the chemistry of precipitation in Greenland from 1300 to 1975 A.D. Found a continuing trend of increasing sulfate and lead concentration beginning about 1800 and rising even more rapidly after 1945. (Cragin et al., 1975)
1976	Schofield, U.S.	Reported the results of lake surveys showing a decline in fish populations associated with acidification of lakes in the Adirondack Mountains of New York State (Schofield, 1976)
1976	Kucera, Sweden	Summarized evidence that acid precipitation accelerates the corrosion of metals (Kucera, 1976)
1976	Summers and Whelpdale, Canada	Summarized earlier studies of precipitation chemistry in Canada and identified northwest Alberta, southern Ontario and Quebec, and the Atlantic Provinces as areas of present or potential impact by acid rain and snow (Summers and Whelpdale, 1976)
1976	Leivistad and Muniz, Norway	Documented a massive fish kill on the Tovedahl River associated with snow melting in the spring of 1975 and established that dead and dying fish had lost control of their blood salt balance. (Leivistad and Muniz, 1976; Leivistad et al., 1976)
1976	Tyler, Sweden	Demonstrated that heavy metals in the litter layer of forests inhibit microbial processes, especially decomposition of organic matter (Tyler, 1976)
1976	Galloway, U.S.; Berry, Canada; Granat, Sweden	Developed standardized protocols for precipitation collectors and collection techniques (Galloway and Likens, 1976; Berry et al., 1976; Granat, 1976)
1976	Hultberg and Grahn, Sweden	Discovered a correlation between acidification of lakes and the mercury content of fish (Hultberg and Grant, 1976)
1976	Pough, U.S.	Showed that reproduction of salamanders is inhibited by acidity of surface waters (Pough, 1976)
1977	Hagström, Sweden	Showed that reproduction of frogs is inhibited by acidity of surface waters (Hagström, 1977)
1977	Rosenqvist, Norway	Enunciated a general theory that acidification of soils and surface waters is due mainly to natural processes in soils and to changes in patterns of land use (Rosenqvist, 1977)
1978	Greszta, Austria	Demonstrated accumulation of heavy metals in forest soils leading to injury to young pine and spruce seedlings (Greszta, 1978)
1978–1980	Several investigators, U.S.	Showed that acid precipitation occurs in both urban and certain rural areas in the western U.S. (Liljestrand and Morgan, 1978; McColl and Bush, 1978; Lewis and Grant, 1980)

Year(s)	Investigator and country	Principal contribution
1979	Altshuller, U.S.; McBean, Canada	Documented the transboundary exchange of sulfur and nitrogen oxides between the U.S. and Canada (Altshuller and McBean, 1979)
1979	Odén, Sweden	Showed by studies of surface waters in Sweden that acidification due to sulfur deposition had begun during the early 1900s (Odén, 1979)
1979	Liljestrand and Morgan, U.S.	Completed a rigorous statistical analysis of trends in precipitation chemistry in the eastern and western U.S. (Liljestrand and Morgan, 1979)
1979	Cronan and Schofield, U.S.	Discovered that aluminum ions are leached by acid precipitation from soils into streams and lakes in concentrations toxic to fish (Cronan and Schofield, 1979)
1979	Galloway, U.S.; Whelpdale, Canada	Developed a new sulfur budget for eastern North America and showed that atmospheric sulfur in this region is predominantly of anthropogenic origin (about 95%) and that a substantial fraction (about 30%) of sulfur emissions in this region are deposited outside this region (Galloway and Whelpdale 1979)
1979	Carter, U.S.	Established a presidential initiative on acid rain calling for a 10-year-long, \$10 million-per-year interagency program of research on acid precipitation and its environmental consequences in the U.S. (Carter, 1979)
1979	Henriksen, Norway	Developed a simple descriptive model for determining the extent to which acidification decreases the alkalinity of lake waters and applied this method to predict the vulnerability of lakes to acid deposition (Henriksen, 1979)
1980	Hultberg and Wenblad, Sweden	Discovered acidification of groundwater in western Sweden, postulated acid precipitation as the probable cause, established by surveys of 1300 wells the frequency of heavy metal accumulation and plumbing problems associated with these wells (Hultberg and Wenblad, 1980)
1980	Abrahamsen, Norway	Summarized many years of research on the effects of acid precipitation on forests and concluded that fertilization effects, particularly by atmospheric deposition of nitrogen, tend to offset nutrient leaching and other detrimental effects. Also emphasized that negative effects of atmospheric deposition on growth are most likely when nutrient deficiencies or imbalances are increased by acid deposition (Abrahamsen, 1980)
1980	Wetstone, U.S.	Summarized the biological and materials damage of acid precipitation in relation to the pollution control laws in North America (Wetstone, 1980)
1980	Schindler et al., Canada	Established an experimental system for controlled acidification of whole lakes (Schindler et al., 1980). Demonstrated that acidification eliminated organisms of several trophic levels at pH values as high as 5.8–6.0 (Schindler, 1980). Also demonstrated that microbial reduction of sulfate could partially protect lakes against acidification (Schindler et al., 1980)
1980	Ulrich et al., Germany	Demonstrated a significant correlation between amount of soluble aluminum in forest soils, death of feeder roots in spruce, fir, and birch forests, and widespread decline in the growth of these forests (Ulrich et al., 1980; Schuck et al., 1979)
1980	Various investigators, U.S.	Established an Integrated Lake Water Acidification Study (ILWAS), to determine detailed chemical budgets for H^+ , SO_4^{--} , NH_4^+ , NO_3^- , Cl^- , and other ions in three lake watersheds with differing degrees of acidification (see Drablos and Tollan, 1980, pp. 252–267; and EPRI, 1981)
1981	Norton et al., U.S.	Demonstrated by analysis of lake sediments that increased depletion of soil nutrients and increased atmospheric deposition of lead and zinc in northern New England started prior to 1880 (Hanson et al., 1981; Johnston et al., 1981)

- to investigate the effects of air pollutants on soils, vegetation, and water to the extent required to support the primary objective.

Lars Overrein of the Norwegian Forest Research Institute was appointed research director for this project from 1972–1980. The project produced a steady stream of technical and scientific reports on various aspects of acid precipitation and its effects. The SNSF project also sponsored two major international scientific conferences—one at Telemark, Norway, in June 1976 and the second at Sandefjord, Norway, in March 1980. Braekke (1976) and *Ambio* (1976) published major reports in connection with the conference at Telemark. The Sandefjord conference was designed to provide a forum for evaluation not only of recent research within the SNSF Project, but also the large amount of research currently being done elsewhere in the world (Drablos and Tollan, 1980). A final report and bibliography from the SNSF Project was published at the end of 1980 (Overrein, Seip, and Tollan, 1980; Tollan, 1981).

The second major scientific initiative was conducted by the Organization for Economic Cooperation and Development (OECD) from 1973–1975. This was a study of the long-range transport and deposition of atmospheric sulfur in eastern and western Europe. The OECD findings, published in 1977, showed that the area of acid precipitation included almost all of northwestern Europe. The findings confirmed the idea that pollutants are transported long distances and showed that the air quality in each European country is measurably affected by emissions from all other European Countries (OECD, 1977).

In October of 1977, the Economic Commission for Europe originated the Cooperative Programme for Monitoring and Evaluating the Long-Range Transmission of Air Pollutants in Europe, which is now in operation. The Economic Commission has nearly completed formulating a multinational convention governing nations' responsibilities for combating the long-range transboundary transport of air pollutants. Arne Tollan and Brunjulf Ottar of the SNSF project were commissioned to develop working papers concerning both the atmospheric and biological influences of sulfur in the air and in precipitation.

North American awareness

Concern about acid precipitation and its ecological effects in North America developed first in Canada and

then later in the U.S. Initial interests were focused on the effects of sulfur dioxide exposure and associated acid precipitation and heavy metal deposition in the vicinity of metal smelting and sintering operations (Katz, 1939; Gordon and Gorham, 1963), especially those near Sudbury, Ontario—the largest point source of sulfur in the world (Gorham and Gordon, 1960; Hutchinson and Whitby, 1974). During the early 1970s, interest spread to other parts of Canada as declining fish populations were discovered in more and more lakes of southern Ontario and Nova Scotia, remote from local sources of atmospheric sulfur (Beamish and Harvey, 1972). Very early measurements of nitrogen compounds in rain and snow were made by Shutt and Hedley (1925); the first measurements of the pH of precipitation in Canada were reported by Herman and Gorham (1957). A summary of acid precipitation studies in Canada was published in 1976 by Summers and Whelpdale (1976).

The first detailed research on precipitation chemistry in the U.S. was completed by MacIntyre and Young (1923). Emphasis was given to the importance of airborne nutrients for the growth of crops. This work was followed by the work of Junge and other atmospheric scientists during the 1950s (Junge and Werby, 1958). The earliest regional monitoring network for precipitation chemistry was maintained by a group of State Agricultural Experiment Station scientists from 1953–55 (Jordan et al., 1959) and the first national monitoring program was established under the auspices of the Air Pollution Program within the Public Health Service Laboratory at Cincinnati, Ohio. The data for 1960–66 were summarized by Lodge (1968). As has been the case for all such studies in North America, however, these early programs were redirected or terminated so that no continuing records are available of long-term trends in precipitation chemistry.

Scientific and public interest in acid precipitation and its ecological consequences were stimulated in North America by Svante Odén with a series of 14 lectures at various institutions in the U.S. during the fall of 1971, and also by Torsten Ahl and Odén at the 19th International Limnological Congress in Winnipeg, Manitoba, in 1974. A series of publications by Gene Likens, Charles Cogbill, James Galloway, Carl Schofield, and others provided further stimulus (Likens et al., 1972; Likens, 1976; Cogbill and Likens, 1974; Schofield, 1976; Gallo-

Year(s)	Investigator and country	Principal contribution
1981	Rodhe, Sweden; Crutzen, Vanderpol, Sweden	Developed a photochemical model for the formation of sulfuric and nitric acid during long-distance transport. The model shows that the transformation of both of these acids are coupled processes and that their transformation rates and distances of transport are influenced by hydrocarbons and various oxidants in the atmosphere (Rodhe et al., 1981)
1981	Rahn, U.S.	Demonstrated that the Mn/V ratio of aerosols can be used as a tracer to determine the source of acid aerosols in the arctic and suggested its use in determining source-receptor relationships for acid deposition in North America (Rahn, 1981)

Major international conferences documenting further progress

1950s	Eriksson, Sweden	The International Meteorological Institute sponsored a series of conferences on various aspects of atmospheric chemistry (Eriksson, 1954)
1975–1976	Dochinger and Seliga, U.S.	U.S. Forest Service sponsored the First International Symposium on Acid Precipitation and the Forest Ecosystem at Ohio State University, Columbus, Ohio (Dochinger and Seliga, 1976a, 1976b)
1976	Overrein et al., Norway	SNSF Project and the Norwegian Ministry of the Environment sponsored the International Conference on Effects of Acid Precipitation, Telemark, Norway (Ambio, 1976; Braekke, 1976)
1977	Husar and Lodge, U.S.; Moore, England	The U.N. Environmental Program and several other organizations sponsored an International Symposium on Sulfur in the Atmosphere, Dubrovnik, Yugoslavia (Husar et al., 1978)
1978	Hutchinson, Canada	NATO sponsored an Advanced Research Institute on Ecological Effects of Acid Precipitation in Toronto, Canada (Hutchinson and Havas, 1980)
1978	Howells, England	The Electric Power Research Institute (U.S.) and the Central Electricity Generating Board (Great Britain) sponsored an International Symposium on Ecological Effects of Acid Precipitation (Howells, 1979)
1978	Hendrey, U.S.	U.S. EPA and Brookhaven National Laboratory sponsored an International Workshop on Limnological Aspects of Acid Precipitation, Sagamore Lake, N.Y. (Hendrey, 1978)
1979	Shriner, U.S.	The Oak Ridge National Laboratory sponsored a symposium on the Potential Environmental and Health Effects of Sulfur Deposition, Gatlinburg, Tenn. (Shriner et al., 1980)
1979	Agle, U.S.; Turnbull, Canada	A group of Canadian and U.S. environmental protection organizations sponsored the Action Seminar on Acid Precipitation, Toronto, Canada (Reid, 1980)
1980	Overrein et al., Norway	The SNSF project sponsored an International Conference on Ecological Impacts of Acid Precipitation, Sande, Norway (Overrein et al., 1980; Tollan, 1981)
1980	Miller et al., U.S.	The U.S. Forest Service and other U.S. and international air pollution organizations sponsored an International Symposium on Effects of Air Pollutants on Mediterranean and Temperate Forest Ecosystems, Riverside, Calif. (Miller, 1980)
1981	Schindler et al., Canada and U.S.	The National Academy of Sciences organized an international committee of scientists to prepare an authoritative overview entitled: "Atmosphere-Biosphere Interactions: Toward a Better Understanding of the Environmental Consequences of Fossil Fuels Combustion." (NAS, 1981)

way and Likens, 1976; Galloway et al., 1978; Likens et al., 1979). Experimental studies of various biological effects of acid precipitation were initiated at Cornell, North Carolina State, and other universities. David Shriner's (1978) dissertation demonstrated both direct injury to vegetation and various indirect effects through pathogens and parasites. Schofield's (1976) research on the extinction of fish populations in the Adirondack Mountains was especially alarming.

Growing awareness of the important impacts of acid precipitation on fish populations and potential effects on forests led the U.S. Forest Service to sponsor the First International Symposium on Acid Precipitation and the Forest Ecosystem in May 1975. The proceedings of this symposium and the associated workshop reports were published by Dochinger and Seliga (1976a, 1976b). At congressional hearings in July 1975, Cowling (1976) testified about the inadequacy of research on acid precipitation in the U.S. Specifically, he said that the lack of coordinated research programs on ecological effects and the absence of a stable monitoring network were the primary causes of the profound ignorance in North America about acid precipitation.

Both Canada and the U.S. have recently started long-term programs for the chemical analysis of precipitation. The Canadian Network for Sampling Precipitation began in 1976; the National Atmospheric Deposition Program was started in the U.S. in 1978 (Galloway and Cowling, 1978). By late 1981, some 50 sampling stations were operating in Canada and 93 in the U.S.

The data from these programs (Figure 1) show that the area receiving acid precipitation now embraces about two-thirds of the total land area of North America. Although sulfuric acid has been found to be the dominant source of acidity both here and in Europe, nitric acid accounts for almost one third, and the fraction is rising.

In 1978, the governments of Canada and the U.S. established a Bilateral Research Consultation Group on the Long-Range Transport of Air Pollutants to coordinate the exchange of scientific information on acid precipitation. This group documented the transboundary flow of air pollutants in eastern North America, and showed that about 11 times more oxides of nitrogen and two to four times more sulfur oxides are transported from the U.S. to Canada than the reverse (Altshuller and McBean, 1979, 1980).

In the late fall of 1978, Congress passed a resolution calling for bilateral discussions with Canada to preserve and protect mutual air resources. A joint statement on the issues was prepared in July 1979, and on Aug. 5, 1980, the governments of Canada and the U.S. signed a Memorandum of Intent to develop a bilateral agreement on transboundary air pollution including "the already serious problem of acid rain." To provide a suitable technical and scientific foundation for the formulation of such an agreement, five bilateral workgroups were established to prepare scientific reports on the following specific aspects of the problem: impact assessment; atmospheric modeling; strategies development and implementation; emissions, costs, and engineering assessments; legal, institutional arrangements; and drafting. Preliminary drafts of the first four of these reports were completed in early 1981 and are presently being refined in preparation for their submission to the Canadian Department of External Affairs and the U.S. Department of State in early 1982.

Coordinated research programs

During the past five years, significant efforts have been made in North America to develop well-coordinated programs of research on both the atmospheric and biological aspects of the acid precipitation problem. In the spring of 1976, a cadre of more than 100 scientists from various state agricultural experiment stations and other federal, state, private university, and industrial research agencies in the U.S. began the process of creating the organization now known as the National Atmospheric Deposition Program (NADP) to meet the need for a coordinated and long-term precipitation chemistry monitoring and effects research program. In mid-1976 the Department of Energy initiated the Multistate Atmospheric Power Production Pollution Study (MAP3S) to improve understanding of the transport, transformation, and fate of pollutants released by energy-related activities.

In the fall of 1977, the President's Council on Environmental Quality contracted with the NADP to draft "A National Program for Assessing the Problem of Atmospheric Deposition (Acid Rain)" (Galloway et al., 1978). This document provided the basis for a presidential initiative on acid precipitation, which former President Carter announced on Aug. 2, 1979, in his Second Environmental Message (Carter, 1979). The presidential initiative called for a 10-year program of

research on the causes and consequences of acid precipitation. The Energy Security Act (PL 96-264) passed by Congress in June 1980 provided a legislative mandate for a national effort. Title VII of this act (the Acid Precipitation Act of 1980) also called for development of a National Acid Precipitation Assessment Plan. The purpose was to develop a firmer scientific basis for environmental and energy policy decisions regarding acid precipitation. After extensive interagency discussions, a formal proposal was issued in draft form by the Interagency Task Force on Acid Precipitation (ITFAP, 1981) in January 1981. Title VII also authorized additional financial support from Congress for a comprehensive national program of acid rain research. Leadership for this interagency program was vested with administrators of the National Oceanic and Atmospheric Administration (NOAA), the Department of Agriculture (DOA), and the EPA.

In 1981 the three designated co-chairmen were Ferris Webster, an assistant administrator in NOAA; Anson Bertrand, director of the Science and Education Administration at DOA; and Andrew Jovanovich, an acting assistant administrator in EPA. The other agencies comprising the Interagency Task Force included the following: the Council on Environmental Quality (CEQ); the Departments of Commerce (DOC), Energy (DOE), Interior (DOI), State (DOS), and Health and Human Services (DHHS); the National Aeronautics and Space Administration (NASA); the National Science Foundation (NSF); and the Tennessee Valley Authority (TVA).

The National Acid Precipitation Assessment Program is now operational. It is designed as a 10-year-long, multiagency program of policy-oriented research. In the 1982 fiscal year, its cost will be about \$18 million. This program is governed by the Federal Interagency Task Force on Acid Precipitation, which sets policy for the national program and oversees its implementation. The task force also has administrative responsibility for federally sponsored efforts and their coordination with ongoing research and monitoring conducted by the states, universities, industry, environmental organizations, and other groups in the U.S., Canada, Mexico, and Europe. The task force will annually report to the president and Congress on the status of knowledge, additional research needs, and alternative strategies for management of acid precipitation and its effects.

TABLE 2

Research tasks in the National Acid Precitation Assessment Program

Areas and specific tasks	Priority	Leading agency	Participating agencies							Contributing agencies						Duration Start (years)		
			NOAA	DOA	EPA	DOI	DOE	TVA	NOAA	DOA	EPA	DOI	DOE	NSF	TVA		NASA	Other
Natural Sources		NOAA																
Assessment of natural sources	High	NOAA	X							X	X	X	X		X		1981	2
Neutralizing materials in the atmosphere	High	NOAA	X							X	X		X	X	X		1982	3
Man-made sources		DOE																
Modeling and economic analysis of emissions	High	DOE			X		X							X			1982	8
Synthesis of emissions data	Medium	DOE			X		X							X			1982	3
Atmospheric processes		NOAA																
Long-distance transport and dispersion	High	NOAA	X			X				X			X	X	X		1982	5
Global circulation of acid substances	High	NOAA	X				X			X			X		X		1980	6
Aqueous-phase conversion processes	High	NOAA	X	X			X	X		X			X		X		1980	10
Scavenging of gases and aerosols	High	NOAA	X				X			X			X		X		1980	10
Atmospheric modeling	Low	NOAA					X		X	X				X			1981	4
Deposition monitoring		DOI																
Global and national trends networks	High	DOI	X	X	X	X		X				X					1980	10+
Improving of research networks	High	DOI	X			X	X			X				X			1980	5
Dry deposition measurement methods	High	DOI	X		X		X			X		X					1982	3
Aquatic impacts		EPA																
State and regional water surveys	High	EPA			X	X								X			1980	4
Modeling lake and stream responses	High	EPA			X	X						X	X	X			1981	5
Tolerance and susceptibility of lakes	High	EPA		X	X	X							X	X			1980	5
Effects on watershed productivity	High	EPA		X	X	X		X				X	X				1980	10
Identification of vulnerable life stages	Medium	EPA				X				X		X	X				1980	5
Mitigation strategies for lakes	Low	EPA		X		X				X				X			1984	5
Acidification of drinking water	High	EPA			X	X										HHS	1980	4
Monitoring drinking water quality	Medium			X	X											HHS	1983	3
Treatment of drinking water	Medium	EPA			X							X					1983	3
Mobilization of toxic metals	Medium	EPA		X	X	X						X					1982	5
Metal contamination of fish	Medium	EPA				X				X	X						1981	2

TABLE 2 (continued)

Research tasks in the National Acid Precipitation Assessment Program

Areas and specific tasks	Priority	Leading agency	Participating agencies						Contributing agencies						Duration (years)					
			NOAA	DOA	EPA	DOI	DOE	TVA	NOAA	DOA	EPA	DOI	DOE	NSF		TVA	NASA	Other	Start	
Terrestrial impacts			DOA																	
Effects on growth and productivity of forests	High	DOA		X	X	X		X						X	X				1980	10
Identification of vulnerable life stages	Medium	DOA		X									X	X					1980	10
Effects on plant metabolism	Medium	DOA		X									X	X					1982	5
Effects on forest diseases and insects	High	DOA		X									X						1982	5
Effects on growth and productivity of crops	High	DOA		X	X	X		X					X	X					1980	5
Dose-response relationships of crops	Medium	DOA		X	X								X						1982	5
Effects on crop diseases and insects	Low	DOA		X									X					HHS	1982	5
Metal contamination of crops	Medium	DOA		X									X					HHS	1982	2
Predicting soil vulnerability	High	DOA		X	X	X													1982	3
Effects on soil nutrient status	High	DOA		X	X			X							X	X			1980	5
Effects on soil buffering capacity	High	DOA		X	X								X	X	X	X			1981	5
Mechanisms and amelioration of soil impacts	Low	DOA		X															1982	5
Effects on materials			DOI																	
Effects on construction materials	High	DOI			X	X													1980	5
Costs of materials effects	Medium	DOI			X			X											1984	3
Use of protective coatings	Low	DOI			X	X													1983	3
Control technologies			EPA																	
Development of limestone injection burner	High	EPA			X			X								X			1981	4
Assessments and policy analysis			EPA																	
Computer simulation models	High	EPA			X			X		X									1980	5
Models to guide policy decisions	High	EPA			X			X		X									1980	5
Analysis of emissions dispatching	Medium	EPA			X								X		X				1982	3
Special scientific and policy assessments	High	EPA	X	X	X	X	X							X	X	X		HHS, DOS	1981	10

Table 2 outlines the research efforts in the National Acid Precipitation Assessment Program. Note that a total of 43 specific research tasks are being undertaken. For purposes of coordination and planning, these 43 tasks have been grouped into nine general categories. Research on each specific task and area of scientific work is coordinated by an Interagency Task Group consisting of scientists and program leaders from the relevant member agencies. Each task group functions under the leadership of a representative from one of the eight agencies. The task group leaders for each area of research and their institutional affiliations are listed in Table 3. Chris Bernabo of NOAA has the interagency role of executive director of the task force. He is located at the Council on Environmental Quality and his responsibilities include coordinating the efforts of the nine task groups, overseeing interagency planning, and providing liaison with the task force.

Similarly comprehensive, well-

coordinated, and well-funded programs of acid rain research have been initiated by the Province of Ontario and the federal Department of Environment in Canada and by the Electric Power Research Institute in the U.S. Especially noteworthy among these efforts are the Experimental Lakes Studies initiated in northern Ontario by David Schindler et al. (1980) and the Integrated Lake-Watershed Acidification Study sponsored by the Electric Power Research Institute (EPRI, 1981; see also Drabljøs and Tollan, 1980, pp. 252-267).

Future research

We have come a long way since the earliest attempts of Smith, Gorham, and Odén to alert the scientific community and the public at large to the causes and consequences of acid rain. Much has been learned both in Europe and in North America. But much more remains to be learned about the many aspects and effects of the phenomenon. The pathway that has led to our

present understanding has been illuminated by the remarkable insights of a few imaginative scientists as well as those of many others who have filled lesser voids in our knowledge.

Today, public interest in acid rain research is at an all-time high in many parts of the world. The challenge for us as scientists is to satisfy that curiosity by providing a more extensive understanding of the atmospheric processes, soil transformations, vegetational changes, alterations in water chemistry, effects on materials, and physiological influences of acid precipitation (ITFAP, 1981; NAS, 1981).

Research is the key to improved understanding. Improved understanding is the key to wiser public and private decisions that relate to the use of energy and to the quality of life in our society. Let us get on with the job of learning so that the challenge of managing acid precipitation and its effects can begin as soon as possible.

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TABLE 3

Task group leaders in the Federal Interagency Task Force on Acid Precipitation

Area	Task group leader
Natural sources	Dr. Daniel Albritton Environmental Research Laboratory National Oceanic and Atmospheric Administration Boulder, Colo.
Synthetic sources	Dr. David J. Beecy Office of Fossil Energy U.S. Department of Energy Washington, D.C.
Atmospheric processes	Dr. John Miller Air Resources Laboratory National Oceanic and Atmospheric Administration Silver Spring, Md.
Deposition monitoring	Dr. R. J. Pickering Water Quality Branch U.S. Geological Survey Reston, Va.
Aquatic impacts	Dr. Ray Wilhour Air Pollution Effects Branch Environmental Protection Agency Corvallis, Ore.
Terrestrial impacts	Dr. Leon Dochinger Forestry Sciences Laboratory U.S. Forest Service Delaware, Ohio
Effects on materials	Dr. Ray Herrman Field Support Laboratory National Park Service Fort Collins, Colo.
Control technology	Dr. Kurt Riegel Environmental Engineering and Technology Environmental Protection Agency Washington, D.C.
Assessments and policy	Dr. Lowell Smith Program Integration and Policy Staff Environmental Protection Agency Washington, D.C.



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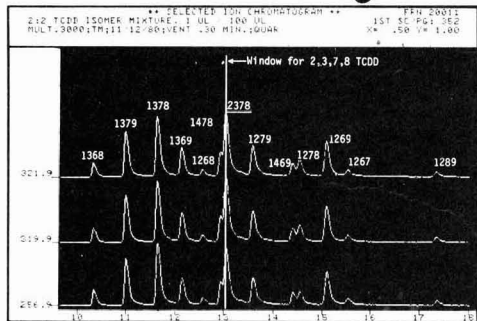
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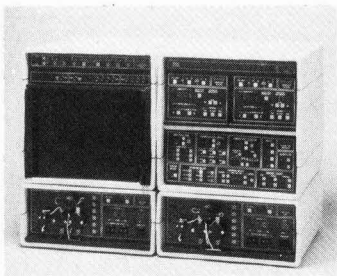
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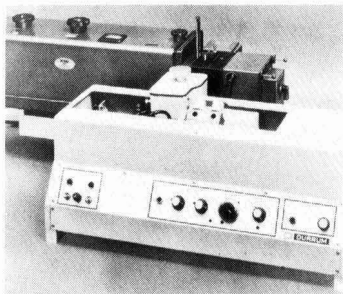
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Vertical recorder

Available in single or dual channel models, this recorder has all controls and connectors mounted on the front panel and can be placed in a stack with similar recorders to save bench space. The chart is covered with a clear plexiglass door. Linear Instruments **114**



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Graphics system

Interactive graphics system supports several plotters/printers. The system consists of a desktop computer, a graphics generator, a large screen display, a graphics tablet, an interactive graphics library, and connecting cables. Hewlett-Packard **120**

Mass spectrometer

Triple-stage quadrupole instrument is capable of performing four types of experiments including daughter, parent, neutral loss/gain, and standard GC/MS experiments. The types of analysis and their sequence may be preselected by the operator. The system features a direct exposure probe for rapid vaporization of compounds not readily introduced to the ion source by conventional methods. Finnigan MAT **122**

Wastewater sampler

Sampler avoids freezing problems by pneumatically ejecting samples at high velocity and then blowing the tubing dry. The system has been used in air temperatures as low as –30 °C. The sampler head is available in stainless steel, aluminum or PVC and portable systems are available. Markland Specialty Engineering **128**

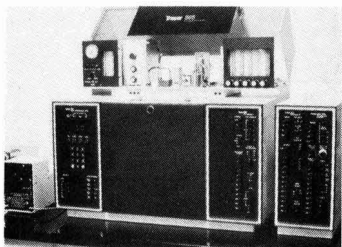
Tubing connectors

Made of chrome-plated brass, these connectors are available for ½-in. and ¼-in. standard laboratory rigid or flexible tubing. They shut off automatic-

ally when disconnected and are available in eight styles. Manostat **129**

Programmable collector

Collects samples in all types of liquid chromatography into many different sizes of containers, from small tubes to carboys. The collector has a programmable peak sensing system that permits peak collections in all chromatographic situations. Five complete programs can be stored in the memory, enabling the collector to be switched between applications. LKB Instruments **124**



Gas chromatograph

Compact instrument is only 25 in. wide but can accommodate up to three detectors and five detector gas controllers. An automated split/splitless capillary system and single or dual autosamplers are available as options. Tracor Instruments **125**

Preparation cylinder

Blends multiple gas mixtures in parts per million by volume or percentage ranges. Gas standards can be prepared in one minute to 0.1% accuracy for chromatograph calibration or environmental chamber studies. The system consists of a nickel-plated graduated 10-L cylinder that has a free-floating piston. Houston Atlas **126**

Relative humidity instrument

Contains five independent channels for monitoring relative humidity at five different locations. The signals can be fed directly to a multichannel recorder or data logger. Measurements can be made over the range of 0–100% relative humidity with automatic temperature compensation from –5 °C to 65 °C. Phys-Chemical Research **127**

Digital conductivity meter

Research-grade instrument has digital switches on the front panel to allow precise settings for cell-constant adjustments from 0.5–1.9cm⁻¹, temperatures from 0–99 °C, and temperature coefficients from 1.0–9.2% °C. A back-off device provides sensitivity from 0.1–1%, permitting the measurement of small changes in conductivity. Orion Research **123**

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ES&T LITERATURE

Energy management. Bulletin announces systems for energy management, such as those measuring temperature, humidity, and solar energy. Calibration facilities are also available. Hy-Cal Engineering **151**

X-ray microanalysis. Illustrative brochures describe new capabilities in energy-dispersive X-ray microanalysis, with advanced techniques for electron column beam control, other advantages. Princeton Gamma-Tech **152**

Anaerobic identification. Brochure describes Series 550 gas chromatograph that identifies metabolic products of anaerobes (volatile or nonvolatile) quickly and accurately. GOW-MAC **153**

Emergency spill service. Information explains on-site analytical capabilities for spill assessment, chemical waste sites, and cleanup projects, on an emergency or long-term basis, with 24-h/d availability. ALERT **154**

PAC. Technical Bulletin 102 tells about use of powdered activated carbon (PAC) as a precoat with a lower pressure drop, as a way to allow substantially longer filter runs. Good resistance to cracking. Lower costs. Ecodyne/Graver **155**

Respirator maintenance. Brochure tells how to set up a maintenance program for reusable respirators and enjoy considerable cost savings. Custom Ultrasonics, Inc. **156**

Fugitive emissions. Laboratory Applications Data reports detail features and procedures of OVA-108 and OVA-128 fugitive emissions monitoring systems. Emphasis is on volatile organic carbon (VOC). Foxboro Analytical **157**

Infrared spectroscopy. Literature discusses infrared spectroscopy applications and methods for analyzing water

pollution, pesticides, many organic compounds, other substances. Beckman Instruments, Inc. **158**

Membrane liners. Technical bulletin describes testing for tear propagation and tear initiation resistance for flexible membrane liners with wastewater and potable water applications. Tests follow ASTM D-751. Burke Rubber Co. **159**

Engineering/management services. Brochure details environmental audits, engineering reviews for environmental impairment liability insurance, hazardous waste trucking insurance services, other needs. ECOSystems **160**

Industrial valves. Announcement describes 3-in., heavy-duty industrial valves with 3-50-psi, 10-125-psi, and 50-175-psi adjustments. Water treatment and cooling towers are among applications. Griswold Controls **161**

Line-scan recorder. News bulletin describes SR-8000 line-scan recorder with real-time recording up to 40 scans/s; scan speed 25 ms-50 s. Many applications, including environmental. Geophysical Survey Systems, Inc. **162**

Energy saving. Brochure describes ways to save energy in heating, ventilation, and air conditioning systems with "EFACT" computerized program. Johnson Controls **163**

Hazardous waste alert. Announcement describes full hazardous waste alert service with surveys, customer files, regulatory warnings, many other services for \$500/y. EEW Management, Inc. **164**

Leak-preventing valves. Bulletin V-31 describes SG4 valves for sealing, and preventing leaks for lethal substance, toxic, and sub-zero°F service. The Duriron Co., Inc. **165**

Waste biotreatment. Brochure explains CTX "BioX Treatment System" for biotreatment of organic hazardous waste for small flows of 1500-150 000 gpd. Works on fixed-film system. Cytox Equipment **166**

Safety supplies. December 1981 catalog lists safety supplies necessary for meeting OSHA regulations. Interex **167**

Pumps and motors. Fluid power catalog lists pumps and motors for many applications, some where fire resistance is required. Delavan **168**

Servo recorder. Bulletin describes Model 304 4-in. servo recorder that prints out in plain language. Applications include pollution monitoring and quality control. Chessell **169**

Pinch valves. Bulletin LEF-10 describes pinch valves for on/off and throttling control in abrasive and corrosive medium service. Robbins & Myers **170**

Polyelectrolyte. Literature describes Series 35-300 Polyelectrolyte System. Takes up less than 7 ft² of floor space, has precise feed rate, and other controls. Wallace & Tiernan **171**

Gel permeation. Brochure describes gel permeation chromatography (GPC) with hardware and software to provide graphical comparison plots of individual runs. Nelson Analytical **172**

Ion exchange. Announcement tells about more than 22 inorganic ion exchangers that the company says is more resistant to radiation, heat, and corrosive media. Amorphous and hydrated forms are both available. Atomergic Chemetals **173**

Stir-tester. Bulletin 8140 describes a stir-tester for precision speed control and measurement. Special application to thixotropic and semisolid materials. G. K. Keller **174**

Fluorescence. Bibliography lists entries for fluorescence applications from acetone to zinc protoporphyrin. Useful for fluorescence spectroscopists. Farand Optical **175**

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

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.

Fuel cost cutting. Industrial Report 128 explains how two single-boiler retrofits saved a chemical company fuel and allowed it to meet emission standards at the same time. Peabody Engineering 176

Source emission monitors. Brochure describes sample handling systems for source emission monitors, and tells how to select the right system for mild, moderate, or severe gas environments. Du Pont Company 177

Hazardous waste. Brochure explains how seven common hazardous waste problems are pinpointed and alleviated. Mobile field laboratory and analytical capabilities are also discussed. York Wastewater Consultants 178

HPLC column. Technical bulletin describes direct connect guard column (DCGC) as a means to protect costly high performance liquid chromatography (HPLC) columns. Screws directly into analytical column inlet; minimizes column effects even with 3- μ HPLC columns. Applied Science 179

Hazardous waste. Information on company's volume reduction and so-

ludification (VRS) system for treating hazardous waste details safety and reduced volume of the encapsulated end product. Werner & Pfleiderer 180

Chloride measurement. Procedure No. 507 sets forth a step-by-step procedure for measuring chloride in drinking water, wastewater, and brines by the electrode method. Orion Research 181

2,4-D herbicides. "Queensland Report" says there is no health hazard. National Coalition for a Reasonable 2,4-D Policy, 435 North Michigan Ave., Suite 1717, Chicago, Ill. 60611 (write direct)

Waste exchange. Brochure discusses November 1981 catalog of Northeast Industrial Waste Exchange. Northeast Industrial Waste Exchange, 700 East Water St., Room 711, Syracuse, N.Y. 13210 (write direct).

Metals in sewage. Project summary outlines heavy metals sources in a municipal sewage treatment plant. EPA-600/S2-81-224. Municipal En-

vironmental Research Laboratory (MERL), U.S. EPA, Cincinnati, Ohio 45268 (write direct).

Biodegradability. Project summary EPA-600/S2-81-175/176 outlines a literature study of biodegradability of chemicals in water (two volumes). MERL, U.S. EPA, Cincinnati, Ohio 45268 (write direct).

Nuclear plant workers. Paper, "The Temporary Worker in the Nuclear Power Industry: An Equity Analysis." Center for Technology, Environment, and Development, Clark University, Worcester, Mass. 01610 (write direct).

Refinery effluent. Report 10/81, "The Statistical Representation of Refinery Effluent Quality Data—A Case Example." CONCAWE, Babylon Kantoren A, Koningin Julianaplein 30-9, 2595 den Haag, the Netherlands (write direct).

Chemical publications. August 1981 catalog lists publications for analytical chemists. The Royal Society of Chemistry, Burlington House, Piccadilly, London W1V 0BN, England (write direct).



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ES&T BOOKS

Organic Chemical Contaminants in Groundwater: Transport and Removal. Cat. No. 20156. Francis A. DiGiano, Ed. 123 pages. AWWA Data Processing, 6666 West Quincy Ave., Denver, Colo. 80235. 1981. \$10.50 (\$8 for AWWA members), softbound.

This book is a set of proceedings that introduce important concepts in groundwater contamination. Case histories are presented concerning solutions to current problems. The sharp differences between surface water and groundwater management and treatment aspects are shown.

Natural Systems for Water Pollution Control. Ray Dinges. 272 pages. Van Nostrand Reinhold, 135 W. 50th St., New York, N.Y. 10020. 1981. \$22.50.

Sometimes nature and its ecosystems can provide a water cleanup pathway whereby an antipollution goal is achieved, and the environment actually benefits. The economy could also benefit. The "power" is provided by enriched water, sunlight, wind, and gravity. Possibly, with proper management, this approach would be amenable to aquaculture; indeed, experiments in this direction have already been conducted. Wildlife habitat may also be enhanced.

Hazardous Substances Advisor. Periodical, monthly, J. J. Keller & Associates, Inc., 145 W. Wisconsin Ave., Neenah, Wis. 54956. \$7.50/mo.

This periodical covers OSHA regulations, toxic substances, pesticides, hazardous waste, and handling/transport. The stress is on regulatory activity, and how it would bear upon an affected business. The aim is to advise industry of changes and new procedures *before* they become law or iron-clad regulations.

Water Crisis in the United States. Cassettes, 3 parts, 42 min. National Public Radio, 2025 M St., N.W., Washington, D.C. 20036. 1981. \$9.

New York City wants to conserve water and rebuild or repair its water systems, but had to cut water consumption by 325 mg/d. Long Island groundwater is being contaminated. South Florida is the scene of fights between developers and those who maintain that the fragile water re-

source is in real trouble. The roles of weather, industry, and politics are discussed. Ask for AT-81-07-09, part of NPR's "All Things Considered" series.

Life for Sale. Sharon and Kathleen McAuliffe. 243 pages. Coward, McCann & Geoghegan Publishers, 200 Madison Ave., New York, N.Y. 10016. 1981. \$12.95, hard cover.

In June 1980, the U.S. Supreme Court ruled that synthetic microbes could be patented. This led to a bio-business "take-off with an unprecedented 'bang.'" This book examines the field of recombinant DNA or "gene-splicing" in easy-to-understand terms, and postulates that genetic engineering and "the biotechnological revolution" could account for as much as 70% of the U.S. GNP by the year 2010.

Building a Sustainable Society. Lester R. Brown. xiii + 433 pages. W. W. Norton & Co., Inc., 500 Fifth Ave., New York, N.Y. 10036. 1981. \$14.95, hard cover.

What is the most serious single threat to humanity? Perhaps the widespread loss of topsoil, the author warns. He adds that while world food output has more than doubled since 1950, the way the land was abused to bring the increase about reduced world topsoil by perhaps 20-33%. Ultimately, this will undermine productivity. The author has certain recommendations on how to combat the strain on earth bioresources.

The Design of Air Quality Monitoring Networks. R. E. Munn. xiii + 109 pages. Macmillan Co., 866 Third Ave., New York, N.Y. 10022. 1981. \$20, hard cover.

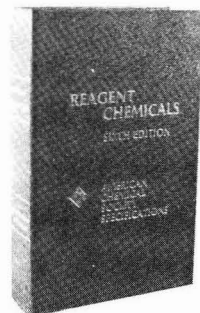
This book offers a unified view of siting of air quality monitoring stations, and optimization of the design of the station network. Case studies are presented, as are three general network design methods: statistical, modeling, and combined statistical/modeling.

A Holist Pilgrimage. Kelvin Van Nuy. ix + 433 pages. Philosophical Library, Inc., 200 West 57th St., New York, N.Y. 10019. 1981. \$19.95, hard cover.

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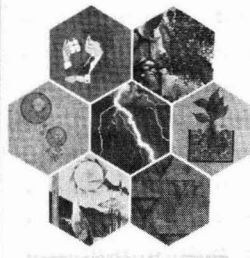
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"Since the earth is finite, human population and environmental use are in for a great contraction, especially if we are to be able to maintain the quality of our lives on a planet that is rapidly being exhausted." That is the essence of this book, which warns that a catastrophic collapse is due when the world's capacity to sustain the present rate of population and economic growth is finally overwhelmed.

Indoor Pollutants. National Research Council. xv + 537 pages. National Academy Press, 2101 Constitution Ave., N.W., Washington, D.C. 20418. 1981. \$16.25, paper.

Indoor pollution has become a "hot topic" of late. This work examines types of pollutants, both chemical and biological; asbestos; radioactive materials; and agents of contagion. Factors that influence exposure to indoor pollutants are discussed, as are recommendations for countermeasures.

Environmental Risk Analysis for Chemicals. Richard A. Conway, Ed. xxiv + 558 pages. Van Nostrand Reinhold Co., 135 West 50th St., New York, N.Y. 10020. 1981. \$37.50, hard cover.

The aim of this book is to provide a systematic approach to gathering information about potentially dangerous substances. Data so gathered can help to prepare an overall plan for basic testing. A step-by-step method of determining any chemical's environmental risk is presented, and recognition of "early warning" signs is explained.

Scientific Basis for Nuclear Waste Management. Vol. 3, John G. Moore, Ed. xvii + 632 pages. Plenum Press, 227 West 17th St., New York, N.Y. 10011. 1981. \$49.50, hard cover.

In this volume, studies characterizing the nature of nuclear waste repositories are set forth. Vitreous and crystalline high-level waste forms, as well as non-high-level management processes are also examined. Natural analogues, leach studies, radionuclide migration, and other related and pertinent topics are also covered.

Ozone Treatment of Wastewater. R. G. Rice, M. E. Browning. xi + 371 pages. Noyes Data Corp., Mill Rd. at Grand Ave., Park Ridge, N.J. 07656. 1981. \$32, hard cover.

The aim here is to acquaint the reader with state-of-the-art technology in ozone wastewater treatment. Oxidation processes are reviewed; funda-

mental principles of ozone technology are set forth; and many different industrial water/wastewater applications of ozone, from aquaculture to textiles, are discussed. Organic oxidation products and biological activated carbon are also covered.

Detection and Measurement of Hazardous Gases. C. F. Cullis, J. G. Firth, Eds. xi + 226 pages. Heineman Educational Books, Inc., 4 Front St., Exeter, N.H. 03833. 1981. \$35, hard cover.

Why detect such gases? Aside from health and safety considerations, laws and regulations require this to be done. This book looks at how to do this task through measurement of flammable gases and vapors; oxygen deficiency; toxic gases in the workplace; and the like. Personal monitoring, statistics, and standard atmospheres are also discussed.

Patty's Industrial Hygiene and Toxicology. 3rd ed. Vol. 2B. George D. Clayton and Florence E. Clayton, Eds. xviii + 937 pages. John Wiley & Sons, Inc., 605 Third Ave., New York, N.Y. 10016. 1981. \$70, hard cover.

This volume is part of the toxicology set. It considers occupational carcinogenesis, halogens, boron, silicon, alkaline materials, *N*-nitrosamines, aliphatic/alicyclic amines, and many hydrocarbons.

Biogas: Production and Utilization. Elizabeth C. Price, Paul N. Cheremisinoff. vi + 146 pages. Ann Arbor Science Publishers, P.O. Box 1425, Ann Arbor, Mich. 48106. 1981. \$29.95, hard cover.

One principal advantage of biogas is that it is a renewable resource. This work looks at microbiology and biochemistry, the anaerobic process, denitrification, process kinetics, methane applications, anaerobic digester design, offgas determination, and sludge treatment with soil conditioning and composting.

What Price Incentives: Economists and the Environment. Steven Kelman. xiv + 170 pages. Auburn House Publishing Co., 131 Clarendon St., Boston, Mass. 02116. 1981. \$19.95, hard cover.

Many economists speak in terms of economic incentives, such as the "polluter pays" principle, to control pollution. Noneconomists are often skeptical about the incentive approach. This book looks at the philosophical and practical concerns of both sides.

Water Quality Measurement. Harry B. Mark, Jr., James S. Mattson, Eds. vii + 485 pages. Marcel Dekker, Inc., 270 Madison Ave., New York, N.Y. 10016. 1981. \$57.75, hard cover.

This book examines modern analytical techniques. Its aim is to furnish chemists with methods needed to clean up water; regulate water quality; determine trace constituents' health hazards; and correlate ecological changes caused by trace substances. Latest developments in analytical instrumentation and chemistry for carrying out these tasks are set forth.

The Possible Share of Soft/Decentralized Renewables in Meeting the Future Energy Demands of Developing Regions. A. M. Khan. 40 pages. IIASA, A-2361 Laxenburg, Schloss Laxenburg, Austria. 1981. \$5, paper.

This report assesses the maximum size of the share of soft/decentralized technologies based on renewable energy sources, that could meet demands of developing world regions, perhaps 20-50 years from now.

Solar World Forum: Solar Technology in the Eighties. D. O. Hall, Ed. 3 volumes, about 3000 pages. Pergamon Press, Maxwell House, Fairview Park, Elmsford, N.Y. 10523. 1981. \$450/set.

These volumes contain the proceedings of the International Solar Energy Congress held at Brighton, England, in August. Topics covered include passive heating/cooling, solar resources, biomass, active heating/cooling, implementation, photochemistry, industrial applications, and many related subjects.

Environment: Latin America, Facing the Realities of Rapid Growth. Dick Riley with Chris Kerrebrock. 72 pages. World Environment Center, 300 East 42nd St., New York, N.Y. 10017. 1981. \$25 (add \$5 for overseas postage).

In Latin America, the authors describe developments that have changed the ecological face of the region, often adversely. Efforts to reverse these trends are also described. Deforestation, water resources, fish and wildlife conservation, alternative energy sources, and many other related matters are discussed.

OECD Guidelines for Testing Chemicals. About 700 pages. OECD Publications & Information Center, 1750 Pennsylvania Ave. N.W., Washington, D.C. 20006. 1981. \$80, looseleaf format.

These guidelines explain testing in physical chemistry, ecotoxicology, and health effects. The latest methods in testing are described. A common basis for international test data acceptance is suggested. This work will be updated periodically.

Mankind in Amnesia. Immanuel Velikovsky. Doubleday & Co., Inc., 245 Park Ave., New York, N.Y. 10017. 1982. \$14.95, hard cover.

This book has been published posthumously. The author asks the questions: Why are we racing toward a self-destructive nuclear confrontation? Can we be saved from our appetite for apocalypse? He also says that only if humanity accepts painful truths about the past, can it hope to avert horrifying cataclysm. The truth may be that any approaching nuclear confrontation and poisoning of the earth is no more than a human response to primal anxieties.

Aquaculture Economics: Basic Concepts and Methods of Analysis. Yung C. Shang. 176 pages. Westview Press, 5500 Central Ave. Boulder, Colo. 80301. 1981. \$20.

The author is at the University of Hawaii at Manoa. He discusses benefits of aquaculture, economic factors, farm-scale culture, recordkeeping needs, investment planning, and strategies for promoting aquaculture development, along with many other related topics.

Applying for a Permit to Destroy PCB Waste Oil: Volumes 1 and 2. S. G. Zelenski, et al. Vol. 1 is Order No. PB 81-173 346; Vol. 2 is Order No. 81-234 874. National Technical Information Service, 5285 Port Royal Rd., Springfield, Va. 22161. 1981. Vol. 1, \$9.50; Vol. 2, \$17.

Volume 1 is a summary, while Volume 2 covers documentation. They explain the permit process required and tried out before PCBs can be run through a burn.

The Occupational Medicine Sourcebook. Report #DR201. Technic Research, 21 Wyman Terrace, Arlington, Mass. 02174. 1982. \$220 (prepaid orders get a 10% discount).

This sourcebook lists 180 producers and 300 service providers. Also, 1800 medical directors are listed, as well as government agencies; research grants or contracts; medical, industrial, and union organizations; and reference sources.

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National Conference on Formaldehyde and Building-Related Illness. Indiana Chapter of the Air Pollution Control Association and Ball State University

Write: Dr. Thad Godish, Department of Natural Resources, Ball State University, Muncie, Ind. 47306; (317) 285-7161

March 6-7 Berkeley, Calif.
Hidden Health Hazards in the Environment. California Occupational Health and Safety Administration (Cal-OSHA) and others

Fee: \$80. *Write:* Health/Environment Conference, P.O. Box 486, Orinda, Calif. 94563; (415) 428-2894

March 8-9 Chicago, Ill.
International Conference on Working Together to Evaluate the Atmospheric Deposition Problem. Illinois Environmental Protection Agency and others

Write: Eileen L. Johnston, Conference Chairman, 505 Maple Ave., Wilmette, Ill. 60091; (312) 793-7694

March 8-10 Ft. Mitchell, Ky.
8th Annual Research Symposium on Land Disposal Incineration and Treatment of Hazardous Wastes. Solid and Hazardous Waste Research Division, U.S. EPA

Write: Robert Landreth, EPA, SHWRD, MERL, Cincinnati, Ohio 45268; (513) 684-7876

March 8-13 Atlantic City, N.J.
1982 Pittsburgh Conference and Exposition on Analytical Chemistry and Applied Spectroscopy. Society for Analytical Chemists of Pittsburgh and the Spectroscopy Society of Pittsburgh.

Write: Pittsburgh Conference, Department J-161, 437 Donald Rd., Pittsburgh, Pa. 15235

March 10-11 Williamsburg, Va.
Hazard Potential of Chemicals. ASTM

Write: Bill F. Hulse, ASTM, 1916 Race St., Philadelphia, Pa. 19103; (215) 299-5507

March 15-16 Washington, D.C.
4th Annual Conference on Hazardous Waste Management. The Energy Bureau, Inc.

Write: Carol A. Hertzoff, Planning Manager, The Energy Bureau, Inc., 41 East 42nd St., New York, N.Y. 10017; (212) 687-3177

Courses

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PAGE NO.

- 1 Beckman Instruments OBC
- 4 Foremost-Mckesson Research Labs. 102A
 Oliver Smith Advertising, Inc.
- 2 Foxboro Analytical, A Division of The Foxboro Company 93A
 Sheperd Tibball & Galog
- 3 Indiana University 128A
- 10 ISCO 101A
 Farneaux Associates
- 9 Martek Instruments IFC
 Tekmar Marketing Service
- 7 Matheson 86A
 Kenyon Hoag Associates
- 12 Monsanto Research Corporation 123A
- 14 Oceanography International 97A
 Gianturco & Michaels

CIRCLE

INQUIRY NO.

PAGE NO.

- 11 Rockwell International 84A
 Campbell-Ewald Company Advertising
- 6 Weathertronics 128A

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Subsurface Distributions of Petroleum from an Offshore Well Blowout. The Ixtoc I Blowout, Bay of Campeche

Paul D. Boehm* and David L. Fiest

Energy Resources Co., Inc. (ERCO), Environmental Sciences Division, 185 Alewife Brook Parkway, Cambridge, Massachusetts 02138

■ Concentrations of oil were measured in seawater in the vicinity of the blowout of the exploratory well Ixtoc I located in the Bay of Campeche (Gulf of Mexico) during the month of September 1979. Seawater samples from more than 20 stations located within 100 km of the blowout were analyzed aboard ship for petroleum hydrocarbons by synchronous fluorescence spectroscopy. Concentrations of oil ranged from 5 $\mu\text{g/L}$ at a distance of 40 km to 10600 $\mu\text{g/L}$ within several hundred meters of the blowout. A subsurface plume of oil droplets suspended in the top 20 m of the water column extended 25 km to the northeast of the blowout. The physical processes which might be controlling the behavior of the oil in the plume are discussed.

Introduction

A significant part of the oil released to the marine environment from a tanker spill or a well blowout may be retained and dispersed in the water column. The relative amount of oil which resides in the water column is a function of a number of factors including the chemical and physical nature of the oil, the point of release, the sea surface turbulence, and other hydrographic conditions. During an undersea well blowout, very favorable conditions exist for retention and transport of particulate, dispersed, and dissolved oil in the water column. For example, the turbulent subsurface release of the oil is expected to enhance the formation of small droplets of oil. These droplets can be retained in the water column for a period of time during which ocean currents can carry them away from the blowout. The formation of droplets increases the surface area of the oil, thereby increasing the rates of physical/chemical and biological processes such as dissolution and microbial attack. Measurements of the concentrations of oil in seawater are important for assessing the potential impact on marine organisms and for predicting the dispersion and weathering pattern of the oil.

Concentrations of high-molecular-weight hydrocarbons ($n\text{-C}_{10}$ to $n\text{-C}_{32}$) in seawater have been measured in coastal water following oil spills (1-6), in oil-spill test tanks (7), and in uncontaminated seawater (5, 8, 9, 10). Reported concentrations generally are $<1 \mu\text{g/L}$ for "clean" open ocean seawater, 2-100 $\mu\text{g/L}$ for oil spills in nearshore environments, and 100-800 $\mu\text{g/L}$ in heavily polluted urban environments (e.g., Boston Harbor). Before this study of the Ixtoc I blowout, few measurements of oil concentra-

tions in the vicinity of a well blowout had been reported. The notable exceptions are those reported after the Ekofisk blowout (11, 1). Gaseous and volatile hydrocarbons in seawater have been examined after a gas well blowout in the northwestern Gulf of Mexico (12), and as part of the Ixtoc I blowout research program (13, 14).

The exploratory well Ixtoc I, located in 48 m of water and 80 km northwest of Ciudad del Carmen, Mexico, in the Bay of Campeche (Gulf of Mexico), blew out on June 3, 1979. Estimates of the rate of release of oil during the first 4 months range from 10 000 to 30 000 barrels per day (15). The oil slick was transported to the north and west of the well from June until early September 1979. In mid-September, a shift in prevailing currents transported the spilled oil to the east and south of the platform (14). Floating booms and chemical oil dispersants were used periodically in the vicinity of the blowout to mitigate the impact of the oil. A continuous fire covering $\sim 4000 \text{ m}^2$ at the blowout site consumed an unknown fraction of the gaseous and volatile components of the oil. The liquid portion of the oil underwent emulsification with seawater either during or subsequent to its release to the water column.

The data presented here were collected as part of a National Oceanic and Atmospheric Administration sponsored study of the Ixtoc I well blowout. Scientists aboard the ships NOAA ship R/V *Researcher* and contract vessel *G. W. Pierce* conducted a research cruise in the western Gulf of Mexico from September 11 to October 3, 1979 (14). While samples were being collected near the well, no booming or dispersant spraying operations were being conducted. Hurricane Henri passed near the well on September 15-16 and caused extensive flooding in and subsequent freshwater runoff from adjacent onshore areas. The locations of sampling stations are shown on the chart of the study area (Figure 1) and were oriented for the most part along the observed axis of the surface oil plume. The extent and location of observed surface oil and sheen emanating from the wellhead (16) varied during the September 18-21 sampling period. The surface slick was oriented to the northeast ($\sim 45\text{-}55^\circ$ true) through September 20 and then shifted southeasterly.

This study addresses the subsurface nature of high-molecular-weight ($>C_{10}$) hydrocarbon compounds observed during this period of the blowout event. The results presented consist mainly of data obtained on the oil concentrations in seawater samples. The dissolved and par-

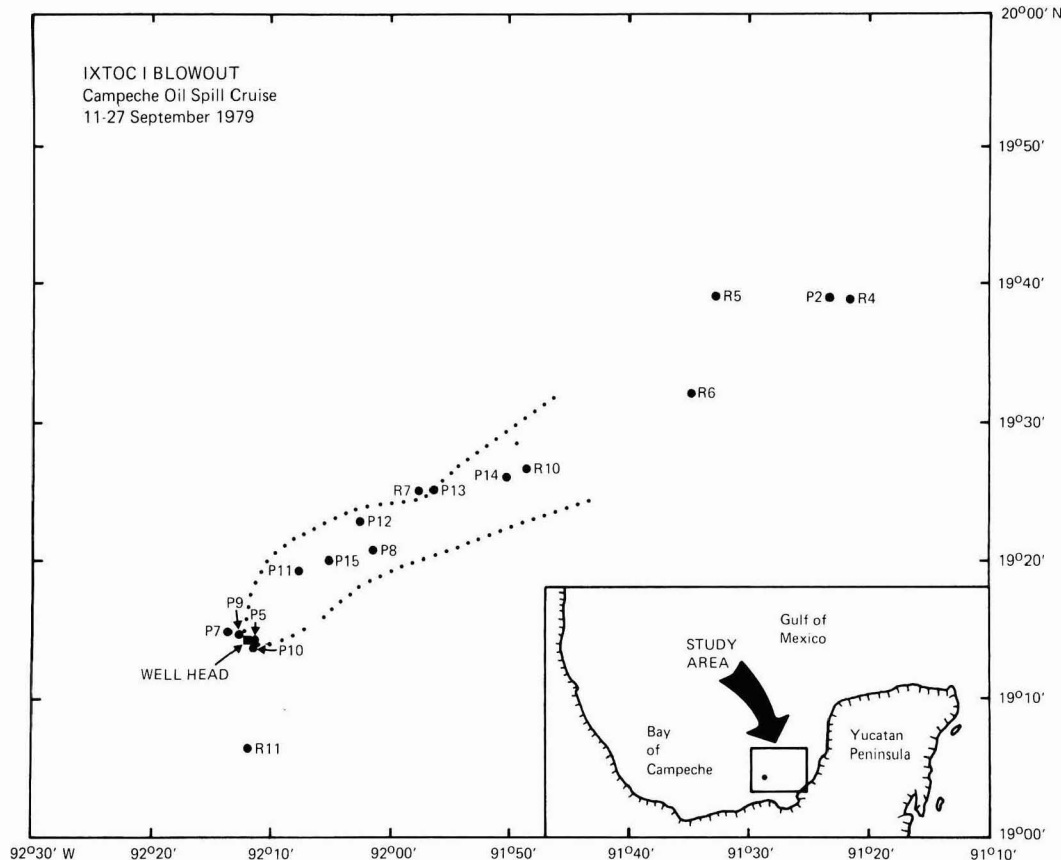


Figure 1. Map showing locations of samples taken in wellhead region (....) approximate extent of observed coherent surface oil slick.

ticulate fractions thereof and the weathering of the surface and subsurface petroleum hydrocarbons are presented elsewhere (17, 18).

Experimental Section

Samples from the immediate vicinity of the Ixtoc I blowout were collected between September 14 and 21, 1979. Seawater was collected with either a 10-L Teflon-lined GO-FLO Sampler (General Oceanics), a 30-L glass Bodman bottle (19), a 90-L aluminum Bodega Bodman bottle (20), or a submersible pumping system (17). The pumping system consisted of a submersible pump (Cole Parmer Model 7111: nylon impeller, silicone rubber gaskets, Viton seals) and 2-m sections of stainless-steel tubing (0.5-in. o.d. type 903) connected with 0.5-m flexible stainless-steel joints and stainless-steel quick connects (Swagelock: Viton seals). Immediately following collection, a 1-L sample was drawn from each sampler, preserved with 100 mL of dichloromethane (Burdick and Jackson, UV grade), and stored at ambient temperature awaiting extraction.

Precautions were taken to ensure that the water samples were not contaminated with surface oil. The GO-FLO, Bodega Bodman, and glass Bodman samplers were deployed in the closed position in which valves or seals prevent surface oil from contaminating the inner surfaces of the sampler during deployment. The pumping system was deployed through an unoiled or lightly oiled sea surface and all tubing purged at each depth by pumping for

several minutes before a sample was collected. All surfaces of the samplers which contacted the water sample were constructed of noncontaminating materials (glass, aluminum, stainless steel, Teflon, silicon rubber, and Viton rubber). Cross contamination due to carryover between samples was minimized by cleaning bottle samplers between deployments. An in-line Turner fluorimeter on the pumping system indicated that response to oil "hot spots" was rapid and that any subsequent bleed was nondetectable. Thus, oil sorption was not a significant problem. Cross calibration between bottle- and pump-obtained samples indicated good reproducibility between devices in all but the most heavy oil concentrations (17, 13), the latter situation most likely owing to heterogeneity within the water column.

All samples were collected in light seas from a stationary vessel. Surface samples (1 m) were taken during these light sea state conditions. Uncertainty as to sampling depth was on the order of ± 1 m.

The unfiltered water sample was transferred to a 1-L separatory funnel and extracted 3 times with 50 mL of dichloromethane. At a few stations, the seawater collected by the pumping system was pressure filtered through a 142-mm, 0.45- μ m, glass-fiber filter held in a stainless-steel filter holder (Millipore) prior to extraction. The solvent extract was dried over sodium sulfate, transferred to a Kuderna-Danish apparatus, and concentrated to 1 mL. The dichloromethane was displaced by repeatedly adding hexane (Burdick and Jackson, UV grade) and evaporating

under a stream of purified nitrogen.

The hexane extracts were analyzed for petroleum hydrocarbons by using a synchronous fluorescence spectroscopy technique (21, 22). In summary, a measured aliquot of the sample extract was dissolved in a known volume of hexane. The intensity of the fluorescence emission was measured from 250 to 500 nm while synchronously scanning at an excitation wavelength 25 nm shorter than the wavelength at which the emission was measured. This technique measures aromatic hydrocarbons with a two- to five-ring aromatic structure (23). The analyses were performed on board the R/V *Researcher* by using a Farrand Mark I spectrofluorometer equipped with corrected excitation and emission modules. The instrument conditions were as follows: excitation slit, 2.5 nm; emission slit, 5.0 nm; scan speed, 50 nm min⁻¹; sample cell, single 10-mm nonfluorescing quartz cell. The instrument was calibrated daily by analyzing a series of dilutions of a standard solution of the API Reference No. 2 fuel oil.

The intensities of the fluorescence spectra were measured at several wavelengths which correspond to peak maxima present in an Ixtoc I reference oil sample. The fluorescence spectra were converted to relative concentration units by comparing the peak height at 312 nm to that of the appropriate No. 2 fuel oil standard curve. No. 2 fuel oil was initially used as the calibration standard as it yields a very reproducible and available standard, and due to the lack of an appropriate Ixtoc oil reference prior to the sampling effort. As many of the fluorescence measurements were made on board, and, as the two-ringed aromatic fluorescence signal was strongest in all samples encountered, a strategy was adopted to base all measurements made at sea using fuel oil as the calibration standard and after returning to the laboratory to recalibrate the method using actual microgravimetric measurements on samples. Use of a fresh Ixtoc I oil standard was deemed inappropriate because of rapid compositional changes occurring at the blowout site itself. A more accurate calibration was achieved by using a series of microgravimetric measurements on actual Ixtoc I subsurface oil samples rather than a single reference oil, as the subsurface oil collection more accurately reflects the compositional characteristics of the oil actually present in the sample collection.

The concentrations of oil in No. 2 fuel oil equivalents were converted to absolute concentrations by multiplying by a factor of 2.30. This factor was determined from a linear regression of oil concentrations in No. 2 fuel oil equivalents vs. concentrations of Ixtoc I oil in the actual samples measured by microgravimetry using a Cahn electrobalance. The samples used for this calibration had concentrations of Ixtoc I oil which ranged from 74 to 1700 µg/L by gravimetry. The fluorescent material in samples with low concentrations (<20 µg/L) differs chemically from the material in the samples used for the regression. Although a lower conversion factor should have been used because of this discrepancy, none is available from existing data and the same conversion factor was used for all calculations.

Results

The concentrations of oil in the water column ranged from values of less than 5 µg/L at a distance of 80 km from the blowout to peak values of 10600 µg/L within a few hundred meters of the blowout. The highest concentrations were observed within 25 km of the blowout in the top 6 m of the water column. The higher values reported here may be an underestimate since some oil was visibly

adsorbed onto the walls of the bottle samplers during sampling in the plume.

The concentration data are summarized in Figure 2, which is a contoured vertical cross section of the oil concentrations along the plume axis, and in Table I. Elevated concentrations of subsurface petroleum hydrocarbons occurred from the wellhead out to 40 km to the northeast of the well. At distances greater than 40 km to the northeast and 16 km to the south and west, concentrations were less than 5 µg/L. The northeastern orientation of the oil-contaminated seawater plume coincided with the observed direction of movement of the surface plume of oil. However, emulsified oil was observed floating on the ocean surface at distances greater than the apparent extent of the oil-contaminated seawater plume. Whereas surface oil was found 80 km or more to the northeast of the well, elevated concentrations of oil in the water column were limited to within 40 km. It is apparent that somewhat dissimilar processes are controlling the transport of surface and subsurface oil. Subsurface petroleum concentrations are heterogeneous in the vicinity of the wellhead as evidenced by the concentration contours in Figure 2. Sorption of oil onto sampling bottle walls probably caused an underestimate of petroleum concentrations at station P05.

Several distinct spectral patterns were observed among the samples which were collected. Samples containing low concentrations (<5 µg/L) had a spectrum with a single fluorescence peak at 308 nm (type A). This spectrum results from either background fluorescent material in seawater or low-level contaminants from the sample workup. Most samples containing Ixtoc-related petroleum hydrocarbons exhibited spectral types B and D (Figure 3). Samples with concentrations from 5 to 20 µg/L had a unimodal spectrum with a peak maximum at 312 nm (type B). This peak results from a predominance of petroleum-derived two-ring aromatics which fluoresce from 310 to 330 nm (23). As discussed below, this spectral type reflects the selective dissolution by seawater of two-ring aromatics from the whole oil released from the blowout. Spectral type D is characterized by a series of fluorescent peaks at 312, 328, 355, and 405 nm. This spectrum was predominant for samples with concentrations greater than 20 µg/L. The series of peaks results from two-, three-, four-, five-, and larger-ring polycyclic aromatic compounds (23). Type D spectra were similar to spectra of the whole oil collected from surface mousse samples.

At a few stations, samples of both whole seawater and filtered seawater through a 0.45-µm glass-fiber filter from the same depth were analyzed. At stations with low concentrations of oil (P1, P2, and P14), no systematic differences between the filtered and unfiltered samples were found. However, at station PIX 08, the concentrations of oil in the filtered samples were 21% and 28% of the concentrations in unfiltered samples collected at 6 and 16 m, respectively (Table II). In both cases, the spectrum of the filtered sample was depleted in the three- to five-ring region compared to the unfiltered sample.

The distinction between the three spectral types was confirmed by glass capillary gas chromatography analysis (17). The saturated and unsaturated (aromatic) fractions of samples with type D, whole oil, spectra contain petroleum hydrocarbons in a boiling range equivalent to that of <n-C₁₀-n-C₃₀. The glass capillary gas chromatogram combined with gas chromatographic mass spectrometry data (17) of the aromatic fraction confirms the presence of polycyclic aromatic hydrocarbons (PAHs) with two to five rings (Figure 4). Normal alkanes from <n-C₁₀ to n-C₃₄ and a low-boiling unresolved complex mixture predominate

Table I. Sample Description and High-Molecular-Weight Petroleum Hydrocarbon Concentrations (0-30 km from the Wellhead)

station	collection date	depth, m	wind velocity (direction), knot	sea surface condition ^a	sampling device ^b	petroleum concn, µg/l	spectral type ^c	distance from wellhead, ^d km	sample type ^e
P7	09/17/79	1	NM ^f	A	P	11	B	-2.0	W
		6	NM	A	P	40	B	-2.0	W
		14	NM	A	P	4	B	-2.0	W
		14	NM	A	P	10	B	-2.0	W
		20	NM	A	P	5	B	-2.0	W
P9	09/18/79	6	7-9 (75-90° true)	A	GF	11	B	-1.0	W
		20	7-9 (75-90° true)	A	GF	9	B	-1.0	W
P5	09/17/79	2	NM	HO	30B	2100	D	+0.5	W
		6	NM	HO	30B	7000	D	+0.5	W
		20	NM	HO	30B	1500	D	+0.5	W
P10	09/19/79	2	11 (295° true)	HO	P	10500	D	+0.8	W
P11	09/19/79	1	11 (295° true)	BO/S	GF	300	D	+0.8	W
		1	11 (295° true)	BO/S	GF	340	D	+0.8	W
		6	11 (295° true)	BO/S	GF	530	D	+0.8	W
		20	11 (295° true)	BO/S	GF	110	D	+0.8	W
P15	09/21/79	2	14 (300° true)	BO/S	P	1000	D	+16.0	W
		20	14 (300° true)	BO/S	P	50	D	+16.0	W
P8	09/18/79	6	7-9 (75-90° true)	S/BO	P	87	B	+22.0	F
		6	7-9 (75-90° true)	S/BO	P	416	D	+22.0	W
		6	7-9 (75-90° true)	S/BO	30B	60	D	+22.0	W
		16	7-9 (75-90° true)	S/BO	P	37	B	+22.0	F
		16	7-9 (75-90° true)	S/BO	P	133	D	+22.0	W
		19	7-9 (75-90° true)	S/BO	P	50	D	+22.0	W
P12	09/19/79	20	7-9 (75-90° true)	S/BO	30B	20	D	+22.0	W
		40	7-9 (75-90° true)	S/BO	30B	19	B	+22.0	W
		1	11 (295° true)	S/BO	GF	71	C	+23.0	W
		1	11 (295° true)	S/BO	GF	12	D	+23.0	W
R7	09/18/79	6	11 (295° true)	S/BO	GF	22	C	+23.0	W
		20	11 (295° true)	S/BO	GF	19	C	+23.0	W
		2	7-9 (75-90° true)	S/BO	30B	3	A	+32.0	W
		35	7-9 (75-90° true)	S/BO	30B	12	C	+32.0	W
		43	7-9 (75-90° true)	S/BO	90B	11	D	+32.0	W

^a A = absence of surface oil; HO = heavy oil/mousse coverage (>50%); BO = broken oil/mousse patches (<50%); S = sheen observed. ^b P = pump; GF = 30-L GO-FLO (Teflon-lined); 30B = 30-L glass Bodman; 90B = 90-L Bodman. ^c See text for explanation. Type C intermediate between B and D. ^d (-) = southwest of wellhead (opposite to surface oil movement); (+) = in direction of surface oil and currents. ^e W = whole (unfiltered) water; F = filtrate. ^f NM = not measured.

Table II. Concentrations of Oil in Filtered vs. Unfiltered Water Samples

station	depth, m	concn, µg/L		filtered/unfiltered
		unfiltered sample	filtered sample	
PIX 08	6	416	87	0.21
	16	133	37	0.28

in the saturated fraction which does not account for any observed fluorescence. Samples with type B, dissolved oil, spectra contain predominantly substituted one- and two-ring aromatic hydrocarbons (Figure 4). Relatively small amounts of PAHs with more than two rings and saturated hydrocarbons are present. Samples with type A spectra contained very low amounts of material.

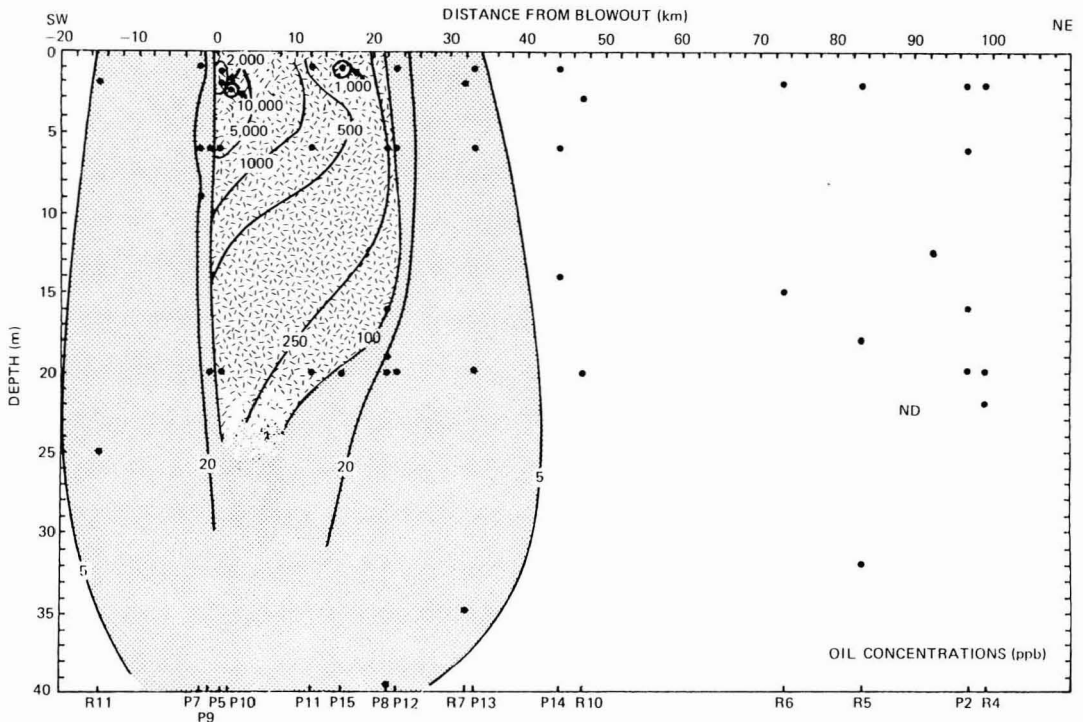
In summary, higher concentrations (>20 µg/L) of oil were associated with type D (whole oil) spectra and were found at shallow water depths (<20 m) within 25 km northeast of the well. Moderate concentrations of oil (5-20 µg/L) occurred to the south and west of the well and from 25 to 40 km to the northeast of the well. Samples collected in this region were of spectral type B, which is characterized by soluble two-ring aromatics. A comparison of oil concentrations in filtered and unfiltered seawater supports the contention that oil in the water column occurred in both a whole-oil (droplet) form and in a fractioned-oil ("dissolved") form, although the operational definition of the material in the filtrate can include dissolved and

colloidal oil as well as small oil droplets if the filter is overwhelmed.

Discussion

The high concentrations of oil in samples collected near the blowout probably resulted from suspension of oil droplets in the water column (spectral type D). This hypothesis is consistent with laboratory studies of the formation of oil-in-water dispersions (24-26). These studies have shown that, under vigorous mixing conditions, droplets of oil, which contain two-, three-, four-, and five-ring aromatic compounds, are entrained in the water, and a type D spectrum results. Since the high shear associated with an undersea blowout enhances the formation of oil-in-water dispersions (i.e., droplets), the predominance of oil droplets in the water samples is not unexpected.

Seawater samples with less than 20 µg/L of oil were collected farther than 25 km from the blowout and have type B spectra which are dominated by two-ring aromatic hydrocarbons. Two-ring aromatic hydrocarbons are 1-2 orders of magnitude more soluble than three- and four-ring structures (27). Laboratory studies have confirmed that, under gentle mixing conditions, two-ring aromatics in oil are selectively dissolved by seawater which would result in a type B spectrum dominated by a single peak. The same selection for two-ring aromatics occurs if the large (>1 µm) droplets are removed from the vigorously mixed dispersion by filtration (25) or centrifugation (24). In samples with type B spectra, oil is present in a "dissolved" state. Two of the three filtered seawater samples collected



(Vertical exaggeration 5,000x;  = area of concentrations >100 µg/l;  = area of concentration 5–100 µg/l).

Figure 2. Concentrations of oil along a transect oriented to the northeast of the Ixtoc I blowout, September 1979.

within the oil plume also had type B spectra. These two samples contained approximately 20–30% (37 and 87 µg/L) of the oil in the unfiltered sample.

We postulate that, within the subsurface oil plume (within 5 km), high concentrations (>600 µg/L) of oil droplets predominated. The diameters of the oil particles are estimated to be greater than 0.7–1.0 µm, which has been shown to be the effective pore size of glass-fiber filters (28). Near the leading edge of the oil-contaminated plume, 25 km from the blowout, moderate concentrations (100–300 µg/L) of oil droplets with diameters generally about 1 µm comprised 70–80% of the oil in the water. The remaining 20–30% consisted of two-ring aromatics dissolved in the water. Droplets of whole oil with diameters less than about 1 µm (i.e., passing through the filter) were not found near the edge of the plume, and low concentrations (<20 µg/L) of dissolved two-ring aromatics predominated.

The absence of high concentrations of oil at depths below 20 m in the plume may have been the result of several processes. The plume of oil and water streaming from the blowout in the sea bed had a net upward velocity which probably caused it to rise quickly to the surface where it spread horizontally in response to prevailing currents. In addition, the positive buoyancy of the oil droplets within the plume may have caused them to move vertically within the plume and remain close to the surface. The possibility that droplets of oil generated by turbulence were formed at the air/oil interface and subsequently driven down into the water column has been largely ruled out through comparisons of the detailed chemistry of surface and subsurface oil (17). The synoptic 20-kHz

acoustic reflectance measurements (29) obtained during chemical sampling in addition to detailed GC- and GC/MS-based chemical measurements (17) support the facts that droplets were present in discreet subsurface plumes within the top 20 m of the water column and that significant subsurface horizontal movement (~20 km) of this oil occurred before buoyancy and dilution caused the droplets to rise to the surface or become nondetectable by acoustic reflectance techniques.

Laterally, the chemically detected subsurface oil plume was limited to within 25–40 km to the northeast of the blowout. Although rigorous physical oceanographic measurements were generally lacking, visual observations of surface and subsurface current velocities which were made indicated that surface and subsurface oil were both transported in the same direction (northeast) largely due to a ~0.5-knot current. Movement of surface oil appeared to be more influenced by currents than by winds, the wind vector generally being perpendicular to the direction of surface and subsurface oil movement. Based on the supportable assumption that the subsurface oil was moving to the northeast at a minimum speed of 0.5 knot, it would take approximately 28 h for the oil to reach stations PIX 08 and PIX 12 at the edge of the plume. Mathematical modeling of the weathering of surface and subsurface oil supports this rate of movement (18). Since all stations were sampled 2–4 days after Hurricane Henri had left the study site, oil streaming from the blowout would have had more than ample time to travel beyond these stations and reestablish a quasi-steady-state subsurface plume. Processes other than simply the rate of advection of the oil

Table III. Mass Balance of Oil in the Top 20 m of Water Column (Wellhead to 40 km)

distance, km	approximate width of plume, m	water depth, m	mean whole water concn, $\mu\text{g/L}$	total amt oil in water, g	% of total	total amt oil spilled during oil transit, ^a bbl
0-1	1000	20	1000	20×10^6	23	20 000
1-12	500	20	500	60×10^6	69	
12-25	100	20	250	6.5×10^6	7.5	
25-40	100	20	10	0.2×10^6	0.2	
				86.7×10^6 ^b		

^a Rate of spillage = 10000 bbl/day (OSIR, 1980); at 0.5-knot current, oil travels ~ 22 km/day; study region (~ 40 km) is therefore equivalent to 2-day transit distance; hence, 20 000 bbl figure. ^b ~ 530 bbl.

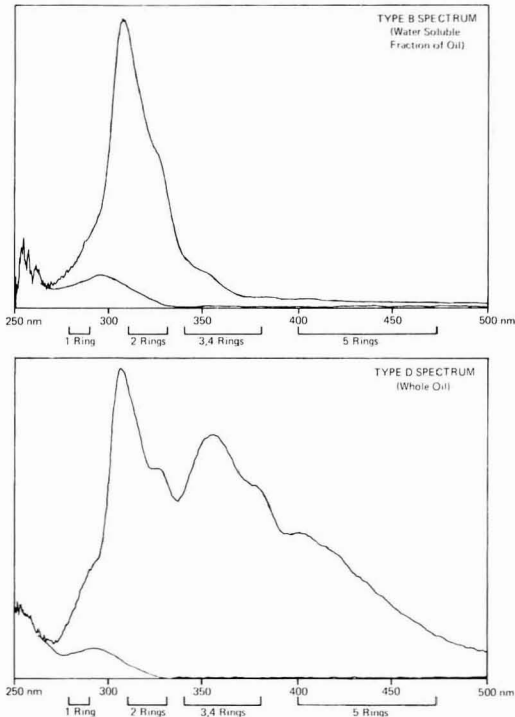


Figure 3. Representative synchronous fluorescence spectra of sea-water samples collected near the Ixtoc I blowout.

must have been responsible for the horizontal limitation (~40 km) of the subsurface plume.

As previously mentioned, one such process may have been a progressive agglomeration of smaller droplets to form larger droplets as oiled seawater was carried away from the blowout. According to Stokes' law, the formation of larger droplets would increase the positive buoyancy and upward velocity of the oil (30). Such a process would remove oil from the subsurface plume to the ocean surface as the oiled water moved away from the blowout.

Alternately, one of the many frontal zones observed from the air in the region may have restricted the horizontal advection or diffusion of the plume. Such fronts have been observed (31) to affect the lateral movement of surface oil slicks. A vertical cross section of σ_T (seawater density) along the plume axis (Figure 5) suggests the possibility of the existence of such a front through the sampling region. The profile, which was generated from STD profiles and salinity and temperature measurements of discrete water samples at stations occupied over a 5-day period, suggests the presence of a lens of less saline, less dense water to the northeast of the blowout. This lens may have resulted

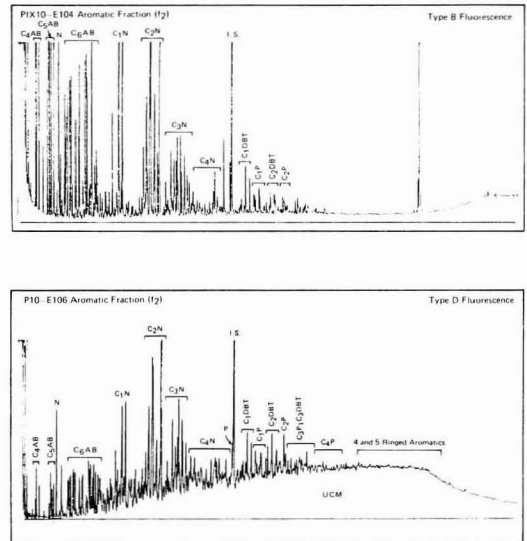


Figure 4. Glass capillary gas chromatograms of aromatic fractions of water samples with types B and D fluorescence spectra (N = naphthalenes; P = phenanthrenes; DBT = dibenzothiophenes; AB = alkylated benzenes; I.S. = internal standard (deuterated anthracene); C₁, C₂, C₃, C₄, C_n = alkylated compounds with n carbons; UCM = unresolved complex mixture).

from freshwater runoff from the adjacent land which had experienced heavy rains and flooding both prior to and during Hurricane Henri. The extent of the lens to the southwest (i.e., toward the blowout site) occurred between 25 and 40 km from the blowout, which was the location of both the strong subsurface oil concentration gradient and the loss of definition of the surface oil plume. While the hydrographic data were collected over several days and hence are not synoptic, the constancy of aerial observations of blue water/turbid water interfaces (i.e., fronts) suggests that gross changes in the hydrographic regime probably did not occur within the 4-day sampling period. Samples were not taken on either side of the transect near the gradient which would allow the three-dimensional behavior of the oiled seawater plume to be better defined.

Low concentrations (<20 $\mu\text{g/L}$) of oil occurred to the south and west of the well (stations PIX 07, PIX 09, PIX 06, and RIX 11). The lack of significant oil at these stations indicates the strong influence of advection on the dispersion of subsurface oil from the blowout driving the oil to the northeast. During the sampling period, the subsurface plume of oiled seawater and the surface plume were similarly aligned to the northeast under the presumed influence of oceanic currents.

Based on the determined subsurface oil concentrations, a mass balance was constructed (Table III) to determine

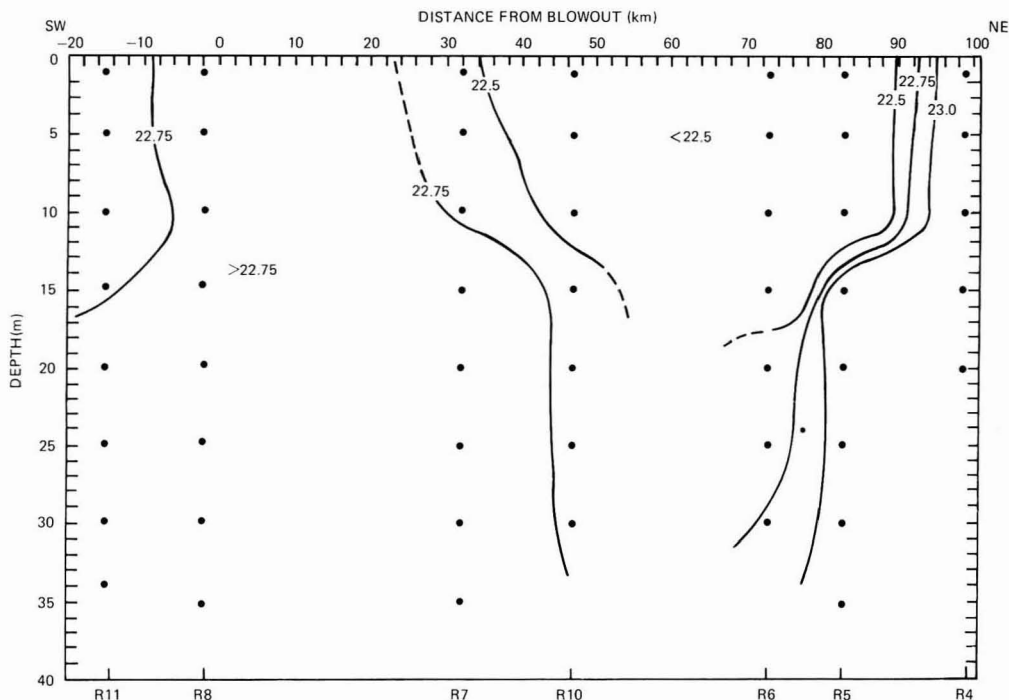


Figure 5. σ_T along a transect oriented to the northeast of the Ixtoc I blowout, September 1979 (vertical exaggeration, 5000X).

the quantity of Ixtoc I oil present in the water column within 40 km of the wellhead at any given time during the blowout event (i.e., a "standing crop" of subsurface oil). Using the assumptions of plume width and spillage rate shown in the table which ignore oil beneath 20 m and at distances greater than 40 km from the wellhead, we calculate that at any given time ~3% of the oil introduced from the blowout existed in the top 20 m of the water column. Most of this 3% was located within 25 km of the wellhead. This calculation would not be significantly altered by inclusion of petroleum in the water column outside of the observed surface plume as measurements of outside plume oil concentrations were very low (generally $< 1 \mu\text{g/L}$ (32)). The mass balance considers only the oil's behavior within the study region. Subsequent dispersion of surface oil by natural physical processes driving oil into the water column are not incorporated.

Conclusions

Oil released from the Ixtoc I blowout tended to form a subsurface plume of oil droplets suspended and laterally advected in the top 10–20 m of the water. The subsurface petroleum hydrocarbons, representing ~3% of the introduced oil, moved in a northeasterly direction in response to ocean currents rather than wind. The northeasterly horizontal advection of the oiled seawater plume may have been inhibited or deflected by a lens of less saline water situated to the northeast of the blowout.

Concentrations of oil within the plume ranged from 20 to $>10000 \mu\text{g/L}$. The highest concentrations of oil (up to $10600 \mu\text{g/L}$), which may have been underestimated because of adsorption in the sampling systems, were found within the oiled seawater plume near the Ixtoc I blowout. These values were in the same range as concentrations found underneath oil slicks during experimental surface spills in the New York Bight (33). During the experimental

spills maximum concentrations within the top 3–9 m of water ranged from $950 \mu\text{g/L}$ under an untreated slick to $17800 \mu\text{g/L}$ under a slick treated with dispersant. Maximum concentrations of oil ($300 \mu\text{g/L}$) measured in the vicinity of the Ekofisk blowout in the North Sea (11, 1) and in the *Amoco Cadiz* ($350 \mu\text{g/L}$) and *Argo Merchant* ($450 \mu\text{g/L}$) tanker spills (2, 6) were comparable to concentrations at the outside edge of the oil plume at the Ixtoc I blowout. The higher concentrations of subsurface oil found during the Ixtoc I blowout resulted from the subsurface release of oil, rather than at or above the ocean's surface as occurred during the Ekofisk blowout or during the tanker spillages.

The horizontal and vertical limitations of the size of the oiled seawater plume from the Ixtoc I blowout suggest that both the physical properties of the oil (i.e., droplet size and density) and the density and current structure of the seawater controlled the dispersal of oil from this undersea blowout. Oceanic frontal systems may act as barriers to subsurface transport of oil and may also act as conduits for subsurface movement of oil along the frontal axis.

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Isosteric Heats of Adsorption of Selected Compounds on Diesel Particulate Matter

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■ Isosteric heats of adsorption were determined for 18 compounds with low injection volumes. The isosteric heats of adsorption of benzene and hexane on the pretreated Diesel samples were compared with those of the same compounds on a graphitized carbon black. The peak shapes of the Diesel-sample chromatograms and the relationship between the injection volume and the retention volume are evidence of a heterogeneous surface and a type II adsorption isotherm. For two compounds, benzene and hexane, the effect of varying the surface coverage, by changing the injection volume, on the adsorption heats was determined. The differences between the heats of adsorption measured for the two Diesel samples is attributed to the difference in the quantities and identities of the extractable compounds (or presorbed materials) on the particulate samples. The adsorption energies reported are significant with respect to the bioavailability of the sorbed species.

Introduction

In 1977 the U.S. Environmental Protection Agency (1) projected that by 1985 25% of new automobiles sold in the United States of America would be equipped with Diesel engines. This change from gasoline engines to Diesel engines may be environmentally significant since it is known that combustion in a compression-ignition engine produces 70 times more particulate matter than in a conventional spark-ignition engine. Therefore, it is important to investigate the Diesel engine and its emissions for its potential effect on public health as a result of the different future air pollution.

From the time in the Diesel combustion process where the particles are formed in a heterogeneous turbulent flame until they are exhausted into the atmosphere, the Diesel particles are in contact with numerous organic and inorganic compounds in an environment of rapidly decreasing temperature. A number of studies have estimated that more than 10 000 different compounds can be found in Diesel exhaust (2), and many of these are known to be potentially carcinogenic or mutagenic. The majority of these compounds have been shown to be associated with the particulate matter, and, depending upon the engine operating parameters, as much as 50% by mass of the particulate matter can be extracted with dichloromethane. The particles alone are potential health hazards since 80-90% by mass are less than 1 μm in diameter (3) and are, consequently, easily respired into the deep alveolar regions of the lung (4). Since these particles have significant lifetimes in the lung and could possibly have toxic species sorbed on their surfaces, there is a probability that

adverse health effects could arise from their inhalation. In this context, a number of studies have reported on the elution of polycyclic aromatic hydrocarbons from carbon soot particles by biological fluids (5, 6). Also, there have been many investigations into the chemistry that can take place at the gas-solid interface between adsorbed compounds, pollutants present in the atmosphere, and sunlight (7-11). The bioavailability of the adsorbed species, the probability of certain substances adsorbing onto the particle surfaces, and the likelihood of atmospheric reactions will to a great extent be determined by the energy of adsorption and the nature of the adsorbate-adsorbent forces involved in the sorption.

Although much work has been done in the area of chemical analysis of the particles emitted by a variety of sources using ESCA, SIMS, AES, and GC/MS (12-15, 3), fewer reports have dealt with their physical properties. Diesel particulate matter was determined to have a high surface area, implying a high adsorptive capacity (16, 17), but, since these reports, there have been relatively few additional studies on the particulate porosity, surface area, and adsorption characteristics of particles. These fundamental physical properties of particulate matter should enable a better understanding of the chemistry of the particles and of their resultant environmental health implications.

This paper represents the initial step in the determination of the physical characteristics of Diesel particulate matter. In this work, gas-solid chromatography was used to measure the heats of adsorption of some selected compounds on a standard graphitized carbon black and particles collected from two different Diesel engines. This dynamic adsorption measurement technique was employed so that the results obtained could be compared with those obtained with the standard static method, which are currently in progress in this laboratory. It is important to make both measurements in order to characterize the particle surface.

One aspect of this study was treatment of particulate samples by heating and flushing with helium in the column and heating under vacuum prior to adsorption measurement. The effects of the variation of the injection volume on the measured adsorption heats was also determined. The heats of adsorption for some basic hydrocarbons on different carbon particle samples at varying pretreatments are expected to allow insight into the nature of the particulate surfaces and into the gas-solid interactions involved in the adsorption of vapors onto Diesel particulate matter.

Theory

The specific method used in this study has been reported previously by Ross et al. (18) to measure the heats of adsorption for molecules on graphitized carbon blacks. These workers showed that, if adsorbate surface concen-

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tration tends to zero, then the following expression can be derived:

$$d(\ln t_r')/d(1/T_c) = q_{st}/R \quad (1)$$

where t_r' is the corrected retention time and T_c is the column temperature. Therefore, if a plot of $\log t_r'$ vs. $1/T_c$ is made, then the resulting straight line has a slope equal to $q_{st}/2.303R$ (where q_{st} is the limiting isosteric heat of adsorption). This value of the heat of adsorption was determined to be appropriate for comparison with those measured by the static method.

Since the flow rate changed from sample to sample as a result of differences in the packing densities of the adsorbents, the specific retention volume was used instead of the retention time. The specific retention volume was calculated by using the following standard expression:

$$V_g = \frac{t_r' F}{m} \frac{T_c}{T_i} \frac{3}{2} \frac{[(P_i/P_o)^2 - 1]}{[(P_i/P_o)^3 - 1]} \quad (2)$$

where t_r' is the corrected retention time, F is the flow rate, m is the mass of the adsorbent in the column, T_c is the column temperature, T_i is the temperature at the bubble flowmeter, and P_i and P_o are the pressure at the inlet and the outlet of the column, respectively.

Experimental Section

A gas chromatograph with a thermal conductivity detector (Varian 920) was used for all of these studies with a glass column (2-mm i.d., 25 cm long) packed with the adsorbents (Spheron, 0.3 g; DPM-PSU, 0.1 g; and DPM-EPA, 0.06 g). Helium (HP, Matheson) was used as the carrier gas with a flow rate in the range of 1.5–3 mL/min. The retention times of the various compounds were measured over a range of column temperatures (50–300 °C) with the various adsorbents.

Three adsorbents were investigated in this study. The first was graphitized Spheron 6 (Graphon), with an approximate surface area of 80 m²/g (19) with no pretreatment. The second was Diesel particulate matter collected from an Avco-Lycoming Bernard W-51 industrial engine at The Pennsylvania State University with a fuel consisting of a 1:1 by volume mixture of *n*-tetradecane and 2,2,4-trimethylpentane with an approximate surface area of 104 m²/g (19). The third adsorbent was Diesel particulate matter collected from an Oldsmobile 350 engine by the U.S. Environmental Protection Agency (run nos. 8311–8319) with an approximate surface area of 112 m²/g (19). In addition to measuring retention volumes of various compounds and columns packed with raw Diesel particles, we also obtained chromatographic data after each of the following pretreatments: (1) 300 °C with helium flow, in the column, for 15 h and (2) 500 °C under vacuum (10⁻² torr) for 15 h followed by the first treatment.

The following compounds were used as the adsorbates: benzene, cyclohexene, cyclohexane, hexene, hexane, methanol, octane, ethylbenzene, benzaldehyde, acetophenone, naphthalene, phenol, phenanthrene, fluorenone, fluoranthene, and anthracene (all 99+ % Aldrich reagents). The liquid compounds were introduced separately onto the column in a pulse size of 0.01–10.0 μL. The solid compounds were introduced in solution (25% in methylene chloride) in a pulse size of 1.0 μL. The column void volume was obtained from the air peak.

Results and Discussion

The specific retention volumes of each adsorbate on the various adsorbents were calculated from corrected retention times by the application of eq 2. These data were then

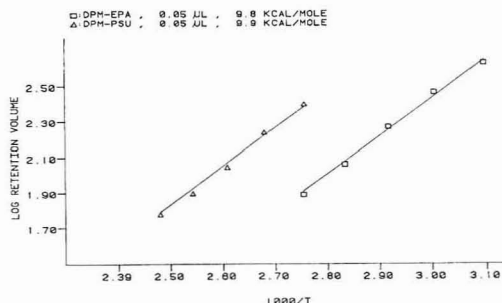


Figure 1. Gas-chromatographic $\log V_r$ vs. $1/T_c$ plots for benzene.

Table I. Isosteric Heat of Adsorption (kcal/mol) for Various Graphitized Carbon Blacks

adsorbate	adsorbent		
	Spheron 6	ref 20	ref 21
benzene	8.7	9.4	9.8
<i>n</i> -hexane	9.4	10.1	10.4

plotted against column temperature by using the relationship expressed in eq 1 to obtain the apparent heats of sorption or the isosteric heats of adsorption. Examples of these plots are shown in Figure 1. The major source of error in the determinations was the variation of the retention time. Consequently, the error associated with the heats is $\pm 5\%$.

Isosteric Heat of Adsorption on Spheron 6. Preliminary experiments were performed with Spheron 6 to compare the values obtained for the isosteric heats of adsorption for benzene and *n*-hexane with the heats obtained with gas chromatography by other workers (20, 21) for similar adsorbents. Injection volumes (1.0 μL) of adsorbates, which correspond to $\sim 1\%$ coverage of the available surface area of the adsorbent, were used since this coverage falls within the Henry's law region of the adsorption isotherm (22). The chromatographic peaks obtained with Spheron 6 were sharp and symmetrical with very little tailing which is characteristic of a homogeneous and relatively nonporous surface. The values of the heats obtained in this study as compared to the previous studies are contained in Table I. The heats for the Spheron 6 are low compared with the heats on completely graphitized carbon blacks since graphitized Spheron 6 is known to have residual heterogeneity (i.e., it is not 100% C + H) in its surface.

Pretreatment of Diesel Particulate Matter. The samples of Diesel particulate matter which were used in this and subsequent studies have significant quantities of sorbed materials on their surfaces (PSU $\sim 5\%$ extractable (22) and EPA $\sim 18\%$ extractable into dichloromethane (2)). These sorbed species will play significant roles in the surface properties of the particles. Therefore, the effects of various pretreatments were studied, and the apparent heats of sorption of selected hydrocarbons were used to monitor these pretreatments. Unfortunately, the injection volume used (1.0 μL) yielded heats of adsorption less than the adsorbate heat of vaporization. The adsorbate surface coverages were calculated (on the basis of BET surface areas of the adsorbents (19)) to be quite high ($\sim 40\%$), which must exceed the Henry's law region of the isotherm. The heats measured, therefore, have very little significance and are not reported here. Yet, since the DPM-EPA

particles do have a larger quantity of presorbed material than the DPM-PSU particles, high-temperature pretreatment should affect the adsorption heats on the former to a greater extent. This has been found to be the case with the static measurements which have been reported elsewhere (19). The peak shapes for the adsorbates after all pretreatments were characteristic of heterogeneous, porous surfaces and type II isotherm adsorbents (24). The presence of type II isotherms was confirmed by the observation that as the injection volume was increased the retention volume decreased (23). The equilibrium constant decreases as the amount of the adsorbate increases, and the isotherm is concave with respect to the pressure axis.

Effect of Surface Coverage on the Apparent Heats of Sorption. A Diesel particle is formed in the cylinder as a result of the combustion conditions present in the turbulent, heterogeneous flame. The particles once formed are transported from the cylinder to the ambient air in the exhaust gas which contains high concentrations of species in the gas phase. Therefore, during the process of emission, the particles will be undergoing numerous collisions with the gas-phase molecules and as a result the molecules will condense or adsorb onto the surfaces of the particles. The extent of condensation will be dependent upon the vapor pressure of the adsorbate and the temperature of the exhaust gases. Typical emission rates of particulate matter of 0.622 g/mi have been observed by other workers (25) for light-duty automobile Diesel engines of which 0.0715 g/mi is extractable into organic solvents. Similarly, total hydrocarbon emission rates of 0.50 g/mi have been observed with a hot flame ionization detector. If this hydrocarbon fraction is separated by gas chromatography, 50% of the total hydrocarbons have sufficient molecular weight to adsorb or condense on the particles. These figures suggest that approximately 28% of the available gas phase adsorbs or condenses on the surfaces of the particles. The extent of the adsorption of the molecules will be related to the surface properties of the adsorbent and the heat of adsorption of the adsorbate. However, once the particles have adsorbed molecules on their surfaces, the heat of sorption of multilayers is lower than the heat of adsorption of the monolayer. The particles, which are collected on the filter, contain at least 18% by weight of organic extractable compounds, which means that the particles have multilayers of molecules sorbed on their surfaces. It is reasonable to expect that, once a particle enters the ambient air, it has sufficient sorbed molecules on its surface that its properties are solely dependent upon the nature of the sorbed species.

Since the bioavailability of sorbed molecules is dependent upon the nature and the energy of sorption of the active species, a study was performed in which the apparent heat of sorption was measured as a function of concentrations of the adsorbate. The following adsorbates were investigated: acetophenone, benzaldehyde, benzene, cyclohexane, cyclohexene, ethylbenzene, *n*-hexane, 1-hexene, and *n*-octane. The adsorbents used in this study have been subjected to the highest-temperature activation pretreatment. Table II lists some examples of the results of this study. These apparent heats of sorption suggest that the adsorbate first sorbs on the most energetic adsorption sites and then sorbs on sites with lower energies. The heats continue to decrease until there is a sufficient quantity of sorbed molecules on the surface that the energy of sorption becomes the differential heat of evaporation from solution. Therefore, this study suggests that the history of collisions between the exhaust gases and the particles will have a major effect on the energy of sorption.

Table II. Variation of Apparent Heats of Sorption with Concentration of Adsorbate

adsorbate	adsorbent	injection vol, μL	apparent heat of sorption, kcal/mol
benzene	DPM-EPA	0.01	12.8
		0.05	9.8
		0.10	9.1
		1.0	5.9
		10.0	8.7
	DPM-PSU	0.01	12.0
		0.05	9.9
		0.10	10.4
		1.0	7.6
		10.0	10.5
<i>n</i> -hexane	DPM-EPA	0.01	15.0
		0.05	10.6
		0.1	10.4
		1.0	5.4
		10.0	12.8
	DPM-PSU	0.01	11.4
		0.05	11.4
		0.1	11.9
		1.0	8.4
		10.0	10.7

Table III. Isosteric Heats of Adsorption

adsorbate	heat of vaporization, kcal/mol	heat of adsorption, kcal/mol		
		DPM-PSU	DPM-EPA	graphitized carbon blacks (27)
water	9.72	10.3	6.9	5.6
methanol	8.98	9.0	4.8	5.3
dichloromethane		8.6	5.0	
<i>n</i> -hexane	7.63	11.4	15.0	10.4
1-hexene	7.79	10.6	10.2	
benzene	8.15	12.0	12.8	9.8
cyclohexene		10.2	9.7	9.1
cyclohexane	7.83	8.7	9.3	8.7
ethylbenzene	9.3	15.2	8.3	12.7
acetophenone	11.73	16.1	15.1	13.0
benzaldehyde	11.66	17.4	12.2	
<i>n</i> -octane	9.2	15.2	8.4	13.4
phenol	11.89	16.4	12.2	13.0
naphthalene	12.31	16.4	12.3	17.3
anthracene	16.82		11.1	
phenanthrene	14.18		19.0	

Isosteric Heats of Adsorption for Diesel Particulate Matter. The small injection volumes (0.01–0.05 μL) which were used in the previous study correspond to coverage in the Henry's law region of the adsorption isotherm and can therefore be used to quantify the isosteric heats of adsorption. Table III lists these heats for various adsorbates on the two samples of Diesel particulate matter activated at the highest-temperature pretreatment. There are significant increases in the heats of adsorption for the activated DPM-PSU as compared to the activated DPM-EPA for every compound investigated, and as a result the higher molecular weight adsorbates phenanthrene, fluorone, fluoranthene, and anthracene could not be eluted from the column containing DPM-PSU. These results can be rationalized by the fact that the DPM-EPA sample is expected to have sorbed materials on its surface which cannot easily be desorbed. These materials will probably result from partially combusted lubricating oils (25).

Summary and Conclusions

The isosteric heats of adsorption determined for benzene and hexane on Spheron 6 are close to those reported in the

literature for graphitized carbon blacks. The heats for the same two compounds on both Diesel samples are somewhat greater, and this is probably due to the presence of higher-energy adsorption sites on the heterogeneous porous Diesel particles. This heterogeneity is confirmed by the peak shapes and increasing retention volumes with decreasing injection volumes, indicative of a type II adsorption isotherm. The difference between the isosteric heats of adsorption may be explained by the increased quantity of sorbed species on the DPM-EPA particle surfaces. Therefore, with the DPM-EPA samples, there is a higher probability of the adsorbate interacting with substances condensed on the particles than with the carbon particles themselves. The variation of adsorption energies with injection volumes indicates a similar phenomenon. With increasing surface coverage, adsorbate molecules will be encountering fewer unoccupied adsorption sites and more adsorbed molecules. Multilayer adsorption will then occur and the corresponding interaction energies should be less. This has significance when considering the bioavailability of the sorbed species on inhaled particles. The molecules adsorbed on the high-energy carbon sites will be tightly held as indicated by the isosteric heats. But, additional layers of sorbed substances may be more easily liberated. This is currently being investigated by measurement of multilayer adsorption isotherms in this laboratory.

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Identification of Atmospheric Particulate Sources in Washington, D.C., Using Chemical Element Balances

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■ During the summer of 1976, 130 air-filter samples were collected at 10 sites in the Washington, D.C., area and analyzed for 39 elements, with 37 samples also being analyzed for SO_4^{2-} , NO_3^- , and NH_4^+ . Concentration patterns were interpreted by using chemical element balances for seven sources: coal, oil and refuse combustion, soil dust, motor-vehicle emissions, limestone, and marine aerosols. For 35 nonvolatile elements, predicted concentrations were, on the average, within a factor of 1.93 of observed values. Predicted concentrations of primary particulate matter plus SO_4^{2-} , NO_3^- , and NH_4^+ account for 65% of measured total suspended particulate (TSP) matter, the remainder presumably being condensed water, organic material, and sources not included. The largest fraction of primary TSP matter is soil dust, much of which is entrained by urban activities. The limestone component may originate from agricultural liming, construction projects, or abrasion of concrete. Most elements are reasonably well fitted, major exceptions being Cr, Cu, Ni, and a small-particle component of Mn.

Introduction

To design optimal control strategies for atmospheric particles, air-pollution authorities need models that relate observed concentrations of total suspended particulate (TSP) matter, or of certain species on particles, to the sources of particles. At present, source-emissions inventories are usually coupled with dispersion models to predict source contributions to TSP matter. However, emissions inventories are often inaccurate for ducted sources, especially those with pollution-control devices; fugitive emissions are often neglected, and dispersion models add to the overall error. If it becomes necessary to control particles of certain sizes or compositions in addition to TSP matter, present methods will be even less adequate.

Because of large uncertainties of source-based models, several investigators have been developing receptor models, which use concentrations of species at sampling sites and their fluctuations to estimate contributions for various classes of sources (1, 2). Sources of urban particles are identified by analyzing urban particulate samples for many elements, some of which can be associated with specific types of air-pollution sources. Three basic types of particle receptor models have mainly been used: chemical element balances (CEBs) (3-8), factor analysis (9-11), or target-transformation factor analysis (12, 13).

According to the CEB model, the composition of particles at the receptor is a linear combination of concentration patterns of particles from the contributing sources; i.e., the concentration of element i in the particulate sample is given by

$$C_i = \sum_j m_j x_{ij} \quad (1)$$

where m_j is the mass of material from source j in the

sample and x_{ij} is the concentration of element i in particles from source j .

Source-strength coefficients, m_j , are determined by a least-squares fit to the observed concentrations of several elements (the "marker" elements). In a previous study, Kowalczyk et al. (6) used 8 marker elements to fit compositions of 10 samples collected in the Washington, D.C., area in 1974 with 6 components. Concentrations of 15 nonvolatile elements not used in the fitting procedure were predicted, on the average, to within a factor of 2. The fit was not perfect, but it was a considerable improvement over previous attempts to apply CEBs to other urban areas (3-5, 14, 15). In part, the improvement resulted from the fact that the Washington area has little industrial activity. Thus, reliable components are needed only for sources common to most urban areas to test the procedure, e.g., coal- and oil-fired power plants, incinerators, motor vehicles, soil, and marine aerosols.

Here, we report on a more detailed study of airborne particles in the Washington area collected during the summer of 1976: 130 samples from 10 sites analyzed for 39 elements and for 37 samples, NH_4^+ , SO_4^{2-} , and NO_3^- . Results were interpreted by using more detailed CEBs for 39 elements and 7 components. Our major aim was to test the fundamental question of the CEB method: can compositions of ambient particles be accurately accounted for by a linear combination of the compositions of particles from major sources? Only secondarily have we been concerned with contributions of TSP matter from the sources, which has been the focus of other studies. For this reason, and because of the small masses of samples needed for analysis by the methods used, we have not determined total mass concentrations of the samples.

Sampling and Analysis

The 10 sampling sites used are shown in Figure 1. Some were on the edges of the metropolitan area for measurements on incoming "background" air and several were in the midst of the city. Some were on tall buildings and others on low buildings to check for vertical gradients. At each site, samples were collected on the roof of the building.

Filter samples were collected at all sites each sampling day for ~24-h periods in most cases. Cascade-impactor samples were collected at two sites each day over the same sampling period as the corresponding filter samples. Twin-piston, oilless Gast vacuum pumps were used at seven locations (sites 1-6, and 8) and Tempest rotary carbon-vane vacuum pumps at sites 7, 9, and 10. Pumps were calibrated before and after the study by using a Sprague dry-gas meter to ensure consistent relationships between airflow and pressure readings. Nuclepore filters with 0.4- μm pore diameter were used. Sampling sites with twin-piston pumps employed 47-mm diameter filters, and 110-mm filters were used at sites 7, 9, and 10. Field blanks were taken every day at each site. Filters were suspended about 2 m above the vacuum pump during sampling to minimize Cu contamination from pump motors. Scientific Advances six-stage cascade impactors with rotary vacuum pumps were used for collection of size-segregated samples. Collection surfaces were polycarbonate films, and the

[†] Present address: Northeast Utilities Co., P.O. Box 270, Hartford, CT 06101.

[‡] Present address: General Software Corp., Landover, MD.

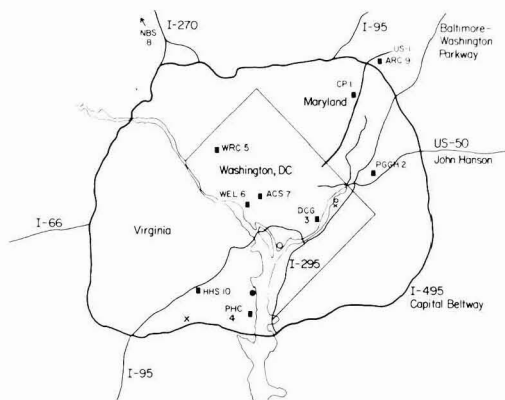


Figure 1. Map of the Washington, D.C., metropolitan area showing locations of the sampling sites and major point sources. Sites shown by number and letter abbreviation were on the following buildings: site 1, 5-story Chemistry Building on University of Maryland campus, College Park; site 2, 9-story Prince George's General Hospital, Cheverly, MD; site 3, 8-story District of Columbia General Hospital; site 4, 2-story Public Health Center, Alexandria, VA; site 5, 2-story WRC-TV studio; site 6, 2-story West End Library; site 7, 8-story American Chemical Society Building; site 8, 2-story Nuclear Reactor Building, National Bureau of Standards, Gaithersburg, MD (see Figure 2); site 9, 14-story USDA Library, Beltsville, MD; site 10, 2-story Hammond High School, Alexandria, VA. The two major refuse incinerators in the metropolitan area (shown as X's) are in Alexandria, VA, and the District of Columbia. Locations of the coal-fired power plant (●) and two oil-fired plants (O) are also shown.

backup filter was 0.4- μ m pore Nucleopore. Eighteen sets of impactor samples were collected, eight at site 7 and at least one at each other site.

Samples collected on 18 days between August 10 and September 13, 1976, were chosen for analysis: August 10-12, 16-25, 30, and 31 and September 4, 5, and 13. On only 4 of the 15 sampling days in August were samples collected at all sites; however, most days had samples from 8 of the 10 sites. Sampling began on August 10, the first clear day after three days of rain. Air quality deteriorated rapidly, and, by the afternoon of August 12, a pollution alert was called. Heavy rain occurred from August 13 to 15 and sampling resumed on August 16. Air quality deteriorated more slowly in this period; however, on August 24, a pollution alert was called and lasted until rain came on August 27. The remaining days were not part of a pollution alert, but samples were analyzed because of fairly constant wind directions on those days.

Samples were analyzed for 36 elements by instrumental neutron activation analysis (INAA) at the National Bureau of Standards (NBS) 10-MW reactor using procedures similar to those previously described (6, 16). Pb, Ni, and Cd were measured by atomic absorption spectrophotometry. After INAA measurements were completed, filters were leached in redistilled concentrated HNO₃ for 1.5 h. The material was centrifuged and rinsed 3 times with dilute HNO₃ and diluted to 25 mL with triple-distilled water. Analyses were performed with a double-beam Perkin-Elmer 360 spectrophotometer using a heated graphite atomizer, HGA-2100, following procedures previously described (17, 18). Analyses for Pb, Cd, and Ni employed the 283.3-, 228.8-, and 232.0-nm lines, respectively.

Analyses for SO₄²⁻, NO₃⁻, and NH₄⁺ employed procedures similar to those of Moyers et al. (19). Filters were refluxed in 10 mL of triple-distilled water for 1 h at 100 °C. After being cooled, the mixture was centrifuged, rinsed, transferred to a volumetric flask, and diluted to 25

mL. All three species were determined from pipetted aliquots. Sulfate was determined by flash pyrolysis (20). Nitrate was measured by forming a stable pink azo dye and measuring its absorbance at 535 nm (18). The NH₄⁺ ion was determined by the phenate method (21, 22).

Results and Interpretation

Elemental Concentrations. Average concentrations at the 10 sites are given in Table I. The highest concentrations for most elements are found at PHC (site 4), which may be due, in part, to the coal-burning Potomac River power plant about 2 km north of the site. Lowest concentrations are usually found at NBS (site 8), the most rural station. Average concentrations over the network are given in Table II.

Chemical Element Balances. The 6 components from our previous CEBs of Washington particles (6) were first used (soil, sea salt, motor vehicles, and combustion of coal, oil, and refuse), with the list of elements expanded to 39. Preliminary results indicated the need for a high-Ca source to account for that element. Following Dzubay (7), we added a limestone component of composition given by Mason (23). Changes were made in the motor-vehicle component based on a recent evaluation of studies in the Baltimore Harbor Tunnel (24). Mg, Mn, Cd, and Sb were added to the motor-vehicle component, and the Ca/Pb ratio was raised from 0.050 to 0.11. The value of K/Pb of 0.03 is based on wind-trajectory analyses (25) of dichotomous sampler data taken in connection with the St. Louis Regional Air Pollution Study (26). Potassium was not measured in studies by Greenberg et al. (27, 28) upon which the refuse component is based. Wind-trajectory analysis, however, indicates that incinerator particles contain large amounts of K, so we have included it in the component based on K/Zn = 0.92 from those results.

Previously, our philosophy was to determine source strengths by fitting concentrations of a minimum of carefully chosen marker elements in order to leave many "floating" elements to test the fit (6). Other researchers, notably Watson (8), use nearly all nonvolatile measured elements as markers, arguing that one should take full advantage of the information content of the data to establish source strengths. In work published elsewhere (29), we explored that question by performing CEBs of the Washington data with the present 7 components, but with 9-30 marker elements. Briefly, the results indicated that the number of marker elements used makes little difference in the quality of fit or strengths of the sources if certain elements are retained as markers and others excluded. Specifically, Na, Pb, and V are essential as markers for the marine, motor-vehicle, and oil components. The ratio of coal/soil strengths is influenced by removal of As or Mn as markers, but the effect is small if many others elements are designated as markers. With 25 or more marker elements, the CEBs have such stability that even Cr, Cu, and Ni (which we show below to be very poorly fitted) can be used as additional markers without appreciably altering the results. However, the use of Br and Ba as markers decreases the strength of the motor-vehicle component and causes serious underprediction of Pb concentrations. Bromine is so volatile that some of it leaves particles to enter the gas phase. As Ba of the motor-vehicle component arises mainly from diesel trucks (24, 30), the Ba/Pb ratio depends on the ratio of diesel trucks to vehicles burning leaded gasoline in local traffic.

Table II summarizes results of individual CEBs of the 130 samples using the 28 marker elements designated in the table. A least-squares fit determined values of m_j in eq 1 that minimized sums of the squares of the deviations

Table I. Average Trace-Element Concentrations^a Observed at Each of the 10 Sampling Sites

element	CP (1)	PGGH (2)	DCG (3)	PHC (4)	WRC (5)	WEL (6)	ACS (7)	NBS (8)	ARC (9)	HHS (10)
Na	280 ± 200	260 ± 220	290 ± 160	460 ± 270 ^b	270 ± 200	350 ± 270	340 ± 220	150 ± 150 ^c	270 ± 200	310 ± 240
Mg	460 ± 210	360 ± 430	870 ± 630 ^b	610 ± 330	310 ± 170	530 ± 200	340 ± 170	270 ± 220	270 ± 120	230 ± 90 ^c
Al	1250 ± 620	1390 ± 2210	1660 ± 1900	2610 ± 1300 ^b	1060 ± 740	1810 ± 1120	1170 ± 570	570 ± 330 ^c	840 ± 420	1000 ± 480
K	410 ± 180	360 ± 370	430 ± 370	690 ± 320 ^b	350 ± 220	560 ± 320	390 ± 180	210 ± 90 ^c	250 ± 130	340 ± 160
Ca	1040 ± 460	750 ± 530	770 ± 460	1290 ± 510 ^b	770 ± 430	1180 ± 570	910 ± 360	430 ± 240 ^c	740 ± 490	620 ± 240
Sc	0.29 ± 0.15	0.33 ± 0.51	0.40 ± 0.45	0.70 ± 0.65 ^b	0.25 ± 0.16	0.46 ± 0.29	0.26 ± 0.14	0.18 ± 0.18 ^c	0.18 ± 0.08 ^c	0.23 ± 0.12
Ti	110 ± 50	120 ± 160	120 ± 130	200 ± 90 ^b	78 ± 55	170 ± 130	94 ± 47	44 ± 26 ^c	81 ± 41	85 ± 44
V	20 ± 21	22 ± 32	34 ± 29	34 ± 32	21 ± 22	37 ± 38 ^b	30 ± 18	9.1 ± 8.1 ^c	15 ± 9	29 ± 27
Cr	16 ± 18	11 ± 12	15 ± 12	31 ± 35 ^b	13 ± 14	25 ± 34	9.4 ± 6.1	3.1 ± 2.8 ^c	9.7 ± 4.4	7.4 ± 7.2
Mn	28 ± 14	20 ± 13	25 ± 14	38 ± 16 ^b	21 ± 12	34 ± 19	23 ± 11	15 ± 8 ^c	24 ± 23	21 ± 10
Fe	1060 ± 470	940 ± 870	1130 ± 750	1860 ± 840 ^b	770 ± 460	1380 ± 720	910 ± 390	460 ± 260 ^c	640 ± 270	780 ± 350
Co	0.70 ± 0.39	0.96 ± 1.82	1.3 ± 1.1	1.4 ± 0.8 ^b	0.56 ± 0.13	1.1 ± 0.8	0.79 ± 0.46	0.35 ± 0.22 ^c	0.44 ± 0.17	0.54 ± 0.31
Ni	20 ± 28	21 ± 15	29 ± 33	22 ± 11	15 ± 10	35 ± 35 ^b	8.0 ± 4.1	9.4 ± 3.7	5.7 ± 1.8 ^c	6.6 ± 2.9
Cu	13 ± 12	27 ± 40 ^b	14 ± 10	21 ± 12	12 ± 5	21 ± 19	27 ± 41 ^b	8.6 ± 7.7	8.0 ± 3.4 ^c	23 ± 19
Zn	99 ± 96	89 ± 67	73 ± 48	113 ± 50 ^b	100 ± 115	110 ± 70	77 ± 47	94 ± 54 ^c	54 ± 31 ^c	84 ± 66
Ga	1.3 ± 0.6	1.4 ± 1.4	1.2 ± 1.3	1.8 ± 0.9 ^b	1.0 ± 0.7	1.0 ± 0.7	0.86 ± 0.44	0.75 ± 0.29	0.70 ± 0.21 ^c	1.1 ± 0.6
As	2.9 ± 1.6	3.3 ± 2.5	3.3 ± 2.9	4.3 ± 2.0	3.1 ± 2.2	3.7 ± 2.6	4.6 ± 2.3 ^b	1.5 ± 0.6 ^c	2.3 ± 1.0	3.4 ± 1.6
Se	2.3 ± 1.3	2.4 ± 2.5	2.7 ± 2.8	3.5 ± 2.4	2.3 ± 1.2	3.8 ± 2.0 ^b	2.4 ± 1.2	1.4 ± 0.4 ^c	1.6 ± 0.6	2.1 ± 1.2
Br	150 ± 100	120 ± 70	120 ± 90	190 ± 140	110 ± 70	220 ± 110 ^b	190 ± 90	45 ± 31 ^c	65 ± 32	170 ± 120
Rb	2.1 ± 1.5	2.5 ± 2.1	3.4 ± 2.7	3.7 ± 3.8 ^b	1.9 ± 1.0	2.2 ± 1.6	1.6 ± 1.4	1.5 ± 1.0	1.1 ± 0.6 ^c	1.5 ± 0.8
Sr	9.4 ± 6.1	12 ± 15	13 ± 17	17 ± 10 ^b	8.2 ± 4.7	14 ± 15	7.8 ± 3.7	4.0 ± 1.2 ^c	4.8 ± 2.4	6.5 ± 2.6
Ag	0.24 ± 0.20	0.21 ± 0.17	0.24 ± 0.11	0.28 ± 0.15	0.24 ± 0.22	0.31 ± 0.14 ^b	0.16 ± 0.12	0.086 ± 0.049 ^c	0.091 ± 0.068	0.18 ± 0.18
Cd	2.5 ± 1.5	2.7 ± 2.3	2.8 ± 2.1	3.6 ± 2.6	2.0 ± 1.3	4.2 ± 4.0 ^b	2.5 ± 2.1	1.1 ± 0.8 ^c	1.6 ± 0.9	1.4 ± 0.6
In (pg/m ³)	22 ± 15	20 ± 17	20 ± 13	27 ± 17	21 ± 18	31 ± 20 ^b	13 ± 8	17 ± 16	11 ± 7 ^c	14 ± 7
Sb	1.9 ± 1.2	2.8 ± 2.9	1.9 ± 1.2	3.0 ± 1.5 ^b	2.1 ± 1.9	2.9 ± 1.9	2.3 ± 1.2	1.1 ± 1.4 ^c	1.2 ± 0.8	1.6 ± 0.8
I	2.7 ± 1.6	2.4 ± 1.6	1.7 ± 0.9	2.9 ± 2.3 ^b	1.7 ± 1.1	2.4 ± 1.2	1.3 ± 0.5	1.1 ± 0.5 ^c	1.2 ± 1.0	1.3 ± 0.7
Cs	0.11 ± 0.09	0.11 ± 0.11	0.12 ± 0.12	0.19 ± 0.11 ^b	0.68 ± 0.58 ^d	0.16 ± 0.11	0.081 ± 0.057	0.047 ± 0.030 ^c	0.060 ± 0.031	0.077 ± 0.058
Ba	15 ± 9	25 ± 35	21 ± 24	37 ± 21 ^b	13 ± 9	29 ± 20	18 ± 7	7.1 ± 1.9 ^c	9.6 ± 4.0	12 ± 6
La	1.4 ± 0.9	1.4 ± 1.8	1.6 ± 1.3	2.8 ± 1.6 ^b	1.3 ± 0.9	2.3 ± 1.5	1.6 ± 0.8	0.67 ± 0.51 ^c	1.1 ± 0.5	0.96 ± 0.66
Ce	1.9 ± 1.0	2.0 ± 2.6	2.3 ± 2.1	3.8 ± 2.2 ^b	1.4 ± 1.1	3.5 ± 1.9	2.1 ± 1.1	0.72 ± 0.38 ^c	1.2 ± 0.5	1.5 ± 0.9
Sm	0.18 ± 0.10	0.19 ± 0.27	0.22 ± 0.21	0.35 ± 0.21 ^b	0.15 ± 0.10	0.31 ± 0.16	0.23 ± 0.11	0.079 ± 0.046 ^c	0.12 ± 0.06	0.13 ± 0.07
Eu (pg/m ³)	29 ± 22	30 ± 45	37 ± 47	48 ± 27 ^b	23 ± 25	45 ± 24	29 ± 16	12 ± 7 ^c	16 ± 8	23 ± 15
Yb (pg/m ³)	28 ± 19	44 ± 58	40 ± 38	68 ± 51 ^b	32 ± 14	52 ± 39	25 ± 12	19 ± 9	15 ± 10 ^c	20 ± 11
Lu (pg/m ³)	5.3 ± 2.5	6.3 ± 9.9	6.5 ± 6.3	11 ± 6 ^b	4.5 ± 3.1	8.9 ± 7.3	3.7 ± 1.8	3.4 ± 1.5	2.7 ± 1.6 ^c	3.7 ± 1.7
Hf (pg/m ³)	120 ± 50	100 ± 150	120 ± 120	200 ± 80 ^b	68 ± 50	130 ± 70	90 ± 46	37 ± 24 ^c	66 ± 34	65 ± 36
Ta (pg/m ³)	23 ± 13	39 ± 39	50 ± 44	68 ± 87 ^b	24 ± 19	64 ± 33	27 ± 23	25 ± 8	20 ± 12 ^c	27 ± 19
W	0.22 ± 0.17	0.29 ± 0.24	0.29 ± 0.25	0.44 ± 0.26 ^b	0.20 ± 0.10	0.28 ± 0.12	0.29 ± 0.27	0.18 ± 0.19	0.12 ± 0.09 ^c	0.20 ± 0.09
Pb	500 ± 320	430 ± 280	410 ± 230	690 ± 320 ^b	440 ± 210	610 ± 170	520 ± 280	130 ± 40 ^c	210 ± 110	420 ± 150
Th	0.22 ± 0.14	0.29 ± 0.47	0.30 ± 0.37	0.49 ± 0.29 ^b	0.18 ± 0.12	0.36 ± 0.24	0.21 ± 0.11	0.13 ± 0.15 ^c	0.14 ± 0.07	0.19 ± 0.11

^a Units are ng/m³ unless otherwise indicated. Uncertainties are standard deviations of a single observation. ^b Highest station average for element. ^c Lowest station average for element. ^d Contamination suspected in some samples.

Table II. Average Results of Chemical Element Balances of 130 Samples from Washington, D.C., Area for Summer 1976

element	predicted contributions, ^a ng/m ³							total, ng/m ³		larger/ smaller ^b	missing values ^c
	soil	limestone	coal	oil	refuse	motor vehicle	marine	predicted	observed ^d		
Na ^e	43	0.83	8.3	12	35	-	201	300	300 ± 20	1.00 ^f	0
Mg ^e	74	101	27	3.8	5.4	32	26	270	440 ± 30	1.63 ^f	3
Al ^e	812	9	517	0.4	6.1	-	<0.01	1340	1350 ± 110	1.16 ^f	0
K ^e	154	6	67	0.4	47	13	7	295	400 ± 20	1.38 ^f	0
Ca ^e	66	635	47	8.2	7.1	47	7.6	820	860 ± 40	1.09 ^f	0
Sc ^e	0.15	0.002	0.18	0.0002	0.0006	-	<0.0001	0.33	0.33 ± 0.03	1.19 ^f	0
Ti ^e	52	0.83	31	0.03	1.0	-	<0.0001	85	110 ± 10	1.35 ^f	0
Ve ^e	1.06	0.042	1.6	23	0.013	-	<0.0001	26	25 ± 2	1.07 ^f	0
Cr	0.81	0.023	0.84	0.062	0.21	-	<0.0001	2.0	14 ± 2	7.07 ^f	5
Mn ^{e,g}	13	2.3	1.6	0.10	0.31	1.3	<0.0001	18	17 ± 2 ^g	1.26 ^f	0
Fe ^e	511	8.3	362	2.8	2.8	34	0.0002	920	1000 ± 60	1.17 ^f	0
Co ^e	0.22	0.0002	0.25	0.16	0.003	0.034	<0.0001	0.68	0.83 ± 0.08	1.19 ^f	0
Ni	0.46	0.042	1.04	4.0	0.07	0.35	<0.0001	6.0	17 ± 2	4.35 ^f	1
Cu	0.23	0.009	2.2	0.89	0.71	3.0	0.0001	7.1	17 ± 2	2.68 ^f	23
Zn ^e	1.14	0.04	2.6	1.6	51	7.3	<0.0001	64	85 ± 6	1.42 ^f	0
Ga ^e	0.38	0.008	0.46	0.0001	-	-	<0.0001	0.85	1.29 ± 0.17	1.89 ^f	42
As ^e	0.061	0.002	3.1	0.028	0.10	-	0.0001	3.32	3.25 ± 0.2	1.58 ^f	0
Se	0.0009	0.0002	0.78	0.035	0.016	0.035	0.0001	0.87	2.5 ± 0.2	4.10	0
Br	0.097	0.013	2.1	0.054	0.66	167	1.25	171	136 ± 9	1.84	0
Rb ^e	1.19	0.0064	0.60	0.0001	-	-	0.0023	1.8	2.1 ± 0.2	1.54 ^f	17
Sr ^e	3.65	1.29	3.5	0.09	0.027	-	<0.0001	8.6	10 ± 1	1.40 ^f	32
Ag ^e	0.0007	0.0001	-	0.006	0.23	-	<0.0001	0.24	0.20 ± 0.01	1.44 ^f	26
Cd ^e	0.0011	0.0001	0.13	0.0028	0.64	1.03	<0.0001	1.80	2.4 ± 0.2	1.89 ^f	0
In	0.0007	0.0001	0.0023	<0.0001	0.0024	-	0.0004	0.0059	0.020 ± 0.001	5.12 ^f	3
Sb ^e	0.0081	0.0004	0.13	0.007	0.89	0.60	<0.0001	1.6	2.1 ± 0.2	1.39 ^f	0
I	0.058	0.0026	2.1	-	-	-	1.14	3.3	2.0 ± 0.1	2.41	12
Cs ^e	0.028	0.0011	0.039	0.0005	0.0025	-	<0.0001	0.07	0.17 ± 0.05	3.36 ^f	2
Ba	7.1	0.02	4.7	2.0	0.30	6.4	0.0006	21	19 ± 2	1.42 ^f	1
La ^e	0.75	0.014	0.31	0.016	0.0016	-	<0.0001	1.1	1.5 ± 0.1	1.42 ^f	0
Ce ^e	0.98	0.024	0.62	0.014	0.007	-	<0.0001	1.6	2.0 ± 0.2	1.30 ^f	1
Sm ^e	0.068	0.0027	0.057	0.0012	0.0003	-	<0.0001	0.13	0.20 ± 0.02	1.59 ^f	0
Eu ^{e,h}	0.015	0.0004	0.014	0.0005	0.0002	-	<0.0001	0.030	0.030 ± 0.003	1.32 ^f	5
Yb	0.037	0.0011	0.030	0.0004	0.0009	-	<0.0001	0.070	0.034 ± 0.003	2.60 ^f	19
Lu	0.0067	0.0004	0.0080	0.0001	0.0004	-	<0.0001	0.016	0.0056 ± 0.0006	3.34 ^f	1
Hf ^e	0.031	0.0006	0.022	0.0008	0.0004	-	<0.0001	0.055	0.10 ± 0.01	1.80 ^f	1
Ta ^{e,h}	0.041	0.0008	0.0077	0.0011	0.0018	-	<0.0001	0.052	0.036 ± 0.004	1.84 ^f	39
W	0.014	0.0013	0.038	0.0004	0.0072	-	<0.0001	0.061	0.24 ± 0.02	4.76	23
Pb ^e	0.15	0.019	2.1	0.39	34	428	<0.0001	465	440 ± 20	1.28 ^f	0
Th ^e	0.11	0.0036	0.10	0.0016	0.0008	-	<0.0001	0.22	0.25 ± 0.02	1.19 ^f	1

av value = 1.93

^a Contributions designated by "--" indicate that concentration of the element in particles from the source is not known. ^b larger/smaller is the average of the ratio of predicted/observed or vice versa, whichever is larger, over all samples.

^c Number of samples for which no value is available because peak is not strong enough in spectra for determination or concentration is not above filter blank. ^d Uncertainty is standard deviation of mean value. ^e Element fitted by least-squares procedure. ^f larger/smaller value included in average given below. ^g For reasons described in text, all observed values reduced by factor of 0.69 prior to fitting. Actual average observed value was 26 ± 3 ng/m³. ^h As noted in text, three observed values were eliminated from fits.

of predicted from observed concentrations of the marker elements. Concentrations were weighted by $1/\sigma^2$, where σ is the estimated uncertainty of the concentration value, including uncertainties of the analytical measurements and in filter blank values. We did not include the estimated 20% uncertainty arising from the air-volume measurements, which affects all concentrations from a sample uniformly. It is vital to include weighting; otherwise, the least-squares procedure ignores elements of small concentration, which provide the best indicators of some sources. Uncertainties must be estimated accurately, as results are sensitive to the choices made. For example, the 20% volume is larger than the analytical and blank errors for most elements; thus, when it is included, fractional errors for most elements are about 21-25%. The resulting CEBs do not yield as good fits to the most accurately measured elements as they do when the volume error is left out. We calculated σ values for each element in each sample, as the errors depend on the absolute concentration, the total volume collected, and the blank values for the filter used. Fractional uncertainties ranged from 5% to

7% for the elements that could be most accurately measured (Na, Mn, Fe, Co, La) to about 25% or more for the most difficult to measure (Mg, Cd, Ga).

Watson (8) and Dunker (31) have correctly noted that one should also include weighting factors based on uncertainties of concentrations of each element in each component. However, we feel that too little is now known about fluctuations of source compositions to make realistic estimates of them. For example, the best-characterized anthropogenic source is coal-fired power plants, but particles from only about a dozen of them have been studied in detail (29). The plants studied burned various types of coal and had different types of boilers and pollution-control devices. Fluctuations over this broad spectrum of plants would be too large for use in a local area in which the ranges of coals used and perhaps the types of plants were much narrower. However, the number of plants studied is too small to subdivide them into categories to obtain fluctuations for the appropriate group. As better and more data are being obtained on particles from certain types of sources (8, 12, 13, 25), we may soon have sufficient

data to assign reasonable uncertainties.

For reasons discussed below, the observed concentrations of Mn were reduced by a factor of 0.7 prior to running the CEBs. Three datum points each for Eu and Ta appeared to be incorrect, but examination of the raw data yielded no justification for removing them from the data set. However, as they would have greatly distorted the CEBs for their samples, we had the fitting routine ignore those points.

As a measure of the quality of the fits, we calculate the larger/smaller (L/S) ratio for each element in each CEB, where L/S is defined as the predicted/observed ratio or the inverse, whichever is larger. Thus, L/S always has a value of unity or greater whether the concentration is over or underpredicted. The average L/S ratio is a better indicator of the quality of fits than the average predicted/observed ratio. For example, the average predicted concentration of Sc agrees with the average observed value, but the L/S value of 1.2 shows that this is achieved by a balancing of over- and underpredictions. But, for Na, the average L/S is 1.00, indicating that Na is predicted correctly in every CEB as expected, as the marine component fits any Na not accounted for by other sources. The last column of Table II indicates the number of samples for which the element was not measurable.

Tests of the CEB Results. It is virtually impossible to test the accuracy of receptor-model results absolutely. It would require a very accurate source-emissions inventory for an area coupled with a highly reliable dispersion model. Core et al. (32) demonstrated reasonable agreement between the two approaches in the Portland area, and below we do so for some of our results. However, errors of source-emissions inventories and dispersion models are so great that agreement, although gratifying, is not a stringent test of the receptor model. Because of the lack of a reliable independent test, one should perform as many internal tests of self-consistency as possible. Tests can be performed to answer the following questions: (1) Are the source strengths for any components frequently negative? (2) Are concentrations of all elements predicted correctly? (3) Are the observed size distributions of particles bearing each element consistent with those of particles from the sources predicted to be major contributors of the element? (4) Are elements that are predicted to have the same major sources strongly correlated with each other? (5) Are distributions of source strengths at the receptor sites consistent with known locations of sources? (6) Are vertical gradients consistent with known locations and release altitudes of sources? (7) Are the source strengths vs. wind direction consistent with the locations of sources with respect to receptors?

Our fitting routine does not prevent negative source strengths. In the 9-marker fit (29), out of the 910 source strengths (7 components for 130 samples), 9 were negative. Most were for the marine component on days when the wind was never from an easterly direction, so the marine component was surely quite small, if present. For the 28-marker fit, there is only one negative source strength, a small negative coal component at station 10. This result indicates that all components used are reasonably close in composition to components actually present. It does not, however, indicate whether or not all major components present have been included in the CEBs.

In the previous Washington study, we used the average L/S of 15 nonvolatile, floating elements as a test of the quality of the fit, obtaining $\bar{L/S} = 2.0$. With 28 marker elements, there are too few floating elements for a test. Thus, in Table II, all except the volatile elements (Se, Br,

I, and W) were included in the average L/S. The result for this study, 1.93, is essentially the same as the value of 2.0 obtained previously. The new study includes many additional elements, whose concentrations in the source components are not well established. But we now include marker elements in the average, some of whose concentrations are almost perfectly fitted. These effects approximately cancel each other to yield about the same overall quality of fit. The average L/S for the same 15 elements as included previously is 2.1 for the present study vs. 2.0 for the previous one. The increase is largely caused by poorer fits to Cr and Ni concentrations.

Of the 35 elements included in the average L/S, 20 have $L/S \leq 1.5$, and 28 have $L/S \leq 2.0$. The fit is reasonable, although one would like to fit every element to within $\pm 20\%$, i.e., $L/S < 1.2$. However, the fit includes some very obscure elements, so it is not surprising that some are fitted poorly. Important sources of some elements may have been missed or their concentrations in some components may be incorrect. There is no particular pattern of the quality of the fit at various stations: some of the best are for urban stations ($\bar{L/S}$ of 1.68 and 1.71 at stations 10 and 7), as well as some of the worst (2.29 and 2.19 at stations 5 and 6, respectively). Fits at the three rural or suburban stations, 1, 8, and 9, have $\bar{L/S}$ values of 1.90, 2.05, and 1.83, which are about average for the network.

The elements most poorly fitted ($L/S > 1.6$) are Mg, Cr, Cu, Ni, Ga, Cd, In, Cs, Yb, Lu, Hf, and Ta. So little is known about concentrations of Ga, In, Cs, Hf, and Ta in source materials that their poor fits are of little concern. Magnesium is a fairly major element and should be fitted better. Another potential source of Mg plus K and Ca is cement plants. Small (33) determined compositions of particles from a cement plant near Frederick, MD, northwest of Washington, D.C. However, we have not included it as a component as the K/Ca ratio on the particles (about 0.8) is so large that one could not fit both K and Ca on ambient particles with such a component. Also, station 8 is closest to the cement plant but has the lowest concentrations of Ca and K in the network, and nearly the lowest of Mg. We ran eight-component CEBs that included both limestone and cement-plant components. As usually occurs when a reasonable component is added, the L/S value dropped slightly, from 1.93 to 1.88, and fits to K were improved. The average predicted TSP matter for limestone dropped from 1.76 to 1.35 $\mu\text{g}/\text{m}^3$, but most other predictions were little affected. However, we do not consider this set of CEBs acceptable, as 26 source strengths were negative, including 6 for limestone and 16 for cement.

The origin of the limestone component is unclear, as there are several potential sources of that sort of material: agricultural liming, construction projects, abrasion of streets and buildings. The limestone component should account for K from cement as its K/Ca ratio is 0.009 vs. the ratio of 0.006 from Phelan's (34) compilation of compositions of NBS standard cements. However, it would overpredict the Mg contributed by cement, as the Mg/Ca ratio is 0.16 for limestone vs. 0.027 from Phelan's cement compilation.

Among the most poorly fitted elements are Cr, Cu, and Ni. As Baltimore is heavily industrialized and only 60 km to the northeast, we thought that substantial quantities of these and other elements might be transported to the Washington area when the wind was from the northeast (see Figure 2). However, there was no evidence for substantial increases in levels of industrially related elements during sampling periods when the wind was from that

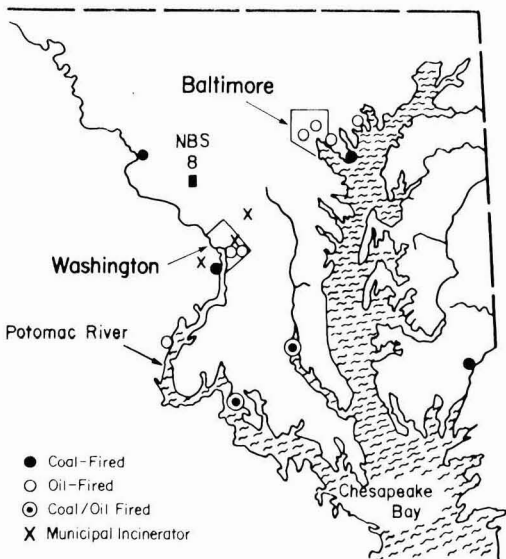


Figure 2. Map showing location of Washington area in relation to Baltimore, Chesapeake Bay, and major point sources in the area. Site 8 is also shown.

direction for a portion of the time. Nor do we find unusually high average concentrations of them at stations on the Baltimore side of Washington (stations 1 and 9). Thus, we have probably missed important sources of these elements within the Washington area. A possible source of Cr is $K_2Cr_2O_7$ biocide added to the water of cooling towers to prevent growth of organisms. Most roofs used for sampling had cooling towers on or near them, but we do not know which were using the biocide. In support of this hypothesis, Cr had the greatest station-to-station variability of any element measured, ranging from an average of 3.1 ng/m^3 at station 8 to 31 ng/m^3 at station 4. This variability suggests that Cr sources are very localized rather than area wide. Chromium does not correlate strongly with any element (see Table III), but its fourth-highest correlation is with K. The second-highest correlation is with V, so perhaps the Cr concentration in the oil component is too low.

A problem with many Cu measurements is contamination of filters by Cu particles abraded from brushes of the pump motors (35). We avoided this problem by placement of the motors away from the filters, and our Cu concentrations are among the lowest reported for urban areas (2). The possibility of contamination cannot be excluded, but it is surely small. Three sites (sites 7, 9, 10) had pumps and filters different from the others but showed no systematic differences of Cu. As average concentrations are 9.9 ng/m^3 at the rural stations (sites 1, 8, 9) and 21 ng/m^3 for the urban stations, the Cu not accounted for is probably real and originates in the urban area.

We had thought that the serious underprediction of Ni resulted from use of too large a V/Ni ratio, 5.8, for the oil component. Breger and Zoller (36) prepared a histogram of V/Ni ratios for 72 crude oils. The highest values observed were in the range of 5.5–6.0, and the histogram has maxima at 0.25, 1.75, and 3.75. Our value, based on studied of the Vienna, MD, power plant (37), is at the extreme of the values reported by Breger and Zoller. Also, Watson (8) obtained $V/Ni = 0.64$ from source studies.

Table III. Highest Binary Correlation Coefficients among Elemental Concentrations for 130 Samples

element	most strongly correlated element (and r value)	other correlated elements (and r values)
		Original Marker Elements
Al	Th (0.97)	Ti, Sm (0.95), Ba, Co (0.94), Ce, Sr, Hf (0.92), Sc, Eu (0.91), Fe, La (0.88), Lu (0.83)
Na	V (0.54)	La (0.53), Mn (0.52), Fe (0.50)
V	Ag (0.71)	Al (0.71), La (0.70), Sr (0.65), Th (0.64), Ce (0.62)
Zn	Ag (0.70)	Fe (0.56), Ta (0.56), Sb (0.53), La (0.51), Mn (0.51)
Pb	Br (0.66)	Ca (0.58), Fe (0.55), Ce (0.52), K (0.51)
Ca	Fe (0.80)	Hf (0.78), Ti (0.76), K (0.75), Ce (0.74), Sm (0.73), Al, La (0.70)
Fe	K (0.93)	Ce (0.91), La, Hf, Ti (0.90), Sm (0.89), Al (0.88), Th (0.86), Ba (0.84), Co, Sc (0.82)
Mn	Fe (0.77)	La (0.71), Ta (0.67), Ca, Ti (0.66), Hf (0.65), Ce (0.64)
As	Se (0.76)	Sm (0.74), Al, Eu (0.73), K, Ba, Co, Th (0.71)
		Other Elements
Cr	Ga (0.70)	V (0.63), Fe, K, Ti (0.49)
Cu	Sb (0.64)	Zn (0.45), Ta (0.44)
Ni	Cd (0.40)	Mg (0.32), Fe (0.31), Ti, Sb (0.30)
Cd	Sb (0.41)	Ni (0.40), Zn, Ti, Fe (0.39), Pb (0.38)
Sb	Cu (0.64)	V (0.54), Zn (0.53), La (0.52), Fe, Ti (0.48), Ag, Ce (0.47)

Thus, we would be justified in using a lower V/Ni ratio for oil, yielding a better accounting for Ni. However, we have not done so, as the correlation coefficient of Ni with V is only 0.26 and the highest correlation of Ni is with Cd ($r = 0.40$), which appears to arise mainly from refuse incineration and motor vehicles. Wind-trajectory analysis (25) yields a Ni/Zn ratio for incinerator particles that is 10 times the value used in the CEBs, based on in-stack measurements (27, 28). Possibly much of the Ni in the hot stack gases is in the vapor phase and condenses on particles upon cooling. However, even with a 10-fold increase of Ni in the incinerator component, we would still seriously underpredict Ni.

We do not regard the underprediction of Cd as serious. A major source of Cd is refuse incineration. As incinerators have high stack temperatures, typically $>200 \text{ }^\circ\text{C}$ (27), some Cd may be in the gas phase when particles are collected but condense upon cooling in ambient air.

Rare earths are chemically very similar to each other and usually behave as other lithiophiles, but their concentrations are not predicted as well as for most other lithiophiles. Light rare earths are slightly underpredicted and the heavy ones considerably overpredicted. Rahn (38) finds that the ratio of heavy-to-light rare earths on particles is often lower than for soils or crustal abundance patterns, especially for urban particles. This result is not understood but may be caused by fractionation of rare earths on soil particles of different sizes or enrichment of light rare earths with respect to heavy ones on particles from high temperature combustion sources. Indeed, the heavy/light ratio for the coal component is much smaller than for the soil component; however, the strength of the coal component relative to soil is too small to yield agreement with observed rare-earth patterns. Thus, light rare earths may be en-

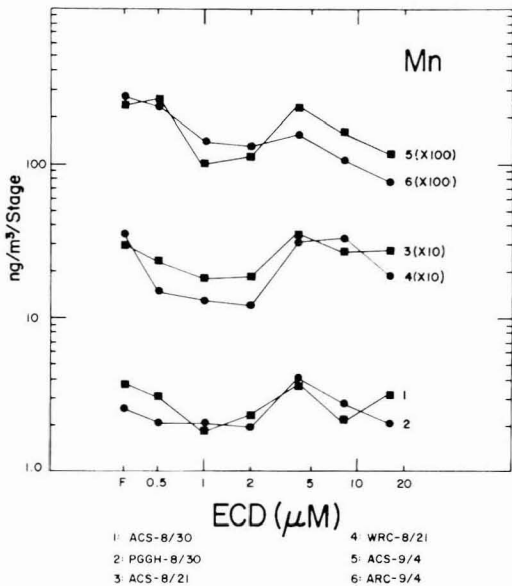


Figure 3. Typical size-distribution curves observed for particles bearing Mn.

riched relative to heavy ones on suspended soil particles with respect to bulk soil.

Particle Size Distributions. Space does not permit a detailed discussion of particle size distributions, which is the subject of a forthcoming paper. However, size distributions for particles bearing the various elements determined from the cascade-impactor results were compared with size distributions for particles released from the various sources (see ref 6 for references to data on sources). For most elements, size distributions of ambient particles agree well with those of particles from the major sources of the elements predicted by the CEBs in Table II. A major exception is Mn, which is important in making a distinction between soil and coal particles. In Figures 3 and 4 are shown the size distributions of particles bearing Mn and Al, respectively. The Al curves are representative of most lithophile elements, showing that these elements are predominantly associated with large particles as expected for elements whose major sources are soil and the aluminosilicate portion of coal. By contrast, the Mn curves show both large- and small-particle components. However, our CEBs indicate that the major source of Mn is soil. By fitting the Al curves to the large-particle end of the Mn distributions, we resolved the latter into large- and small-particle components, finding that the large-particle component typically accounts for only 70% of the total Mn. As the fine-particle component is not soil, it would distort the CEBs if we allowed them to fit the total Mn concentration. Thus, Mn concentrations were reduced by a factor of 0.7 before attempting the fits.

We have not identified the source of the fine-particle Mn. One possible source was the Mn-containing gasoline additive MMT, which was in use during 1976. The fine-particle Mn amounts to about 9 ng/m³. From measurements in traffic tunnels during the peak of MMT use (30), we estimate that, at most, 3.5 ng/m³ of Mn could be accounted for by motor vehicles, so there is probably an additional source of fine Mn.

Binary Correlations of the Elements. If two elements are predicted to arise mainly from the same source,

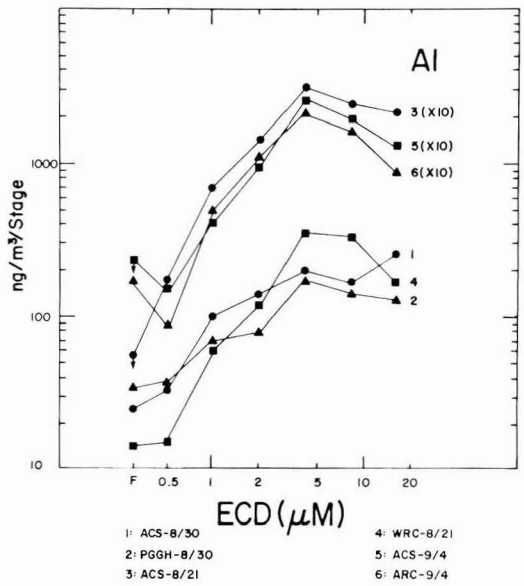


Figure 4. Typical size-distribution curves observed for particles bearing Al.

their concentrations are expected to be highly correlated. Important binary correlation coefficients are listed in Table III. The first group of elements includes the most sensitive markers for the seven components. Most elements show reasonably high correlations with most other elements, the major exception being Br, which is correlated strongly only with Pb. Mixing heights and wind speeds exert a strong influence on concentrations of particles from all sources simultaneously, forcing at least modest correlations to occur (39, 40). Most elements are correlated with lithophile elements such as Al and Fe, as soil is the major source of atmospheric material and its concentration tends to rise and fall along with those of particles from other sources.

No element correlates strongly with Na, but its major source is marine aerosol, which is not a major source of other measured elements. The correlation with V is not surprising, as comparable amounts of Na and V are released by oil combustion. Probably more important, winds that bring marine aerosol into the area also bring particles from oil-fired plants to the east and south of Washington (see Figure 2). The strong correlation of Ag with V probably arises because of the close proximity of an oil-fired plant and a municipal incinerator in the city, which is the major source of Ag.

Correlations with Zn agree reasonably with the CEBs, as the highest is with Ag and that with Sb is among the highest. The CEBs indicate that these elements arise mainly from refuse combustion, although we cannot be certain that there are not other sources of Zn and the other elements that were not included as components. The correlations with Pb are reasonable: as expected Br is the strongest and the group includes other elements present in the motor-vehicle component. As expected, Ca and Mn correlate mainly with lithophile elements. It is gratifying that Se correlates most strongly with As, as both are predicted to originate mainly from coal combustion.

The second group of elements includes several whose concentrations were not well predicted by the CEBs. The lack of strong correlations of Cr suggests that it has an additional source. The fact that K is among the stronger correlations of Cr weakly supports the suggestion that

Table IV. Average Contributions of TSP Matter ($\mu\text{g}/\text{m}^3$) from Various Sources at Each Site As Indicated by CEBs^a

site no.	soil	limestone	coal	oil	refuse	motor vehicle	marine	total
Urban Sites								
2	11.8 ± 2.1	1.5 ± 0.2	4.1 ± 2.2	0.30 ± 0.12	0.65 ± 0.12	4.2 ± 0.8	0.55 ± 0.14	23.1 ± 3.2
3	16.1 ± 2.6	1.5 ± 0.2	4.7 ± 1.8	0.56 ± 0.11 ^b	0.57 ± 0.10	4.3 ± 0.7	0.57 ± 0.11	28.3 ± 3.3
4	27.5 ± 4.3 ^b	2.4 ± 0.3 ^b	6.7 ± 1.5 ^b	0.41 ± 0.11	0.84 ± 0.12 ^b	6.6 ± 0.9 ^b	0.96 ± 0.23 ^b	45.4 ± 4.7 ^b
5	12.0 ± 2.4	1.7 ± 0.3	2.9 ± 0.8	0.26 ± 0.08	0.56 ± 0.14	4.1 ± 0.5	0.60 ± 0.15	22.1 ± 2.6
6	23.0 ± 4.4	2.3 ± 0.3	5.0 ± 1.5	0.50 ± 0.18	0.80 ± 0.17	6.1 ± 0.8	0.66 ± 0.23	38.4 ± 4.7
7	11.7 ± 2.0	2.0 ± 0.2	4.1 ± 0.65	0.41 ± 0.08	0.50 ± 0.10	5.5 ± 0.9	0.79 ± 0.18	25.0 ± 2.3
10	11.4 ± 1.5	1.3 ± 0.2	2.8 ± 0.7	0.31 ± 0.08	0.61 ± 0.17	3.1 ± 0.5	0.70 ± 0.22	20.2 ± 1.8
av urban	16.2 ± 2.5	1.8 ± 0.16	4.3 ± 0.5	0.39 ± 0.04	0.65 ± 0.05	4.8 ± 0.5	0.69 ± 0.05	28.9 ± 3.6
Rural or Suburban Sites								
1	15.2 ± 2.0	2.3 ± 0.3	3.5 ± 0.6	0.26 ± 0.08	0.64 ± 0.13	4.7 ± 0.8	0.59 ± 0.13	27.2 ± 2.3
8	7.8 ± 1.5 ^c	1.0 ± 0.2 ^c	1.3 ± 0.3 ^c	0.13 ± 0.04 ^c	0.27 ± 0.04 ^c	1.3 ± 0.1 ^c	0.34 ± 0.15 ^c	12.1 ± 1.6 ^c
9	9.0 ± 1.6	1.6 ± 0.2	2.6 ± 0.4	0.19 ± 0.03	0.35 ± 0.07	2.1 ± 0.4	0.69 ± 0.17	16.5 ± 1.7
av rural	10.7 ± 2.3	1.6 ± 0.4	2.5 ± 0.6	0.19 ± 0.04	0.42 ± 0.11	2.7 ± 1.0	0.54 ± 0.10	18.6 ± 4.5
av 10 sites	14.6 ± 2.0	1.7 ± 0.2	3.8 ± 0.5	0.33 ± 0.04	0.58 ± 0.06	4.2 ± 0.5	0.64 ± 0.05	25.8 ± 3.1
urban/rural av	1.51	1.13	1.72	2.05	1.55	1.78	1.28	1.55
site-to-site variation, %	13.7	8.5	12.5	13.0	9.8	12.3	8.1	11.9

^a Uncertainties are standard deviations of the mean values. contribution for component.

^b Highest TSP contribution for component. ^c Lowest TSP

cooling-tower biocides are a source of Cr. The correlation with V suggests that oil may be a stronger source of Cr than indicated by the CEBs. Iron and Ti are associated with all lithophile sources, so their correlation with Cr could result from the general interelement correlations discussed above. Copper's strongest correlations are with Sb and Zn, perhaps indicating that refuse is a stronger source of Cu than shown by the CEBs. The Cu/Zn ratio from incinerator particles observed by wind-trajectory analysis (25) in St. Louis, 0.03, would raise the Cu contribution from refuse to 1.5 ng/m³. Kleinman (40) used Cu as a marker element for refuse incinerators in CEBs of New York City particles, but we feel that Zn is a much more reliable marker.

Nickel exhibits no strong correlations. The weakness of its correlation with V (0.26) is surprising and argues against the unexplained Ni being from oil-fired plants. Its correlations with Cd and Sb suggest that more Ni comes from refuse incineration than shown by the CEBs, although it may be caused by the close proximity of the oil-fired plant and the refuse incinerator. Correlations of Cd, although not strong, agree reasonably well with the CEBs, especially those with Sb, Zn, and Pb. Note that correlations with Pb can arise from both incinerators and motor vehicles. Correlations of Sb include both Zn and Ag, in agreement with the CEBs.

In summary, most correlations (including those not shown or discussed) agree with the predictions of the CEBs. Correlations among the group of elements including V with Sb and Ag and of Cu and Ni with Cd and Sb may be imposed by the close location of an oil-fired plant and an incinerator within the city, or it may indicate that a larger portion of these elements is released by refuse incineration than indicated by the CEBs.

Source Strengths at Stations. Average TSP contributions from the various sources at each station as indicated by the CEBs are shown in Table IV. The TSP contributions are calculated from the CEBs with knowledge of the concentration of a prominent element in particulate material from each source. The same concentrations as in the 1978 paper (6) were used for five sources: Al, 5.6% in soil and 13% in particles from coal combustion; 8.8% Zn in refuse-combustion particles; 7% V in particles from oil combustion; 31% Na in marine aerosol. We reduced the assumed Pb concentration in

motor-vehicle particles from 15% to 10% because of the decreasing use of leaded gasoline. Pierson and Brachaczek (30) report a value of about 7% from Tuscararo Mountain Tunnel studies in 1977, but the fraction of diesel-truck traffic was 16%, which is much larger than the 5% value that they recommend for general traffic. The limestone component is assumed to contain 36% Ca (23).

Soil is the dominant source of primary TSP matter, yielding a mass concentration more than 3 times as great as the closest competitor, motor-vehicle emissions. However, the secondary species, NH₄⁺, NO₃⁻, and SO₄²⁻, contribute nearly as much as soil, about 12 $\mu\text{g}/\text{m}^3$ (see below). Highest concentrations of particles from most sources are recorded at station 4, which was 2 km south of a coal-fired power plant and 7 km south of an oil-fired power plant. One of two major incinerators in the area is located northwest of the site. As the sampler was only two stories above ground level, it received more suspended soil than other, usually higher sites. Site 3 has the highest oil component, as it is closer to two oil-fired plants than other stations. The lowest TSP contributions for all components are observed at the most rural site, site 8, at the National Bureau of Standards, which is surrounded by large, grass-covered fields. The sampler was on the roof of the NBS reactor building at the west end of the property, about 2 km from most employee traffic. Although site 1, on the College Park campus, is a suburban site, contributions from many sources are rather high, especially motor vehicles. Traffic levels are very high in the area, and the Chemistry Building, on which the sampler was placed, is in the midst of several large parking lots and less than 1 km from the heavy traveled U.S. Route 1.

With one exception, urban/rural ratios of source strengths are about as expected. Coal, oil, and motor-vehicle strengths are about twice as high in the urban area. Soil is about 50% stronger in the urban area. In remote rural areas, soil may be a natural component caused by entrainment of soil by the wind. However, in urban areas, the soil is not simply blown in from the countryside, as the urban/rural ratios for soil-associated elements range up to factors of 4 or 5 in some cities (10). Much of the soil in urban atmospheres is entrained by human activities such as traffic and construction projects. The most surprising result is that the refuse component is only 53% stronger in the urban area, whereas the two major incin-

Table V. Matrix of Average Intercomponent Binary Correlation Coefficients (%)

soil	marine	coal	oil	refuse	motor vehicle	limestone	soil	45
100	25	35	56	73	29	52	marine	14
	100	-9	41	26	4	-4	coal	25
		100	34	24	20	44	oil	39
			100	65	23	14	refuse	39
				100	14	32	motor vehicle	19
					100	25	limestone	27
						100		

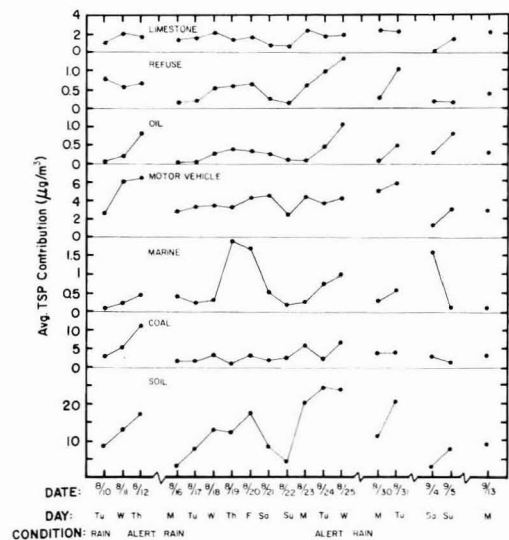


Figure 5. Daily average TSP contributions by various sources in the network as indicated by CEBs.

erators are in the urban area. (By contrast, the largest power plants are located outside of the city.) This may indicate that some "unofficial" refuse incineration occurs in rural areas or that the incinerator component is in part accounting for a source not included in the CEBs.

If the marine component represents sea salt brought into the area from the sea and Chesapeake Bay, its strength should be uniform over the network. Indeed, its urban/rural ratio is among the lowest; however, its strength is 32% greater in urban areas, so there may be another source of Na. That source is probably not road salt, as the samples were taken during August and September. The limestone component is only 19% higher in the urban area, suggesting that agricultural liming and crustal erosion are major sources of the component.

Correlations among Source Strengths. Average coefficients for correlations between strengths of each pair of sources are listed in Table V. This table represents the averages from a similar matrix constructed for each of the stations. These data can be understood somewhat in terms of the average strength of each component throughout the network for each sampling day, as plotted in Figure 5. The soil component is most strongly correlated with other components. Soil is strongly influenced by wind speed and mixing height that also influence the other sources. As expected, the weakest correlations are for marine aerosol, which comes into the area from outside. The highest average intercomponent correlation coefficient is for soil with refuse ($r = 0.73$). Perhaps a portion of the refuse component is, in fact, contributed by resuspended urban dust. The high correlation of refuse with oil probably results

Table VI. Concentrations of Secondary Aerosol Species^a

quantity	site 7 (urban)	site 9 (suburban)	site 10 (urban)
no. of samples	14	13	10
av concn, $\mu\text{g}/\text{m}^3$			
NH_4^+	1.2 ± 0.1	0.75 ± 0.10	0.80 ± 0.11
NO_3^-	2.7 ± 0.6	2.1 ± 0.7	1.5 ± 0.4
SO_4^{2-}	9.8 ± 1.3	7.6 ± 1.3	9.4 ± 1.4
av molar ratio (NH_4^+)/(SO_4^{2-})	0.73 ± 0.09	0.56 ± 0.10^b	0.52 ± 0.23

^a Uncertainties are standard deviations of the mean values. ^b One value not included in average.

from the close proximity of the municipal incinerator to an oil-fired power plant in the eastern part of Washington D.C. (see Figure 1). Oil is also correlated with marine aerosols, probably because of the locations of oil-fired plants to the south and east of the city (see Figure 2).

Vertical Distributions. One would expect higher strengths near ground level for particles released at ground level, e.g., soil, limestone, and motor-vehicle emissions. Sources with tall stacks might yield higher strengths at elevated receptors or, if well mixed before arrival at receptors, uniform vertical distributions. We divided the receptor sites into four high-level sites (sites 2, 3, 7, and 9), on buildings of ≥ 8 stories, and five low-level sites (sites 1, 4-6, and 10), on buildings of ≤ 5 stories. Site 8 was not included as it is much more rural than the other sites. Averages of source strengths for all CEBs for each group of sites were computed and the ratios of averages called the high/low (H/L) ratios of source strengths.

The H/L averages obtained were as follows: oil, 1.05 ± 0.55 ; coal, 0.93 ± 0.43 ; marine, 0.93 ± 0.25 ; limestone, 0.83 ± 0.23 ; motor vehicle, 0.82 ± 0.37 ; refuse incineration, 0.75 ± 0.23 ; soil ± 0.32 . Uncertainties are large, but, with one exception, the trends are in the expected directions; i.e., the coal, oil, and marine strengths are uniform or slightly stronger at high-level sites, and limestone, motor-vehicle, and soil strengths are greater at low-level sites, with soil being the most strongly enriched at low levels. The only unexpected result is the lower high-level strength of refuse incineration, which is thought to arise from two major incinerators with tall stacks.

Secondary Aerosols. Analyses for NO_3^- , SO_4^{2-} , and NH_4^+ in 37 samples from three sites are reported in Table VI. Concentrations are similar to those measured in other urban areas (7, 8, 10, 40). Sulfate levels at urban sites are slightly lower than the average third-quarter value for northeast urban sites, $13 \mu\text{g}/\text{m}^3$ (41). A molar ratio for $\text{NH}_4^+/\text{SO}_4^{2-}$ of 1.0 would correspond to the stoichiometry of NH_4HSO_4 . As shown, the average ratios at all three stations correspond to a more acidic material than NH_4HSO_4 . This result agrees with the measurements by Pierson et al. (42) in rural southwestern Pennsylvania except that we observe even lower $\text{NH}_4^+/\text{SO}_4^{2-}$ ratios, implying greater acidity. Also, $\text{NH}_4^+/\text{SO}_4^{2-}$ ratios decrease with increasing SO_4^{2-} concentration, suggesting higher

Table VII. Prediction of Total Suspended Particulate Material in Urban Washington ($\mu\text{g}/\text{m}^3$)

observed concn of TSP		65 ± 7
primary aerosol mass from CEBs (from Table IV)		
soil	16.2 ± 2.5	
limestone	1.8 ± 0.16	
coal	4.3 ± 0.5	
oil	0.39 ± 0.04	
refuse	0.65 ± 0.05	
motor vehicle	4.8 ± 0.5	
marine	0.69 ± 0.05	
	28.8 ± 3.5	
secondary aerosol mass (sites 7 and 10)		
NH ₄ ⁺	1.0 ± 0.2	
NO ₃ ⁻	2.1 ± 0.6	
SO ₄ ²⁻	9.6 ± 0.2	
	12.7 ± 0.7	
total accounted for		42 ± 4
balance not accounted for		23 ± 8

acidity with increasing SO₄²⁻, again in agreement with Pierson et al. Although experimental uncertainties of these measurements are much smaller than observed variations, the lack of direct acidity measurements makes it impossible for us to draw firm conclusions on these points.

The SO₄²⁻ concentrations have rather high binary correlations with most elements, generally ranging from 0.5 to 0.8 for the 37 samples. The major exceptions were for the marine element, Na ($r = 0.11$), and motor-vehicle elements, Pb ($r = 0.11$) and Br ($r = -0.14$). The NH₄⁺ concentrations have modest correlations with most elements, but generally weaker than those of SO₄²⁻. These results suggest that these species have some correlation with most other source materials because of correlations imposed by meteorological conditions. The fact that the highest SO₄²⁻ correlation is with Se ($r = 0.83$) may indicate some association of SO₄²⁻ with emissions from coal-fired power plants. The NO₃⁻ correlations are weak or negative for most elements, the major exceptions being with (values of r are given in parentheses) Na (0.32), Mn (0.56), Br (0.32), Cd (0.33), I (0.34), and Pb (0.41). Many of these are elements associated with motor vehicles, which also are a major source of NO_x, some of which is converted to NO₃⁻ in the air or possibly as an artifact on filters.

Correlations among the three secondary species are negative, except for NH₄⁺ with SO₄²⁻, for which $r = 0.46$. These results agree with those of Pierson et al. (42), except they find a stronger NH₄⁺-SO₄²⁻ correlation, $r = 0.84$.

Comparison with Measured TSP Matter. We did not measure masses of samples and have not emphasized predictions of TSP levels; we can check predicted TSP values against those measured by local air pollution agencies. The average of 12 TSP values measured during August and September, 1976, by Virginia, Maryland, and D.C. agencies in the Washington metropolitan area was 65 $\mu\text{g}/\text{m}^3$. Table VII summarizes the average TSP contributions indicated by CEBs for the urban stations. We fail to account for 23 of the 65 $\mu\text{g}/\text{m}^3$. Note that we do not include several species in our account, e.g., condensed water and carbonaceous material other than that associated with motor vehicles. Furthermore, the TSP measurements were made with high-volume samplers, which collect some particles larger than those collected by our filters.

Comparison with Source-Emissions Inventories. For some sources, there are emissions inventories with which we can compare results of the CEBs. Estimated emissions from refuse incineration, motor-vehicle emis-

Table VIII. Predicted TSP Contributions for Anthropogenic Sources Based on Source-Emissions Inventories

source	particulate emissions, ^a ton/yr	predicted TSP contribution, $\mu\text{g}/\text{m}^3$	
		box model	CEBs ^b
refuse incineration	1717	0.41	0.58 ± 0.06
motor vehicles	8435	2.0	4.2 ± 0.5
coal and oil	16365	3.9	4.1 ± 0.6

^a Reference 43. ^b Average over all 10 stations.

sions, and coal- and oil-fired power plants (not available separately) in the metropolitan area are listed in Table VIII. To predict ambient levels, we approximated the area as a box of (36 × 36)-km² area with an average mixing height of 1 km (44) and average wind speed of 13 km/h, observed during the study period. The predicted TSP levels agree surprisingly well with CEB results, perhaps fortuitously, for refuse incineration and coal- and oil-fired plants. The motor-vehicle component from CEBs is about twice as great as predicted from the source-emissions inventory, perhaps because motor vehicles are a ground-level source and the particles are not uniformly distributed in the mixing layer as assumed by the box model (as shown by the H/L ratios discussed above).

Uncertainties of source-emissions inventories are so large that one cannot place great emphasis on the agreement, but it is important for refuse incineration. Particles from refuse incineration contain such high concentrations of many trace elements that a very small TSP contribution can account for large fractions of many elements. Thus, it is gratifying that the TSP contribution obtained from the CEBs is reasonable in terms of the source-emissions inventory.

Correlations of Source Strengths with Wind Directions. Several sites should be strongly influenced by nearby major point sources when the wind is blowing from the sources toward the sites. Sites 3 and 4, especially, should show strong influences from power plants and/or an incinerator when the wind is from the north. In fact, these sites, as well as site 2, are sometimes heavily influenced by emissions from coal combustion, with coal TSP contributions up to 35, 29, and 19 $\mu\text{g}/\text{m}^3$ at sites 2-4, respectively. We looked for correlations of source strength with average wind direction during the sampling periods for days having reasonably small fluctuations of wind direction. The results were largely inconclusive because 24-h sampling periods nearly always have considerable wind fluctuation. Our studies (25) of the St. Louis network data (26) show that sampling periods of ≤12 h along with detailed wind measurements are needed to obtain directional information on sources. About the only directional information that can be obtained with our 24-h periods is general observations such as the small marine concentration in the network when the wind is never from the east during a sampling period.

Conclusions

The CEBs satisfactorily account for sources of most elements, the major exceptions being Cr, Ni, and Cu and fine-particle Mn. Although rare earths are generally thought to follow changes in concentrations of other lithophile elements, the CEBs do not fit observed rare-earth patterns precisely, perhaps because of fractionation between bulk and suspended soil. If this were better understood, rare-earth patterns would help distinguish between otherwise similar components, e.g., entrained soil

and particles from coal combustion.

A small set of carefully chosen marker elements yields CEBs that are almost identical with those obtained by using nearly all nonvolatile elements as markers (29). The CEBs have remarkable stability against changes of designated marker elements if certain key ones are retained, especially Pb for the motor-vehicle component and Na for marine aerosol. With the 7 components used, only 1 of the 910 source strengths obtained was negative. Thus, the components used are reasonable representations of materials actually present. When a cement component was added, we obtained many negative source strengths for it and the chemically similar limestone component.

Uncertainties of source-emissions inventories are probably greater than those of CEB results, and they provide no information about components such as soil and marine aerosol. These uncertainties are further compounded by those of dispersion models used to relate emissions to ambient concentrations. For what it is worth, the CEB results agree rather well with ambient levels of TSP matter predicted for three sources (motor vehicles, refuse incineration, and power plants) from source-emissions inventories and an atmospheric box model.

As CEBs cannot be tested absolutely, we applied many internal consistency tests to the Washington area CEBs, and most results were satisfactory. Except for a small-particle component of Mn, observed size distributions of particles bearing the elements agree with size distributions of particles from the predicted sources. Ratios of TSP contributions observed at high-level sites to those at low-level sites are greater for particles released from tall stacks than for those from ground-level sources. This test would be more definitive in a city with taller buildings. Most elements that are predicted to originate from a given source have large correlation coefficients with other elements thought to arise from the same source.

A major exception to the good results obtained from most tests is the refuse-incineration component. There are two dominant incinerators, with tall stacks, located well inside the metropolitan area. However, the urban/rural ratio is among the lower values obtained, the H/L ratio is not typical of an elevated source, and the interstation correlation is third highest (whereas it is expected to be among the lowest). Possibly, the refuse component is attempting to account for contributions from sources not included in the CEB.

Attempts to correlate component strengths with wind directions during sampling periods were not successful because of the large changes in meteorology, especially wind directions, that occur during 24-h sampling periods. The data do not cover enough days to permit us to observe correlations with weekdays vs. weekend days.

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Method for Detecting Trace-Element Contamination of Fish Samples from Handling

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■ A statistical method to detect handling (surface) contamination of fish tissue and whole fish samples with trace elements is presented. The method was applied to whole body and axial muscle samples of bluegill that were acid digested and analyzed for Cd, Cu, Mn, Pb, and Zn. Handling contamination of whole fish samples was not evident for any of the five trace elements, whereas handling contamination of muscle samples by Pb was indicated. This contamination was not revealed by the combined analyses of a reference standard (NBS bovine liver) and procedural blanks. Lead contamination of muscle samples probably resulted from contact with mucosal surface slime, which contains high concentrations of Pb relative to muscle tissue.

Introduction

Determination of trace-element concentrations in fish and other aquatic biota has become an integral part of many research and monitoring programs. Trace-element analyses of biological samples are routinely conducted in many laboratories, and most analysts use procedural blanks and one or more reference standards to validate their results and ensure quality control over laboratory procedures. Analysis of procedural blanks allows detection of contamination both from reagents used for sample digestion and storage and from container walls. Analysis of reference standards containing known concentrations of specified trace elements permits the analyst to evaluate the accuracy and the precision of his or her concentration estimates.

In certain cases, the combined use of procedural blanks and reference standards does not indicate contamination that has occurred during sample processing. This is especially true for samples that are subjected to surface contamination from extensive handling (e.g., dissection), because it is not possible to subject procedural blanks and reference standards to the same physical treatment that the samples receive during processing. Errors in concentration estimates caused by contamination during sample handling can be quite large (1), especially for samples such as fish muscle, which contain low concentrations of most trace elements.

In this paper, a statistical method for detecting surface contamination of samples is presented and applied to

samples of axial muscle tissue and whole fish that were collected from a relatively uncontaminated pond and analyzed for Cd, Cu, Mn, Pb, and Zn.

Methods

Collection and Analysis of Samples. Bluegill (*Lepomis macrochirus*) analyzed in this study were collected at various time intervals after release into Skinface Pond, a 2-ha soft-water impoundment near Jackson, SC. Before being stocked (pond stocked on November 21, 1975), the pond was twice treated with rotenone to eliminate resident fishes. Skinface Pond and other details of the study have been described elsewhere (2). Fingerling, hatchery-reared bluegill were collected for trace-element analysis during stocking of the pond. Thereafter, stocked bluegill were periodically collected with seines and fish traps. Fish were transported live to the laboratory in polyethylene bags containing pond water and were stored in polyethylene bags at -4 °C until dissection and/or lyophilization.

Samples of axial musculature from bluegill collected 216, 360, and 511 days after stocking were dissected with stainless-steel implements on a clean polyethylene work surface. Polyethylene gloves were worn during dissections to reduce surface contamination of muscle samples. After dissection, muscle samples were placed into acid-washed and tared plastic vials, weighed, and lyophilized to a constant dry weight. Dry weights of muscle samples for individual bluegill ranged from 0.44 to 1.75 g (Table I). Muscle samples were digested in porcelain crucibles with distilled HNO₃. Lyophilized whole fish were also digested with distilled HNO₃. Methods employed for digesting fish samples and cleaning glassware and polyethylene bottles have been described elsewhere (2, 3). After digestion, digestates were diluted to known volumes (Table I) and stored at 4 °C in washed polyethylene bottles until analysis. Concentrations of Cd, Cu, Mn, Pb, and Zn in diluted digestates were determined by atomic absorption spectrophotometry (2, 3). Procedural blanks were used throughout sample digestions, storage, and analysis to evaluate contamination from reagents and container walls. Procedures for sample preparation and analysis were validated with U.S. National Bureau of Standards (NBS) bovine liver as a reference material. Results were within the range of concentrations given by NBS for each element studied.

Evaluation of Sample Contamination. The following rationale and statistical approach were used for each trace element and sample type (whole fish and axial muscle

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Table I. Dilution Volumes of Digestates and Biomass of Axial Muscle and Whole Body Samples of Bluegill Collected from Skinface Pond

sample type	residence time in pond, days		range of sample dry weights, g	dilution vol, mL
	n			
whole fish	0	12	0.02-0.41	10
	97	12	0.04-0.27	10
	220	15	3.64-13.97	100
	340	11	3.97-15.13	100
	499	10	6.6-23.8	250
axial muscle	216	13	0.44-1.04	25
	360	11	0.81-1.17	25
	511	11	0.45-1.75	10

tissue) to evaluate surface contamination from handling. Because digestates were diluted to known volumes, the concentrations (corrected for concentrations in procedural blanks by subtraction, if detectable in blanks) of each element in the diluted digestates should be approximately proportional to the sample mass/dilution volume ratios, unless surface contamination of the samples occurred. For sets of digestates diluted to equal volumes, the blank-corrected concentration of a trace element in the diluted digestate should be proportional to the mass of sample digested. For each sample type, a simple linear regression of blank-corrected concentration in the diluted digestate against sample mass (or mass/dilution volume ratio) in the diluted digestate should produce a regression equation with a significant, positive slope and an intercept that does not differ greatly from zero. Given adequate sample size, lack of a positive regression slope and/or occurrence of a large nonzero intercept would suggest surface contamination during sample handling. Concentrations of a trace element can vary considerably within a given species and sample type (3); however, given a wide range of sample mass, a positive correlation between trace-element concentration and sample mass in the diluted digestate (or mass/dilution volume ratio) should occur.

As a test of the method, blank-corrected concentrations in diluted digestates were regressed against sample mass for each sample type, trace element, and time of collection. If the coefficient of determination (r^2) for a given regression

equation was substantially reduced by a single outlying observation, the outlying data point was removed and the regression equation was recalculated. This was done to improve the reliability of the regression estimates, because a single outlying observation can have a substantial effect on estimates of least-squares regression parameters (4). Data analyses were conducted with the general linear models (GLM) procedure of the Statistical Analysis System (5).

Results and Discussion

Contamination Indicated by Procedural Blanks.

Analyses of procedural blanks indicated substantial Cd contamination of samples of whole bluegill collected 220 and 340 days after stocking. Cadmium contamination was not evident in either samples of whole bluegill collected 0, 97, and 499 days after stocking or samples of axial muscle. Data on cadmium concentrations in whole bluegill collected 220 and 340 days after stocking will consequently not be analyzed further in this report. Later investigation indicated that Cd contamination occurred during sample digestion and was caused by leaching of Cd from Pyrex watch glasses under conditions of high temperature and strong acid. No Cd contamination occurred if samples were digested in porcelain crucibles with porcelain covers or in Teflon beakers with Teflon watch glasses. Analysis of procedural blanks produced no evidence of contamination of any samples with Cu, Mn, Pb, or Zn. Concentrations of these metals in procedural blanks were either below detection limits or very low relative to concentrations in samples.

Contamination Indicated by Regressions. Surface contamination of samples of whole bluegill was not evident for the five elements studied. A single outlying data point was removed before calculation of each of three regressions for whole fish samples (Cu, 220 days; Pb, 0 and 97 days). Slopes of all regressions for whole bluegill samples were positive (Table II). All regression slopes for Cu, Mn, and Zn and two of three regression slopes for Cd differed significantly from zero. Regression slopes for Pb were highly significant ($P < 0.01$) for two sets of samples (0 and 97 days) and were nearly significant ($0.05 < P < 0.10$) for the

Table II. Summary Statistics from Simple Linear Regressions of Trace-Element Concentrations (mg/L) in Diluted Digestates against Sample Dry Weight (g) for Whole Bluegill from Skinface Pond

element/regression statistics	time of collection, ^a days after stocking				
	0	97	220	340	499
cadmium					
slope	0.0054**	0.0037*			0.00022
intercept	ns	ns			ns
r	0.94**	0.71*			0.41
copper					
slope	0.77**	24.9**	0.014**	0.010**	0.012*
intercept	ns	0.63*	ns	0.062*	ns
r	0.81**	0.97**	0.70**	0.80**	0.72*
manganese					
slope	2.46**	1.62**	0.18**	0.15**	0.062*
intercept	ns	ns	ns	ns	ns
r	0.93**	0.88**	0.96**	0.77**	0.75*
lead					
slope	0.013**	0.082**	0.0019	0.0012	0.0018
intercept	ns	ns	ns	ns	ns
r	0.94**	0.91**	0.45	0.53	0.55
zinc					
slope	18.8**	14.6**	0.94**	0.85**	0.31**
intercept	0.76**	0.82**	ns	ns	ns
r	0.99**	0.93**	0.99**	0.98**	0.89**

^a One and two asterisks (*) indicate departure of individual statistics from zero at the 5% and 1% levels of significance, respectively. Nonsignificant ($P > 0.05$) intercepts are indicated by ns.

Table III. Summary Statistics from Simple Linear Regressions of Trace-Element Concentrations (mg/L) in Diluted Digestates against Sample Dry Weight (g) of Axial Muscle Samples from Bluegill

element/regression statistics	time of collection, ^a days after stocking		
	216	360	511
cadmium			
slope	0.00017	0.0010*	0.00089*
intercept	ns	-0.00081*	ns
r	0.27	0.72*	0.67*
copper			
slope	0.0094	0.037**	0.055**
intercept	ns	ns	ns
r	0.20	0.78**	0.91**
manganese			
slope	0.020**	0.0048	0.047**
intercept	ns	ns	0.022**
r	0.80**	0.15	0.93**
lead			
slope	-0.0037**	-0.0025	-0.0045
intercept	0.0055**	ns	ns
r	-0.85**	-0.28	-0.31
zinc			
slope	1.21**	1.40*	2.16**
intercept	ns	ns	0.81*
r	0.82**	0.69*	0.92**

^a One and two asterisks (*) indicate departure of individual statistics from zero at the 5% and 1% levels of significance, respectively. Nonsignificant ($P > 0.05$) intercepts are indicated by ns.

other three sets. Only 4 of the 23 regressions for whole bluegill samples had intercepts that differed significantly from zero (Table II).

The occurrence of smaller coefficients of determination (r^2) for regressions for Cd and Pb (nonessential elements) relative to those for Cu, Mn, and Zn (essential elements) is not surprising. Concentrations of nonessential trace elements in whole fishes are generally more variable than concentrations of essential trace elements (3). Increased variability in whole body concentrations would increase the scatter around the regression lines and decrease the coefficients of determination of the regression equations.

A single outlying data point was removed before calculation of two of the linear regression equations for axial muscle samples (Cd, 216 days; Cu, 216 days). Regression slopes for axial muscle samples were positive for all elements studied except Pb, which had negative slopes for all sets of samples analyzed (Table III), indicating surface contamination by Pb. Contamination of muscle samples by Cd, Cu, Mn, and Zn was not evident; 9 of the 12 regressions for these four elements had significant (nonzero) slopes and only 3 had nonzero intercepts (Table III). It should be emphasized that the combined analysis of procedural blanks and the NBS reference standard did not reveal Pb contamination of muscle samples. This contamination probably occurred during dissection because of contact of muscle samples with mucosal surface slime, which contains high concentrations of Pb relative to axial musculature (6). A detailed description of techniques for reducing sample contamination by Pb during collection, handling, and analysis has since been published by Patterson and Settle (1).

These results indicate the utility of this method for detecting surface contamination of fish samples by trace elements. The technique was effective even for sets of samples that had relatively little variation in mass among samples. For example, dry weights of muscle samples for bluegill collected 360 days after stocking only ranged from

0.81 to 1.17 g (Table I), a difference of less than 50%. However, regression slopes for this set of samples were significant for Cd, Cu, and Zn. A broader range of sample weights would have probably increased the accuracy of the regression equations. This technique has also been successfully applied to samples of resident fishes from the pond, with similar results (2), and has potential for general application to analyses of other biological samples.

In this study, regressions were calculated for sets of samples of fish of a single species and, presumably, of equal age. Individual regressions should be calculated only for samples from a single species and location, because differences in trace-element concentrations in whole fish and fish tissues among species and locations can be considerable (2, 7). For certain elements such as mercury, concentrations in fish tissues can be strongly correlated with age or body size (8). If concentrations of a trace element in fish tissues are known to be size dependent, individual regressions should be calculated for sets of samples of fish of approximately equal size or age.

The method presented in this paper should be used only to detect contamination of sets of samples that have been processed and analyzed as a unit. If surface contamination by a given trace element is indicated, the data for that element for the entire set of samples are suspect and should be treated summarily. Substantial departure of a single data point from a regression line should not be used as a criterion for deleting that observation from a data set. To reemphasize, removal of single outlying observations before calculation of certain regression equations was done only to improve the reliability of the method, because a single outlying observation can have a considerable effect on least-squares estimates of slope, intercept, coefficient of determination, and other regression parameters. Frequency distributions of trace-element concentrations in whole fishes and fish tissues often exhibit considerable positive skewness (3). Such skewness results in occasional occurrence of data points well above the regression line. Because the underlying frequency distributions of trace-element concentrations in populations are commonly "outlier-prone", removal of such outlying observations from data sets on trace-element concentrations is not advisable (3, 9).

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Sorption of Amino- and Carboxy-Substituted Polynuclear Aromatic Hydrocarbons by Sediments and Soils[†]

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■ The sorption of 2-aminoanthracene, 6-aminochrysene, and anthracene-9-carboxylic acid on 14 sediment and soil samples exhibiting a wide range of physicochemical properties was studied. The equilibrium isotherms were linear, and the Freundlich partition coefficients (K_p) for each compound were found to be highly correlated with the organic carbon content of the soil/sediment tested. No other significant correlations with soil/sediment properties were observed. The sorption constants (K_p), when normalized to organic carbon content of the substrate (K_{oc}), could be predicted within a factor of 2-3 from the octanol-water partition coefficients or water solubilities of the compounds using equations developed in earlier studies. However, both equations tended to underestimate the K_{oc} values for the two amines tested. The amount of deviation from predicted sorption was highly correlated with the % organic carbon/% montmorillonite clay ratio of the substrates. Experimental values of the water solubility and octanol-water partition coefficients for the three compounds are reported.

Introduction

Polynuclear aromatic hydrocarbons (PAHs) are ubiquitous products of the combustion of carbon-based substances. In addition to the purely aromatic and alkyl-substituted PAHs, a wide variety of PAHs exist which are substituted with polar functional moieties such as primary amino groups or carboxyl groups. Like the normal PAHs, these substituted PAHs are of concern environmentally because many individual compounds within this group have been demonstrated to cause mutations and certain types of cancer (1, 2). In one recent report, the amino-PAHs were identified as the most mutagenic fraction in a variety of synthetic fuels (1).

Although the sources and distribution of PAHs in the environment have been studied extensively (3-7), the transport and the fate of substituted PAHs in sedi-

ment/water systems are poorly understood. In addition, the physical and chemical properties of the substituted PAHs which govern their interactions with substrates have not been characterized or quantitated. In water/sediment and water/soil systems, sorption is recognized as one important factor in the determination of the fate of organic molecules (8). Karickhoff et al. (9) and Means and co-workers (10-18) have described the sorption behavior of a number of hydrophobic molecules on sediments and soils. The compounds included normal PAHs, nitrogen and sulfur heterocyclic PAHs, and some substituted aromatic compounds (i.e., 1-naphthol, acetophenone, benzidine). These studies suggested that the sorption of hydrophobic molecules (benzidine excepted) was governed by the organic carbon content of the substrate. Furthermore, the solubility of the compound and its solvent-partitioning characteristics (e.g., octanol-water partition coefficient, K_{ow}) were found to be significantly correlated to the sorption constant K_{oc} , which is derived from the linear partition coefficient K_p and the organic carbon content of the sorptive substrate. Conversely, the sorptive behavior of these compounds was found to be independent of substrate pH, cation-exchange capacity (CEC), textural composition, or clay mineralogy. We concluded that sediment/soil K_{oc} values could be reliably predicted from either the K_{ow} or the water solubility of the compound and from the organic carbon content of the individual substrates.

Benzidine, a fairly polar aromatic molecule, did not exhibit the same type of sorptive behavior (16) but instead yielded curvilinear isotherms. This result suggested multiple mechanisms of sorption. Further investigation indicated that, although the fraction of benzidine which existed in a neutral form sorbed to organic matter in accordance with the above relationships, the sorption of charged forms was observed to be independent of organic matter and dependent upon sediment surface area. As might be expected, the sorption of benzidine was largely controlled by the pH of the aqueous phase in the isotherm mixtures. These data suggested that the sorption of substituted PAHs might be a multimechanistic process which would not be amenable to the predictive relationships outlined above (13, 14).

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Table I. Characteristics of Soils and Sediments

sample	pH (1:1) ^b	CEC, mequiv/100 g	organic carbon, %	sand, %	clay, %	silt, %	montmorillonite clay, %
EPA-B2	6.35	3.72	1.21	67.5	18.6	13.9	2.0
EPA-4	7.79	23.72	2.07	3.0	55.2	41.8	40.1
EPA-5	7.44	19.00	2.28	33.6	31.0	35.4	25.7
EPA-6	7.83	33.01	0.72	0.2	68.6	31.2	60.8
EPA-8	8.32	3.72	0.15	82.4	6.8	10.7	6.1
EPA-9 ^a	8.34	12.40	0.11	7.1	17.4	75.6	16.3
EPA-14 ^a	4.54	18.86	0.48	2.1	63.6	34.4	13.8
EPA-15	7.79	11.30	0.95	15.6	35.7	48.7	10.1
EPA-18	7.76	15.43	0.66	34.6	39.5	25.8	29.7
EPA-20 ^a	5.50	8.50	1.30	0.0	28.6	71.4	21.9
EPA-21	7.60	8.33	1.88	50.2	7.1	42.7	2.8
EPA-22	7.55	8.53	1.67	26.1	21.2	52.7	14.8
EPA-23	6.70	31.15	2.38	17.3	69.1	13.6	57.6
EPA-26	7.75	20.86	1.48	1.6	42.9	55.4	37.1

^a Soils; all others are sediments. ^b Equilibrium pH of 1:1 (water/substrate) slurries.

In the present study, we have investigated the detailed sorptive behavior of three substituted PAH compounds with varying chemical and structural characteristics on a group of 14 sediments and soils. Linear partition coefficients (K_p) and K_{oc} values for each compound on each sediment/soil are reported. The relative influence of chemical and physical properties of the compounds and substrates on the sorptive process is discussed. The reliability of the K_{ow} and water-solubility parameters for predicting the sorption of substituted PAHs is evaluated. Water solubilities and octanol-water partition coefficients for the three compounds were determined experimentally.

Experimental Section

Collection and Characterization of Samples. The soil and sediment samples used in this study were collected from sites along the Missouri, Ohio, Wabash, Illinois, and Mississippi Rivers (see Figure 1 in ref 13). Fourteen samples were selected for the sorption studies following the detailed characterization described below. Each soil/sediment sample was analyzed for a number of physical and chemical properties including reaction pH, cation-exchange capacity, percent total nitrogen, percent organic carbon, and texture and clay mineralogy using methods outlined in Means et al. (10). The complete characterization was reported in our earlier paper (13).

Water Solubilities and Octanol-Water Partition Coefficients of Selected Substituted PAHs. The water solubilities and octanol-water partition coefficients of 2-aminoanthracene (2-AA) (M_r 193.25, mp 238–241 °C), 6-aminochrysene (6-AC) (M_r 243.31, mp 209–212 °C), and anthracene-9-carboxylic acid (9-CA) (M_r 222.24, decomposes 214 °C) were determined by using the procedures outlined by Means et al. (10). In each determination, the final data were corrected for trace impurities by using methods outlined by Wood and Means (17).

Reagents and Chemicals. The three substituted PAHs studied were obtained in pure form from Aldrich Chemical Co. Each pure compound (99+%) was tritiated by using the $BF_3\text{-}^3H_3PO_4$ procedure described by Hilton and O'Brien (19). The individual radiolabeled compounds were purified by microdistillation followed by preparative thin-layer chromatography. In each case, the final materials were assayed for purity and specific activity by liquid scintillation counting and gas chromatography. The compounds 2-aminoanthracene (97.1% pure; specific activity, 24.9 mCi/mmol), 6-aminochrysene (99.4%, pure; specific activity, 55.2 mCi/mmol), and anthracene-9-carboxylic acid (97.4% pure; specific activity, 0.928 mCi/mmol) were further purified by preparative thin-layer chromatography.

Table II. Water Solubilities and Octanol-Water Partition Coefficients for Three Substituted PAHs

compd	water solubility, $\mu\text{g/L}$	K_{ow} ^a
2-aminoanthracene	1.30 ± 0.159	13 400 ± 930
6-aminochrysene	0.155 ± 0.018	96 600 ± 4200
anthracene-9-carboxylic acid	85.0 ± 1.9	1 300 ± 180

^a Octanol-water partition coefficient.

All materials used for these studies were 99+ % pure.

All reagents used in these experiments were reagent grade, and certain solvents (e.g., 1-octanol, methanol) were redistilled in glass. The water used in all experiments was generated by a Milli-Q purifying system (Millipore).

Sorption Isotherms. Batch equilibrium sorption isotherms (see Figure 1) were determined for five concentrations of each compound on each soil/sediment sample by using the techniques outlined in Means et al. (13). A soil/sediment to water ratio of 4 g to 40 mL was employed. Kinetic studies on each compound/substrate combination indicated that equilibrium was achieved in 20 h or less.

The initial and final solution concentrations of the compound were determined by liquid scintillation counting, and the amount sorbed was calculated by difference. A mass balance for the 3H label was performed for each set of isotherms to verify that there were no losses of labeled material during the isotherm experiments. Techniques for these mass-balance determinations are discussed by Means et al. (10) and Wood and Means (17).

It should be noted that studies of this type require handling of relatively large quantities of radioactive substances and compounds which are known or suspected carcinogens. Investigators are cautioned that experiments of this type should be conducted only in approved laboratory facilities with stringent supervision by personnel who have been trained specifically in the safe handling of radioactive and toxic compounds.

Results and Discussion

The physicochemical characterization of the 11 sediments and 3 watershed soils selected for this study revealed that the samples possessed a broad range of values for all parameters tested (Table I) (13). Matrix correlation of the major substrate characteristics (Table I) associated with sorption indicated that the 14 substrates were random with respect to all characteristics except for the % clay/CEC interaction.

The water solubilities and octanol-water partition coefficients of the three substituted PAH compounds used

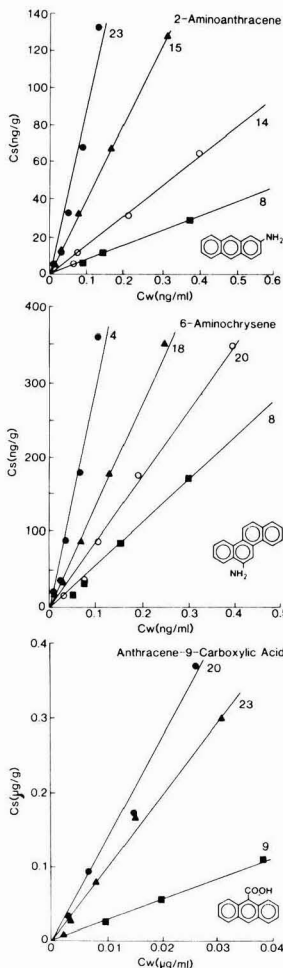


Figure 1. Representative sorption isotherms for 2-aminoanthracene, 6-aminochrysenes, and anthracene-9-carboxylic acid.

in these studies are presented in Table II. The three compounds span a range of approximately 2 orders of magnitude for water solubility (0.16–85 ppm) and approximately 2 orders of magnitude for K_{ow} (1.3×10^3 – 9.5×10^4). The water solubilities and the octanol-water partition coefficients determined in this study for 2-AA, 6-AC, and 9-CA are the first experimental values to be reported.

The data obtained from the batch equilibrium sorption experiments for the three substituted PAH compounds on the sediments and soils are presented in Table III. The linear Freundlich equilibrium constants (K_p) were obtained as discussed in Means et al. (13). The partition constants (K_p) and corresponding coefficients of determination (r^2) for all compound/substrate combinations are contained in Table III.

For 2-aminoanthracene (2-AA), the K_p values range from 79 to 875 on the 14 substrates. These K_p values were regressed against the values of each of the substrate properties reported in Tables I. The only significant relationship found was that between K_p and % organic carbon. The K_{oc} value thus derived was 28129 ($r^2 = 0.871$). Individual K_{oc} values from 2-AA on each sediment/soil are presented in Table III.

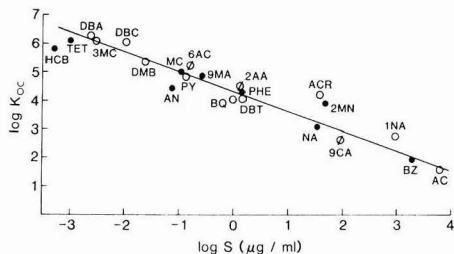


Figure 2. Relationship between sorption constant (K_{oc}) and the water solubility (S) of 22 compounds (TET = tetracene, HCB = hexachlorobiphenyl, DBA = dibenzanthracene, 3MC = 3-methylcholanthrene, DBC = dibenzocarbazole, DMB = 7,12-dimethylbenzanthracene, 9MA = 9-methylanthracene, AN = anthracene, 6-AC = 6-aminochrysenes, PY = pyrene, PHE = phenanthrene, BQ = biquinoline, DBT = dibenzothiophene, MC = methoxychlor, 9AA = 9-aminoanthracene, ACR = acridine, 2MN = 2-methylnaphthylene, NA = naphthylene, 9-CA = anthracene-9-carboxylic acid, 1NA = 1-naphthol, BZ = benzene, and AC = acetophenone). ● = data from Karickhoff et al. (9). ○ = data from ref 12–15 and 18. φ = data from this investigation.

The sorption of 6-aminochrysenes (6-AC) yielded K_p values ranging from 573 to 3973, indicating much stronger sorption than was observed for 2-AA. The K_p values were highly correlated with organic carbon content of the substrates. No other significant correlations were observed. The K_{oc} values calculated for the individual substrates tended to converge on an average of 162900 when the K_{oc} value for soil EPA-9 was omitted. This value was dropped because it was more than two standard deviations above the mean. Regression of K_p vs. % organic carbon for all 14 samples yielded a K_{oc} value of 143355 ($r^2 = 0.944$).

In previous work, we have demonstrated that the K_{oc} is a unique constant for a variety of nonpolar compounds which is dependent upon the physical properties of the compound being sorbed and on the organic carbon content of the sorbent but independent of the other sorbent properties (10, 13, 14). We have demonstrated that a significant relationship exists between K_{oc} and K_{ow} (13–15, 18) for the sorption of 22 nonpolar compounds by various soils and sediments (eq 1).

$$\log K_{oc} = \log K_{ow} - 0.317 \quad (r^2 = 0.980) \quad (1)$$

The calculated K_{oc} values for 2-AA and 6-AC obtained by using eq 1 are 6468 and 46556, respectively. These values are both significantly lower than the observed regressed K_{oc} values, which were 28129 and 143355, respectively. These data suggest that, although the sorption of these aromatic amines is highly correlated with the organic carbon content of the substrates, the strength of the sorption is greater than can be accounted for based on hydrophobic association of neutral aromatic nuclei to sediment organic matter as was observed for neutral PAHs (10, 13). This increase in sorption was also observed for benzidine (16) and for one heterocyclic amine compound, acridine, studied by our group on the same set of substrates and reported in another paper ($K_{oc} = 12910$ observed vs. 2020 calculated) (14). Hydrophobic sorption appears to be the result of a weak solute/solvent interaction rather than a strong sorbate/sorbent interaction. Chiou and co-investigators suggested that the solubility of a hydrophobic organic molecule should therefore be a good estimator of the organic-water partitioning coefficients (21). By inference, we concluded that the log solubilities (S) should be a reliable means of estimating $\log K_{oc}$ (13, 14). Regression of the water solubilities ($\mu\text{g}/\text{mL}$) and K_{oc} values

Table III. Equilibrium Sorption Constants for Selected Substituted PAHs on 14 Soil/Sediment Samples

soil/sed.	% OC ^b	2-aminoanthracene			6-aminochrysene			anthracene-9-carboxylic acid		
		K _p	r ²	K _{oc}	K _p	r ²	K _{oc}	K _p	r ²	K _{oc}
EPA-B2	1.21	321.6	0.996	26 580	1735.5	0.942	143 427	5.27	0.877	436
EPA-4	2.07	329.2	0.986	15 904	3115.7	0.979	150 519	5.49	0.741	265
EPA-5	2.28	304.1	0.989	13 336	3972.5	0.963	174 232	7.96	0.976	349
EPA-6	0.72	259.5	0.946	36 039	1078.7	0.988	149 817	5.47	0.868	760
EPA-8	0.15	79.0	0.943	52 659	573.3	0.999	382 185	1.84	0.940	1227
EPA-9 ^a	0.11	103.7	0.943	94 276	686.4	0.995	624 022	2.82		2564
EPA-14 ^a	0.48	145.1	0.922	30 225	924.3	0.972	192 553	10.03	0.976	2090
EPA-15	0.95	391.9	0.999	41 248	1292.2	0.985	136 025	2.66	0.841	280
EPA-18	0.66	283.0	0.899	42 878	1424.5	0.999	215 835	1.78	0.330	270
EPA-20 ^a	1.30	458.7	0.964	35 287	871.9	0.990	67 070	13.27	0.988	1021
EPA-21	1.88	531.9	0.984	28 292	2616.0	0.997	139 149	6.45	0.956	343
EPA-22	1.67	502.1	0.970	30 069	1459.0	0.876	87 363	5.59	0.997	335
EPA-23	2.38	875.2	0.972	36 772	3923.3	0.941	164 844	9.88	0.990	415
EPA-26	1.43	688.7	0.985	46 537	1688.8	0.967	114 108	7.50	0.728	507
mean				33 500 ± 10 800 ^c			162 900 ± 74 000 ^c			517 ± 304 ^d

^a Soils; all others are sediments. ^b % organic carbon. ^c Without EPA-9. ^d Without EPA-9 and -14.

of 22 compounds yielded the following linear relationship (10, 12-14, 18) (Figure 2):

$$\log K_{oc} = -0.686 \log S (\mu\text{g/mL}) + 4.273 \quad (r^2 = 0.933) \quad (2)$$

The calculated K_{oc} values using eq 2 for 2-AA and 6-AC are 15 662 and 67 384, respectively. Although these values are higher than those calculated from eq 1, they are still much lower than the observed K_{oc} values for these two compounds. This further supports the hypothesis that there is an enhancement of the sorption of these two amines above that expected based on hydrophobic bonding but which is nevertheless associated with the organic carbon content of the substrate.

A close examination of the K_{oc} values for 2-AA in relationship to the % organic carbon revealed an inverse relationship. Those substrates with higher organic carbon contents tended to give lower K_{oc} values (closer to the values predicted from eq 2), while low organic carbon containing substrates generally gave higher K_{oc} values. Substrates EPA-8 and -9, which had a very low % organic carbon (0.15% and 0.11%, respectively), gave anomalously high K_{oc} values of 52 659 and 94 276, respectively. From these data, it appears that the amount of sorption of 2-AA is dependent primarily upon the amount of organic carbon in the substrate, as well as upon the relative coverage of the inorganic particle surfaces by the existing organic matter. This hypothesis is further supported by the fact that, while the solubilities of anthracene (9) and 2-AA differ by over 2 orders of magnitude, the K_{oc} values are essentially the same (Figure 2).

In a previous paper, we reported that the % organic carbon/% montmorillonite clay ratio was critical in interpreting the sorption of 1-naphthol on these same substrates (15). When observed values of K_{oc} of 2-AA on each substrate were plotted against the % organic carbon/% montmorillonite clay ratio of the substrates (Figure 3, upper half), it was noted that at ratios below 0.1 there is a very strong inverse relationship, suggesting that clay mineralogy may be important in the sorption of 2-AA. Similar trends were observed for the data for 6-AC (Figure 3, lower half) although they were less pronounced and the relative positions of various substrates differed for the two compounds (2-AA vs. 6-AC). This may be due to steric hinderance effects of the larger 6-AC molecule.

The mechanisms for enhanced sorption of 2-AA and 6-AC must involve one or more specific interactions of the

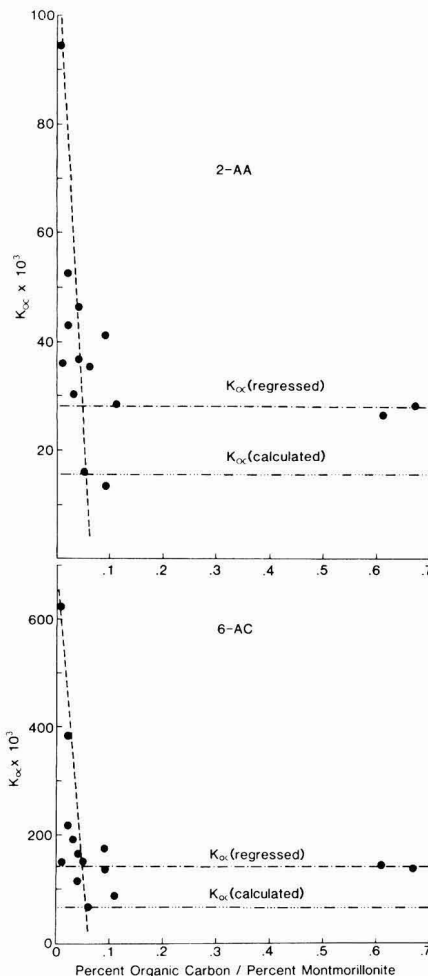


Figure 3. Relationship between the sorption constant (K_{oc}) and the % organic carbon/% montmorillonite ratio.

amine functional group with components of either the substrate organic matter or associated clay minerals.

Parris has shown that amines may undergo both reversible and irreversible reactions with humates to yield a variety of products (22). Benzidine and other aromatic amines are known to react with components of the clay minerals (16, 23, 24). Reactions of these types may account in part for our observations.

The third compound, 9-CA, exhibited linear isotherms with K_p values which ranged from 1.78 to 13.27 on the 14 substrates (Table III). The K_p values were highly correlated with % organic carbon of the sediments. All three soils tended to give high K_p values. No other significant correlations were observed. The K_{oc} values calculated for the sediments tended to converge on an average value of 517 when the anomalously high values obtained on soils EPA-9 and -14 were dropped because they fell more than two standard deviations above the mean. Regression through the origin of K_p vs. % organic carbon for all 11 sediments yielded a K_{oc} value of 422 ($r^2 = 0.751$).

The values of K_{oc} predicted for 9-CA using eq 1 and 2 were 626 and 889, respectively. The close agreement of the observed value of K_{oc} with the calculated values suggests that the sorption of 9-CA to a variety of substrates is controlled by the neutral aromatic portion of the molecule rather than the polar carboxyl anionic moiety. This is consistent with the fact that the surface charge on soils and sediments tends to be negative and therefore the negatively charged carboxyl group on the 9-CA molecule would be expected to be oriented away from the particle surface.

Of the 14 substrates tested, 9-CA tended to be sorbed most strongly to the 3 soils (EPA-9, -14, and -20) and to 1 sediment (EPA-8) which had a very low organic carbon content (0.15%). No consistent pattern of substrate properties was observed which could explain the enhanced sorption of 9-CA on these four substrates. However, various combinations of low % organic carbon, low CEC, low pH, and high silt/clay content may contribute to the high observed values of K_{oc} in these cases. In the case of EPA-14 and -20, the low pH of the soils may result in partial protonation of the 9-CA present, thus reducing the effective solubility and enhancing sorption.

The contrast of the physical properties and sorptive behavior of 2-AA and 9-CA is significant. Although they are similar in molecular size and volume and each exhibits a single but opposite charge in solution at circumneutral pHs, their solubilities and octanol-water partition coefficients differ by approximately 1 order of magnitude and their sorptive behavior expressed as K_{oc} differs by approximately 2 orders of magnitude. In a previous paper, the effective chain length of a series of neutral PAHs was found to be important in determining the relative strength of sorption to a sorbent (13). In the case of these substituted PAH compounds, it is clear that the nature and charge of the polar functional groups contained in molecules of similar size can profoundly influence the sorptive properties of the molecules. In spite of the large differences observed, the predictive value of eq 1 and 2 (particularly of eq 2) remained reasonably high for substrates with high % organic carbon but was reduced for substrates with low organic carbon contents.

Summary and Conclusions

The sorption of 2-aminoanthracene (2-AA), 6-aminochrysene (6-AC), and anthracene-9-carboxylic acid (9-CA) has been studied on 14 sediment and soil substrates. In all cases, the equilibrium isotherms were linear and the resulting partition constants (K_p) for each compound were found to be significantly correlated with the organic carbon

content of the 14 substrates. The K_p values appeared to be independent of any other single substrate characteristics. The enhanced sorption of 2-AA and 6-AC on certain substrates, however, was well correlated with the % organic carbon/% montmorillonite ratio, suggesting that these compounds may be interacting with the inorganic matrix of the sorbent when the ratio is low (<0.1).

Water solubilities (S) and octanol-water partition coefficients (K_{ow}) were determined experimentally for each compound. Predicted sorption constants (K_{oc}) were calculated from S and K_{ow} by using equations developed and reported in a previous series of papers (10, 11, 13, 14). In general, the predicted K_{oc} values were within a factor of 2-3 of the observed values for the three compounds on most of the 14 substrates. For these three compounds, the solubility of the compound was a better predictor of K_{oc} . The reliability of these predictive equations appears to be impaired for substrates with very low carbon contents. The fact that both predictive equations consistently underestimated K_{oc} values for the aromatic amines, 2-AA and 6-AC, suggests that the sorptive mechanisms active for this class of compounds need further study and that caution should be observed in applying these predictive relationships to the sorption of other members of this class of toxic chemicals.

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Optimal Emission Control Strategies for Photochemical Smog

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■ A study of certain aspects of the selection of reactive hydrocarbon and nitrogen oxide emission reductions for photochemical oxidant abatement is carried out. Optimal emission control paths are defined as those minimizing a total cost function consisting of control cost and ozone dosage contributions. Los Angeles County ozone air quality and control cost data are used to formulate an optimal emission reduction path. The analysis is presented primarily to provide insight into the factors involved in designing oxidant control strategies.

Introduction

The determination of hydrocarbon and nitrogen oxide emission reduction levels needed to meet National Ambient Air Quality Standards (NAAQS) for ozone and nitrogen dioxide in major urban areas is a central problem in implementing the Federal Clean Air Act (1-4). The problem involves two major aspects, determining the relationship between hydrocarbon and nitrogen oxide (NO_x) emissions and ozone (O_3) and nitrogen dioxide (NO_2) air quality and identifying available emission control measures. The approach that in many cases is being employed for relating emissions to air quality for photochemical smog in control strategy determinations is the US Environmental Protection Agency's EKMA (Empirical Kinetic Modeling Approach) method that is based on the relationship between peak ozone concentrations achieved during a multihour period and the initial concentrations of reactive hydrocarbons (RHCs) and NO_x (5-8). Figure 1 shows ozone isopleths generated by the EKMA method, the use of which for determining emission reduction levels is described in the caption. A similar ozone-precursor relationship determined by Trijonis (1) from Los Angeles monitoring data is shown in Figure 2.

The basic emission control problem is to select a path from a starting point on Figure 1 (or Figure 2) to the region representing the desired air quality goal, e.g., in Figure 1, the 0.12 ppm isopleth, while at the same time not violating the air quality standard for NO_2 . The purpose of this communication is to demonstrate some properties of optimal paths in the RHC- NO_x plane. To do so requires that optimality be carefully defined, and we will propose a measure of optimality. It is important to note that the analysis that we will present is not intended as a ready framework for the determination of optimal control strategies for photochemical smog. Rather, we hope to provide some insight into the factors entering into such a complex decision and, by demonstrating an example in detail, to show the possibility of applying classical techniques to this problem. This work is, of course, not the first on deter-

mining optimal air pollution control strategies. For additional material we refer the reader to some available literature on this subject (1-4, 9-13). In particular, Bilger and Post (4, 14, 15) have also considered the use of isopleth diagrams relating ozone formation to precursor concentrations for determining control strategies.

Formulation of the Problem

For the purpose of our discussion let us focus on Figure 2, the ozone-precursor relation expressed in terms of the number of days per year of violation of a given O_3 level, and RHC and NO_x emission levels. Although our analysis will apply without conceptual change to Figure 1, the standard EKMA representation, we choose to use the data of Figure 2 because Trijonis (1) developed detailed control costs associated with the emission levels on the ordinate and the abscissa. The availability of control cost data is essential to our analysis.

The isopleths shown in Figure 2 can be assumed to be obtained from a surface $z = f(x, y)$ where z = number of days per year that hourly-average ozone concentrations exceeded 0.10 ppm, x = Los Angeles County RHC emissions (ton/day), and y = Los Angeles County NO_x emissions (ton/day). The function f can be approximated in principle by fitting a polynomial $f(x, y)$ to the data used to construct the surface on the isopleths.

The emission control problem is then as follows: If t represents time (in years), it is desired to determine a path $\alpha(t), \beta(t)$ that proceeds from (α_0, β_0) , the emission levels at the starting point, i.e., current air quality, to desired air quality. We use $\alpha(t)$ and $\beta(t)$ to denote the emission reduction path in the x - y plane; thus, $\alpha(t)$ and $\beta(t)$ refer to the RHC and NO_x emissions, respectively. In Figure 1 desired air quality is represented by any point on the 0.12 ppm isopleth. One would also ordinarily require that the desired air quality also satisfy the constraint that the NO_x concentration not exceed the value corresponding to the NAAQS for NO_2 . That aspect will not be explicitly considered here, although it can in principle be treated through the introduction of a constraint on the terminal NO_x concentration. In Figure 2 the goal is taken to be the line corresponding to 50 day/yr violations. We are interested in determining an optimal path; therefore, we must define the basis for judging optimality. In general, we define a cost or "performance index", J that consists of two components, J_1 and J_2 , J_1 representing the control costs and J_2 representing the costs associated with the air quality level. The optimal path will then be that path minimizing J .

Let us consider the development of a form of the control cost portion, J_1 , of the overall performance index J . The control costs determined by Trijonis (1) are shown in Figure 3. The form of the control cost curves in Figure

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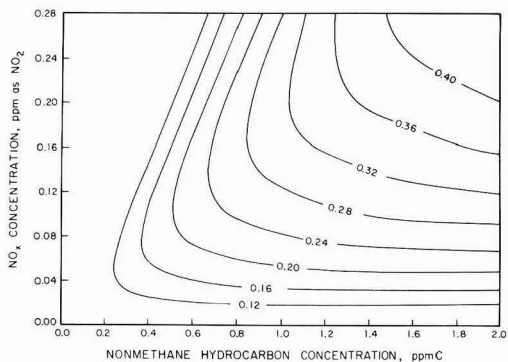


Figure 1. Standard ozone isopleth diagram for US Environmental Protection Agency EKMA Method (5-β). The reactive hydrocarbon composition in the chemical mechanism used to generate this figure is represented by a surrogate mixture of propylene, *n*-butane, and aldehydes. The standard isopleth diagram is generated by assuming an initial propylene-butane split of 25% propylene and 75% *n*-butane as carbon. It is also assumed that 5% of the initial carbon atoms are present as aldehydes, 40% formaldehyde, and 60% acetaldehyde as carbon. The composition of the precursors can be altered by changing the aldehyde fraction of the initial NMHC concentration, the hydrocarbon mix, or the fraction of the initial NO_x concentration that is added as NO₂, the standard isopleth value of the initial NO₂/NO_x ratio for the pre-0800 emissions is 0.25. The concentrations shown on the axes can be related to ambient values by assuming that they result from pre-0800 emissions. This figure can be used to predict the percent reductions in NMHC and NO_x emissions needed to achieve a desired ozone concentration based on a measured ozone value. Only a NMHC/NO_x ratio and an observed maximum 1-h average ozone concentration (the so-called design ozone value) are needed. The design ozone value is the maximum 1-h average concentration observed by all monitoring stations within the area 15–30 km downwind of the central business district during the base year. The NMHC/NO_x ratio is determined from the 6–9 a.m. average NMHC and NO_x concentrations.

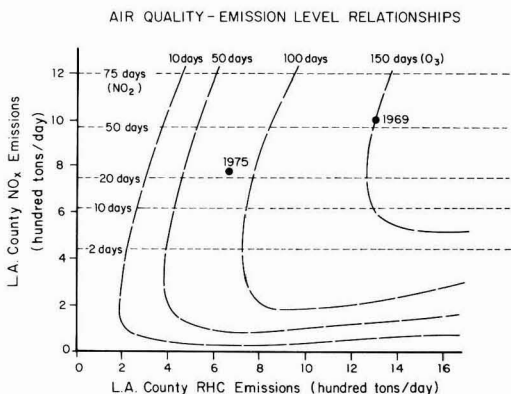


Figure 2. Estimated numbers of days per year of midday ozone concentrations exceeding 0.10 ppm and of NO₂ concentrations exceeding 0.25 ppm in Los Angeles as a function of Los Angeles County RHC and NO_x emissions (1).

3 suggests that J_1 can be represented by a modified path length. It can be shown that the introduction of a factor k affecting one of the coordinates of the velocity of the path ($d\alpha/dt, d\beta/dt$) can generate constant cost curves qualitatively similar to those of Figure 3. Therefore, we are led to propose the following form of J_1 :

$$J_1 = \int_0^{t_f} \{(\alpha/dt)^2 + k(t)(d\beta/dt)^2\}^{1/2} dt \quad (1)$$

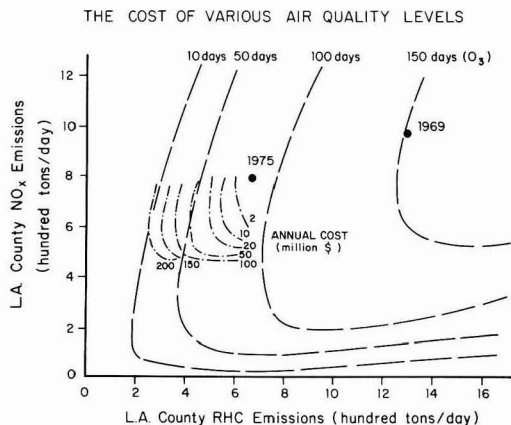


Figure 3. Ozone air quality lines of Figure 2 with annual control costs superimposed relative to the 1975 Los Angeles County emission levels (1).

The dependence of k on t in J_1 accounts for interactions in the control costs that are reflected in the cost curves in Figure 3. The form of J_1 given in eq 1 is versatile enough to fit numerical control cost data. The determination of $k(t)$ as equal to γ_0^2 , a constant, is discussed in Appendix A.

The form of J_2 can be defined as the cost of the ozone "dosage" over the time period of interest, $[0, t_f]$

$$J_2 = \int_0^{t_f} f dt \quad (2)$$

The problem that we wish to solve is as follows. Determine the emission reduction path $\alpha(t), \beta(t)$, over the time period $[0, t_f]$ starting at point $(x_0, y_0) = (\alpha_0, \beta_0)$ and ending on the target curve $f(x, y) = \xi$ such that $J = J_1 + \kappa J_2$ is minimized. The constant κ measures the relative importance between the two factors of the cost and is considered as given. The family of admissible paths $(\alpha(t), \beta(t))$ consists of those for which $\alpha(t)$ and $\beta(t)$ are smooth and, in fact, can be expressed as $\alpha(t) = x(\beta(t))$. This condition excludes paths with $d\beta/dt = 0$ at some time t , a restriction introduced only to simplify the mathematical treatment. The admissible paths can then be expressed as $(x(\beta), \beta)$, where time need no longer be explicitly indicated. The target curve can be expressed as $x = g(\beta)$.

To make the formulation specific to our interests, a functional form for $f(x, y)$ must be determined. In an attempt to obtain the best second-order polynomial in x and y approximating f for the region in Figure 3 covered by the dash-and-dot curves, the following linear form was found to be sufficiently accurate

$$f(x, y) = c_0 + a_1x + b_1y \quad (3)$$

with $c_0 = 5.535$, $a_1 = 13.21$, and $b_1 = -2.56$.

With the expressions for f and k , J becomes

$$J = - \int_{\beta_1}^{\beta_2} F(x, dx/d\beta, \beta) d\beta \quad (4)$$

where

$$F(x, dx/d\beta, \beta) = [\gamma_0^2 + (dx/d\beta)^2]^{1/2} + \kappa(c_0 + a_1x + b_1\beta) \quad (5)$$

and where the minus sign in eq 4 arises because of the change of integration variable from time to NO_x emission level β and because x must be an increasing function of

β ; i.e., neither RHC nor NO_x emission increases are allowed. The initial point (α_0, β_0) is selected as that corresponding to 1975 emission levels in Figure 2, namely, (6.66, 7.86) with $z_0 = 73.39$. The target curve is $z_1 = \xi = 50$.

Optimal Paths

The problem posed above lies in the domain of the classical calculus of variations (16). The application of the Euler-Lagrange equation

$$\frac{\partial F}{\partial x} = \frac{d}{d\beta} \left(\frac{\partial F}{\partial x'} \right) \quad (6)$$

where x' denotes $dx/d\beta$, leads to the following family of candidate optimal paths

$$x(\beta) = K_2 - \frac{\gamma_0}{\kappa \alpha_1} [1 - (\kappa \alpha_1 \beta + K_1)^2]^{1/2} \quad (7)$$

subject to the boundary conditions

$$x(\beta_0) = \alpha_0 \quad x(\beta_1) = g(\beta_1) \quad (8)$$

and to the transversality condition

$$f(\beta_1, x(\beta_1), x'(\beta_1)) = [g'(\beta_1) - x'(\beta_1)] (\partial F / \partial x)(\beta_1, x(\beta_1), x'(\beta_1)) \quad (9)$$

which must be added to account for the freedom of the optimal path to terminate at any point on the target line $z = \xi$, where $\xi = c_0 + a_1 g(\beta_1) + b_1 \beta_1$. Equations 8 and 9 permit the determination of the three unknown constants, K_1 , K_2 , and β_1 . This determination is shown in Appendix B.

Before the optimal paths are studied, it is instructive to examine the behavior of the problem when only J_1 or only J_2 constitutes the performance index J . In the case in which $J = J_1$, it is readily determined that the optimal path from (α_0, β_0) to the $z = \xi$ line is the straight line

$$x = (\alpha_1 \gamma_0^2 / b_1) (\beta - \beta_0) + \alpha_0 \quad (10)$$

For the numerical values that we intend to study ($\alpha_0 = 6.66$, $\beta_0 = 7.86$, $\xi = 50$), we find $\beta_1 = 7.87$, a value slightly greater than β_0 . (The restriction of nonincreasing β is not imposed in this case.) With $J = J_2$, an optimization problem does not result. Nevertheless, we can obtain information about the qualitative behavior by considering straight-line trajectories of different final points β_1 on the target line $z = \xi$

$$x(\beta) = \frac{\beta - \beta_0}{\beta_1 - \beta_0} (x_1 - \alpha_0) + \alpha_0 \quad (11)$$

Letting $\Delta\beta = \beta_1 - \beta_0$, $\Delta\beta^2 = \beta_1^2 - \beta_0^2$, $\Delta x = x_1 - \alpha_0$, we find

$$J_2 = \frac{1}{2} (a_1 \Delta x / \Delta\beta + b_1) \Delta\beta^2 + (c_0 + \alpha_1 \alpha_0) \Delta\beta - a_1 \beta_0 \Delta x \quad (12)$$

Since Δx and $\Delta\beta$ are related by $a_1 \Delta x + b_1 \Delta\beta + \delta = 0$, a final form of J_2 depending only on β_1 is obtained, from which $dJ_2/d\beta_1$ can be evaluated. For the numerical values listed above, $dJ_2/d\beta_1 = 61.70$, a value independent of β_1 , which indicates that β_1 should be reduced to reduce J_2 . Thus, a problem with $J = J_2$ will lead to paths for which β is decreased.

The optimal path for $\kappa = 0.5$ is shown in Figure 4. We observe that the path is close to the $\beta = \beta_0$ line. This result is consistent with the paths expected from the interplay between the J_1 and J_2 terms in J . The influence of J_2 is small because the admissible values of κ (between 0 and about 0.6) are small. Paths for other values of κ are quite

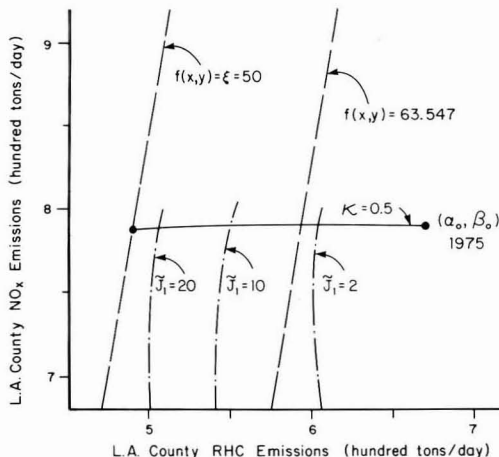


Figure 4. Optimal RHC and NO_x emission reduction path from 1975 Los Angeles County emission levels to a condition of 50 day/yr of O_3 levels exceeding 0.10 ppm. The path is determined for the weighting coefficient $\kappa = 0.5$. The figure is an enlargement of the region from that in Figure 3.

close to that for $\kappa = 0.5$. Some of the numerical values associated with the optimal path can be determined simply, including J_1 and J_2 , from

$$J_1 = \frac{\gamma_0}{\kappa \alpha_1} [\sin^{-1} u_1 - \sin^{-1} u_0] \quad (13)$$

$$J_2 = \kappa (c_0 + a_1 K_2) \Delta\beta + \frac{\kappa b_1}{2} \Delta\beta^2 - \frac{\gamma_0}{2\kappa \alpha_1} [u_1 (1 - u_1^2)^{1/2} - u_0 (1 - u_0^2)^{1/2}] + \frac{\gamma_0}{2\kappa \alpha_1} [\sin^{-1} u_1 - \sin^{-1} u_0] \quad (14)$$

An interesting feature of the optimal path is that little NO_x reduction is called for relative to RHC reduction. This behavior is dictated virtually totally by the structure of the control cost curves of Figure 3, since these curves were used to form the control cost contribution J_1 to the overall performance index J . Other control cost data that indicate a more equitable relative cost per pound of reduction between RHC and NO_x would most likely lead to paths with more NO_x control. Furthermore, had we introduced a constraint β^* on the terminal NO_x value corresponding to the NAAQS for NO_2 , and if the starting point β_0 exceeded that value, the paths would, of necessity, satisfy $\beta_1 \leq \beta^*$. We chose not to study that aspect here so as to be able to examine paths for which only O_3 was of concern.

With slight variations, the same approach can be used for related problems, such as that with a fixed final point. Notice that the choice of k as independent of t (see Appendix A) makes the entire problem explicitly independent of time. In fact, time explicitly enters the problem only through $k(t)$ in J_1 . If k is dependent on t , the problem can be treated in its original form, e.g., $(\alpha(t), \beta(t))$. In different regions of the x - y plane, second-order approximations for f may also be necessary.

Conclusions

A study of the qualitative features of optimal RHC and NO_x emission reduction paths for control of photochemical smog has been performed. A total cost or performance index consisting of the sum of control cost and ozone dosage contributions was proposed. The minimization of

the performance index was carried out by classical calculus of variations procedures. The ozone air quality and control cost data of Trijonis (1) were used to compute optimal Los Angeles County RHC and NO_x emission reductions from 1975 levels to achieve 50 day/yr of peak hourly-average ozone values exceeding 0.10 ppm at downtown Los Angeles. The analysis presented is not intended as a ready framework for the determination of optimal control strategies for photochemical smog; rather we hope to provide some insight into the factors entering into emission reduction policies. The differentiable-path integral-cost formulation permits the determination of analytical solutions and bounds on the parameters of the problem, allowing one to examine the properties of different paths.

Acknowledgments

We extend appreciation to Glen Cass for helpful discussions.

Appendix A

Determination of $k(t)$. The control cost component of J, J_1 , is given by eq 1, in which $k(t)$ is an empirical function to be determined from control cost data, such as those in Figure 3. The fact that the cost curves in Figure 3 do not deform significantly leads one to propose a simple expression for $k(t)$

$$k(t) = (\gamma_0 + \gamma_1 t)^2 \quad (A.1)$$

where γ_0 and γ_1 are parameters to be determined from the data. Let us assume for the moment that $0 < \gamma_1 \ll \gamma_0$, and consider the linear paths, $\alpha(t) = \alpha_0 + rt$ and $\beta = \beta_0 + st$. Then, selecting $t_f = 1$, one can consider J_1 as a function of r and s

$$J_1 = \int_0^1 [r^2 + k(t)s^2]^{1/2} dt$$

$$= \frac{1}{2\gamma_1} \left\{ (\gamma_0 + \gamma_1)[r^2 + (\gamma_0 + \gamma_1)^2 s^2]^{1/2} - \gamma_0(r^2 + \gamma_0^2 s^2)^{1/2} + \frac{r^2}{|s|} \ln \frac{|s|(\gamma_0 + \gamma_1) + [r^2 + (\gamma_0 + \gamma_1)^2 s^2]^{1/2}}{|s|\gamma_0 + (r^2 + \gamma_0^2 s^2)^{1/2}} \right\} \quad (A.2)$$

By defining $h = |s|/r, \bar{r} = r - 2, \bar{h} = h - 1$, and linearizing J_1 by

$$J_1(r, s) = L(\bar{r}, \bar{h}) \simeq L(2, 1) + \bar{r}(\partial L/\partial r) + \bar{h}(\partial L/\partial h) \quad (A.3)$$

we can estimate γ_0 from

$$\gamma_0 \simeq [(\partial L/\partial r)^2 - 1]^{1/2} \quad (A.4)$$

and γ_1 from the appropriate root of

$$\frac{2\gamma_0}{(\partial L/\partial r)\gamma_1^2} + \left[2\gamma_0^2 - \left(\frac{\partial L}{\partial h} \right) \right] \gamma_1 - \frac{\gamma_0^2}{(\gamma_0 + \partial L/\partial r)^2} = 0 \quad (A.5)$$

For the data in Figure 3, we find $\gamma_0 = 33.8$ and $\gamma_1 = 0.005$, confirming the earlier hypothesis.

Appendix B

Determination of K_1, K_2 , and β_1 . Letting $u_1 = \kappa a_1 \beta_1 + K_1$ and $u_0 = \kappa a_1 \beta_0 + K_1$, in eq 7-9 we obtain

$$\alpha_0 = K_2 = \frac{\gamma_0}{\kappa a_1} (1 - u_0^2)^{1/2} \quad (B.1)$$

$$\frac{\xi - c_0 - b_1 \beta_1}{a_1} = K_2 - \frac{\gamma_0}{\kappa a_1} (1 - u_1^2)^{1/2} \quad (B.2)$$

$$\gamma_0 / (1 - u_1^2)^{1/2} + \kappa \xi = u_1 [\gamma_0 u_1 / (1 - u_1^2)^{1/2} + b_1 / a_1] \quad (B.3)$$

From these equations, u_1 is obtained as the appropriate root of $Au_1^2 + Bu_1 + C = 0$, where $A = (b_1/a_1)^2 + \gamma_0^2$, $B = -2\kappa \xi b_1/a_1$, and $C = (\kappa \xi)^2 - \gamma_0^2$. The discriminant of the quadratic equation should be nonnegative for real solutions, and thus the following bounds are obtained for the group $\kappa \xi$:

$$0 < \kappa \xi \leq [(b_1/a_1)^2 + \gamma_0^2]^{1/2} \quad (B.4)$$

For the parameters of the problem, the value of the upper limit is 33.81. To be consistent with the hypothesis of nonincreasing α and β , the sign of the resolvent must be positive, and u_1 is determined uniquely by

$$u_1 = \frac{\kappa \xi b_1/a_1 + \gamma_0 [(b_1/a_1)^2 + \gamma_0^2 - (\kappa \xi)^2]^{1/2}}{\{ (b_1/a_1)^2 + \gamma_0^2 \}^{1/2}} \quad (B.5)$$

By similar manipulations, another equation, $D\beta_1^2 + E\beta_1 + F = 0$, is obtained, where $D = \kappa^2 [(b_1/\gamma_0)^2 + a_1^2]$, $E = -2\kappa [b_1(1 - u_1^2)^{1/2}/\gamma_0 + a_1 u_2 + \kappa (b_1 \lambda/\gamma_0^2 + a_1^2 \beta_1)]$, $F = \kappa [2a_1 \beta_0 + 2\lambda(1 - u_1^2)^{1/2}/\gamma_0 + \kappa (a_1^2 \beta_0^2 + \lambda^2/\gamma_0^2)]$, and $\lambda = \xi - c_0 - a_1 \alpha_0$. For physically plausible solutions the following two conditions must hold:

$$\delta = b_1 \beta_0 - \lambda > 0 \quad (B.6)$$

$$4\kappa^2 (b_1(1 - u_1^2)^{1/2}/\gamma_0 - a_1 u_1)^2 + 8\kappa^2 a_1 [(1 - u_1^2)^{1/2} - b_1 u_1/\gamma_0] (\delta/\gamma_0) - 4\kappa^4 a_1^2 (\delta/\gamma_0)^2 \geq 0 \quad (B.7)$$

The reductions that can be obtained are bounded by these conditions, which depend on the starting point and the data of the problem.

By solving the two quadratic equations, $Au_1^2 + Bu_1 + C = 0$ and $D\beta_1^2 + E\beta_1 + F = 0$, one can determine u_1 and β_1 . The two constants K_1 and K_2 can then be evaluated and the optimal path is completely defined. Equations B.4, B.6, and B.7 result from the condition that a physically plausible solution exists. Equation B.4 is particularly interesting in that it places a bound on the largest value of κ that can be used in J consistent with a particular target line $z = \xi$.

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Characterization of Polycyclic Ketones and Quinones in Diesel Emission Particulates by Gas Chromatography/Mass Spectrometry[†]

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■ The chemical composition of two neutral, mutagenic subfractions of a diesel particulate extract sample was examined by capillary gas chromatography/mass spectrometry. Most compounds identified were polar derivatives of three- to five-ring polynuclear aromatic hydrocarbons. Ketone, quinone, carboxaldehyde, and hydroxy derivatives and their alkyl homologues were characterized. 9-Fluorenone and its C₁-C₄ alkyl homologues were the single largest family of compounds detected. Some of the compounds characterized are bacterial mutagens; the mutagenicity of others is not known at this time.

Introduction

Particulates originating in vehicular engine emissions are major contributors to air pollution, and the projected increase in the use of diesel automobiles will increase this contribution. The composition of organic compounds adsorbed onto such particulates is enormously complex.

The possible adverse health effects of diesel emission particulates have recently received considerable attention (1, 2). Diesel particulates are mostly of respirable size (1) and may constitute a significant inhalation health hazard to the human population. Recent studies utilizing the Ames *Salmonella* mutagenesis assay and other short-term bioassay methods have indicated that organic extracts of these particulates possess significant mutagenic activity (3, 4) even in the absence of mammalian enzymes. These findings have stimulated an intensive research effort to identify mutagens in diesel particulates.

The major class of mutagenic compounds reported (5-7) in automobile emission particulates at the time that this work was initiated was polynuclear aromatic hydrocarbons (PAHs). We have reported (8, 9) our preliminary findings on the composition of PAHs in diesel particulate extracts. However, since PAHs require enzymatic activation to express mutagenicity, we anticipated that other potential mutagens, as yet unrecognized, may be present in diesel particulate adsorbates. By utilizing the *Salmonella* mutagenesis assay and chromatographic methods, we have isolated fractions of diesel particulate extracts showing

higher mutagenic potency than the PAH fraction (4). A comprehensive characterization of the potential mutagens in each mutagenic fraction has therefore been initiated.

In this paper we describe the chemical composition of two highly mutagenic subfractions of the neutral fraction of a diesel particulate extract, as determined by high-resolution gas chromatography/mass spectrometry (GC/MS). Our objective was to characterize all compounds detected by GC/MS, since there was no indication of the possible identity of the mutagens in the two fractions. Once chemical identities are established, the compounds' mutagenic properties can be determined, if they are not already in the literature. Control strategies can then be developed to make the emissions toxicologically safer.

Experimental Section

Particulate Collection and Sample Preparation. Diesel emission particulates were collected from a Volkswagen Rabbit by the dilution tunnel method (10) on (20 × 20) in.² Teflon-coated Pallflex T60A20 glass-fiber filters. The filters were Soxhlet extracted with dichloromethane for 24 h, and several extracts were combined to give a composite sample.

The two subfractions whose chemical characterization is reported here were isolated by silica gel chromatographic fractionation of the neutral extract. The fractionation method and the mutagenicity of the subfractions have been briefly described elsewhere (4).

Gas Chromatography/Mass Spectrometry. GC/MS experiments were performed on a Finnigan 4000 electric quadrupole mass spectrometer equipped with an INCOS 2300 data system and a Finnigan gas chromatograph. The samples were chromatographed on a 45-m SE54 wall coated glass capillary column, programmed from 110 °C (2 min) to 170 °C at 10 °C/min, to 240 °C at 5 °C/min, to 290 °C at 7 °C/min. The mass spectrometer was operated at 70 eV. In the electron impact (EI) mode, it was scanned from 50 to 400 amu every 2 s. In the chemical ionization (CI) mode it was scanned from 100 to 400 amu every 2 s. Methane was used as the reagent gas.

Chemicals. Anthraquinone, phenanthrenequinone, 9-fluorenone, anthrone, 7H-benz[de]anthracen-7-one, and benz[a]anthracene-7,12-dione were purchased from Aldrich Chemical Co. and purified if necessary by recrystallization. 4-Methyl-9-fluorenone and three dimethyl-9-fluorenone isomers (3,6-, 1,8-, and 2,4-) were obtained from Dr. R. A. Zweidinger of the Mobile Sources Emissions Research Branch, U.S. Environmental Protection Agency.

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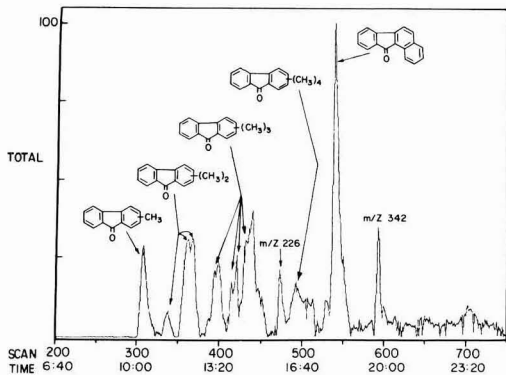


Figure 1. Total ion chromatogram (EI) of subfraction 4.

Results and Discussion

The neutral fraction constituted 94% by mass of the total diesel particulate extract. Seven subfractions of this fraction were prepared by silica gel column chromatography. Ames *Salmonella* mutagenesis assays of the subfractions indicated that subfraction 4 (3.8% of the neutral fraction by mass) had the highest specific mutagenicity (revertants/ μg of extract) and accounted for 52% of the direct-acting mutagenicity of the neutral fraction. Subfraction 5 (6.8% of the neutral fraction by mass) also had significantly high specific activity, accounting for 13% of the direct mutagenicity of the neutral fraction. The specific activities of these subfractions were higher than that of the PAH subfraction, which showed minor activity only in the presence of microsomal enzymes.

Bioassay results also indicated that these subfractions contained direct-acting mutagens, as well as promutagens which require metabolic activation. The elution patterns of these subfractions suggested that they contained compounds more polar than parent and alkyl-substituted PAHs. Considering the chemical manipulations involved in the preparation of the subfractions, it was inferred that the mutagens were apparently stable chemicals and unlikely to be alkylating agents, a common type of reactive, direct-acting mutagen. No other information regarding the chemical nature of the compounds was available at the outset.

Glass capillary GC with flame ionization detection showed that each subfraction had an extremely complex composition. Chromatographic conditions could not be completely optimized, since not even possible identities of the constituents were known. The column used was excellent for difficult-to-separate PAH isomers. To obtain maximum structural information about the constituents, we examined the subfractions by capillary GC/MS under both EI and CI conditions. A thorough search of the reconstructed ion chromatograms was made to identify the mass spectra of as many compounds as possible. Fragments of parent ions were identified by time-concurrent elution of the parent and the appropriate fragment ions in the mass chromatograms. Background levels were high, possibly from decomposition of some constituents of the sample. Interference-free spectra were obtained by using computer-assisted techniques.

Subfraction 4. The total ion chromatogram of subfraction 4 in the EI mode is shown in Figure 1. The EI mass spectrum of a major component (Figure 2, scan 308) showed the parent ion at m/z 194, with a relative abundance (RA) of 1.0. This compound was identified as methyl-9-fluorenone. The molecular ion lost 29 amu (CO

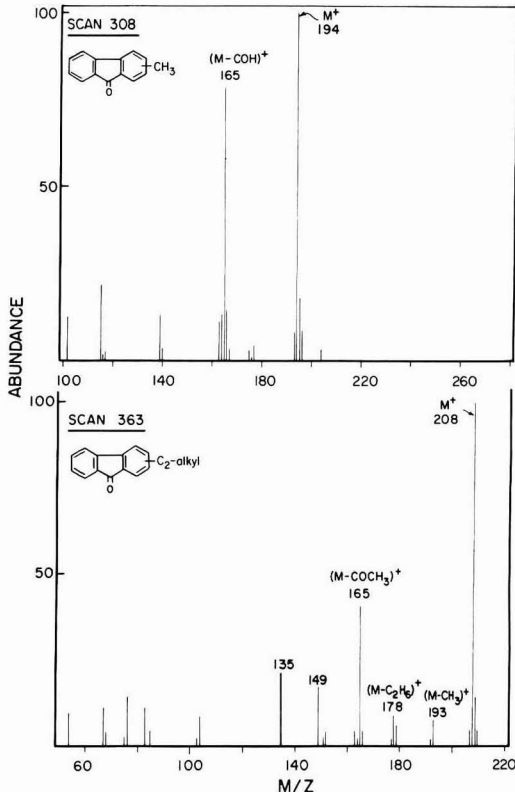


Figure 2. Mass spectra (EI) of scans 308 and 363, subfraction 4.

+ H) to give a m/z 165 ion (RA = 0.7). The spectrum is in agreement with the observed spectrum of 4-methyl-9-fluorenone, as determined in our laboratories, and with literature spectra of methyl-9-fluorenone (11). In the CI spectrum ($M + 1$)⁺ ion was observed at m/z 195, confirming the molecular weight. Other possibilities, such as anthrone/phenanthrone or methylbenzo[*c*]cinnoline, were less likely because of their different elution volumes from the silica gel column.

The most abundant constituent of this subfraction (scan 539) was identified as benzo[*a*]fluorenone (m/z 230, RA = 1.0). The major fragment was observed at m/z 202 (RA = 0.17), corresponding to loss of CO. The ($M + 1$)⁺ ion at m/z 231 in the CI mass spectrum confirmed this basic structure, and its GC retention time and silica gel chromatographic elution volume corroborated this assignment.

Three compounds (scans 338, 363, and 368) with parent ions at m/z 208 (RA = 1.0) and key fragment ions at m/z 193 (RA = 0.07) and m/z 165 (RA = 0.48) were assigned a C_2 -alkyl-9-fluorenone structure. (See Figure 2 for the spectrum of scan 363.) The EI mass spectra were in agreement with the spectra of two isomeric dimethyl-fluorenone, as determined in our laboratories, as well as with mass-spectral data in the literature (11, 12). Since the mass spectra of isomeric C_2 -alkyl-9-fluorenone are strikingly similar, isomer-specific identification was not possible by GC/MS. Indeed, no definite isomeric structure could be assigned to any alkyl-9-fluorenone, since only a few isomers were available to us and fragmentation was not homologue specific. Some alkyl-9-fluorenone have been reported by Erickson et al. (12) in a diesel particulate extract.

TABLE I. Compounds Characterized by GC/MS in Subfraction 4

scan no.	EI parent peak	compd
308	194	methyl-9-fluorenone
338	208	C ₂ -alkyl-9-fluorenone
363	208	C ₂ -alkyl-9-fluorenone
368	208	C ₂ -alkyl-9-fluorenone
394	222	C ₃ -alkyl-9-fluorenone
400	204	4 <i>H</i> -cyclopenta[<i>def</i>]phenanthren-4-one
415	222	C ₃ -alkyl-9-fluorenone
422	222	C ₃ -alkyl-9-fluorenone
431	222	C ₃ -alkyl-9-fluorenone
433	212	9 <i>H</i> -thioxanthen-9-one
438	206	anthracene/phenanthrene-9-carboxaldehyde
440	218	hydroxypyrene/fluoranthene
452	236	C ₄ -alkyl-9-fluorenone
473	226	C ₂ -alkylnaphthofurancarboxaldehyde
475	236	C ₄ -alkyl-9-fluorenone
488	226	unidentified, hydroxy - <i>m/z</i> 210
492	236	C ₄ -alkyl-9-fluorenone
497	220	methylanthracene/phenanthrene-carboxaldehyde
539	230	benzo[<i>a</i>]fluorenone
594	342	unidentified

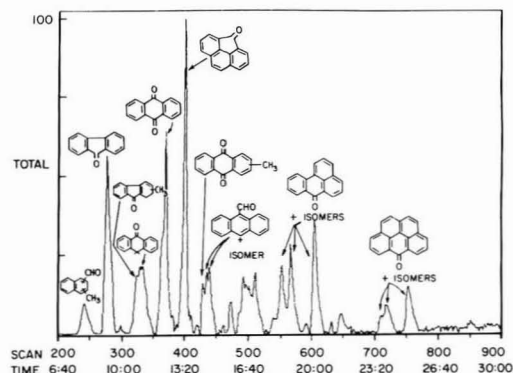
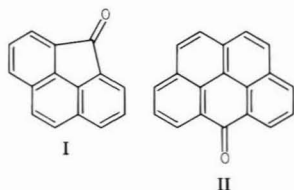


Figure 3. Total ion chromatogram (EI) of subfraction 5.

Other compounds characterized in this subfraction are also listed in Table I. In all cases the assigned molecular weights were confirmed by the presence of the corresponding (M + 1)⁺ ions in the CI mass spectra. Additional compounds will presumably be found in this subfraction. The mass spectra of some should be assigned appropriate structures, but others may not be amenable to GC/MS analysis.

Subfraction 5. The total ion chromatogram of subfraction 5 determined under EI conditions is shown in Figure 3; the CI chromatogram was virtually identical.

A major constituent at scan 400 (Figure 4, *m/z* 204, RA = 1.0) was characterized as 4*H*-cyclopenta[*def*]phenanthren-4-one (I). The assignment was corroborated



by the presence of a key fragment at *m/z* 176 (M⁺ - CO,

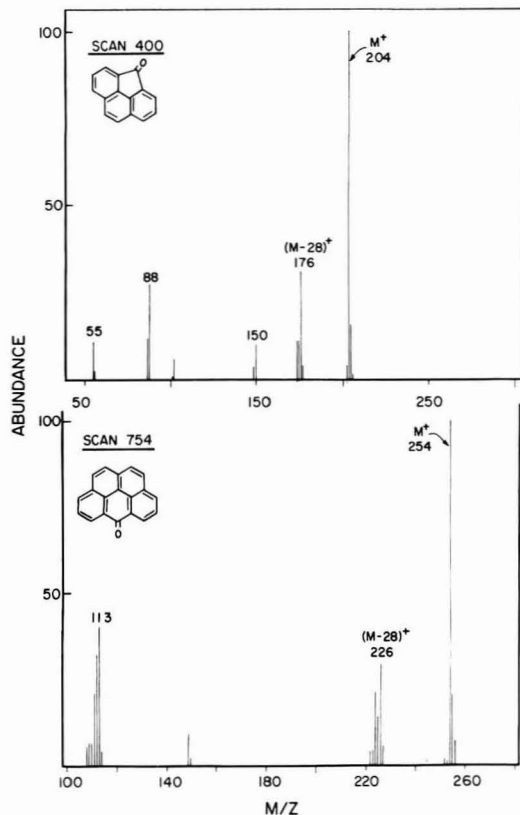


Figure 4. Mass spectra (EI) of scans 400 and 754, subfraction 5.

RA = 0.3) and the (M + 1)⁺ ion at *m/z* 205 in the CI mass spectrum. This compound had not been reported in any diesel particulate sample but had been found in carbon-black adsorbates (13). Our EI mass spectrum is in agreement with the reported spectral data. A small amount of this compound was also detected in subfraction 4.

Three compounds with parent ions at *m/z* 254 were detected. The mass spectra of all three were virtually identical; the parent ion in each case lost 28 amu (CO) to give the *m/z* 226 fragment (Figure 4). These spectral features are consistent with the reported (13) mass spectrum of 6*H*-benzo[*cd*]pyren-6-one (II), although several isomers of this basic structure are possible. For all three compounds the CI mass spectra showed (M + 1)⁺ ions at *m/z* 255.

Three significant components with parent ions at *m/z* 222 were detected. Two had major fragment ions at *m/z* 207 (M - CH₃, RA = 0.08), *m/z* 194 (M - CO, RA = 0.42), *m/z* 166 (M - C₂O₂, RA = 0.31), and *m/z* 165 (M - C₂O₂H, RA = 1.0). These two were characterized as methylanthraquinone/phenanthrenequinone. The mass spectrum of the third was significantly different and was in agreement with C₃-alkyl-9-fluorenone.

Anthracene-9-carboxaldehyde and phenanthrene-9-carboxaldehyde (*m/z* 206, RA = 1.0) were abundant in this subfraction. Both spectra showed strong fragment ions at *m/z* 205 (M - H, RA = 0.52), *m/z* 178 (M - CO, RA = 0.3), and *m/z* 177 (M - CHO, RA = 0.46), indicative of an aromatic aldehyde. Since the retention times of these compounds are very close, a definite assignment to either

TABLE II. Compounds Characterized by GC/MS in Subfraction 5

scan no.	EI par-ent peak	compd
245	170	methylnaphthaldehyde
276	180	9-fluorenone
284	184	C ₂ -alkylnaphthaldehyde
328	194	methyl-9-fluorenone
332	194	anthrone/phenanthrone
365	196	9H-xanthen-9-one
370	208	anthraquinone
400	204	4H-cyclopenta[def]phenanthren-4-one
436	206	anthracene/phenanthrene-9-carboxaldehyde
441	206	anthracene/phenanthrene-9-carboxaldehyde
421	222	C ₃ -alkyl-9-fluorenone
431	222	methylanthraquinone/phenanthrenequinone
439	222	methylanthraquinone/phenanthrenequinone
454	218	hydroxypyrene/fluoranthene
462	218	hydroxypyrene/fluoranthene
474	236	C ₄ -alkyl-9-fluorenone
492	236	C ₂ -alkylanthraquinone
511	220	methylanthracene/phenanthrene-9-carboxaldehyde
549	256	unidentified (an oxy-PAH)
553	230	benz[de]anthracene/benzofluorenone
567	230	benz[de]anthracene/benzofluorenone
604	230	7H-benz[de]anthracen-7-one
633	278	dibutyl phthalate
648	258	benz[a]anthracenedione
663	244	hydroxychrysen/benz[a]anthracene/triphenylene
710	254	benzo[cd]pyrene
717	254	benzo[cd]pyrene
754	254	benzo[cd]pyrene

was not possible. Other isomeric structures cannot be completely discounted since reference standards were not available.

Two compounds of *m/z* 194 were characterized as anthrone/phenanthrone and methyl-9-fluorenone. The only difference in their mass spectra was that the former had a slightly higher relative abundance of the *m/z* 165 ion. The methyl-9-fluorenone isomer in this subfraction was different from the one in subfraction 4. The presence of anthrone/phenanthrone in this subfraction is consistent with the elution volume of these two compounds from the silica gel column. We are seeking additional evidence to differentiate among these and methyl-9-fluorenone.

Additional compounds identified in this subfraction are also listed in Table II. In all cases the EI and CI mass spectra were consistent with the assigned structures. For 9-fluorenone, anthraquinone, and 7H-benz[de]anthracen-7-one the GC retention times were in agreement. Other compounds not amenable to GC/MS detection could also have been present.

Virtually all compounds characterized in these subfractions are oxy-PAH derivatives; 9H-thioxanthen-9-one and 9H-xanthen-9-one are the only two oxyheterocyclics detected. Although some of these compounds could conceivably be formed by oxidation of the corresponding parent PAHs during sample collection, the array of oxy-PAHs is much wider than that expected from the parent PAHs detected in the extract. It appears likely that many of the oxy-PAHs are formed during combustion. Also since a wide variety of PAHs are frequently detected in airborne particulates, it is less likely that the particulate-adsorbed PAHs will be oxidized extensively during the relatively

short sample-collection period.

After our study was completed, Schuetzle et al. (14) reported several oxy-PAHs in two diesel particulate extract samples. They and others (15) have also reported a few mutagenic nitro-PAHs in some diesel particulate extracts. We have made an extensive search for nitro-PAHs in the reconstructed ion chromatograms of the two subfractions of the sample examined, but none was detected. In low concentrations, however, these and some other compounds could go undetected by full-scan mass spectrometry, particularly because operating conditions were not optimized for any specific class of compounds. Also composition of particulate-adsorbed organics from different vehicles is likely to be different, and complementary studies of similar particulate extracts from other vehicles are desirable. The high polarity and the low vapor pressure of these compounds and other polar derivatives of PAHs (e.g., epoxides, anhydrides, etc.) make them less suitable for GC/MS detection. PAH derivatives with reactive functionalities may also be unstable to varying degrees on silica gel and may thus escape detection.

The mutagenicity of most compounds reported here is unknown. A few benzopyrene ketones have been reported to be direct-acting mutagens (16), as are oxidation products of pyrene and some hydroxy-PAHs (17). Pyrene-3,4-dicarboxylic acid anhydride, recently reported in a diesel particulate extract, is also a weak direct-acting mutagen (18). Additional information regarding the mutagenicity of polycyclic carbonyl compounds is needed before the mutagenic contributions of the characterized compounds can be assessed. Research should be directed to studies of the mutagenicity of a wide variety of oxy-PAHs.

Our present efforts are being directed to obtaining better structural confirmation of oxy-PAHs in various mutagenic subfractions, differentiating among isomeric species, and identifying nitro-PAHs and other constituents that are presumably less amenable to GC/MS. In-depth characterization will also be extended to particulate extracts from several other vehicles.

Acknowledgments

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Formation of Methyl Nitrite in Engines Fueled with Gasoline/Methanol and Methanol/Diesel

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■ The concentration of methyl nitrite in the exhaust emissions from vehicles fueled with methanol and methanol blends was determined by gas chromatography with electron capture detection. The concentration was found to vary between 0.02 and 0.1 ppm for methanol/gasoline blends and 0.02 and 5 ppm for a methanol/diesel-fueled engine. The amount of methyl nitrite in the exhaust emissions was reduced by the use of a catalytic conversion system. Secondary formation of methyl nitrite during dilution of the exhaust emissions with air was found to be negligible.

Introduction

An increasing emphasis on methanol as an alternative motor fuel has called upon comprehensive investigations of the exhaust emissions. Methyl nitrite (MN) has been identified in exhaust emission samples from an automobile fueled with a gasoline/methanol blend (1). Unburned methanol can form MN after reaction with nitrogen oxides, which are present in the exhaust gas from internal-combustion engines. Stoichiometry of the reaction is shown in eq I. At temperatures above 450 K, only a small



fraction of the methanol is supposed to form MN (2). At the high temperatures normally encountered in the engine and in the exhaust system, only small amounts of MN may be formed. However, as the exhaust gas enters the atmosphere, there is a simultaneous cooling and dilution of the exhaust. While the former favors the formation of MN, the dilution will cause a decrease in the reaction rate. Because of the third-order kinetics of reaction I (3), this decrease will be very rapid.

It is of interest to further investigate the presence of organic nitrites in engine exhaust emissions. Ethyl nitrite, a homologue to MN, has been shown to be mutagenic in *E. coli*, *Salmonella typhimurium*, and barley (4). Furthermore, the weak N-O bond in MN is readily dissociated upon UV exposure, making MN a potential source of atmospheric methoxyl radicals. The reactions of this radical

are significant in photochemical smog formation (5, 6).

The main objective of this work was to determine the actual concentration of MN at the exhaust-pipe exit during realistic driving conditions. In addition, the formation of MN as the exhaust gas enters the atmosphere during dilution with ambient air was investigated.

Experimental Section

Engines and Fuels. With minor changes to the engine, gasoline/methanol blends can be used in automobiles designed to run on gasoline. Emission tests were carried out with a Volvo 244 GL, 1977 year model, according to Swedish specifications (vehicle A). The engine was not optimized to run on the blend fuel. Only the CO concentration of the tailpipe exhaust at idling was altered to the same level as prescribed by the car manufacturer for gasoline. This was done to compensate for the "leaning-out effect" caused by the addition of methanol to gasoline. Tests were also performed on a Volvo 244 GL, 1978 year model, built according to Volvo's Federal Specification, equipped with a three-way conversion catalyst (vehicle B). The vehicle had a closed-loop control system with oxygen sensor, which automatically compensates for the change in fuel stoichiometry and enables the vehicle to be operated on the gasoline/methanol blend (7). The test fuel was a blend of 15 vol % methanol, 2% 2-methyl-1-propanol, and 83% lead-free gasoline.

Methanol can also be used as a fuel in diesel engines. In a dual-fuel system diesel oil is used as pilot fuel with methanol as the main fuel (8). During normal driving conditions methanol supplied 70-80% of the required energy input. A Volvo TD 100A truck (10 L, six-cylinder, direct-injection engine) equipped with a dual-fuel system was used (vehicle C). The vehicle was later equipped with an oxidation catalyst (vehicle D). The test fuels were methanol and a commercial diesel oil.

Test Procedure. Vehicles A and B fueled with gasoline/methanol were run on a chassis dynamometer at idling and at 40 and 80 km/h. Vehicles C and D, fueled with methanol/diesel, were run on a chassis dynamometer ac-

according to the 13-mode Federal Test Procedure (FTP), which includes constant loads and idling in 13 different steps (9). Sampling of the exhaust gas for MN analysis was made at the driving modes 3, 6, 7, 8, 10, and 12.

Exhaust Gas Sampling. During driving tests on the chassis dynamometer, the tailpipe of the test vehicle was connected to a dilution tunnel in conjunction with a CVS (constant-volume sampler) test equipment, which enables the exhaust gas stream to be continuously diluted with filtered ambient air to give a constant volume. For vehicles C and D only part of the exhaust gas stream was led into the dilution tunnel. Samples for the MN analysis were taken before and after dilution with air.

The conventional exhaust gas components, hydrocarbons (HC), nitrogen oxides (NO_x), and carbon monoxide (CO), were sampled and analyzed according to standardized procedures for light-duty vehicles (10) and heavy trucks, respectively (9). Samples for methanol analysis for vehicles C and D were taken before dilution of the exhaust gas stream.

Apparatus. MN was analyzed on a laboratory-made gas chromatograph equipped with a Packard (10 mCi of ⁶³Ni) electron capture detector (ECD). The column was made of Teflon (1 m × 1.8 mm i.d.) and packed with 8% Fluorad FC-430 (3M Co., Saint Paul, Minnesota 55101)-0.5% H₃PO₄ on Tenax GC (60/80 mesh). To confirm the identification of MN, we used a silanized glass column (1 m × 1.8 mm i.d.) packed with 6% poly(*m*-phenyl ether) (six-ring)-1% H₃PO₄ on Tenax GC (60/80 mesh).

Sampling and Analysis. Samples for the gas-chromatographic analysis of MN were taken with a 500- μ L gas-tight syringe. The 500- μ L aliquot was immediately injected into the gas chromatograph. The time delay between sampling and injection varied from 5 to 10 s. The gas chromatograph was operated isothermally at +40 °C. The temperatures of the injector and the detector were 150 and 100 °C, respectively. The response to MN was found to be enhanced by a low detector temperature.

Methanol was sampled in 70-mL evacuated glass tubes, which were transported to the laboratory for gas-chromatographic-mass-fragmentographic analysis. This method has been described previously (1). Because of the time elapsed between sampling and analysis, the reaction mixture had equilibrated. Hence, the methanol reacted in the sampler with concurrent oxides of nitrogen, to form MN (reaction I). Preliminary studies to the present work showed that only a minor part of the MN found in the equilibrated exhaust samples was originally present in the exhaust pipe. Thus, assuming that the original MN concentration was negligible in comparison to the methanol concentration, and taking into account the stoichiometry of reaction I, it was possible to calculate the original methanol concentration as the sum of methanol and MN found in the sampler.

On a few occasions another analytical method was used for methanol. Exhaust samples were collected on activated molecular sieve 13X and subsequently desorbed with water. The analysis was performed on GC-MS by a method similar to that described earlier (1). The sampling procedure has not yet been fully evaluated, and the results from these analyses (numbers marked with footnote c in Table I) should therefore be considered approximate.

Preparation of Standard and Calibration. MN was prepared by a method similar to that described by Sloan and Sublett (11). The yellowish product was distilled under reduced pressure and stored in the dark under liquid nitrogen. The gas-phase IR spectrum of the product (bp

-12 °C) agreed well with spectra reported in the literature (12). The spectrum is characterized by two strong absorption bands at 1610-1614 and 1670-1690 cm⁻¹, respectively, corresponding to the N=O stretching frequencies, and by two weak bands at 3220 and 3320 cm⁻¹ corresponding to the first harmonics of the N=O stretching frequencies.

A 1000 ppm (1 ppm = 10⁻⁶ by volume) gas standard of MN was prepared by injecting a known volume of pure gaseous MN into a thoroughly cleaned and dried desiccator filled with helium. The desiccator was protected from light in order to avoid photochemical decomposition of MN. After storage for 3 weeks, the MN concentration decreased by 6%. It was considered sufficient to prepare a new gas standard every 2-3 weeks.

The primary gas standard was further diluted for calibration of the ECD response in the pg range (10⁻¹¹-10⁻⁹ g). For this purpose, an all-glass exponential dilution flask, similar to that described by Lovelock (13), was used. In this range the chromatographic system operates linearly.

The detection limit (peak height = 2.5 × noise width) was 6 ppb in a 500- μ L sample, i.e., 8 pg, during the measurements on vehicles A and B. For the analyses carried out 10 months later on vehicles C and D, the detection limit was 17 ppb in a 500- μ L sample.

Precision and Accuracy of the Analytical Method. Repetitive analysis of standard samples containing 0.5 ppm MN in nitrogen gave a relative standard deviation of 2% using a 500- μ L sample volume. For an exhaust sample containing 0.02 ppm MN, the standard deviation was 11%.

Accuracy is mainly dependent on the primary gas standard which in turn depends on the transfer of pure MN by syringe to the glass vessel. Adsorption of MN on the walls of the vessel might occur. The linear calibration plot, however, indicates that MN is not adsorbed. The accuracy of the method is within 10%.

Results and Discussion

Exhaust samples from vehicles A and B, fueled with the gasoline/methanol blend, were taken before and after dilution with air at different driving modes, i.e., idling and at 40 and 80 km/h. Exhaust samples from vehicles C and D, the diesel engine with a dual-fuel system, were taken at driving modes 3, 6, 7, 8, 10, and 12 of the 13-mode test cycle. The results are summarized in Tables I and II.

For all cars a very low MN-to-methanol ratio was found in the exhaust gas. This ratio varied between 0.001 and 0.007 for the methanol/diesel-fueled engine, vehicle C, except for modes 6 and 7, where the methanol concentration was very low (Table I).

Methanol was not measured in the exhaust gas from vehicles A and B. Measurements have, however, been done on vehicle A in an earlier study (1) using a fuel with a slightly higher methanol content, i.e., 80 vol % lead-free gasoline, 18% methanol, and 2% 2-methyl-1-propanol. With that blend the methanol concentration (calculated as the sum of methanol and MN) was 73 ppm at idling, 17 ppm at 40 km/h, and 11 ppm at 80 km/h. The MN concentrations were now found to be 0.12, 0.02, and 0.02 ppm for the same driving modes. The current blend would probably give a somewhat lower concentration of methanol in the exhaust gas. Assuming the same range for the methanol concentration as in the earlier work, i.e., 10-100 ppm, less than 0.2% of the methanol would form MN within the exhaust system.

The results in Table II indicate a decrease in the MN concentration with increased power output, i.e., increased speed. The same pattern is seen for the methanol/diesel engine (Table I) despite the fact that the methanol portion

Table I. Exhaust Emissions (ppm) from a Methanol/Diesel-Fueled Engine without (C) and with (D) an Oxidation Catalyst

vehi- cle	13- mode (FTP), mode	effect, kW	meth- anol/ diesel ^a	ex- haust temp, °C	ex- haust dilution factor	MN	MN after dilution		methanol	NO	NO _x	HC	CO
							found	theoret- ical					
C	3	32.7	2.6	226	6.7	4.8	0.64	0.72	705	429	480	570	400
	6	131.1	9.4	482	5.9	0.6	0.06	0.10	15	1003	1067	75	2000
	7	idle		354	8.2	0.02	ND ^b	0.002	2	494	555	92	179
	8	182.0	12.0	460	4.9	0.07	0.06	0.014	64	546	578	142	167
	10	90.5	5.6	393	6.3	1.2	0.10	0.19	592	252	306	575	292
	12	3.9	1.3	236	5.1	2.6	0.48	0.51	753	163	222	720	492
D	3	32.7	2.0	224	6.6	3.0	0.40	0.45	250 ^c	457	459	168	29
	6	131.1	9.8	480	5.9	0.2	0.07	0.03	1 ^c	921	1067	10	32
	7	idle		360	8.6	0.02	0.04	0.002	ND ^c	187	359	8	5
	8	182.0	13.5	414	5.3	ND	ND	0	10	485	541	14	8
	10	90.5	5.5	400	6.4	0.09	0.04	0.017	0.3	275	304	28	12
	12	3.9	1.6	250	4.8	0.10	0.06	0.02	130 ^c	191	192	141	39

^a Ratio (weight) between the two fuels used at each driving mode. ^b Below detection limit (0.017 ppm). ^c Another analytical technique used.

Table II. Exhaust Emissions (ppm) from Methanol/Gasoline-Fueled Vehicles

vehicle	speed, km/h	exhaust dilution factor	MN before dilution	diluted exhaust emissions					
				MN		HC	NO	NO _x	CO
found	theoretical ^a								
A	idle	26.9	0.12	ND ^b	0.004	29	2.7	3.0	642
	40	11.2	0.02	ND	0.002	19.5		19	435
	40	11				15.5	14.4	15.5	395
	80	6.3	0.02	0.008	0.003	39	158	288	420
B	idle		ND	ND		7.6	0.65	0.70	164
	40		ND	ND		3.6	1.0	1.2	51
	80		ND	ND		4.3	14.5	15	80

^a MN concentration before dilution divided by the exhaust dilution factor. ^b Below detection limit (0.006 ppm).

of the fuel increases with increased power output. At idling the engine is run on diesel oil only—thus the very low methanol and MN concentration. At low and medium load of the engine, the high concentration of methanol is an important factor for the formation of MN. The relatively low exhaust temperature in these driving modes may also play an important role due to the temperature dependence of reaction I. There seems to be no correlation between the concentration of MN and nitrogen oxides in the exhaust gas.

The catalytic converter system used in conjunction with the gasoline/methanol blend (vehicle B) proved to be very effective in decreasing the MN concentration. The oxidation catalyst used on the methanol/diesel engine (vehicle D) was somewhat less efficient in this respect. The catalyst was placed too far from the engine to attain the temperature required for efficiency at low loads.

The MN concentration in the exhaust gas before dilution with air was divided by the dilution factor for each driving mode and was reported as "MN after dilution—theoretical". For vehicle A both theoretical and found values are too low to be significant. For vehicles C and D, however, there is a good overall agreement between theoretical and found values. This reveals that no appreciable amount of MN is formed during the cooling and dilution process in the dilution tunnel.

Exhaust samples were kept at ambient temperature and the MN concentration was monitored in order to elucidate the formation rate of MN in concentrated exhaust gas. Figures 1 and 2 show the formation of MN in 50-mL exhaust samples at 25 °C during the first 30 min after sampling. From these data the approximate initial reaction rate was calculated. This was done by assuming a constant rate between 10 and 30 s (first and second analysis) after

sampling. The difference in concentration at 10 and 30 s, respectively, was divided by the time difference to give the initial rate in ppb/s. Thus, the initial reaction rates at 25 °C in Figures 1 and 2 were not detectable in Figure 1, a and b, 3 ppb/s in Figure 1c, 60 ppb/s in Figure 2a, 19 ppb/s in Figure 2b, and 16 ppb/s in Figure 2c.

The initial reaction rate is markedly higher for the methanol/diesel engine than for the gasoline/methanol engine. However, the absolute rate is very moderate. Assuming an initial exhaust dilution of 10 times/s during normal driving conditions, the reaction rate will decrease by a factor of 1000/s due to the third-order nature of the reaction. Thus, it is not believed that any appreciable amount of MN is formed during the dilution process.

In Figures 1c and 2a the MN concentration in the samples taken before dilution increases progressively during the first minutes of reaction. Vilkins and Lephardt (14) found that the formation of MN in "ageing cigarette smoke" followed a similar course. This increase in reaction rate is due to an increase in the NO₂ concentration by thermal oxidation of NO. The reaction rate will increase rapidly because of the second-power dependence of the NO₂ concentration. The NO oxidation is also a third-order reaction and consequently extremely dependent on concentration. At low load and after dilution with air, the NO concentration of the exhaust gas is low and the above-mentioned effect is not noticeable. The likely reaction scheme is summarized below:



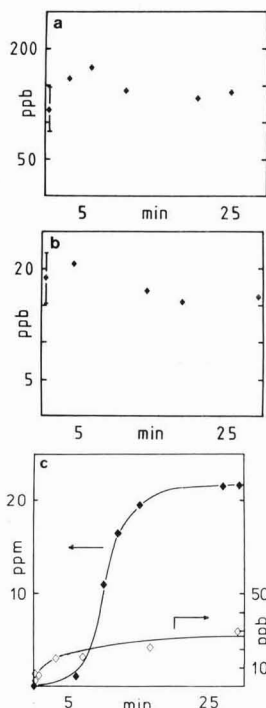


Figure 1. MN concentration in 50-ml exhaust samples 0.1–30 min after sampling; samples stored at room temperature (25 °C). Vehicle A: (a) idling; (b) 40 km/h; (c) 80 km/h; (♦) sample taken in exhaust pipe; (◊) sample taken after dilution tunnel. The first point in each part was obtained by sampling exhaust directly with a 50- μ l syringe. In a and b the standard deviation of repetitive sampling directly from the exhaust stream is shown.

Reaction V is considered the rate-determining step in reaction I (3).

Above we have discussed the possibility of MN formation during the dilution with air that occurs close to the exhaust-pipe exit. It is concluded that this immediate secondary formation of MN is not likely to contribute significantly to the overall exhaust emission of MN during normal driving conditions. Special situations like cold start and warming up of the engine with subsequent increased emissions of unburned fuel, i.e., methanol, might result in increased levels of MN. This is currently being investigated with a neat methanol vehicle during transient cycles.

Conclusion

This work demonstrates a sensitive and accurate analysis method for the determination of MN in auto exhaust by direct injection onto a gas chromatograph equipped with an electron capture detector. The detection limit for a 500- μ l sample is 0.006 ppm. This method was used to measure MN in the exhaust from Otto and diesel engines run on conventional fuels, methanol, or methanol blends. The measured concentrations of MN in the exhaust gas were as follows: Otto engine without catalyst, methanol blended gasoline, 0.02–0.12 ppm; Otto engine with three-way conversion catalyst, methanol blended gasoline, below 0.006 ppm; diesel engine without catalyst, methanol fuel, 0.02–4.8 ppm; diesel engine with oxidation catalyst, methanol fuel, 0.02–3.0 ppm; diesel engine without catalyst, diesel fuel, below 0.006 ppm. Experimental studies on the formation rate of MN in samples of concentrated exhaust gas and during dilution with air indicate that at normal

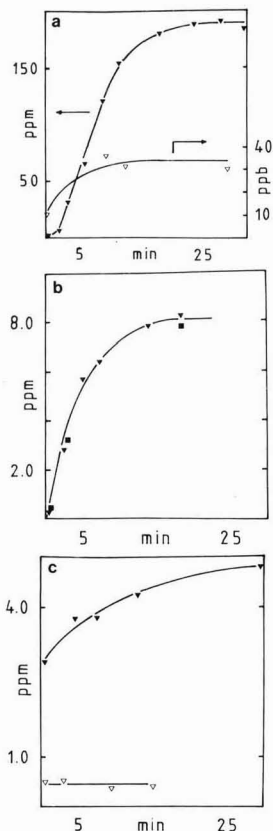


Figure 2. MN concentration in 50-ml exhaust samples 0.1–30 min after sampling; samples stored at room temperature (25 °C): (a) vehicle C, mode 8; (b) vehicle D, mode 8; (c) vehicle C, mode 12; (♦) sample taken in exhaust pipe; (◊) sample taken after dilution tunnel. The first point in each part was obtained by sampling exhaust directly with a 500- μ l syringe.

ambient temperatures the reaction is too slow to produce any significant amount of MN during the immediate dilution process as the exhaust emissions enter the atmosphere. Because of the photochemical stability of methanol, it is not precluded that the atmospheric residence time is long enough to allow reaction with concurrent nitrogen oxides producing secondary MN. This could influence the photochemical activity, as discussed in the Introduction.

Acknowledgments

We are indebted to the Emission Certification Department at Volvo Car Corp. for use of their emission laboratory facilities for light-duty vehicles and a Volvo 244 with a three-way-conversion catalyst. We also express appreciation to the Swedish Environment Protection Board, Vehicle Exhaust Laboratory, for the use of emission test equipment for heavy-duty vehicles.

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Gas-Chromatographic Speciation of Methylstannanes in the Chesapeake Bay Using Purge and Trap Sampling with a Tin-Selective Detector[†]

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■ A method was developed permitting detection and speciation of both volatile and nonvolatile organotin compounds in aqueous media. The method employed a commercial gas chromatograph (GC) with a flame photometric detector (FPD) optimized for tin-selective detection. A commercial automatic purge and trap sampler (P/T) employing a Tenax-GC filled trap concentrated the purged volatiles and species volatilized by hydridization with NaBH₄. The P/T-GC-FPD method was applied to detect varying amounts of methyltin compounds, including tetramethyltin and methyltin hydrides, in polluted sites in Baltimore Harbor. In vitro studies using GC-MS confirmed earlier reports of microbial methylation of inorganic Sn(IV) by a strain of *Pseudomonas* species isolated from the Chesapeake Bay. Consequently, biogenic origins are suspected for the methylstannanes (Me_nSnH_{4-n}, n = 2, 3) found in Chesapeake Bay.

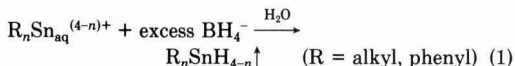
Some workers regard biomethylation of heavy metals or metalloids as a substantial pathway for observed (1) transport of certain elements in the environment. Whether by enzymic or by abiotic chemical means, such translocation of heavy elements, exemplified by methylmercury or methylarsines, can present adverse ecological impacts and human health problems if undetected. This concern is similarly expressed for those metals in widespread commercial use which may enter critical biogeochemical cycles (2).

Recent attention has focused, for example, on reports of biological (3, 4) and abiotic (5) formation of volatile tetramethyllead in aquatic media with its apparent large-scale transport into the atmosphere (6). Tin's chemical similarities to lead also imply its widespread environmental formation and gaseous transport as hydrophobic tetramethyltin (Me₄Sn). Biogenesis of this molecule, though not heretofore detected in the aquatic environment, seems reasonable on the basis of recent evidence for in vitro methylation of various inorganic tin and organotin compounds by microbes isolated from the Chesapeake Bay (7-9) and by viable sediments from San Francisco Bay (10) or Canadian freshwater lakes (11).

[†]This work was presented in part at the 15th Middle Atlantic Regional Meeting of the American Chemical Society, Washington, DC, January 1981, Abstract 191, and at the 181st National Meeting of the American Chemical Society, Atlanta, GA, March 1981, Abstract ENVR 24.

Consequently, just as with the better established biogeochemistry of lead (12), environmental transformations of tin are of current wide interest because of the diverse and significant anthropogenic inputs via commercial materials and effluents (13). Especially important in this connection is development of methods permitting accurate speciation of methylstannanes present in aquatic media, both in field samples and in controlled laboratory experiments. Essential to this problem is the requirement that measurements be capable of both rapid, nondestructive molecular separation and element-selective detection at environmental trace concentrations.

Studies of Braman and Thompkins (14) and Hodge et al. (15) showed that involatile methyltin species, Me_nSn_{aq}⁽⁴⁻ⁿ⁾⁺ (n = 1-3), are ubiquitous at ng L⁻¹ concentrations in natural waters, including both marine and freshwater sources. The latter authors also determined that large quantities of butyltin species occurred in Lake Michigan where anthropogenic sources are believed to be responsible. These findings underscore the significance of methyltins as intermediate transport species and their availability for further biological or nonbiological transformations (16) in aquatic environments. Nonetheless, both of the above reports failed to establish whether tetramethyltin was present in natural waters, because of the inability of the methods used to effectively trap this compound during the combined preconcentration purge and reductive derivatization steps employed to generate volatile organotin hydrides necessary for tin-specific detection



In our continuing studies on the environmental degradation of commercial organotin compounds (17) and the involvement of methylstannanes as metabolic intermediates (7, 8, 18), we have sought to devise trace speciation methods capable of ensuring detection of these tin species along with appropriate preconcentration and derivatization without loss, decomposition, or alteration of their basic molecular features.

In this paper we describe development of a system employing a purge and trap (P/T) sampler, which collects and concentrates volatile organotins from water samples, coupled automatically to a gas chromatograph (GC) equipped with a commercial flame photometric detector (FPD) modified for tin-specific detection (19). The system was

applied to the analysis of a series of water samples obtained from the Chesapeake Bay at both industrially polluted and relatively pristine sites (9) and examined by the P/T-GC-FPD system. The field findings were compared with a laboratory reexamination by an independent GC-mass spectrometric system of the volatile metabolites of a tin-metabolizing *Pseudomonas* isolate from Chesapeake Bay previously described by us (7, 8). In addition to evidence for the presence of variable quantities of tetramethyltin in Chesapeake Bay waters, we unexpectedly found other volatile tin species in the form of methylstannanes, $(\text{CH}_3)_n\text{SnH}_{4-n}$, for which presumptive evidence of microbial mediation is presented on the basis of the *Pseudomonas* study.

Experimental Section

Materials and Chemical Procedures. Laboratory glassware used for preparation, storage, and dilution of inorganic tin and organotin solutions was cleaned before use by leaching with aqueous dilute (5–10%) nitric acid.

The organic and inorganic tin compounds used for the preparation of standard solutions were obtained from commercial suppliers and used with no further purification. Inorganic tin solutions were prepared at concentrations of 1000 mg L⁻¹ in deionized water. Organotin solutions were prepared at concentrations of 200–1000 mg L⁻¹, in spectrograde methanol, depending on each compound's solubility. Deionized water of 15–18 MΩ cm resistivity obtained from a Milli-Q Reagent-Grade water system (Millipore, Bedford, MA) was used for dilution of all stock solutions to working strengths of 0.05–0.2 mg L⁻¹. Working solutions were prepared just before use. Fresh solutions (4% w/v) of sodium borohydride in deionized water were prepared from NaBH₄ pellets (Aldrich Chemical Co., Inc., Milwaukee, WI). Occasionally, trace amounts of stannane were detected in the borohydride solution (14, 15), but these were sufficiently small that no further purification of the borohydride was required.

Calibration solutions of gases, such as $(\text{CH}_3)_4\text{Sn}$, $(\text{C}_2\text{H}_5)_2\text{Sn}$, and $(\text{CH}_3)_2\text{Sn}$, were prepared by direct condensation of measured volumes of each gaseous component into a glass dilution vessel fitted with vacuum-tight glass and Teflon valves (J. Young Scientific Glassware, Ltd., London, England) and septa. A measured volume of gas(es) (about 0.03 mmol, 0.65 cm³, STP) was condensed at liquid nitrogen temperatures into a small side-arm interconnector between the vacuum line and the dilution flask. The dilutor and interconnector sections were valved closed, removed from the vacuum system, and shaken for 30 min. Working solutions of tetramethyltin, with and without combinations of methyl sulfides, were freshly prepared by appropriate 1:1000 dilutions in screw-capped septa vials to give typical concentrations of about 0.1–0.2 mg L⁻¹ as Sn and of about 0.03–0.09 mg L⁻¹ as S. The storage stability of Me₄Sn improved in the mixed solutions with the methyl sulfides, possibly by process of complexation; hence, mixed solutions were used for calibrations. More stable standard solutions of Me₄Sn used for the purge time optimization experiments were prepared. Ten microliters of the 0.1 mg L⁻¹ standard in methanol was added by pipet to 10 mL of deionized water for purging in the analysis. Methanol did not cause detection interferences in these amounts.

Biological Procedures. Pure cultures of a tin-resistant *Pseudomonas* species isolated (7) from the Chesapeake Bay were used as the inoculum in studies of microbiological transformations of inorganic tin(II) and tin(IV). Sterile Nelson's agar medium (8), stressed with 10 mg L⁻¹ of tin(II) (as SnCl₂) or tin(IV) (SnCl₄·5H₂O) (added after autoclav-

ing) or free of tin stress (control), was hardened into slants in sterile 15-mm O-ring, 20-mL borosilicate glass tubes. Immediately after the slants were inoculated, the tubes were capped with sterile 15–9-mm O-ring adaptors incorporating a high-vacuum glass and Teflon Young valve. Experiments were controlled with sterile and inoculated tubes of tin stressed and unstressed media, respectively. After incubation (23 ± 2 °C) for various intervals the respirant atmosphere above the slants was removed for analysis by gas chromatography-mass spectrometry (GC-MS). On the vacuum line, the atmosphere above the slants was expanded into a glass U-trap chilled with liquid nitrogen, and the noncondensable gases were pumped from the sample in the liquid-N₂-cooled trap. After the trap warmed to room temperature, helium carrier gas from the GC was redirected through the trap to carry the contents into the GC-MS system. A calibration mixture for the identification of slant atmospheres was generated by the reduction of the di- and trimethyltin chlorides with NaBH₄ in the presence of gaseous Me₄Sn in a glass culture tube capped tightly with a Mininert valve. One-milliliter gas samples were injected into the GC-MS system by using a gas-tight syringe.

Chesapeake Bay Sample Collection. Chesapeake Bay and Baltimore Harbor water samples were collected in the early spring and late fall aboard the *R/V Ridgely Warfield*. Samples were also collected from shore stations in Baltimore Harbor during the spring, summer, and fall months as indicated in Table I. Surface (5–10 cm below the surface) and bottom (~40 cm above the bottom) samples were taken from each site. Samples were collected in 3.8-L amber glass bottles, held upright in a lead-weighted wooden frame. Before being used, sample collection bottles were cleaned by dilute nitric acid leaching. No tin impurities from the glass sample bottles were observed over repeated use. After collection, the samples were immediately stored in an ice-cooled container, either in the 3.8-L sampling bottles or in smaller 1-L glass bottles. In the laboratory, samples were refrigerated (2–4 °C) until 10–15 min prior to analysis, at which time 10-mL aliquots were transferred into glass sample tubes used as purge vessels and were covered with Teflon-lined screw caps. The samples were warmed to room temperature in a 20 °C water bath.

P/T-GC-FPD System. A Hewlett-Packard (Avondale, PA) (HP) Model 5730 gas chromatograph (GC) equipped with an HP flame photometric detector (FPD) and an HP Model 7675A purge and trap sampler (P/T) was used for this study. Zero grade gases (certified for total hydrocarbon as CH₄ < 0.5 ppm) are recommended by the manufacturer for use as the carrier and purge gas. Aqueous samples, usually 10 mL, were analyzed in 15-mL, 16 × 125 mm borosilicate glass purge vessels. A typical cycle of the automatic (microprocessor-controlled) P/T involved 5-min prepurge with zero grade N₂ flow to equilibrate the sorbent trap at room temperature and 10-min sample purge (gas stripping (20–22)) with zero grade N₂ at 20 mL min⁻¹ flow rate (total purge volume = 200 mL). Volatile trace components purged from the samples were collected in the P/T on a 60/80 mesh Tenax-GC (Alltech Associates, Arlington Heights, IL) (23, 24) filled trap at ambient temperatures. The desorb cycle, which automatically followed the purge cycle, rapidly heated the trap to 250 °C for 5 min while the carrier gas was directed by a six-port valve through the trap and into the GC column. Column temperature programming began automatically with the desorb cycle in the P/T. The Tenax trap was heated an additional 50 °C for 3 min to

TABLE I. Chesapeake Bay and Baltimore Harbor Collection Sites and Water Parameters

sample site	collection method	location	collection dates	station depth, m	$S^{a,b}$	pH ^a
Jones Falls (Baltimore Harbor)	ship	76°36'14''W	03/25/80	6.0	8.29	7.20
		39°16'58''N	12/08/80	3.3		
	land	76°36'19''W	04/22/80	2.0	13.2	8.07
		39°17'14''N	07/09/80	0.7		
			08/08/80	1.0		
			09/09/80	1.0		
			09/30/80	1.3		
			10/07/80	1.0		
			10/15/80	1.2		
			12/15/80	3.3		
Colgate Creek (Baltimore Harbor)	ship	76°32'15''W	03/25/80	8.3	7.78	7.42
		39°15'20''N				
	land	76°32'8''W	04/22/80	1.3		
		39°15'28''N	07/09/80	1.5		
			08/08/80	1.1		
			09/09/80	1.3		
			09/30/80	1.7		
			10/07/80	1.0		
			10/15/80	1.2		
			12/15/80	1.0		
Tolly Point (Chesapeake Bay)	ship	76°25'75''W 38°55'80''N	12/09/80	9.6	16.2	8.27
Bloody Point (Chesapeake Bay)	ship	76°23'90''W 38°49'80''N	12/09/80	30.5	16.6	8.43
Eastern Bay (Chesapeake Bay)	ship	76°17'0.5''W 38°51'0.7''N	12/09/80	10.1	17.2	8.14

^a At 1-m depth. ^b S = salinity, parts per thousand.

vent any residue not removed by the desorb heating.

Chromatographic separations were made on a 2-mm i.d. \times 6 ft glass columns copacked with 3% SP-2401 and 10% SP-2100 on 80/100 mesh Supelcoport (Supelco, Inc., Bellefonte, PA). The column oven was generally maintained isothermally at 30 °C for separating the methylstannanes. Temperature programming ($T_1 = 30$ °C for 4 min to $T_2 = 100$ °C at a rate of 16 °C min⁻¹) was used for organostannanes less volatile than butyltin trihydride or the methylstannanes. Zero grade N₂ was used as the carrier gas with a flow rate of 20 mL min⁻¹.

The HP flame photometric detector was modified to permit tin-selective detection of SnH emission in a hydrogen-rich flame (19). The flame was supported by a mixture of H₂ at 110 mL min⁻¹, air at 70 mL min⁻¹, and N₂ (carrier) at 20 mL min⁻¹. The detector temperature was 200 °C. A 600-nm cut-on interference filter (band-pass 600–2000 nm) (Ditric Optics, Inc., Hudson, MA) was used to transmit the SnH emission lines (25) and bands in the red region with maximum signal. GC-FPD tin selectivity (14) to sulfur, determined from calibrations of Me₄Sn and CS₂, were 46 700 and 101 200 (molar basis) from a nonlinear two-step regression. Water samples were also analyzed in the sulfur mode of the FPD with the flame conditions as recommended by the manufacturer, i.e., 50 mL min⁻¹ for H₂, 50 mL min⁻¹ for air, and 10 mL min⁻¹ for O₂, and with the 394-nm interference filter supplied by the manufacturer for sulfur-selective detection as S₂. Deposits from combustion products which collected in the detector seriously reduced the detector sensitivity. Repeated injections of a fluorine-containing organic compound, in this case, *m*-C₆H₄F₂, generally restored the detector sensitivity. The output signal from the FPD was recorded simultaneously on a strip chart recorder (1-mV full scale) as well as on a Shimadzu Model C-R1A Chromatopac (Columbia, MD) digital integrator-plotter.

GC-MS System. Electron impact (70 eV) mass-spectral data were obtained with an Extranuclear (Pittsburgh, PA) SpectrEL quadrupole mass spectrometer interfaced with a Fisher series 4400 Victoreen gas chromatograph. Sam-

ples were introduced into the GC-MS system by syringe injection or by the vacuum line injection method. The background pressure in the mass spectrometer with helium carrier flow was 10⁻⁶ torr. The GC column, 1/8-in. o.d. \times 6 ft glass-lined stainless steel, was copacked with 3% SP-2401 and 10% SP-2100 on 80/100 mesh Supelcoport. A helium carrier flow rate of 20 mL min⁻¹ was used. The GC oven was operated isothermally at 30 or 70 °C.

The GC-MS system is interfaced with an on-line Computer Automation Inc., computer and software from Teknivent, Inc. (St. Louis, MO). This system provided two modes for data acquisition: mass-spectrum mode and selected ion monitoring or multiple ion detection (ion chromatogram) mode. Major representative peaks in isotope multiplets of tin were selected from fragmentation patterns of mass spectra of tetramethyltin (*m/e* 120, 135, 150, 165) for use in the selected ion monitoring mode.

Minimum detectable amounts of tetramethyltin in the mass-spectrum (*m/e* 100–180) scanning mode were 35 ng (as Sn) in pentane and 50–100 ng (as Sn) in a water matrix, the difference being attributed not only to the varying solubility of Me₄Sn in the matrices but also to the interference of detector response by the solvent. At these concentrations dissimilarity indexes of 0.100–0.300 (0.000 is a perfect fit, 50.00 is not a fit) were obtained upon comparison with MS data for tetramethyltin stored in the user NIH/EPA Chemical Information System (26). One or two data points per second were collected in the multiple ion detection mode to visualize the ion chromatograms. Hard copies of the data stored on floppy diskettes were plotted with a Complot Model DP-1 digital plotter (Houston Instruments, Bellaire, TX).

Volatilization of Organotins in the P/T Cycle. Nonvolatile organotin species (cations) were volatilized by a modified hydride reduction process (14, 15) using an excess of 4% aqueous sodium borohydride solution. Analyses for volatile organotins in water did not require additions of borohydride. The purge vessel, containing water samples to be analyzed for volatile species, was attached to the P/T just before the 5-min prepurge. For

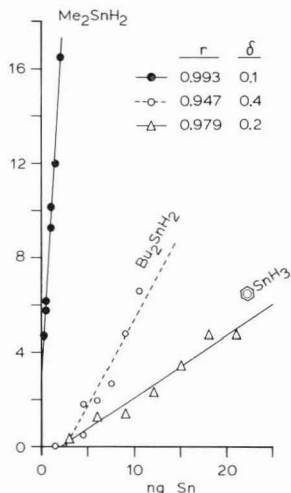


Figure 1. Typical GC calibrations of simultaneously reduced Me₂SnH₂, Bu₂SnH₂, and PhSnH₃ using temperature programming with P/T-GC-FPD system. Correlation coefficients (*r*) and system detection limits in ng (δ) are also indicated.

hydride reduction of the nonvolatile species, 100–500 μ L of 4% NaBH₄ was added to the purge vessel containing the sample within the last minute of the Tenax trap purge, and immediately before initiating the 10-min N₂ sample purge. This procedure kept the reaction time for the reduction process to a minimum of 10 min. It also served to minimize the loss of volatile hydrides possibly formed in the purge vessel on the initial addition of the borohydride. Simultaneous analysis for volatile and nonvolatile organotin species was accomplished by using the procedure for the reduction process. No pretreatment of the water sample is necessary for use with the P/T-GC-FPD system.

Solution Calibrations and Quantitation of Field Samples. Calibrations were made for organostannanes with borohydride reduction of the corresponding organotin chlorides in deionized water and in Bay water. In general, unfiltered Bay water was purged with zero grade N₂ and refrigerated (2–4 °C) before use with the standards. Nanogram quantities of the tin compounds were pipetted in microliter amounts to the purge vessel containing 10 mL of Bay or deionized water. The plots in Figure 1 illustrate typical calibration curves made with Me₂SnCl₂, *n*-Bu₂SnCl₂, and PhSnCl₃ in Bay water with BH₄⁻ reduction employing GC column temperature programming. Typical calibrations for tetramethyltin in Bay water and deionized water are shown in Figure 2. Concentrations of Me₄Sn in Bay water samples were also determined by using the method of standard additions with extrapolation to the negative intercept of the X coordinate (ng/10 mL) as in Figure 3.

Results and Discussion

Analysis of Volatile and Nonvolatile Aqueous Organotins. In environmental studies, it is important to know whether the chromatographically speciated volatile organotin hydrides were present in the environment as hydrides or were generated only during the hydride reduction process. The relatively short analysis time, the absence of sample preparation, and the small sample sizes used in this study facilitated duplicate analyses of water samples for differentiation of organotins as volatile or nonvolatile species. Although both volatile and nonvolatile

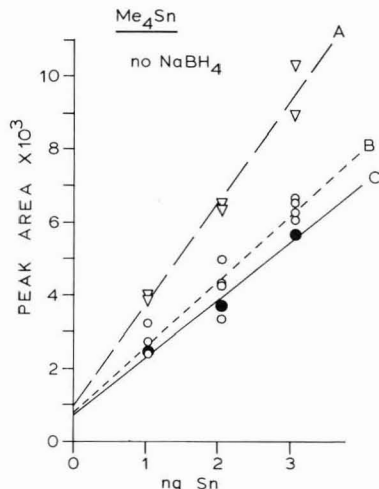


Figure 2. P/T-GC-FPD calibration of Sn response in Me₄Sn/Me₂S mixture in (A) deionized water and (B) Bay water. Curve C shows the additive effect of sequential sample purging of Sn as Me₄Sn in Bay water.

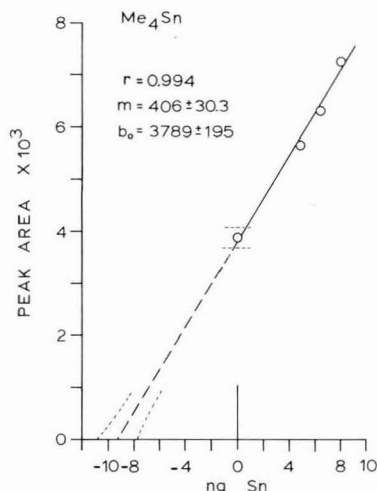


Figure 3. Extrapolation for concentration determination of Me₄Sn in Bay water from Colgate Creek in Baltimore Harbor using method of standard additions with Me₄Sn/Me₂S₂ standard.

species were trapped simultaneously, we analyzed the Bay water samples in duplicate to distinguish between the methylstannanes present in the Bay water and those generated by hydride reduction in the laboratory. Figure 4 shows the chromatogram of duplicate samples of standards in deionized water with the method used for Bay water analysis. Without the addition of NaBH₄, the tetramethyltin standard was purged from the sample while the dimethyltin cation remained in solution. When NaBH₄ was added, both volatile species were observed, there being no apparent loss of Me₄Sn as a result of hydride formation. The chromatographic separation of the methylstannanes (Me_nSnH_{4-n}, *n* = 1–4) mixture is shown in Figure 5. The hydrides (*n* = 1–3) were formed by BH₄⁻ reduction of the corresponding chlorides in the presence of Me₄Sn.

Calibration Results. Regression analyses are given in Table II for various calibration curves of species used in

TABLE II. Regression Analysis of Calibrations in Bay Water

species	mean $t_r \pm$ SE, ^a min	detection limit, ^b $\mu\text{g L}^{-1}$	regression slope \pm SE	N	R	rel sensitivity of regression slopes
SnH ₄	0.88 \pm 0.07	0.030	21.6 \pm 2.8	10	0.937	0.012
MeSnH ₃	11.24 \pm 0.04	0.053	604 \pm 126	6	0.923	0.33
BuSnH ₃	3.98 \pm 0.08	0.018	329 \pm 24	7	0.987	0.18
Me ₂ SnH ₂	11.57 \pm 0.04	0.013	6683 \pm 367	7	0.993	3.76
Bu ₂ SnH ₂ ^c	11.12 \pm 0.06	0.037	726 \pm 110	7	0.947	0.40
PhSnH ₃ ^c	8.27 \pm 0.04	0.023	265 \pm 24	7	0.979	0.14
Me ₂ Sn	2.86 \pm 0.11	0.023	1777 \pm 186	11	0.954	1.00
Me ₂ S	1.71 \pm 0.03					

^a Determined with column oven $T = 30^\circ\text{C}$. ^b P/T-GC-FPD system detection limits based on 10-mL sample solutions.

^c Determined with oven-temperature programming.

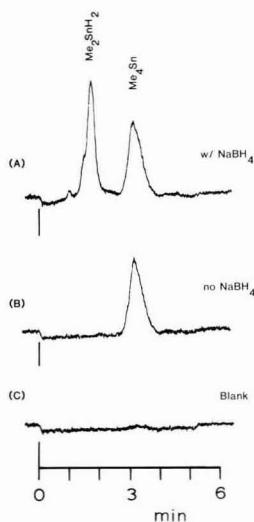


Figure 4. Gas chromatograms of duplicate samples of methyltin standards in deionized water (A) with borohydride reduction for simultaneous analysis of volatile and nonvolatile methyltins and (B) without borohydride volatilization. Curve C shows deionized water blank.

this study. The detection limits of the P/T-GC-FPD system at 95% confidence level (27) are given for various species reduced in sparged Bay water as well as for non-reduced species. A comparison of the slopes indicates not only a trend for the detectability of the various species but also a trend in the relative rates of hydridization. While all hydride reduction reactions were limited to 10 min, it is expected that the more Lewis acidic methyltin cations would undergo a biomolecular electrophilic substitution (S_E2) reaction more completely in the given time than the butyl or phenyl analogues. Comparison of the slopes for the methyltins with the butyl- and phenyltins gives evidence to support this. Figure 6 also shows the difference in completeness of reduction for $\text{Me}_2\text{Sn}^{2+}$ and $\text{Et}_2\text{Sn}^{2+}$ with different purge times. Within a given series, increased alkyl substitution produced larger slopes indicating more efficient production in the same reaction time.

Although Me_2Sn was not affected by the purge time as with organotin hydride formation, it is evident from Figure 2 that the detection limits are lower than for the methyltin hydrides. The tetramethyltin standards in water (see Experimental Section) were not stable because of the hydrophobicity of Me_4Sn . Consequently, the values for Me_4Sn in Bay water samples may be overestimated.

Consideration of Parameters for Optimizing the P/T-GC-FPD Method. Although our results are reported in concentrations of $\mu\text{g L}^{-1}$, only 10-mL samples

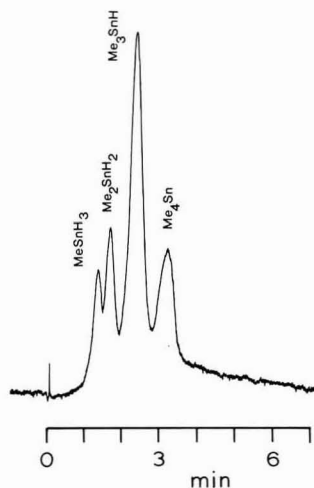


Figure 5. P/T-GC-FPD separation and detection of the four methylstannanes ($\text{Me}_n\text{SnH}_{4-n}$, $n = 1-4$) in deionized water, where $n = 1-3$ are formed by hydride reduction.

were used in present analyses. Larger samples presumably yielding lower detection limits for the system require much longer purge times or faster purge flow rates. This is necessary in order to provide adequate purge volume relative to the size of the sample as defined by eq 2, derived

$$t_{0.05} = 3(V_G + K_1V_L)/F \quad (2)$$

here for 95% trapping efficiency in dynamic gas stripping from a liquid (22). Here $t_{0.05}$ is the time required for 95% analyte recovery, V_G is the headspace volume, K_1 is the partition coefficient of the organotin solute, V_L is the volume of the liquid sample, and F is the purge flow rate. Increasing the purge flow rate for larger samples leads to undesirable breakthrough of the more volatile analyte species (20-22, 24) and less trapping uniformity on the Tenax-GC trap. Increasing the purge time not only makes the analysis tedious but also increases the likelihood of eventual breakthrough of the most volatile species in mixtures, as shown in Figure 6.

Mixtures of Me_2SnCl_2 , Me_4Sn , and Et_2SnCl_2 in 10 mL of deionized water (1 ng as Sn for each compound) were subjected to borohydride reduction during the purge cycle. The purge times were varied to determine the optimal purge time required for a fixed purge flow rate of 20 mL min^{-1} . The relative extent of hydride reduction for $\text{Me}_2\text{Sn}^{2+}$ and $\text{Et}_2\text{Sn}^{2+}$ is also reflected in this series. After a 10-min purge (200-mL purge volume), found to be optimal, quantities of all trapped species appear to decrease as a result of breakthrough of the more volatile species.

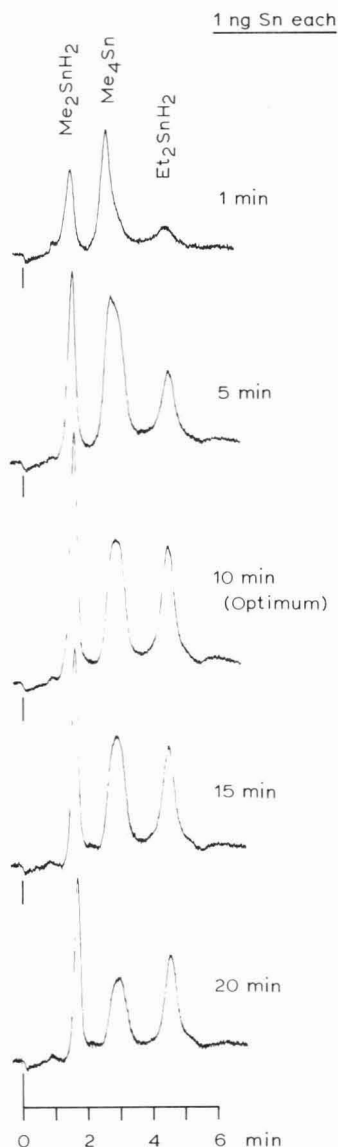


Figure 6. Optimization of purge time for trapping volatiles on Tenax-GC trap using 1 ng (as Sn) each of Me_2SnCl_2 , Me_4Sn , and Et_2SnCl_2 with 4% NaBH_4 added to volatilize $\text{Me}_2\text{Sn}^{2+}$ and $\text{Et}_2\text{Sn}^{2+}$ to the corresponding hydrides. Optimum purge time indicated at 10 min.

Another consideration in our trapping procedure and purge times was the resulting retention times of the components on the GC column. During the trapping process, the purged volatiles flow upward onto the trap and move farther into the trap during the purge time. The flow of the gas through the trap is reversed during desorption into the GC. Consequently, the longer the sample is purged, the longer will be the resulting retention time on the GC column as would be expected because of the longer travel path in the trap.

Figure 6 also demonstrates the relationship between uniform trapping and the (ideal) Gaussian distribution of the analyte peak shape on the GC column. We found the 10-min purge again to be optimal in this test.

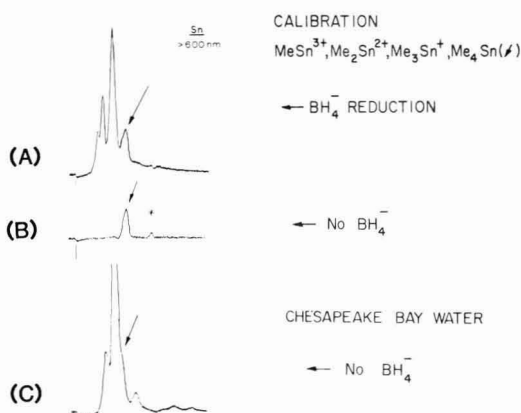


Figure 7. Gas chromatograms of methylstannanes (A) formed in calibration mixture with hydride reduction, (B) formed in calibration solution without hydride reduction showing Me_4Sn , and (C) found in sample from Jones Falls in Baltimore Harbor without hydride reduction as obtained by using P/T-GC-FPD method. Arrow denotes Me_4Sn .

If larger samples are needed for an analysis, sequential purge and trapping offers a possibility. Curve C in Figure 2 is a calibration of Me_4Sn using a collection of one, two, and three 10-mL samples with sequential 10-min purge cycles finally followed by desorption. Compared to curve B, where a single 10-min purge is used for the same total quantity of Sn, sequential purging gives adequate results up to perhaps three consecutive 10-min purges. Deviations between curves B and C then begin to increase because of loss of sample from breakthrough on the trap.

Speciation of Organotins in Bay Water Samples. Results from analyses of samples collected during the spring months from an urban runoff in Baltimore Harbor (Jones Falls) gave evidence of the presence of tetramethyltin as well as tin-containing species more volatile than Me_4Sn (Figure 7). These water samples were also analyzed with the P/T-GC-FPD system in the sulfur mode, thus showing that these additional peaks were not sulfur-containing. A calibration mixture of the methylstannanes ($\text{Me}_n\text{SnH}_{4-n}$, $n = 1-3$) volatilized by hydride reduction in the presence of Me_4Sn was later analyzed by the P/T-GC-FPD method. Comparison of the calibration chromatogram with the results from Jones Falls in Figure 7 indicated that there were methylstannanes ($n = 2, 3, 4$) present in the Bay water. Borohydride was not added to the Bay sample for this analysis. A chromatogram of the calibration mixture analyzed without the addition of NaBH_4 is shown in Figure 7. This resulted in the sparging and detection of only the volatile Me_4Sn . The amounts of methylstannanes present in this sample were estimated from calibration data to be the following (in $\mu\text{g L}^{-1}$): Me_2SnH_2 (0.2), Me_3SnH (0.4), and Me_4Sn (0.48). These were the highest estimates of methylstannanes speciated at this site in Baltimore Harbor.

Tetramethyltin was also detected at another site in Baltimore Harbor, Colgate Creek, during the spring months. The method of standard additions (Figure 3) was used to determine the concentration of Me_4Sn in the sample. As much as $0.93 \mu\text{g L}^{-1}$ of Me_4Sn were present in the Bay water sample within a 95% confidence interval as indicated by the broken lines.

Baltimore Harbor sites were sampled during a consecutive 3-week period to assess possible trends in the water composition over a shorter range than experienced with most of the water sampling. These results are given in

TABLE III. 3-Week Baltimore Harbor Sampling

site ^c	collection date	SnH ₄ (0.88 ± 0.07) ^a		Me ₃ SnH ₃ (1.57 ± 0.04) ^a Me ₂ S (1.71 ± 0.03)		Me ₃ SnH (2.16 ± 0.03) ^a		Me ₄ Sn (2.86 ± 0.11) ^a		BuSnH ₃ (3.98 ± 0.08) ^a	
		mode I ^d	mode II ^{e,f}	mode I ^{g,f}	mode II ^{g,f}	mode I	mode II ^f	mode I ^f	mode II ^f	mode I ^f	mode II ^f
JFS	09/30/80	10-20	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
JFS	10/07/80	0.3-0.5	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
JFS	10/15/80	3-4	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
JFB	09/30/80	0.6-0.7	0.02-0.05	<0.01	<0.01	0.01-0.02	0.01-0.02	0.05-0.1	0.05-0.1	0.05-0.1	0.05-0.1
JFB	10/07/80	0.2-0.3	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
JFB	10/15/80	0.7-0.8	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
CCS	09/30/80		<0.01	<0.01	<0.01	<0.01	<0.01	0.01-0.05	0.01-0.05	0.05-0.1	0.05-0.1
CCS	10/07/80		<0.02	<0.02	<0.02	<0.02	<0.02	<0.01	<0.01	<0.01	<0.01
CCS	10/15/80		<0.005	<0.005	<0.005	<0.005	<0.005	<0.01	<0.01	<0.01	<0.01
CCB	09/30/80		<0.02	<0.02	<0.02	<0.02	<0.02	0.15-0.3	0.15-0.3	0.05-0.1	0.05-0.1
CCB	10/07/80		<0.02	<0.02	<0.02	<0.02	<0.02	<0.01	<0.01	<0.01	<0.01
CCB	10/15/80		<0.005	<0.005	<0.005	<0.005	<0.005	<0.01	<0.01	<0.01	<0.01

^a Identified species with mean $t_r \pm SE$ (minutes) as determined with standards. ^b Mean $t_r \pm SE$ (minutes) determined from samples over 3-week period. ^c S = surface samples; B = bottom samples; JF = Jones Falls; and CC = Colgate Creek. ^d Mode I: samples analyzed for volatile species without addition of NaBH₄ for reduction. ^e Mode II: samples with NaBH₄ added; gives simultaneous analysis for volatile and nonvolatile species. ^f Quantities expressed in concentration of $\mu\text{g L}^{-1}$. ^g Assuming species to be Me₃SnH₃.

Table III. The volatile species shown in the table under mode I were determined by the P/T-GC-FPD method without the hydride reduction step. Nonvolatile species (mode II) were volatilized, trapped, and detected with the volatile species present in the samples. Generally, no changes in the concentration of the volatile species were observed with the hydride reduction step. An increase in the amount detected, as with Me₂SnH₂ and BuSnH₃, indicated that the solvated cations were also present in the water samples along with the respective free stannane. The prevailing GC peak at 1.75 ± 0.04 min has not been completely resolved or identified. The retention time is within the range of both dimethyl sulfide (Me₂S) and Me₂SnH₂. Dimethyl sulfide is known to be a microbial metabolite present in environmental water (28); therefore, this is a possible interference. However, we find that the concentration of Me₂S would have to be extremely high because the selectivity of our FPD detector to tin over sulfur in the red region of the spectrum (>600 nm) is several orders of magnitude. Identification of the peak as Me₂SnH₂ would be consistent with our results from the spring sample collection. Inorganic tin (volatilized to SnH₄) was detected in as much as 10-20 $\mu\text{g L}^{-1}$ quantities at the urban runoff, Jones Falls. None was detected in Colgate Creek in Baltimore Harbor.

The samples collected in the Chesapeake Bay at Tolly Point, Bloody Point, and Eastern Bay (see Table I) showed minimal amounts of methyltin species. A peak corresponding to MeSnH₃ was observed in the water samples collected from these three sites with the least amount detected in Eastern Bay, a relatively nonpolluted area (9). Trace amounts of Me₂SnH₂ were also detected at the same retention times as those observed in the Baltimore Harbor samples. As much as 0.2 $\mu\text{g L}^{-1}$ was detected in the samples collected at Tolly Point and Bloody Point.

At trace levels, as those observed in Bay water, the rate of decomposition of organotin hydrides may equal the rate of production of the stannanes (steady state) which would give the appearance of water-stabilized hydrides. The question that subsequently arises is in regard to the formation of the various organotin hydrides (methylstannanes in this case) in aquatic environments.

If methylstannanes had been present in the environmental samples analyzed by Braman (14) and Hodge (15), they would not have been detected for the same reason that tetramethyltin was not observed, i.e., removal of the volatile methylstannanes during prehydride degassing.

In Vitro Methylation of Inorganic Sn(IV) by *Ps* 244. We have reexamined previous work from this laboratory (7) to determine the extent of methylation of inorganic tin by an aerobic strain of *Pseudomonas* 244 (*Ps* 244) isolated from the Chesapeake Bay. The respirant atmosphere above 10-ppm tin-stressed, Sn(IV) and Sn(II), inoculated agar slants and sterile controls were observed by using GC-MS after incubation for 2 weeks. Results of representative ion chromatograms are shown in Figure 8. These were obtained with the selected ion monitoring mode of the GC-MS data system for all major fragment ions, including m/e 120 and 165 corresponding to the major isotopes of Sn⁺ and Me₃Sn⁺ fragments, respectively. A calibration ion chromatogram showing Me₂SnH₂, Me₃SnH, and Me₄Sn is also give (Figure 8E) to identify the peaks from the respirant atmosphere above the *Ps* sp. slants.

The ion chromatogram of the tin(IV)-stressed *Ps* sp. inoculated slant showed a methyltin compound at ~0.95 min which corresponded to Me₃Sn in the calibration, as well as a very broad methyltin peak obviously more volatile

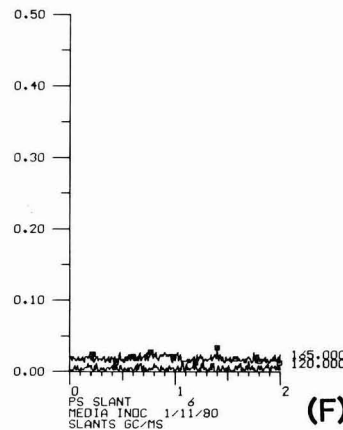
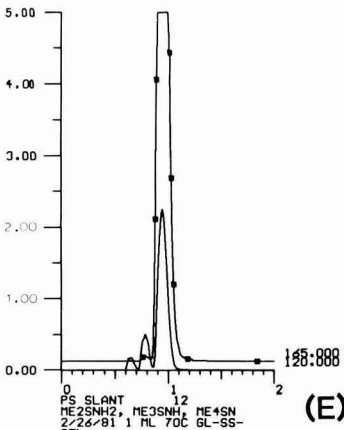
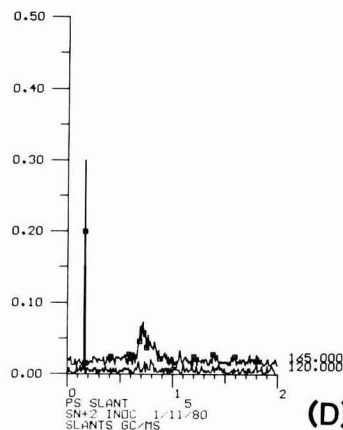
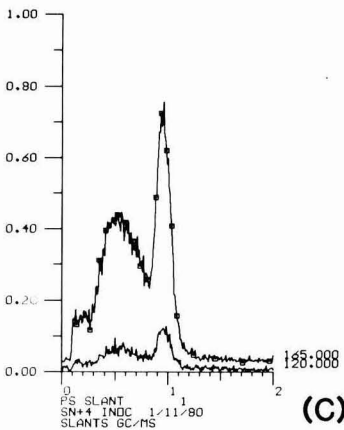
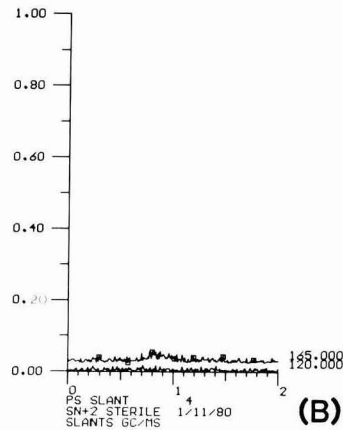
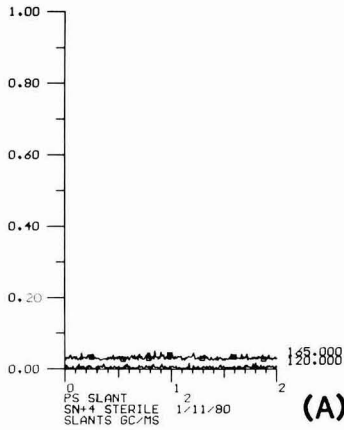


Figure 8. GC-MS ion chromatograms of respirant atmosphere above agar slants: (A) sterile control with Sn(IV) stress, (B) sterile control with Sn(II) stress, (C) *Ps* 244 inoculated with Sn(IV) stress, (D) *Ps* 244 inoculated with Sn(II) stress, and (F) *Ps* 244 inoculated with no tin stress. Part E shows the ion chromatogram from a gaseous calibration mixture of Me_2SnH_2 , Me_3SnH , and Me_4Sn .

than Me_4Sn . The broadness of the peak is indicative of a decomposition reaction of methyltin species on the GC column during elution. Comparison with the ion chromatogram shows an overlap of the broadened peak with

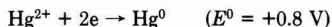
the elution of Me_2SnH_2 and Me_3SnH in the calibration chromatogram. However, the mass spectra of Me_3SnH and Me_2SnH_2 show that the abundance of m/e 165 is small (Me_3SnH) or nonexistent (Me_2SnH_2).

Generally, organotin hydrides are considered to be unstable in aqueous or aerobic environments. In oxidant-free environments, however, their lifetimes are expected to be considerably longer. For example, organotin monohydrides can be stored for a practically unlimited time without decomposition, while the dihydrides are stable for several weeks and the trihydrides only for several days. Upon decomposition, however, the organotin hydrides tend to form R_4Sn , Sn , and H_2 in stoichiometric amounts (29). The appearance of the broadened peak in the ion chromatogram for the $Sn(IV)$ -stressed inoculated slant at m/e 165 would therefore indicate decomposition yielding Me_4Sn since this fragment ion is not a major fragment of Me_3SnH or Me_2SnH_2 .

While a small amount of a volatile methyltin compound corresponding closely to Me_3SnH was also observed above the inoculated slant stressed with tin(II), none was detected in the atmosphere above sterile controls stressed with either tin(IV) or tin(II). These experiments demonstrating methylation of tin by the *Ps* microorganisms not only confirm the previous work from this laboratory regarding the biomethylation of tin(IV) (7) and the more recent reports of others (9–11) but also support the idea that methylstannanes present in the Chesapeake Bay may arise in a microbially mediated pathway.

Repeated experiments using the *Ps* sp. slants stressed with inorganic tin gave irreproducible production of methylstannanes. Because the solidified agar slants are inoculated on the surface, methylation of the tin in the medium depends on the bioavailability of the tin, i.e., the proximity and molecular form of the tin at the surface of the agar slant. Recent studies (9) have indicated a non-uniform bacterial response to $Sn(IV)$ in agar media.

Bioreduction by *Ps* 244. Reduction processes are defined as (1) the addition of hydrogen, (2) the addition of electrons, and (3) the removal of oxygen. Bioreduction of metals and metalloids is considered commonplace in the environment. The *Pseudomonas* strain 244 has been observed to have the capability to reduce mercuric ions to elemental mercury gas under aerobic conditions (7):



Bioreductions have also been known to generate methylmetals as with the production of trimethylarsine (30) involving from two to four electron steps. Chen and Focht (31) reported bioreduction plus biomethylation by *Ps* sp. of $As(V)$ and $As(III)$ in sediments to form arsine and methylarsines and pure cultures. We can therefore presume that the *Ps* organism has the potential to further reduce methylated tin cations to the corresponding hydrides since it seems well within the physiological redox range for the couple $Sn(IV) \rightarrow Sn(II)$ ($E^0 = +0.15 \text{ V}$). The reported instability and decomposition of organotin hydrides (methylstannanes) may well account for the presence of tetramethyltin in Bay water samples as well as in the *in vitro* experiments performed for this study. Kinetic information on decomposition (protolysis or oxidation) rates of Me_nSnH_{4-n} in seawater are now required to evaluate their flux.

Conclusions

We have described a method which combines readily available commercial instrumentation (appropriately modified for tin-selective detection) with classical volatilization processes. This extended method permits non-destructive speciation and detection of trace organotins, including hydrophobic species, in aqueous systems. We have also demonstrated that volatile organotin compounds

(including hydrides presumably unstable in water) can be stored for periods of time on Tenax-GC at ambient temperatures and desorbed for GC analysis without decomposition. The P/T-GC-FPD system detection limits determined from linear calibrations for organotins in water at the 95% confidence level were $0.013\text{--}0.052 \mu\text{g L}^{-1}$, depending on the individual organotin species. However, methyltin species ($n = 2, 3, 4$) were detected on concentrations as low as $0.005 \mu\text{g L}^{-1}$. Greater selectivity of speciation can be achieved by using capillary GC separations.

Water samples collected from the Chesapeake Bay and Baltimore Harbor were analyzed by the P/T-GC-FPD method. We detected varying amounts of methyltin species, including not only hydrophobic Me_3SnH but also, quite unexpectedly, methylstannanes (Me_nSnH_{4-n}) $n = 1\text{--}3$. Although biogenic origins are suspected, there is an apparent relationship between the concentration gradients observed for the methylstannanes in the sampling locations and tidal fluxes, runoff, and anthropogenic activity as indicated by Hallas (9).

Reexamination of previous work from this laboratory by GC-MS has confirmed the biomethylation, possibly coupled with bioreduction, of $Sn(IV)$ by a *Pseudomonas* sp. (isolated from the Chesapeake Bay) to form methylstannanes ($n = 2, 3, 4$). The production of Me_nSn in these experiments may result from decomposition of the methyltin hydrides under aerobic conditions.

The results from this work open new areas of study for determining biological pathways and fluxes of organotins in the service environments.

Acknowledgments

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NOTES

Effect of Pipetting on Mineral Floccs

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■ Floccs of kaolinite and of untreated natural suspended material were produced in a Couette-type reaction chamber using 2% and 30‰ seawater solutions. The diameter of the pipet tip opening directly affected the degree of flocc breakage when samples were extracted. Extremely small pipet tip openings (125-400- μm diameter) disrupted nearly all floccs. In general, pipet tip openings should exceed 2000 μm in order to prevent flocc breakage. Pipet openings should be larger than 3000 μm in diameter in cases of weakly bound or large floccs.

Introduction

Floccs in the marine environment have been observed by Berthois (1), Biddle and Miles (2), Edzward (3), Edzward and O'Melia (4), Gibbs (5), Kranck (6), Krone (7), Schubel and Kana (8), Sheldon (9), and Zabawa (10). Because flocculation affects transportational and depositional processes of materials, it is critical to have accurate as well as precise methods for measuring the floccs.

An important experimental task in the investigation of the flocculation-deflocculation phenomenon of particles is documentation of the size and/or the number of floccs. Because clay floccs are often fragile, utmost care must be taken during the measurement process. While, intuitively, many researchers consider floccs to be fragile, there are no quantitative studies that test what procedures do and do not break floccs during sampling and analysis. Another study (11) showed breakage when using pumps to sample floccs.

There are mainly three techniques for determining the size and the number of particles. The simplest approach is taking a sample by using a pipet and placing it on a slide for microscopic examination. A second approach for measuring the size distribution of suspended material is

the Coulter-counter technique, in which the particles are passed through a tiny orifice, changing the resistance across the orifice in proportion to particle size. The effectiveness of this method in defining the size and the number of floccs has yet to be evaluated. The advantage of the Coulter counter is that large numbers of particles can be counted in a short time and a computer coupled to the counter can produce displays of size distributions rapidly. The third group of methods utilizes optical techniques in an in situ mode. Light scattering generally is considered a nonspecific technique for this purpose, but it can give some useful information (12). Recording the image by either photographic or holographic techniques (13) is useful for some studies, but it is fairly expensive and presently lacks the resolution needed for floccs smaller than 5 or 10 μm in diameter.

The purpose of this study is to evaluate what effects, if any, pipet handling has on the floccs either when taking the sample or when diluting the sample for analysis. Various investigators use pipets of varying diameters without stating reasons for their choice, and in many cases other procedures that may have affected flocc breakage have not been considered in preparing samples. This study's specific objective is to determine the relationship between flocc breakage and the size of pipet tip openings and to develop a procedure that will minimize flocc breakage when using pipets in handling suspended-material samples.

Procedures

The materials utilized to produce the floccs for this study were untreated kaolinite, (API standard no. 3), size-fractionated into 2-4- μm intervals, and an untreated sample of suspended sediment from the Amazon River, obtained from the Atlantic Ocean area off the mouth of the Amazon River. The 2-6- μm size fraction from the Amazon River

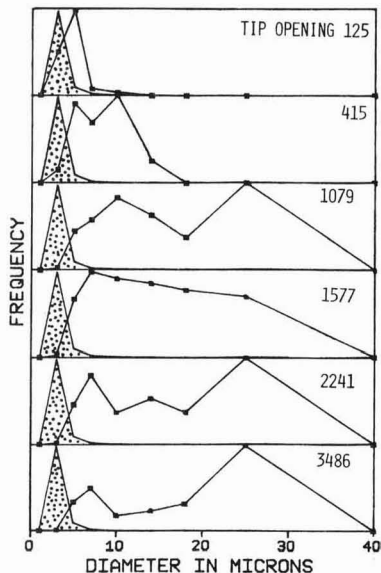


Figure 1. Size distributions obtained for kaolinite flocs by using pipets with tip openings of various diameters at 30‰ salinity. Primary particle size mode is shown by stippling.

sediment was not treated and thus retained its natural organic and iron coatings. The composition of this natural sample was 40% kaolinite, 40% illite, and 20% montmorillonite.

Flocs were produced in a Couette-type reaction chamber with a velocity gradient of 32 s^{-1} for kaolinite and 20 s^{-1} for the untreated natural sample. The solutions were prepared by using filtered natural seawater and diluted to 2‰ with distilled water. The concentration of suspended material was maintained at 15 mg/L for all experiments, a concentration typical of many estuaries.

In an effort to eliminate human error, an automatic mechanical pipet was utilized for sampling and for placing the material on microscope slides having wells 400 μm deep. The number and the size of flocs were determined by using a microscope with 450 \times magnification.

Primary particle-size distributions were determined before the material started to flocculate. The material was then permitted to flocculate and sampled by using pipets with six size openings, ranging from 125 to 3486 μm in diameter. For perspective, the openings of commercially available pipets used for most analytical work range from 800 to 1500 μm in diameter. The samples were permitted to reach an equilibrium size distribution before successive sampling with the various pipets. This minimized the possibility of the sample changing during sampling. The pipetted samples were taken in rapid succession from the same position in the container.

Results and Discussion

The experiments for floc breakage of kaolinite at both 2‰ and 30‰ salinity showed similar results. A 125- μm pipet opening allows breakage of almost all of the 20–30- μm flocs (Figure 1), whereas 2241- and 3486- μm diameter pipets appear to disrupt very few flocs. The 415-, 1079-, and 1577- μm pipet openings appear to cause some breakage. The kaolinite flocs were formed under a high shear (32 s^{-1}) in the reactor, which would produce strong flocs and break weak flocs. The natural environment would have shears below 10 s^{-1} , and as such the experiments are

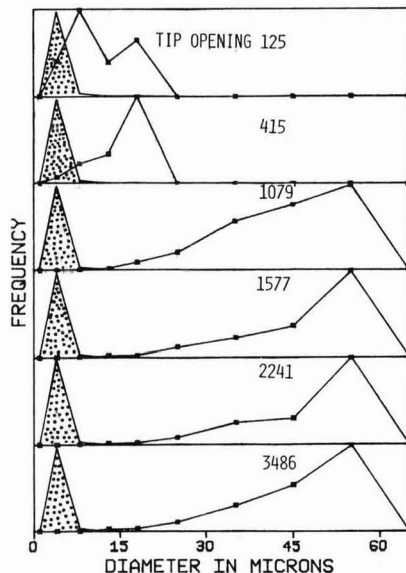


Figure 2. Size distributions obtained for flocs of natural sample by using pipets with tip openings of various diameters at 2‰ salinity. Primary particle size mode is shown by stippling.

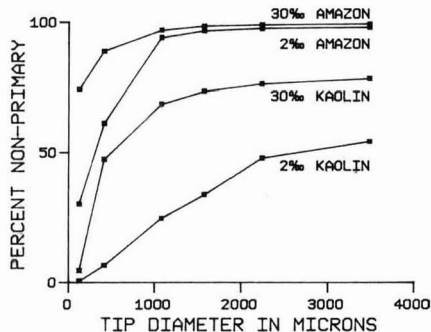


Figure 3. Percent of nonprimary particles (flocs) for pipets with tip openings of various diameters.

considered to be an extreme test for producing least breakage.

The untreated natural material was allowed to grow to an equilibrium size distribution at a lower shear, representative of that found in estuaries. The results (Figure 2) show that the flocs grew to over 50 μm in diameter in both the 2‰ and 30‰ salinity experiments. Results for pipets having 125- and 415- μm openings indicate significant floc breakage, whereas results for 1079- μm diameter openings indicate less breakage; larger-diameter openings do not produce significant breakage of flocs.

In an effort to quantify the degree of floc breakage as a function of the tip diameter of the pipets, the percent of nonprimary particles (flocs) was determined (Figure 3). More breakage of flocs occurred for 2‰ salinity samples than for 30‰ salinity samples, indicating the existence of weaker flocs at the lower salinity. Because the experiments on the two samples (untreated natural material and kaolinite) were conducted at two different shear rates, it is difficult to draw direct comparisons. However, judging from the progressive increase in the curve for the 2‰ salinity solution of the kaolinite sample as opposed to the more rapid rise in the curve for the 2‰ salinity sample of

the untreated natural sample, the kaolin flocs appear weaker. This would be expected because of the composition of the natural sample, which would produce a stronger floc than kaolinite alone.

A pipet having a tip opening less than 2000 μm in diameter can, therefore, produce significant floc breakage; in the case of weak flocs, tip openings larger than 3000 μm in diameter are recommended. It should also be pointed out that, because the maximum floc size studied was only 65 μm in diameter, care in handling should be applied when dealing with larger flocs.

Conclusions

The diameter of the pipet tip opening used for sampling suspended material for flocculation studies directly affects floc breakage. Extremely small pipet tip openings disrupt flocs of all sizes. Therefore, pipet tip openings should be larger than 2000 μm in order to minimize floc breakage. If flocs are large and/or weak, the tip opening of pipets should be larger than 3000 μm . All commercially available pipets have unacceptably small tip openings. Studies of flocs should include measurement to show that sampling methods do not disrupt flocs.

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Improved Method for Polychlorinated Biphenyl Determination in Complex Matrices

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■ An improved method is described for pretreatment of samples for the determination of trace-level polychlorinated biphenyls (PCB's) using conventional gas chromatography. After initial treatment with concentrated sulfuric acid, the samples were subjected to further digestion with potassium permanganate and ultrasound. Removal of digestion products was accomplished with a Florisil microcolumn, and analysis performed by packed-column gas chromatography. Various difficult matrices were subjected to the new procedure. High recoveries of PCB's were obtained with minimal interferences. The method is fast, inexpensive and effective in many cases, particularly for road oils and sludges, where other methods are inadequate. It also provides detection limits well below acceptable tolerances set by current regulations.

Introduction

Polychlorinated biphenyls (PCB's) were originally used as heat-transfer fluids, dielectric fluids for capacitors and transformers, and as hydraulic fluids for diecasting because of their thermal stability and nonflammable properties. They were found to be hazardous to human health, and a massive effort is underway to purge them from the environment. The analyst's job, assisting in locating and quantifying contamination, becomes frustrating and inconclusive as the complexity of the matrix increases. Analysis in water is a fairly straightforward procedure (1, 2): the sample is extracted with a suitable solvent, concentrated to a known volume, and analyzed by electron-capture gas chromatography. Oils and sludges, however, are unsuitable for solvent extraction, frequently contain large amounts of chlorinated hydrocarbons, industrial byproducts, and particulate matter, and at the same time have the highest potential for large concentrations of PCB's.

Table I. Some Analytical Methods for the Determination of PCB's in Complex Matrices

- (1) EPA electrolytic conductivity
- (2) acid, then florisil, alumina, or silica gel (EPA electron-capture procedure)
- (3) florisil addition
- (4) SbCl₅, perchlorination
- (5) oil/methanol partition
- (6) column chromatography
- (7) permanganate digestion

Table I lists several approaches which have been used to separate complex waste materials from PCB's. The Environmental Protection Agency has tentative guidelines which it is evaluating for testing various types of oils (3). The first of these methods is a simple dilution followed by analysis on an electrolytic conductivity detector. Halogenated compounds can interfere in this analysis. The second is a method which has been used with considerable success on biological materials, cleaner oils, and non-chlorinated solvents. This procedure (referred to hereinafter as the EPA electron-capture (EC) procedure) involves weighing an amount of sample, diluting with hexane, shaking with concentrated sulfuric acid, and removing impurities with a small Florisil, silica gel, or alumina column. This new method has been applied particularly to those cases in which the EPA electron-capture procedure was ineffective.

The other methods currently in use for PCB determination require only a brief mention. Florisil addition involves diluting the sample and shaking with Florisil to adsorb impurities. Perchlorination with antimony pentachloride involves converting all of the PCB present to a single compound, decachlorobiphenyl (4). Although effective, the procedure is time-consuming and requires the analyst to use a highly toxic reagent. Oil/methanol

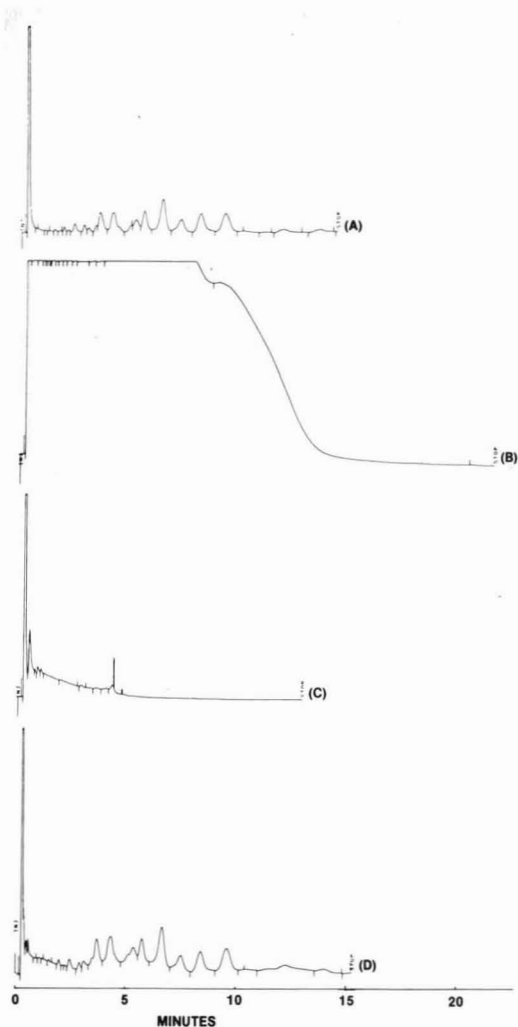


Figure 1. Progressive analysis of a chlorinated alkane mixture in a cutting oil: (A) Aroclor 1254 standard; (B) sample subjected to EPA electron-capture procedure; (C) sample subjected to new procedure; (D) sample subjected to new procedure after being spiked with Aroclor 1254.

partition consists of extracting the oil with a known amount of methanol to extract a consistent 30% of the PCB concentration. Unfortunately, much of the oil dissolves in the methanol, too, making it unusable for determinations at low levels. Column chromatography is time-consuming and uses large amounts of expensive solvent (5, 6). The goal in the development of an analytical procedure is a method that is fast, accurate, and inexpensive and selectively eliminates interferences without significantly altering the measurable PCB concentration. The new permanganate digestion method approximates these conditions rather well, particularly in cases which were not amenable to analysis in the past.

Experimental Section

The instrumentation used in the study consisted of a Hewlett-Packard 5730A gas chromatograph equipped with a Nickel-63 electron-capture detector, an H/P 3380A integrator, and an H/P 7672A autosampler. The following chromatographic conditions were used: 1.5% OV-17/

Table II. Precision and Accuracy Data Based on Quadruplicate Analyses of Virgin Lubricating Oil Spiked with Three Different Aroclor Mixtures

PRECISION & ACCURACY AT 1-10 ug/g			
STANDARD DEVIATION	AVG. % RECOVERY		
	PCB 1242	PCB 1254	PCB 1260
EPA EC METHOD	97%	123%	95%
	—	—	—
NEW KMnO ₄ METHOD	81%	78%	66%
	8%	4%	8%
CONTROL	84%	99%	79%
	1%	1%	1%

1.95% QF-1 on Supelcoport packed in a 6-ft long, 2-mm i.d. glass column with argon/methane carrier gas at 60 mL/min, 200 °C isothermal oven temperature, at attenuation 64. Other equipment and supplies required included concentrated sulfuric acid, 5% aqueous potassium permanganate, 2-dram glass vials with Teflon-lined screw caps, Pasteur pipets, activated Florisil (activated at 130 °C for at least 24 h), glass wool, anhydrous sodium sulfate, and an ultrasonic bath.

Using the EPA procedure as a framework, we added two small but significant steps. Relying on the ability of polychlorinated biphenyls to withstand chemical oxidation, we subjected the samples to various strong oxidizing agents after initial treatment with concentrated acid in an attempt to digest the remaining impurities. The acid was removed from the vial with a pipet before addition of the oxidizing agent. A 5% aqueous solution of potassium permanganate was chosen as the most promising. The most effective method of mixing the sample proved to be an ultrasonic bath. Shaking the mixture vigorously, even for several minutes, was not as effective. Fifteen minutes in the sonic bath appears to be the optimum time for destruction of impurities with highest recovery of PCB's.

The following is the complete permanganate digestion procedure: (1) Weigh 50–100-mg sample into a 2-dram vial. (2) Dilute to 2 mL with hexane. (3) Add 2 mL of concentrated sulfuric acid. (4) Cap tightly with a Teflon-lined cap and shake vigorously for 30 s. Allow layers to separate. (5) With a Pasteur pipet, draw out the acid layer. (The small amount of acid remaining in the vial will not disturb the analysis.) (6) Add 2–3 mL of 5% aqueous potassium permanganate solution. Cap tightly. (7) Suspend the vial in a sonic bath for 15 min, making sure the water level in the bath is above the liquid level in the vial. (8) Allow the layers to settle. (Centrifugation may be necessary if large amounts of particulate oxidation products are present.) (9) Pass the solvent layer through a Florisil microcolumn (made by packing a Pasteur pipet with 6–8 cm of Florisil and 0.5 cm of anhydrous sodium sulfate); wash the permanganate layer thoroughly with

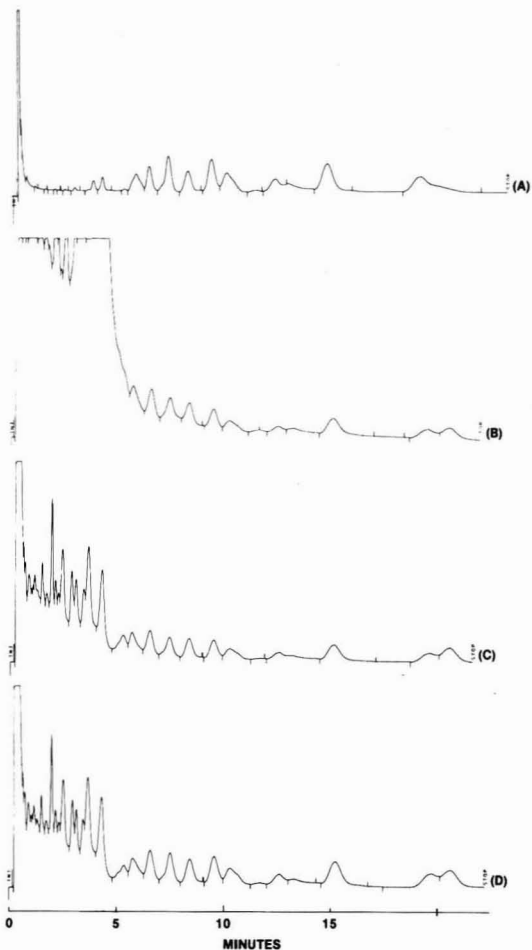


Figure 2. Progressive analysis of a waste crankcase oil: (A) Aroclor 1260 standard; (B) sample subjected to EPA electron-capture procedure; (C) sample subjected to new procedure; (D) sample subjected to new procedure after being spiked with Aroclor 1260.

fresh hexane 2-3 times and add the washings to the top of the column. (10) Elute with 3-4 mL of hexane. (11) Concentrate to a desired volume, if necessary. (12) Analyze by electron-capture gas chromatography.

Three particularly troublesome samples were each analyzed by the EPA procedure, the permanganate digestion procedure, and the permanganate digestion procedure spiked with various PCB mixtures before the analysis. In addition, several samples of a clean oil were spiked with various PCB mixtures and analyzed via the new method to determine precision and percent recovery. Finally, standard solutions of three PCB mixtures were subjected to permanganate and ultrasound without acid or Florisil treatment to determine the loss attributable to the modifications in the method.

Results and Discussion

Figures 1-3 show the progressive improvement in three practical samples. These samples were chosen out of a group actually received at an analytical laboratory because of their particularly troublesome characteristics.

In Figure 1A is a standard Aroclor 1254 mixture, 0.54 ppm by mass. Figure 1B is a chlorinated alkane mixture

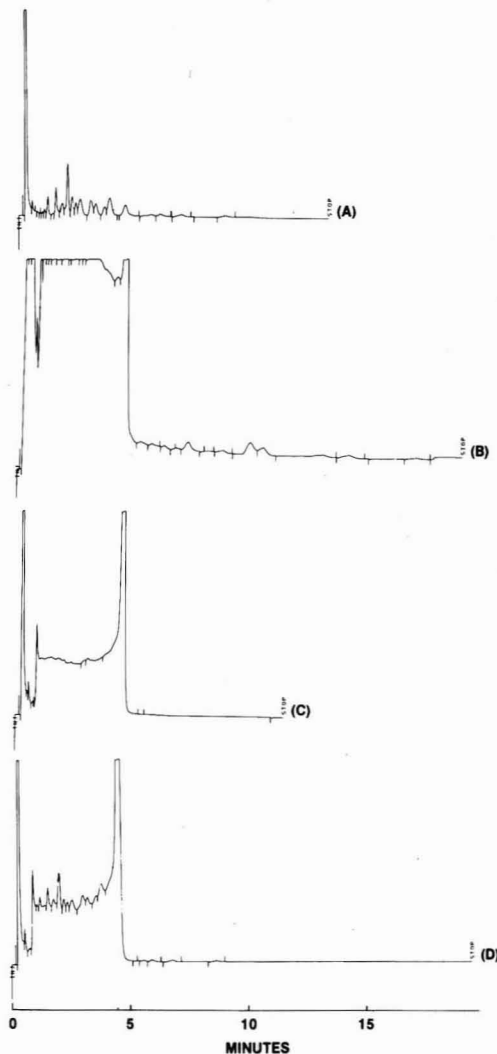


Figure 3. Progressive analysis of a refinery oil sludge emulsion: (A) Aroclor 1242 standard; (B) sample subjected to EPA electron-capture procedure; (C) sample subjected to new procedure; (D) sample subjected to new procedure after being spiked with Aroclor 1242.

in a cutting oil subjected to the EPA electron-capture procedure. The contamination is too severe for any quantitation. Figure 2C is a second similar quantity of the same subjected to the permanganate digestion. The contamination has been noticeably reduced. Finally, Figure 1D is the sample spiked with 1.52 μg of Aroclor 1254 and digested under the conditions of the new method. The recovery of this spike was 96%, somewhat high compared to average recovery from clean oils, indicating that trace contaminants may remain. The sample chromatogram is, however, vastly improved.

Figure 2 shows a similar progression in a used crankcase oil. This particular sample contains a fairly high concentration of Aroclor 1260, but it is only after the permanganate digestion (Figure 3C) that the Aroclor 1248 concentration can be recognized and quantified as well. Figure 2D is the same sample spiked with 0.56 μg of Aroclor 1260. There was a 61% recovery of this spike, close

to the average percent recovery expected.

Figure 3 shows again the same progressive improvement in an emulsified oil sludge sample. This cannot be regarded as a completely satisfactory analysis, but it is possible to establish a detection limit below 50 ppm after the permanganate digestion, allowing at least some information to be gathered.

Finally, Table II shows some precision and percent recovery data obtained by spiking clean lubricating oil with three different Aroclor mixtures. The EPA electron-capture procedure is precise and accurate but, as has been seen, inadequate in some cases. The permanganate digestion method destroys a certain amount of the PCB's, but with reasonable precision. The control data indicates that most of the PCB loss is indeed occurring in the permanganate/ultrasound step of the procedure, at least for Aroclors 1242 and 1260.

As the data indicate, the problems involved in determining PCB's in oil cannot be considered solved, but the permanganate digestion method improves the situation

considerably. Further work should be done to determine the relationship between time in the sonic bath and degradation of PCB concentration. (Although no explosions or other violent reactions have been observed in applying this technique to several hundred samples, care should be exercised whenever acid, permanganate, and organic materials are mixed.)

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Atmospheric Trace Gases over China

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■ Flask sampling, EC/GC, and FID/GC techniques were used to measure the concentrations of CO, CH₄, CH₃Cl, N₂O, CCl₄, CH₃CCl₃, CCl₃F, CCl₂F₂, and CHClF₂ in the air over four urban and three rural areas in the People's Republic of China. The results were compared with the concentrations of these trace gases found over urban and rural areas of Oregon, U.S.A. More CCl₄ and CH₃Cl were found over Chinese cities than over Oregon cities or over rural China. CO, CH₃Cl, N₂O, and CH₄ were all significantly more abundant over rural China than over the clean background site in Oregon. In China rural sources of CO and CH₃Cl include smoldering combustion in homes, whereas rice paddies and biogas conversion may be sources of CH₄. Our results show that China may have significant anthropogenic sources of CH₄, N₂O, and CCl₄, all of which are increasing in the atmosphere and may alter the earth's climate if their increases continue for a long time.

Introduction

For a long time, people living in cities have been aware of hazardous air pollution in the form of smoke and haze, but over the past decade new fears have emerged, that the unseen gaseous emissions from industrialized cities may eventually alter the earth's total atmospheric environment. Concerns have centered around the environmental consequences of depleting the stratospheric ozone layer, altering the temperature of the lower atmosphere and affecting the earth's climate (1, 2). To address these complex issues requires more detailed observations of the atmospheric distributions of trace gases than are currently available (3). In particular, the natural trace gases, CH₄, CO₂, CO, CH₃Cl, and N₂O, likely to be increased by human activities, and the purely anthropogenic gases CCl₃F (F-11), CCl₂F₂ (F-12), CHClF₂ (F-22), CCl₄, and CH₃CCl₃ are among those believed to be important in determining the

effects of human activities on the global environment (4).

Recently it has been established that methane (CH₄) and nitrous oxide (N₂O) are increasing in the earth's atmosphere (5-9). The magnitudes and the locations of the anthropogenic sources of these trace gases can be determined probably by no other means than atmospheric measurements. As a part of this goal we report our first measurements of CH₄, CO, CH₃Cl, N₂O, CCl₄, CH₃CCl₃, F-11, F-12, and F-22 in the urban (Beijing, Hangzhou, Nanjing, and Wuxi) and rural (Xi'an, Luoyang, and Suzhou) areas of the People's Republic of China—a country containing a fourth of the world's human population. We also measured these trace gases over Oregon, U.S.A., cities (Portland, Oregon City, Newberg, Salem, Corvallis, and Beaverton) and over the background site at Cape Meares, OR. Exact locations of the cities are given in the microfilm appendix (see paragraph at the end of the text regarding supplementary material). We recognize that our data are few and we do not have supporting meteorological data; still the results of the experiment suggest that in China there may be significant anthropogenic sources of CH₄, CH₃Cl, CO, N₂O, CCl₄, and even CH₃CCl₃.

Measurements and Analyses

The samples of air were collected in stainless-steel canisters and brought to the Atmospheric Trace Gas Laboratory of the Oregon Graduate Center (OGC), where the halocarbons and N₂O were measured by electron capture-gas chromatography (EC/GC) techniques and CO, CO₂, and CH₄ by FID-M/GC methods (10, 11). The collection techniques, preparation of the canisters with inert internal surfaces, and the methods of analysis have all been designed and experimentally established to provide accurate and precise atmospheric measurements of the nine trace gases which we consider in this study. The

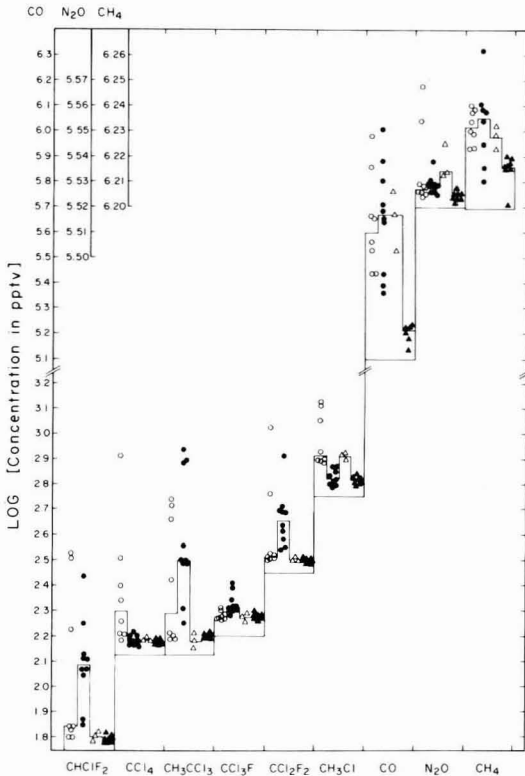


Figure 1. Trace gas concentrations in urban and rural areas of China: (O) urban China; (●) urban U.S. (Oregon); (Δ) rural China; (▲) rural U.S. (Oregon). Medians are marked by horizontal bars.

details of the experimental techniques, especially relevant to this study, are given as supplementary material.

The results of all of the measurements of CHClF_2 (F-22), CCl_4 , CH_3CCl_3 , CCl_3F (F-11), CCl_2F_2 (F-12), CH_3Cl , CO , N_2O , and CH_4 are shown in Figure 1. There are four groups of points for each trace gas: the first column contains concentrations in urban areas of China (CU, O); next to it are the concentrations in urban areas of the U.S. (Oregon) (UU, ●); the third column shows concentrations in rural China (CR, Δ); and the last column contains measurements at the clean air, background U.S. (Cape Meares, OR) site (UR, ▲). Figure 1 contains practically all of the information that we were able to obtain in this study. It shows the variability, the distribution, and the patterns of differences of concentrations in each of the four environments (CU, UU, CR, and UR). The complete numerical data used to obtain Figure 1 are given as supplementary material along with the precision of measurement, the sites to which the measurements correspond, and the average concentrations in each of the four environments.

To support the evidence of differences in the trace gas concentrations among the four environments and to estimate the magnitudes of these differences, we applied statistical techniques to the data. For each trace gas the data were divided into four groups (CU, CR, UU, UR) and we compared concentrations in urban China (CU) with urban U.S. (UU), rural China (CR) with rural U.S. (UR), urban China (CU) with rural China (CR), and urban U.S. (UU) with rural U.S. (UR). The mechanisms responsible for atmospheric variability of trace concentrations are different in areas near the sources compared to areas far

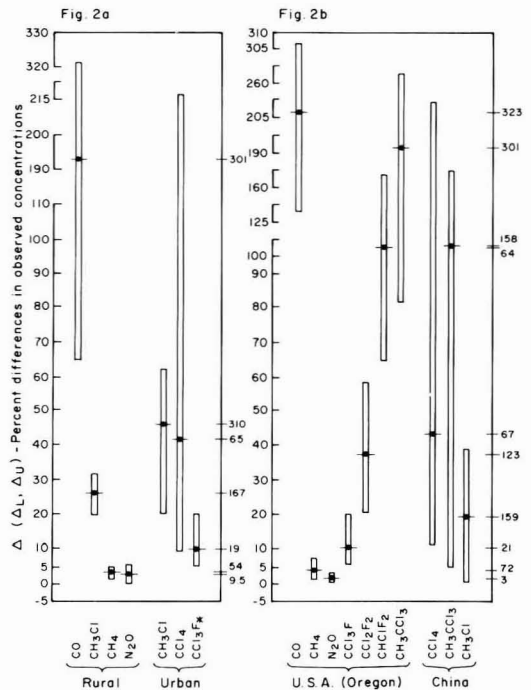


Figure 2. (a) Differences of trace gas concentrations between U.S. (Oregon) and China. The set of results under "rural" are a comparison of rural China with rural Oregon; results under "urban" are a comparison of urban China with urban U.S. (Oregon). Concentrations over China are greater than over U.S. for all gases listed except F-11, which is more abundant over U.S. cities than over Chinese cities. (b) Differences of trace gas concentrations within China and U.S. (Oregon). Differences of concentrations between U.S. (Oregon) rural and U.S. (Oregon) urban areas are reported under "U.S.A. (Oregon)". Similarly comparisons of urban and rural China are reported under "China". For all listings concentrations over urban areas were larger than over rural areas. Scales on the left are estimates of average differences in pptv for the halocarbons and ppbv for CO , CH_4 , and N_2O .

from sources. Therefore, the variances of the concentration distribution, particularly between urban and rural areas, are unequal. We took this into account by using the Welch test (12) to compare the differences of mean concentrations. When any two groups being compared had very different variances, we were able to apply a distribution-free Wilcoxon signed rank test (13) and thus avoid the assumption of normality of distribution inherent in the Welch test. In either case, we calculated the estimated average difference between the concentrations in two groups and the approximately 90% confidence limits of the difference. The results of all of these calculations, along with a discussion of statistical techniques, are given as supplementary material. The differences, which we were able to support statistically, are summarized in Figure 2, a and b, which contains the estimate of average difference along with approximate 90% confidence limits for the difference. Figure 2 is based on the distribution-free Wilcoxon test for all comparisons except comparisons of rural China concentrations with rural U.S., comparison of CH_3Cl concentrations in urban and rural China, and comparisons of CH_4 , N_2O , and CCl_4 concentrations in rural and urban U.S., which are based on the Welch test because in these cases the conditions allowing the application of the Wilcoxon test were not realized. In order to represent all of the calculated differences on the same graph (Figure 2), we calculated $\Delta = (100\%) [\Delta / \min(\bar{x}_1, \bar{x}_2)]$ where Δ is

the estimated average difference between any two sets of data being compared and \bar{x}_1 and \bar{x}_2 are the means of the same two sets of data.

Discussion and Conclusions

The patterns of human influence on trace gas concentrations in the air over China are revealed in Figure 2. Some of these patterns stand in sharp contrast to those found in the U.S. (Oregon).

Even though western Oregon cities, where measurements were made, are not heavily industrialized, the urban concentrations of all but two trace gases were significantly elevated. The exceptions were CH_3Cl and CCl_4 . In contrast, concentrations of CH_3Cl and CCl_4 were much higher in urban China compared to either rural China (Figure 2b) or urban U.S. (Figure 2a). Generally, the urban concentrations of fluorocarbons (F-11, F-12, and F-22) in China are at the same levels as the U.S. clean background except at Beijing, where high F-12 and F-22 concentrations and slightly higher F-11 concentrations were observed. High concentrations of CH_3CCl_3 were sometimes observed in urban China. On the basis of these observations, we believe that CH_3CCl_3 and particularly CCl_4 are probably used in industrial processes in China, whereas the use of fluorocarbons (F-11, F-12, and F-22) does not appear extensive.

Perhaps the most unusual result of this study is the contrast of the rural environments of China and U.S. (Oregon) (Figure 2a). CO , CH_3Cl , CH_4 , and N_2O are more abundant in rural China than in rural U.S. Observations of living patterns suggest that in southeastern China dense population and smoldering fires in homes provide local rural sources of CH_3Cl and CO . Sources of CH_4 in rural China include the 7.5 million biogas installations distributed over China (14) and rice paddies (15). Since CCl_4 can serve as a tracer of urban plumes in China, its low concentrations in rural areas support the contention that local rural sources of CO , CH_3Cl , CH_4 , and N_2O exist.

The slightly higher N_2O concentrations found both in U.S. (Oregon) and in China provide further support that combustion is an anthropogenic source of N_2O (16, 17). Compared to trace gases of purely anthropogenic origin, the natural background levels of CH_4 and N_2O are so high that it takes enormous anthropogenic emissions to raise their levels by a few percent.

Since China is a huge country, in terms of both land area and population, the rural flux of medium-lived gases, CH_3Cl ($\tau \sim 2$ yr), CH_4 ($\tau \sim 10$ yr), and N_2O ($\tau > 15$ yr), could provide a measurable and increasing anthropogenic contribution to the global burden of these gases. Increasing or continuing worldwide anthropogenic emissions of these gases and halocarbons could lead to adverse environmental effects by diminishing stratospheric ozone and changing the earth's climate (2, 5, 6, 9, 18). The implications of our study demonstrate the need to expand the few data that we have from China to cover greater geographical areas and long times so that we may further substantiate and quantify the anthropogenic sources of N_2O , CH_4 , CCl_4 , and CH_3Cl from China.

Supplementary Material Available

Eleven sections (16 pages), described below, will appear following these pages in the microfilm edition of this volume of the journal: (1) summary of experimental techniques; (2) sample collection and number of samples collected; (3) statistical analyses; (4) Table 1, latitudes and longitudes of sampling sites; (5) Table 2, concentrations (pptv) of anthropogenic trace gases in urban

and rural atmospheres of the People's Republic of China; (6) Table 3, concentrations of trace gases in urban and rural atmospheres of the People's Republic of China, April–May 1980; (7) Table 4, concentrations of trace gases in the U.S. (urban areas) at several cities in Oregon, September–October 1980; (8) Table 5 concentrations of trace gases in the U.S. (rural background) at Cape Meares, OR, April–July 1980; (9) Table 6, comparison of trace gases in air samples from the People's Republic of China and the U.S. (Oregon): mean concentration (\pm standard deviations) in urban and rural atmospheres; (10) Table 7, levels of significance (α) and related statistical results in the comparison of trace gas concentrations in China and the U.S. Pacific Northwest; (11) Table 8, estimates of differences (Δ) with approximate 90% confidence limits (Δ_L , Δ_U) in the comparison of trace gas concentrations in China and the U.S. Pacific Northwest. Photocopies of the supplementary material from this paper or microfiche (105 × 148 mm, 24 × reduction, negatives) may be obtained from Business Operations, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Full bibliographic citation (journal, title of article, author) and prepayment, check or money order for \$16.00 for photocopy (\$17.50 foreign) or \$4.00 for microfiche (\$5.00 foreign), are required.

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Mean Residence Time of Plutonium in the Troposphere

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■ Plutonium is injected into the stratosphere by large atmospheric thermonuclear explosions. When aerosols bearing plutonium reenter the troposphere, they are removed by such processes as rainfall and sedimentation. In this work, the mean tropospheric residence time of stratospherically injected plutonium is calculated. A mean residence time of 71 days was obtained for the Northern Hemisphere. Calculated residence times showed little variation by geographic location or for different years.

Introduction

The mean residence time of aerosols in the troposphere is a quantity of considerable importance in relation to atmospheric pollutants, especially for those pollutants which are attached to the aerosol particles. Much effort has gone into the measurement of the aerosol residence time without producing an answer that is generally accepted. Some of the more common methods for estimating residence time use natural radioactive tracers such as ^{210}Pb , ^{210}Bi , and ^{210}Po (1-4). Other estimates have been made by using cosmic-ray-produced nuclides and nuclear weapon debris. The apparent residence times calculated by these methods are often discordant, with the estimates ranging from 4 to 65 days (1-6).

Since 1952, the stratosphere has had an inventory of artificial radioactivity more or less continuously. An estimate of aerosol residence time in the troposphere must then include the effect of the addition of radioactive particles from the stratosphere. Since the transfer process from the stratosphere has not been completely understood, natural radioactive tracers have been favored as a method of estimating the mean residence time of aerosols in the troposphere. The natural radioactive tracers used for this purpose are for the most part confined to the troposphere, and corrections for stratospheric input are not necessary.

During the last 10 years, more information has accumulated concerning the transfer of material from the stratosphere to the troposphere. It now seems possible to estimate the mean tropospheric residence time of aerosols by using artificial radioactive tracers. In this work, an estimate is made of the mean residence time of plutonium, and the results are compared with the residence times obtained by other methods.

Results and Discussion

The calculated residence times shown in Table I are derived from $^{239,240}\text{Pu}$ monthly concentrations in surface air as reported by the Environmental Measurements Laboratory (7). The data are combined into bimonthly averages of concentrations to reduce short-term fluctuations which are not of interest here. Residence times were calculated only for those periods which were free of low-yield atmospheric nuclear explosions, since these explosions would interfere with the removal rate determination.

A June 1974 thermonuclear test by China injected debris into the stratosphere, but very little was detected in the troposphere during the summer and fall of 1974 (8). It

Table I. Mean Residence Time of Plutonium in the Troposphere

	τ , day		
	1971 ^a	1974 ^a	1975 ^b
Mauna Lao, HI	65	65	67
Moosonee, Ontario	85	79	44
New York City	89	81	66
Bimini, Bahamas	66	c	c
Salt Lake City, UT	69	82	c
Miami, FL	58	c	96
av	72 ± 12	77 ± 8	68 ± 21

^a Based on monthly concentrations whose standard deviation of counting was less than 20%. ^b Based on monthly concentrations containing one or more months where the standard deviation was 20-100% and the remaining months less than 20%. ^c Incomplete data.

therefore seemed reasonable to use that year for residence time calculations.

The residence time of plutonium is derived from the rate of decrease of the tropospheric air concentrations during the summer and fall months. The initial concentration is taken to be the average concentration for May and June. This is often the peak concentration during the year, although the spring peak sometimes occurs during March or April.

Assuming that the amount of debris which enters the troposphere from above during the months of July, August, September, and October is insignificant, one can easily obtain the troposphere residence time from the rapidly decreasing concentrations during the summer and fall.

There is considerable evidence which indicates that the transfer of debris from the stratosphere is insignificant during July through October in comparison to the large amounts of debris which enters the troposphere during the spring peak. For example, Krey and Krajewski (9) concluded that the debris injected into the lower stratosphere in June 1967 by a 3-megaton Chinese explosion did not begin to leave the stratosphere until November of that year. Bauer et al. (10) concluded that material injected into the stratosphere in the summer does not leave until the following winter. More recently, Holloway (11) noted that only trace amounts of fallout were deposited in the summer and fall of 1973 in Arkansas even though a substantial inventory of debris existed in the lower stratosphere. The fact that fission product concentrations often decrease by 1 order of magnitude in the months following the spring peak is also evidence that there is relatively little debris entering the troposphere during the summer and fall.

The November-December concentrations are not used in the residence time calculations presented here since there is some evidence suggesting that stratospheric debris may begin to enter the troposphere during November and December (10).

The time (T) required for the tropospheric concentrations of the tracer to be reduced by half is given by the equation

$$T = 0.693t / \ln(Q_1/Q_2) \quad (1)$$

where Q_1 is the concentration of the initial inventory as

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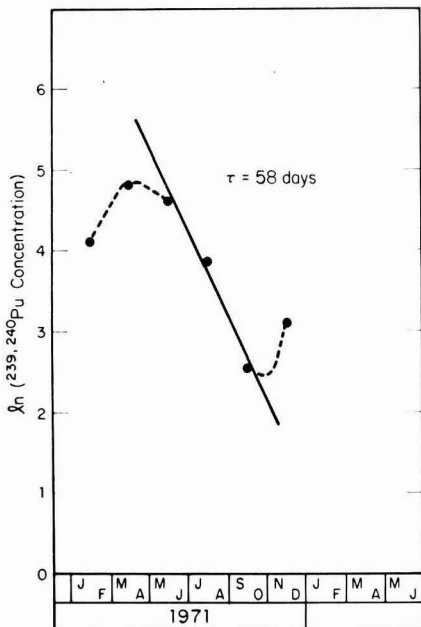


Figure 1. Seasonal variations of the $^{239,240}\text{Pu}$ concentrations in surface air at Miami, FL, in 1971.

measured by the May–June concentration, Q_2 is the concentration at some later time, and t is the time interval in days between Q_1 and Q_2 . The time (T) required to remove half of the debris is less than the mean residence time (τ), and they are related by the equation

$$\tau = T/0.693 \quad (2)$$

The mean residence time then can be expressed as

$$\tau = t/\ln(Q_1/Q_2) \quad (3)$$

At a particular location, the concentration of $^{239,240}\text{Pu}$ in the atmosphere decreases approximately exponentially

during July through October in the Northern Hemisphere. However, the bimonthly concentrations seldom fit precisely on a line corresponding to a specific residence time. To obtain the best estimate of residence time at each location, we converted the bimonthly concentrations for May through October to natural log form, and a line was fitted to the three points by the least-squares method. The mean residence time was calculated by using eq 3 and Q values obtained from the fitted line. The calculated residence times are given in Table I. Figure 1 shows the typical seasonal variations in plutonium concentrations at a single location. Note that the bimonthly concentrations for May through October deviate slightly from a straight line. These deviations are typical for the concentrations measured at a single location and probably result from meteorological factors rather than analytical error. Transient meteorological conditions on a time scale of a few weeks could cause variations in the removal rate over fairly large regions. The result would be variations of the measured concentrations about the line corresponding to the best single residence time.

In order to reduce the influence of regional effects, it seemed appropriate to average the bimonthly concentrations of the widely dispersed sampling locations. The results are shown in Figure 2. The summer and fall bimonthly concentrations fit the line corresponding to a single residence time remarkably well. The air concentration measurements for the locations in Table I were used to obtain the averages plotted in Figure 2. The resulting residence times (τ) in Figure 2 can be considered as typical of the Northern Hemisphere since they are derived from air concentrations at widely dispersed locations.

The average of the three residence times shown in Figure 2 is 71 days. This is higher than most previous calculations of residence time, but it is in good agreement with the results of Marengo and Fontan (2), who calculated a global tropospheric residence time of 65 days based on the $^{210}\text{Po}/^{210}\text{Pb}$ ratio. The longer residence times of 65 and 71 days do not necessarily conflict with estimates in the 30–40-day range. Marengo and Fontan's 65-day result was obtained from the $^{210}\text{Po}/^{210}\text{Pb}$ ratio throughout the entire troposphere (2). The 35-day estimate of Nevissi et al. (4) was based on the same ratio in rain samples. The 71-day

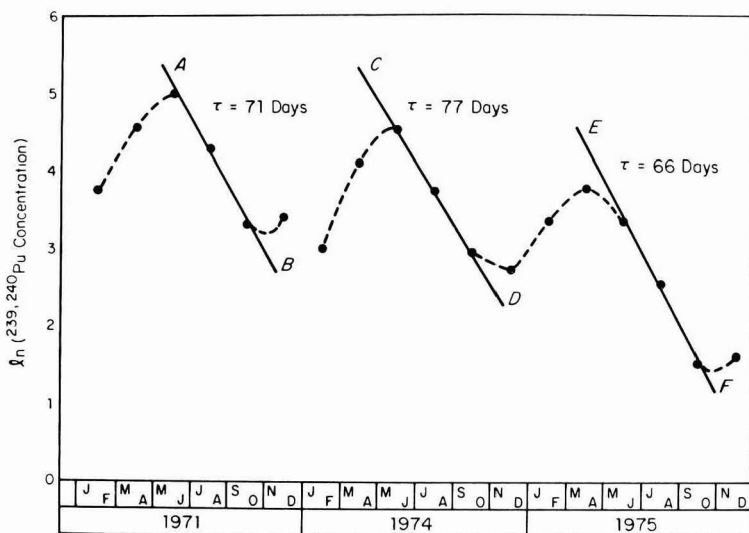


Figure 2. Average bimonthly concentrations of $^{239,240}\text{Pu}$ for the Northern Hemisphere. The locations used to obtain the average concentrations are those listed in Table I.

residence time obtained in this work is derived from particles that have been transported downward from the stratosphere to near the earth's surface. It is reasonable to expect some variations in calculated residence time if the particles being sampled have had quite different origins. In the case of ^{210}Pb and ^{210}Po , both are formed in the troposphere from the decay of ^{222}Rn . An additional source of ^{210}Po from volcanic emission has been suggested recently by Lambert et al. (12). Their results indicate that volcanoes may be a significant source of ^{210}Po compared to the decay of atmospheric ^{222}Rn . Since their estimate of volcanic ^{210}Po is an order of magnitude estimate, the extent to which the tropospheric $^{210}\text{Po}/^{210}\text{Pb}$ ratio is influenced by volcanic emissions is not clear. Moore et al. (13) favor a residence time of only 4–6 days in the troposphere and suggest that soil particles and plant exudates are the major sources of ^{210}Po in the atmosphere.

The particle size distribution of plutonium-bearing aerosols may also be slightly different from the size distribution of particles containing natural radioactive tracers. This might lead to different residence times for each type of aerosol. Fission products in the stratosphere are attached to particles whose average diameter is approximately $0.2\ \mu\text{m}$ (14). After these particles enter the troposphere, a definite shift toward larger mean diameter has been observed. For example, Gasiev et al. (15) found that only 3% of the β activity at ground level was associated with particles with a diameter of less than $0.3\ \mu\text{m}$, while at an altitude of 5–6 km about 48% of the β activity was associated with particles of that size fraction. The shift toward larger particles in the troposphere is thought to be caused by coagulation of the radioactive particles with natural aerosols. Presumably, natural radioactive tracers such as ^{210}Pb and ^{210}Po undergo the same process, though the original attachment of ^{210}Pb and ^{210}Po would be to particles of less than $0.3\text{-}\mu\text{m}$ diameter (16). It should be noted that Moore et al. (17) have found cases where the shift to larger particle sizes did not occur for ^{90}Sr as measured in surface air. Because of the stratospheric source of the plutonium-bearing particles and possible differences in their size distributions compared to other tracers, the residence time of 71 days may be slightly more than the true residence time of natural aerosols. However, our results tend to support these estimates which range from 30 to 65 days rather than the much shorter residence time estimates of 5 to 10 days. There is also the possibility that the 71-day residence time estimated from plutonium-bearing particles is valid for natural aerosols in general. The good agreement with the 65-day estimate of Marengo and Fontan (2)

tends to support this interpretation.

Conclusions

The removal rate of plutonium-bearing aerosols from the troposphere can be calculated from the decrease of the tropospheric inventory present during the spring. The removal rate corresponds to a mean residence time of 71 days. This is a Northern Hemispheric residence time and only slight variability was observed at widely dispersed locations.

The mean residence time for plutonium should be similar to that of natural aerosols, although not necessarily identical.

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CORRESPONDENCE

Correspondence On: Anaerobic Degradation of Halogenated 1- and 2-Carbon Organic Compounds

SIR: We are writing in regard to your article "Anaerobic Degradation of Halogenated 1- and 2-Carbon Organic Compounds" (*ES&T* 1981, 15, 596). The article stated that no aerobic conditions were found under which chloroform in the 10–100 $\mu\text{g/L}$ range could be degraded after 25 weeks of incubation in the dark at 20 °C. For the study, a primary sewage bacterial inoculum in chloroform–mineral salts medium was used.

In July 1980, a 20000-gal chloroform spill occurred which contaminated both soil and groundwater. This spill created a unique situation with regard to the enrichment of chloroform degraders. Using a chloroform-contaminated soil inoculum collected in April 1981 from the spill site, our laboratory recently completed a 27-day study using an electrolytic respirometer which demonstrated chloroform reduction under aerobic conditions. The electrolytic respirometer is a closed system with oxygen generated within the system.

For the study, duplicate 1-L respirometer vessels containing chloroform–mineral salts medium were each inoculated with 50 g of chloroform-contaminated soil. In addition, one of the two vessels received a suspension of commercially available selected microbial strains. A third vessel was prepared which served as an uninoculated control. The soil contained a chloroform concentration of 490 mg/L and a microbial aerobic heterotroph population of 10^6 colony-forming units/g. For the purpose of the study, the chloroform concentration in each of the respirometer vessels was adjusted to approximately 500 mg/L on day 3.

The degradation rates were determined from day 9 to day 27. On day 9, chloroform concentrations in the vessels were 580 and 560 mg/L. On day 27, the chloroform concentrations were 190 and 180 mg/L, respectively, thus demonstrating 67% and 68% chloroform reductions. The uninoculated control had an initial chloroform concentration of 530 mg/L as determined on day 9 and did not show a decrease throughout the study period. Other laboratories have also aerobically degraded chloroform at other concentration levels. We thought that this observation might be of interest to your readers.

Paul E. Flathman, James R. Dahlgran

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Received June 16, 1981

SIR: A finding that chloroform is biodegraded under aerobic conditions is an important one that should be well documented and reported. As our article mentions, we were unable to find aerobic conditions under which chloroform could be biodegraded when present at sub-mg/L concentrations, and a survey of the literature revealed no evidence for aerobic biodegradation of chloroform. However, we think that better documentation of the experiments by Flathman and Dahlgran is needed before positive confirmation of aerobic biodegradation can be claimed. Listed below are four significant problems with the report of Flathman and Dahlgran.

(1) The large amount of soil in the test apparatus (50 g/L) complicates interpretation because of possible sorptive or catalytic effects. Since the control apparently contained no soil, the results could have been related solely to the soil and not the bacteria. The problem is compounded because the report does not differentiate between dry and wet soil, between clayey and sandy soil, or between organic-rich and organic-poor soil.

(2) The relationships among the 490 mg/L of chloroform in the soil, the theoretical 500 mg/L at the start of the test, and the 560–580 mg/L after nine days are unclear.

(3) Despite being carried out in an aerobic respirometer, microanaerobic zones could have existed in the soil/water medium. This would have been especially likely if the soil had not been well mixed.

(4) The amount of oxygen utilized was not reported. Biodegradation of about 380 mg/L of chloroform aerobically would result in a significant and predictable oxygen consumption. Was oxygen consumption observed or observable in the experiments? Also, was chloride released and measured to confirm degradation?

Our reply does not imply that Flathman and Dahlgran's claim is necessarily incorrect. Instead, we stress that confidence in such an important claim can only rest on data from well-controlled and fully documented research. We encourage Flathman and Dahlgran, or others, to submit such a report.

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Received September 8, 1981

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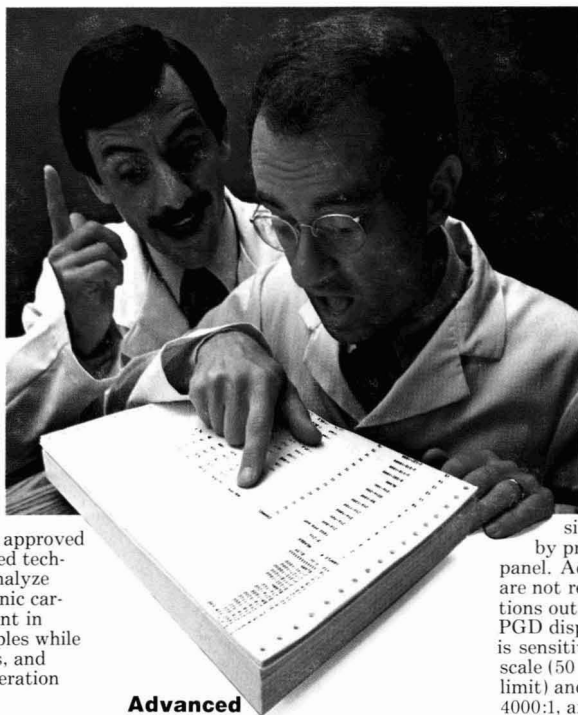
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