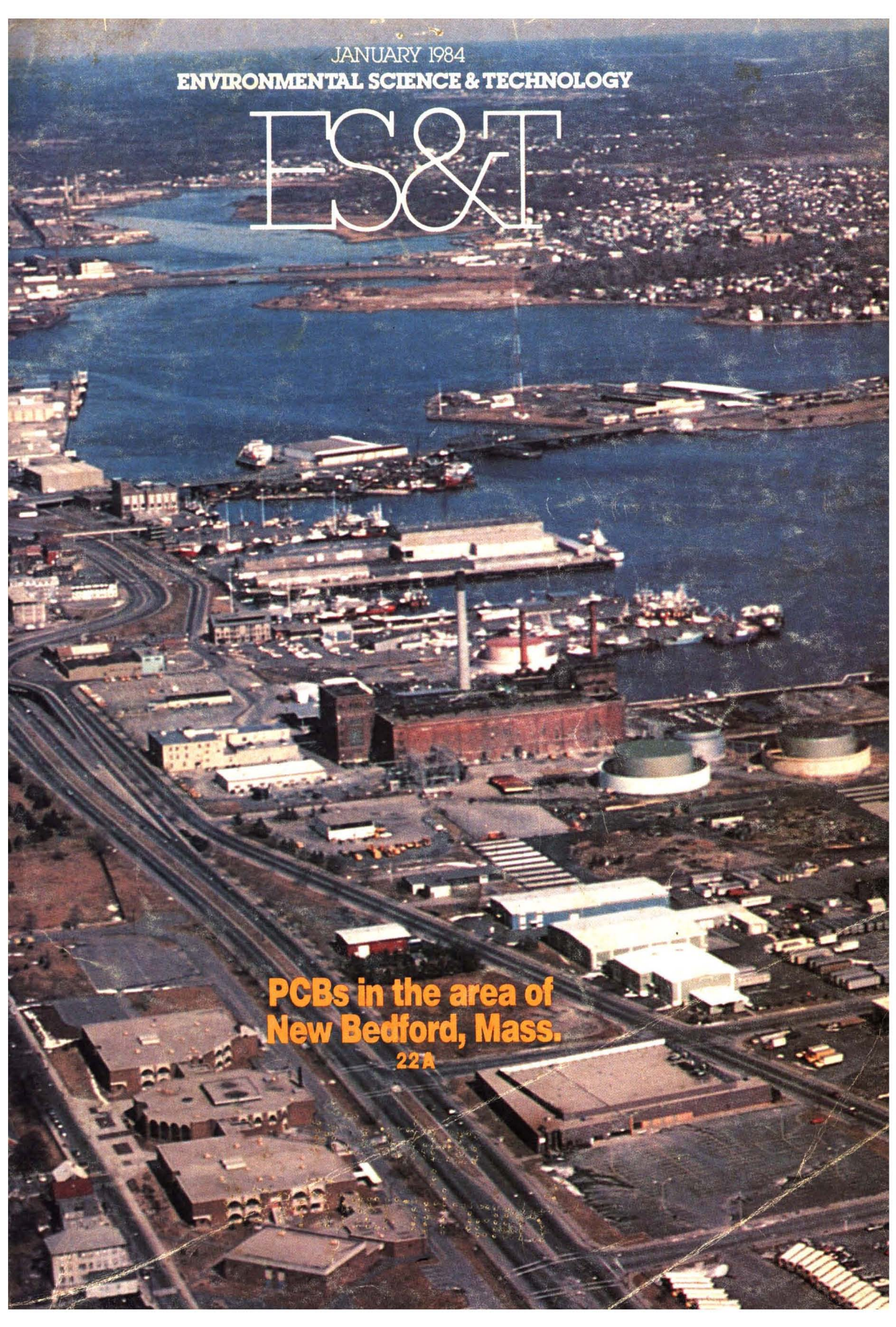


JANUARY 1984  
ENVIRONMENTAL SCIENCE & TECHNOLOGY

ES&T

**PCBs in the area of  
New Bedford, Mass.**

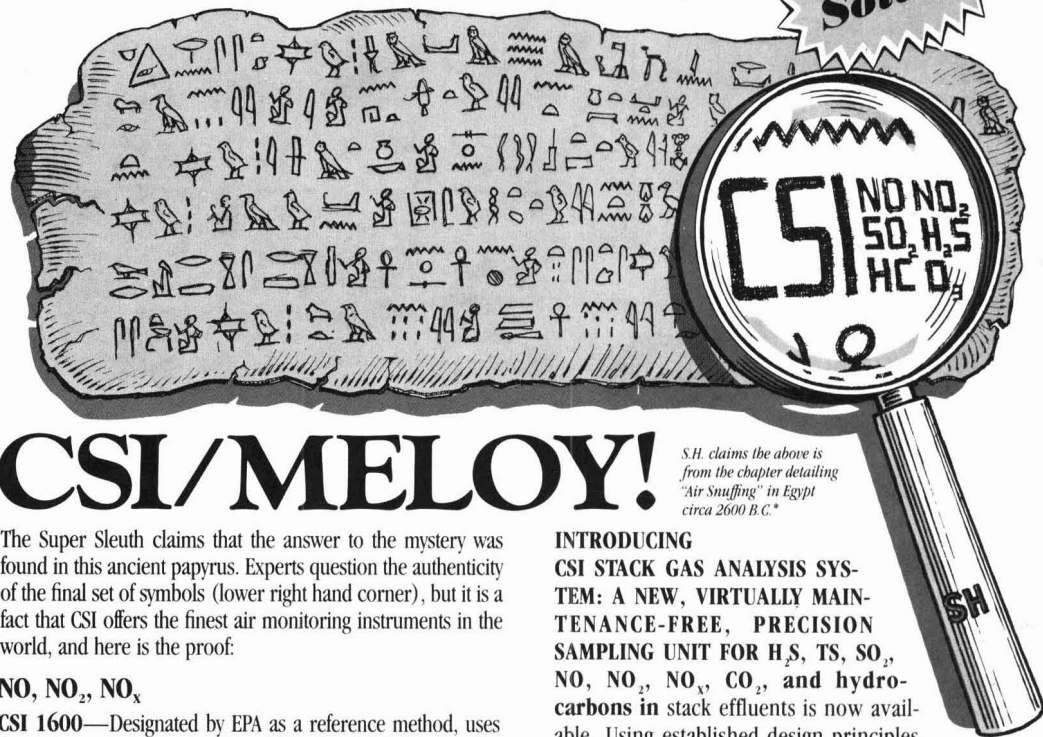
22A



*The Great Investigator does it again!*

## The case of "Who has monitoring instruments for NO, NO<sub>2</sub>, NO<sub>x</sub>, SO<sub>2</sub>, H<sub>2</sub>S, HC and O<sub>3</sub>" is

**Solved**



# CSI/MELOY!

*S.H. claims the above is from the chapter detailing "Air Snuffing" in Egypt circa 2600 B.C.\**

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**CSI/MELOY SA285E**—Continuous flame photometric analyzer, fully tested to EPA specs. Low detection limit of 0.5 ppb. EPA approved ranges from 0–50 ppb to 0–1000 ppb. Can be equipped with internal span check permeation tube option.

**CSI/MELOY SA285H**—Most sensitive H<sub>2</sub>S Monitor built today. Used in Sour Gas fields and plant atmospheres. Detection to 0.5 ppb. Circle 2 on Reader Service Card.

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The analysis system is performance proven, and the EPA designated ambient monitors insure full-time operation at a startup and an annual cost significantly below existing sampling units and systems. The built-in calibration system using SRM referenced gasses is in full compliance with EPA recommendations, and calibration is carried out at stack temperatures and equivalent flow conditions to eliminate temperature and pressure dependent variables. Circle 3 on Reader Service Card.

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Circle 4 on Reader Service Card.

\*Egyptologists may debate assignment of authorship related to portions of this document. But there is no question about who wrote the book on Air Monitoring. CSI/MeLOY did it.

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ES&T

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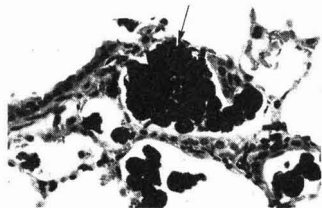
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Cover: Steve Bliven, Massachusetts Coastal Zone Management (Boston, Mass.)

# CHEMTECH

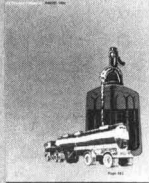
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## RESEARCH

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An increase in adsorptive capacity, resulting from bacterial removal of material adsorbed on carbon, is shown to occur in seeded GAC columns.

**5. Decomposition of organic matter in lake sediments.** Yoram Avnimelech,\* J. Roger McHenry, and John D. Ross

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**12. Elemental partitioning in ash depositories and material balances for a coal burning facility by spark source mass spectrometry.** Robert J. Conzemius,\* Timothy D. Welcomer, and Harry J. Svec

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**18. Physicochemical properties controlling polychlorinated biphenyl (PCB) concentrations in aquatic organisms.** Glen R. Shaw and Des W. Connell\*

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**23. Retrospective analysis of the response of Saginaw Bay, Lake Huron, to reductions in phosphorus loadings.** Victor J. Bierman, Jr., David M. Dolan,\* Robert Kasprzyk, and John L. Clark

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## CORRESPONDENCE

**61. Comment on "Acid fog."** W. B. Innes  
Michael R. Hoffmann

\* To whom correspondence should be addressed.

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

## Equal protection for all

The environmental and public health communities welcomed the passage of the 1974 Safe Drinking Water Act (SDWA) since it authorized the first mandatory quality standards for all publicly supplied drinking water in the U.S. It was assumed by many that development and implementation of quality standards, monitoring requirements, and other protective measures provided for by the act would mean improved drinking water quality for all U.S. consumers. However, extension to all U.S. water consumers of whatever protection compliance with drinking water standards offers has not happened in the nearly 10 years of the act's existence. The reasons for this are concealed in the mechanics and requirements of the act itself.

Congress did not realize just how many small water systems are operating in the U.S. In 1974 it was thought that the total number of community systems was 20 000, whereas today EPA estimates almost 60 000. Well over 90% of these systems serve fewer than 10 000 people. This inaccurate information was derived from state estimates and is a reflection of just how little concern had been extended to the very many small water supply systems in this country. The authors of the SDWA created a serious problem by designing an approach to standard setting based on "large and regional systems" and on the application of technologies that could be considered "generally available." Thus, extension of protection to small water systems has been crippled by the relative diseconomies of small scale. Ironically, it was concern over small-system problems that added substantial pressure to the passage of the SDWA in the first place.

The need for quality regulations for small systems remains as serious as ever even though these systems are not serving the majority of water consumers. EPA is aware of 50 reported outbreaks involving 20 000 waterborne disease cases in 1980 alone; the vast majority of these cases occurred in small systems. Fur-

thermore, the growing statistics for noncompliance with existing regulations show that the majority of failures continue to occur in small systems, especially with regard to high fluoride concentrations, arsenic, selenium, and barium in groundwater systems and, what is more acutely important for the majority of noncompliance cases, coliform and turbidity violations.

Nevertheless, present implementation of the act is failing to exert sufficient pressure on small systems to comply with all quality standards, and as presently constructed there simply is no equity in protection for all consumers of U.S. drinking water. Present technology affordable to large systems is equivalent to outrageous costs for smaller systems. At the regional workshops on the proposed primary regulations, EPA received a clear message from professionals in the field that a cost of \$3 per thousand gallons was simply unacceptable to small-system operators and consumers.

Thus, a serious need exists for some creative alternatives such as appeals to the private sector for the development of package treatment systems, the cost of which could be aggregated over large service areas on a contract basis. In addition, point-of-use treatment devices and bottled water use have not been given sufficient consideration. Unfortunately, the amendments to the SDWA presently proposed by Dennis Eckardt (D-Ohio) in HR-3200 would lock the present small-system problem into concrete by exempting small systems that could demonstrate economic stress. This bill aims to strengthen the SDWA by forcing more standards and more extensive monitoring, which may actually aggravate the present dichotomy.

We need instead to find a way to extend the standards we already have to all water consumers.

*R.F. Christman*

# ES&T LETTERS

## PCB replacements

Dear Sir: The feature by R. F. Addison, "PCB replacements in dielectric fluids" (*ES&T*, October 1983, p. 486A), contains many useful and informative comparisons between various candidate materials. However, Dr. Addison's attribution of the degradative action of soils on silicones to presumed microbial activity requires correction.

The authors of his cited reference (Buch, R. R.; Ingebrigtsen, D. N. *Environ. Sci. Technol.* 1979, 13, 676-79) conclusively established that it was the clay content of the soils that was responsible for the observed catalysis. Microbiological degradation of methylsiloxane polymers has yet to be

demonstrated despite attempts to do so.

C. L. Frye  
Health & Environmental Sciences  
Dow Corning Corporation  
Midland, Mich. 48640

## The Zimmerman Award

Dear Sir: The Central Wisconsin Section of the American Chemical Society in conjunction with Zimpro, Inc., a subsidiary of Sterling Drug, Inc., is seeking nominations for the F. J. Zimmerman Award in Environmental Science. The award, consisting of \$1000 and a plaque, is given annually to an individual whose research has had a significant impact on environmental protection.

The award announcement and presentation will be made at the joint Great Lakes and Central Regional Meeting to be held May 23-25, 1984, in Kalamazoo, Mich. The award recipient will be invited to present an overview of the scientific contributions upon which the award is based.

Any scientist residing in the U.S. is eligible for the award. Nomination forms are available from L. A. Ochrymowycz, Department of Chemistry, University of Wisconsin—Eau Claire, Eau Claire, Wis. 54701. Nomination forms and supporting documents must be received no later than Feb. 1, 1984.

Clarence A. Hoffman  
Zimpro, Inc.  
Rothschild, Wis. 54474

## Openings in Saudi Arabia

NUS Corporation, Environmental Services Division, is staffing a field team for environmental activities in Saudi Arabia. Consultants will work within a Saudi organization to provide technical expertise, management assistance and Saudi staff training. Five openings are:

### Air Quality Monitoring Instrumentation Engineer

BS or MS in related field, 5-10 years experience.

Oversee air quality monitoring instrumentation network - supervise technicians, develop written procedures, coordinate operations and maintenance and review quality of data received.

### Oil Spill Operations Team Coordinator

BS or MS in related field, 10 years experience.

Provide consultation and coordination of oil spill administration, surveillance, and clean up activities. Related oil spill and seamanship experience desired.

### Oil Spill Engineer

BS in Engineering, 5-10 years experience.

Advise on and coordinate - spill response activities, contingency plans, equipment specifications, equipment procurement, spill surveillance, and staff training.

### Marine Ecologist

BS or MS in Marine Ecology, 5-10 years experience

Coordinate and lead - marine environmental assessment of the oil spill impacted Saudi waters. Field experience and ability to train staff required.

### Liquid Effluent Pollution Engineer

BS or MS in related engineering field, 5-10 years experience.

Review and process license and variance requests; recommend water pollution abatement measures; develop and update standard for water pollution and hazardous wastes.

Extended bachelor status can be anticipated. Compensation commensurate with skill and Saudi Arabian competitive levels. Please send your resume, in confidence to:



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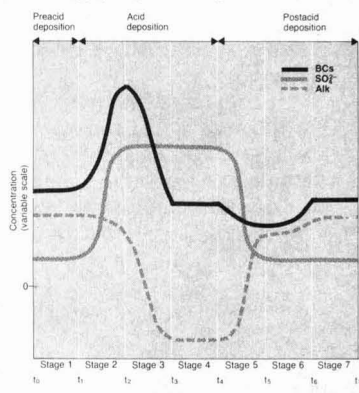
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CIRCLE 8 ON READER SERVICE CARD

## Correction

With reference to "Freshwater acidification from atmospheric deposition of sulfuric acid: A conceptual model" (*ES&T*, November 1983, p. 541A), there is an error in Figure 1. The legends for the Alk and  $\text{SO}_4^{2-}$  lines on the figure were reversed. From top to bottom, the legend should read BCs,  $\text{SO}_4^{2-}$ , and Alk. The correct figure is shown below.

FIGURE 1  
The temporal variation of the concentrations ( $\mu\text{eq/L}$ ) of  $\text{SO}_4^{2-}$ , BCs and alkalinity (alk) during the seven stages of acidification



# ES&T CURRENTS

## INTERNATIONAL

**Concentrations of cadmium, copper, iron, lead, and zinc have decreased** substantially over the past decade at Port Kembla Harbour, Australia. P. J. Moran of the Australian Institute of Marine Science compared recent levels of these metals with concentrations recorded at two industrial sites during 1974 and 1978. Port Kembla Harbour, 80 km south of Sydney, is surrounded by a large number of industrial plants for steel and metal manufacturing and processing. The decrease is attributed to the implementation of water quality control programs undertaken by these industries.

**Total world energy production remained almost unchanged in 1982**, according to a report prepared by the Energy Information Administration of the Department of Energy. The world primary energy production was 218 quadrillion Btu in 1982, a reduction of 0.8% from the 1981 level. Primary energy is defined as petroleum, natural gas, coal, and electricity from hydro and nuclear power. Production of crude oil and natural gas decreased in 1982, while coal production and hydro and nuclear power generation increased. The four largest energy producers are the U.S., the Soviet Union, the People's Republic of China, and Saudi Arabia.

## WASHINGTON

**The EPA has rescinded its 1982 decision not to regulate formaldehyde** as a cancer-causing substance under section 4(f) of the Toxic Substances Control Act (TSCA). As a result, the agency is soliciting public comment to aid in determining whether exposure to formaldehyde presents a significant health risk. In February 1982, EPA decided that formaldehyde did not qualify for priority consideration under TSCA. This decision led to a lawsuit filed by the Natural Resources Defense Council and the American Public Health Association. These

groups criticized the decision and the way it was reached (*ES&T*, October 1982, p. 543A).



*Lavelle: convicted on four counts*

**A federal jury has found former EPA official Rita M. Lavelle guilty** of perjury and of obstructing congressional investigations of hazardous waste programs. Lavelle was the administrator of these programs at EPA until she was forced to resign in February of 1983. She was convicted on four charges and found not guilty of a fifth charge. All four charges involved lying about knowledge that her former employer, Aerojet-General Corporation, was one of the dumpers of hazardous wastes at the Stringfellow Acid Pits near Riverside, Calif. Following the scandal that engulfed the agency in early 1983, Lavelle was the only EPA official to be indicted, and she is the only top official of the Reagan administration to be convicted of a crime committed in performance of official duties.

**The National Clean Air Coalition (NCAC) has charged that EPA** has quietly proposed a major rule that will aggravate the acid rain problem. According to NCAC, a rule proposed in the *Federal Register* in October would allow nearly 300 power plants and factories built between 1971 and 1978 to emit 700 000 tons more sulfur dioxide than is allowed under current regulations. The current rule allows a maximum emission rate in any 3-h period of 1.2 lb of SO<sub>2</sub>/10<sup>6</sup> Btu of coal burned. The proposed relaxation will allow the averaging period

to be 30 days instead of 3 h. At present, the operator must keep the yearly average at 0.63 lb/10<sup>6</sup> Btu to ensure the 3-h average is not exceeded. Under the proposed rule, the yearly average can be 0.95 lb/10<sup>6</sup> Btu, a 50% increase.

**Scientists, by a 7-to-1 margin, believe that some form of acid precipitation control program** should be initiated now rather than postponed, according to a recent survey conducted by the National Wildlife Federation. Questionnaires were sent to 461 U.S. acid precipitation researchers. Of these, 96 replied. Nearly two-thirds of those responding favor a control program aimed at protecting all sensitive areas in the eastern half of the country. They support this approach over a strategy aimed at protecting only the most heavily affected areas. They also favor sulfur dioxide reductions in the range of 5 to 12 million tons and broad reductions throughout most of the eastern states rather than targeted reductions in only a few source states.

**Laboratory standards for testing pesticides and toxic substances** under the Federal Insecticide, Fungicide, and Rodenticide Act and the Toxic Substances Control Act have been set by EPA. These standards are written to ensure that the test data submitted to EPA are reliable. They are consistent with testing procedures developed by the Food and Drug Administration. Rules for the administration of testing labs, the control and management of laboratory test animals, the documentation of tests, and the handling of data are included in these standards.

## STATES

**A panel appointed by New York State Governor Cuomo has prepared** a draft report about the Shoreham nuclear power plant, a unit under construction in Suffolk County, N.Y. The report states that Suffolk County acted reasonably when it decided that no adequate evacuation plan is possible,



the economic difference between operation and abandonment of the plant is small, and the Long Island Lighting Company, owner of the plant, does not have the situation under control. The cost of the plant is now 1000% over budget. The panel also questions the ability of the utility to run the reactor. The report is not complete, however, and several members of the panel disagree with its conclusions. They are already drafting minority reports.

**A Missouri task force recommended that up to 100 000 yd<sup>3</sup> of dioxin-contaminated soil be stored in a building aboveground until technology to destroy the material is developed.** The task force said that Times Beach, Mo., might be a good place to store the material because about 60% of the dioxin-contaminated soil in the state is located on the roadways in the town. The members estimated that soil excavation and storage would cost about \$70/yd<sup>3</sup>, bringing the total cost of storing all of Missouri's dioxin-contaminated soil to \$7 million. The state is seeking to have its 33 dioxin-contaminated sites classified as one site under Superfund.

**A new wastewater treatment plant that uses alternative technology will be built by the city of Las Cruces, N.M.** This alternative technology, which has been proven, is eligible for 85% federal funding. In this plant, the sludge will be digested anaerobically by microorganisms that convert it to harmless material. The sludge will then be plowed into the soil to a depth of 3-4 in., where it will decompose and provide nutrients. The methane gas produced from the sludge during digestion will be used to run a generator. This will power a boiler that heats water to keep the sludge at a temperature at which the microorganisms work effectively.

## AWARDS

**The Regional Scientist of the Year Award of the U.S. Agricultural Research Service (ARS)** was awarded to Malcolm Thompson, a chemist with ARS in Beltsville, Md. The award recognized several agricultural chemicals developed by Thompson, including one that sterilizes boll weevils by blocking egg formation in females, thus providing a "pest population control."

## SCIENCE

**A possible mechanism to explain how acid rain damages forests** has been suggested by Alfred Haug of Michigan State University (East Lansing). Haug conducted experiments which indicate that increased levels of aluminum absorption by tree roots interfere with the structure and function of calmodulin, a protein crucial to the regulation of calcium in the root cells. As the cells deteriorate, the plant begins to die. Scientists theorize that acid rain elevates the levels of aluminum available to plant roots. Thus, says Haug, acid rain may contribute to the decline of forests in the U.S., Canada, and West Germany. He also points out that aluminum toxicity in soil may interfere with food production.

**An instrument to measure minute fluctuations (up to 1 ppm) in the levels of oxygen in the atmosphere** has been designed by Pieter Tans and colleagues at the Lawrence Berkeley Laboratory (University of California). It will be used in an effort to solve the problem of where the "missing" carbon dioxide in the carbon cycle is absorbed. Only 25-40% of the CO<sub>2</sub> generated by human activities remains in the atmosphere. The remainder is dissolved in the oceans or incorporated into plant tissue. But scientists have not been able to learn which sink takes the most CO<sub>2</sub> out of the atmosphere. If oxygen levels in the world rise, it means that the global mass of green plants is increasing, Tans said. If oxygen levels drop significantly, this would indicate that the global mass of green plants is decreasing and that the extra CO<sub>2</sub> is dissolving in the oceans.

**How air pollutants move through an urban area** may become better understood through the release of minute quantities of harmless tracer gases from two sites in the Washington, D.C., metropolitan area. Two air sampling station networks—one with 100 stations and the other with three—will take samples every 8 h for one year. In this way, scientists at the National Oceanic and Atmospheric Administration will learn how the perfluorocarbon tracers are transported during all weather situations and around buildings, how they are dispersed, and what effect the urban "heat island" may have.

**Can safe long-term containment of high-level radioactive waste be demonstrated (ES & T, September 1983, p. 413A)?** Faced with this question, the Organization for Economic Cooperation and Development's Nuclear Energy Agency (Paris, France) defines *direct demonstration* as proof that a containment system can be safely built, operated, and closed at acceptable costs and with available technology. *Indirect demonstration* consists of a convincing evaluation of the system's performance and long-term safety on the basis of predictive analyses, many of them derived from experimental work confirmed by a body of technical and scientific data.

**The reauthorization of the Resource Conservation and Recovery Act would require EPA** to use an analytical system that shows what danger, if any, a landfill poses to people living or working in the surrounding area. Known as the Preliminary Pollutant Limit Value (ES & T, July 1980, p. 778), the method or analytical system should be capable of using site-specific information on single and multiple pathways of exposure from soil, air, and water and of translating this information into a health effects assessment document that non-scientists can understand.

## TECHNOLOGY

**Can a scrubber clean air so efficiently** that a power plant can be built in a Class I or "pristine" air area? Bechtel Power Corporation (San Francisco, Calif.) says that two of its engineers, Bob Sherwin and Jack Abrams, have found a way to remove SO<sub>2</sub> to the extent of 90% with specially treated hydrated dolomitic lime. They set up the scrubber to collect fly ash particles which, in turn, can further remove SO<sub>x</sub> to 96%, thus rendering exhaust gases clean enough for a Class I area. Bechtel explains that scrubbers normally remove up to only 80% of a plant's SO<sub>2</sub>. This enhanced scrubbing capability will be used at Colstrip, Mont., in a pristine area.

**Hazardous landfill leachates and dump liquors can be degraded** by use of indigenous microflora in adjacent soil systems. These microbes are supplemented with an initial addition of a sewage organism

"seed" and additions of a glucose nutrient trace species medium, David Kosson of Rutgers University told the Diamond Jubilee Meeting of the American Institute of Chemical Engineers (AIChE), held in Washington, D.C. Next, glucose is replaced by organic carbon from pretreated landfill leachate. Loading rates, depths of treatment zones, nutrient additions, and the like are controlled. Kosson says that reductions in organic carbon of industrial origin have exceeded 90%.

**Mercury pollution from industrial wastes can be removed** with chitosan from prawn shell waste, S.M.S. Abuthahir Ali of the Central Institute of Fisheries Technology (Cochin, India) told the American Institute of Chemical Engineers. Ground prawn shell waste in the 100-150-mesh fraction only is used. Ali says that a strong affinity for mercury ions on the part of chitosan should make it suitable for industrial applications.

**A new coal-fired fluidized-bed combustion (FBC) system** is being commissioned at Nyköping, Sweden. Built by Wormser Engineering, Inc. (Woburn, Mass.) and Stal Laval of Sweden, the system, which burns coal together with SO<sub>x</sub>-absorbing limestone, can also use wood waste. Particulate matter and fly ash are captured by a fabric filter. Because the process is cooler

than most others—flue gas comes out at 320 °F—little or no NO<sub>x</sub> is formed, according to Wormser. The plant, which is an addition to an existing facility, is rated at 10 MW thermal and will produce hot water at 338 °F.

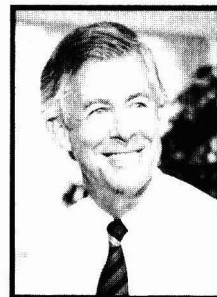
## BUSINESS

**"I would like to see tougher laws concerning the export of hazardous chemicals** passed by nations of the Organization for Economic Cooperation and Development [OECD]," William Brock, U.S. international trade representative, told a Chemical Manufacturers Association Chemical Forum. The U.S. has such laws now, and this, in Brock's view, puts U.S. chemical firms at a competitive disadvantage with firms in other OECD countries that do not have such laws, especially when exports to Third World nations are involved. A tightening of hazardous chemical export laws by OECD countries would, in Brock's view, restore the competitive balance.

**The development of a hybrid diffusion model to predict** and compute pollutant concentration levels in the vicinity of tall stacks is the objective of a contract that Environmental Research and Technology, Inc. (ERT, Concord, Mass.) received from the Electric Power Research Institute (EPRI). A plant in a flat area of Illinois and one at a hilly site in Tennessee will be studied. The model will include state-of-the-art modules on the planetary boundary layer, plume rise and diffusion in convective and stable boundary layers, diffusion in hilly terrain, and dry deposition. Model uncertainty will be estimated through modeling concentration fluctuations in effluent plumes.

**The Environmental Industry Council and the Council on Environmental Quality** have awarded environmental protection awards to five companies. These are Steelcase Inc. (Grand Rapids, Mich.), for air pollution control; Homestake Mining Company (Lead, S.D.), for solid waste management; Miller Brewing Company (Albany, Ga.), for water/wastewater pollution control; Environmental Systems Corporation (Muskegon, Mich.), for hazardous waste management; and Allied Corporation (Metropolis, Ill.), for toxic pollution control.

A sixth award for permitting went to a group consisting of AMAX Corporation (Golden, Colo.), the U.S. Forest Service, the Gunnison County, Colo., Board of Commissioners, and the Colorado Department of Natural Resources.

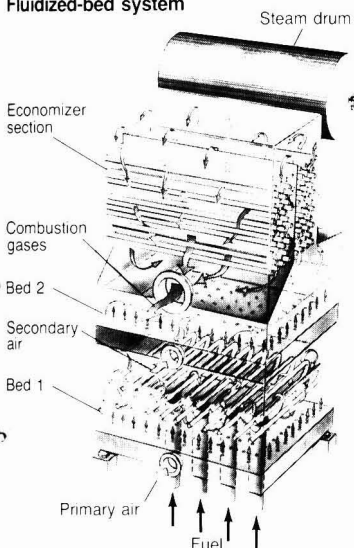


*Addison: can't justify costs*

**"No one can justify the spending of billions of dollars on the problem of acid rain** with solutions that cannot promise success," said Edward Addison, president of The Southern Company (Atlanta, Ga.). He warned that acid rain legislation pending in Congress will add a nonproductive energy cost to the American economy and thereby further damage U.S. ability to compete in foreign markets. Addison suggested that adding higher energy costs to energy-intensive industries will drive them offshore. He added that if there were "solid scientific evidence of danger to human health, plants and animals, and lakes and rivers—that a genuine emergency existed—we would not be arguing about price. But since we don't [have solid scientific evidence], we have to talk about price."

**Major changes in the Clean Water Act** were recommended by the American Society of Mechanical Engineers (ASME). One is a return to standards based on water quality, rather than technology-based standards for conventional pollutants. Dischargers should not be required to expend funds for more equipment unless there would be material improvement in a stream's quality, the society said. But ASME did call for a continuation of technology-based standards for toxic pollutants and, indeed, suggested the development of more stringent technology standards. ASME called on EPA to begin a well-funded research program on toxic pollutants immediately.

### Fluidized-bed system



Source: Wormser Engineering, Inc.

## Forest decline from air pollution

*Scientists are actively puzzling over why the productivity of several species in some eastern U.S. forests has been decreasing over the past few decades. Acid deposition is only one possible answer*

There is a strong consensus that the forests of West Germany are in a state of serious decline. Since the mid-seventies, fir and spruce have been dying back over extensive areas, and in the past two years, a number of other species have begun to show signs of damage. In 1982, West German provincial forestry offices estimated that 1.4 million acres, or 8% of that country's forests, were suffering damage. By 1983, they increased their estimates to 24%.

In the U.S., there is also a growing consensus that some species in the high-altitude forests of the East are declining substantially. During the past 20-25 years, red spruce in the high-elevation forests of Vermont, New York, and New Hampshire have experienced dramatic dieback and a substantial reduction in basal area and density (see *ES&T*, July 1983, p. 294A).

Scientists in both countries are involved in intensive efforts to ascertain the cause or causes of these declines. Ongoing research was discussed at an October 1983 symposium on air pollution and forest productivity, held in Washington, D.C., and sponsored by the Izaak Walton League of America and Pennsylvania State University.

The dieback of spruce in the Northeast is relatively well-known. It was revealed at the symposium, however, that forests in other areas of the U.S. may be showing signs of stress and damage and that species other than spruce are affected. Samuel B. McLaughlin of Oak Ridge National



Laboratory (ORNL) pointed out that red spruce, shortleaf pine, hickory, yellow birch, pitch pine, hemlock, and Fraser fir are declining in East Tennessee. He noted that these declines together with those in New England suggest that decreased productivity in several tree species has been occurring over a broad scale during the past two decades.

One commonly held view is that acid deposition is causing the decline of forests in both Europe and the U.S. (*ES&T*, June 1983, p. 246A). At the symposium, a number of different opinions about possible causes were expressed, ranging from drought to ozone to combinations of pollutants, including acid deposition, ozone, and trace metals. Possible causes that were not subjects of active inquiry were disease and insects. Most researchers in the field believe there is little evidence that one of these is the primary damaging agent.

### Changes since 1950

Scientists working in several different areas of the country using a variety of techniques gave evidence for definite changes in forests since about 1950. Arthur Johnson of the University of Pennsylvania described an abrupt shift in the increment size of red spruce tree rings in cores taken from stands sampled in the Northeast. Forty percent of the red spruce cores "showed a rather abrupt shift to abnormally narrow rings in the early to mid-1960's with no subsequent recovery." About 30-40% of the pitch

pine cores from stands in southern New Jersey also showed this effect. He pointed out that drought may have played a role in these declines but that there are very few data that can be used to answer the question of primary causation.

Trace-metal analysis of tree rings was another area of investigation that revealed marked changes after 1950. Charles F. Baes III, also of ORNL, and McLaughlin analyzed shortleaf pine tree rings from three sites in East Tennessee as a part of the FORAST project (see box). For the analyses they used inductively coupled plasma optical emission spectroscopy, which measures approximately 30 elements simultaneously. At all three sites, the rings contained "steadily increasing concentrations of Al, Cd, Cu, Fe, Mn, Mo, Ti and Zn over the past 20-25 years." The rings showed decreasing growth, which would in itself cause the metal concentrations to go up as long as the accumulation rate did not decline. But even when corrected for growth rate, the annual accumulations of many of these metals were found to increase over the past few decades.

One interesting aspect of this research is that at the site in the Great Smoky Mountains National Park, the concentration of iron in the tree rings was elevated from 1863 to 1912, and the rings revealed a simultaneous growth decline. During this same period, ores containing iron and copper sulfide were being smelted 88 km upwind. (The smelter opened in 1854 and reduced its emissions of SO<sub>2</sub> by 1910 under a Supreme Court order.) After emissions were controlled, iron concentrations in the rings decreased until the late 1950s when they began to rise again. This research suggests that SO<sub>2</sub> emissions and the availability of airborne trace metals could affect metal uptake and growth in trees.

Another interesting aspect of Baes and McLaughlin's research is that the trace-metal concentrations of Al, Cd, Mn, and Zn in the cambial tissues (the layer between the rings and the bark) are currently near levels "that have been associated with toxic effects when found in above-ground tissues of herbaceous plants." The level of trace metals that is toxic to trees is not known because most experiments have been performed on small herbaceous plants. Baes and McLaughlin noted that researchers have not been able to determine whether the metals are getting into the trees through the root structure or the canopy.

Laura E. Conkey of Dartmouth College used X-ray densitometry to

ascertain variations in wood density. In experiments on tree cores from Maine, she noted that the maximum density curve showed a pronounced change after 1950 in cores that dated back to 1670. She hypothesized that this change could be caused by sharply lower spring temperatures in Maine but that it could also result from alterations in the chemical environment of the forest.

Richard L. Phipps of the U.S. Geological Survey (Reston, Va.) also studied tree rings as a part of the FORAST project. Although his work is still in progress, he noted that in the collections of tree rings that have been examined, the variation in tree growth at each site changed significantly in the way it correlated with climatic variation.

The Forest Responses to Anthropogenic Stress (FORAST) project consists of a systematic survey of growth trends in eastern forests. It involves 12 university and government research groups, 10 of which are supported by EPA funding. Increment cores are being collected and analyzed from more than 6000 trees at 12 study sites. With the data obtained from these cores, it is hoped that the following questions will be answered: Has a systematic growth decline occurred? What is the areal extent of the decline? What trends might be expected under future pollutant regimes?

In particular, he discussed a collection of cores taken from Signal Knob near Front Royal, Va. In the pines, there was a pronounced increase in growth rate from 1910 to 1950 and an "equally pronounced decrease in growth rate between 1950 and 1980." The period when growth started to decline varied substantially between trees, but by 1960 all of the pine trees were showing decline. He postulated that deposition of sulfur emitted by a nearby industrial plant caused the decreased growth rate. The plant began operating in the early 1940s.

Nearest neighbor pairs of overstory trees (trees forming the upper canopy) were studied by Thomas W. Doyle of ORNL. He too found that a change had occurred in the past few decades. More than 40 pairs of trees were measured. Up to 1957, in drought years growth of white oak exceeded

that of tulip poplar. After 1957, tulip poplar dominated over white oak. The reason for this change in tree dominance is not known.

### Is ozone a cause?

Several of the speakers described ozone injury to forests in both the western and the eastern U.S. John M. Skelly of Pennsylvania State University studied ozone damage in the Shenandoah National Park (Virginia) where he found surprisingly high levels of ozone. From May to September, concentrations (measured hourly) ranged from 0.06-0.12 ppm at a site in the higher elevations. At lower elevation sites, the average levels were consistently lower. (The health and welfare standards for ozone are both 0.12 ppm for 1 h.) Ozone injury was widespread throughout the park and could be positively correlated with elevation. The first indicators of vegetation effects were reduced needle length and retention and foliar symptoms typical of ozone damage on eastern white pine.

Ozone damage in the San Bernardino Mountains of southern California was discussed by Paul Miller of the USDA Forest Service (Riverside, Calif.). Like Skelly, he found that in rural areas, ozone levels were higher at mountain locations than at low elevations. In the mountains, levels ranged from 0.03-0.04 ppm, which he considers background, to 0.10-0.12 ppm. Ponderosa pine were very sensitive to ozone, followed by, in decreasing order of sensitivity, Jeffrey pine, white fir, black oak, incense cedar, and sugar pine. Ozone damage resulted in decreased photosynthetic activity and eventually led to weakened trees. The sites receiving moderate to severe ozone doses had mortality rates of 2-3% in some years.

### Multiple pollutants

Several of the speakers emphasized that the cause of forest decline could be more than one pollutant. McLaughlin said that "multiple pollutant stress must be considered since acid rain, gaseous pollutants, and trace element loading have increased over the same approximate time span and in the same geographical regions as has industrialization during recent decades." He suggested that trees may be responding bimodally to air pollution. Roots may be responding positively. Shoots may be responding negatively. The net result may be that the whole plant is responding negatively. If this is true, it might explain some of the contradictory results obtained from research

concerning the effects of air pollution on trees.

The strongest evidence that tree decline can be caused by more than one pollutant was presented by George H. M. Krause of the Land Institute for Pollution Control of the Land North-Rhine Westphalia in West Germany. He first described how the extent of forest decline in West Germany "has spread dramatically" in the past two years. For example, in the autumn of 1980, 62% of the fir trees in the Land (state) of Baden-Württemberg were healthy. In the spring of 1982, less than 4% were healthy. In both Bavaria and the Black Forest, several deciduous species have recently become affected—beech, sycamore, mountain ash, and alder. During the past year, spruce damage has spread to a number of areas where it was not previously observed.

For several reasons, the institute has proposed that forest decline may result from a combination of ozone and acid deposition. The trees in a stand that tend to be most affected are those exposed to light and air. The damage occurs in forests on many different types of soils, those with both high and low buffering capacities. The only pollutant known to have increased greatly (~50%) in the past decade is  $\text{NO}_x$ . This also would have caused ozone levels to rise during this time. Ozone is not monitored in most mountainous areas; however, where it has been measured, its average level, though not peak level, is higher than the average in cities. Preliminary laboratory experiments carried out at the institute suggest that damage to trees is not caused by current levels of either acid deposition or ozone alone but that it could be caused by a combination of the two at their current concentrations. Krause discussed his hypothesis that ozone causes increased membrane permeability in the foliage, which in consequence allows acid rain and acid fog to leach nutrient cations from the foliage. This in turn leads to reduced photosynthesis and reduced assimilation and nutrition of the root system, and eventually to reduced root growth and nutrient uptake.

In summary, the symposium provided no final answers about the cause of forest decline, but suggested many avenues of investigation that may yield clearer results. A number of other important papers were presented, which cannot be described in this brief article. The proceedings of the conference will be published this spring by the Izaak Walton League.

—Bette Hileman

# Whither environmental progress?

*Nine out of 10 environmental laws are awaiting reauthorization*

Our environmental laws are not working well. All of these laws, from the Clean Air Act of 1970 to the Superfund Act of 1980, were based on assumptions, none of which have proven completely correct. On Oct. 25, in the Foard Lecture to an audience of several thousand students and faculty at the University of North Carolina at Chapel Hill, EPA Administrator William Ruckelshaus said that these assumptions were that we knew:

- what the bad pollutants were,
- what adverse health and environmental effects they cause and at what levels,
- how to measure these pollutants, and
- how to regulate them to acceptable levels at reasonable costs.

The major flaw in the laws we enacted was that enforcement responsibility was left to the states. They didn't enforce the laws because they competed so strongly for industry to locate within their borders. Thus the solution was to bring in the federal government to overlay enforcement on the state governments. Now, in 1984, it is clear that none of our earlier assumptions were right, at least not completely.

- We recognized some pollutants, but certainly not all of them.
- Our knowledge of the health effects of these environmental pollutants, and of the ones we have discovered since, is sketchy.
- We have trouble establishing a safe level for these pollutants in the environment.
- Early measurement techniques were primitive. We have now discovered a new set of problems by developing measurement techniques that are anything but primitive: We can measure dioxin in parts per quadrillion, but we don't know what to do about it after we've found it.

It was probably a reasonable assumption to make that the controls for all pollutants were available. However, the costs of controls, especially at the upper level, are very high, sometimes even prohibitive.



*William Ruckelshaus*

Further, it was probably reasonable to assume that the laws would be changed once it became apparent to society that the basic assumptions underlying them were questionable. But over the years we have found that it is nearly impossible to get laws changed once they have been enacted. Emotions run so high and the polarization between factions becomes so wide that it is terribly difficult to adjust these laws, even in the light of scientific and administrative difficulties of an enormous magnitude.

—Stanton Miller

# Independent evaluation of monitoring data

*A proposed numerical approach to choosing an analytical laboratory could help, but at low contaminant concentrations, wide differences can be found among even the most meticulous laboratories*

Two principal problems arise in the quest for reliable, independently obtained or evaluated monitoring data. First, there has been no standard, rigorous procedure for selecting a laboratory. Second, where trace concentrations of contaminants are involved, the increase of quantitative variability with decreasing concentration can bedevil the results of work done by even the most excellent, reputable laboratory.

There are a number of reasons why such data are needed. For example, an industrial plant's management may need a "disinterested party's" confirmation that monitoring results show the plant is complying with the terms of its discharge permit issued under the National Pollution Discharge Elimination System (NPDES), a principal provision of the Clean Water Act. Moreover, such monitoring data and any confirmation thereof would have to be obtained by the use of analytical methods approved by EPA (*ES&T*, December 1981, p. 1426). Updated versions of those methods are expected to be promulgated later this year in the Code of Federal Regulations.

On the other hand, a regulatory body or citizen's group may be seeking legally admissible support of an accusation that a plant's discharges are in violation of its permit. Or a discharger might not have the laboratory facilities to do the required monitoring and would need to contract this work out. One can think of many other reasons applicable not only to water discharges, but to air emissions, landfill leachates, and other environmental monitoring requirements.

## Point system

A choice of an analytical laboratory often is made on the basis of casual recommendations from practitioners, names on a regulatory agency's reference list, or even a search of the phone book. Choices made on these bases

entail certain risks and uncertainties.

Roy Ball, of the consulting firm Environmental Resources Management-North Central, Inc. (Park Ridge, Ill.) suggested a methodology for choosing an analytical laboratory to a session of the 56th Annual Conference of the Water Pollution Control Federation (WPCF), held in Atlanta, Ga., last October. This methodology, he said, helps to overcome many uncertainties and risks involved in selecting a laboratory. Although Ball and his associates applied this method to choose a laboratory to perform analyses for metals in water, Ball maintains that it should work for the

selection of a laboratory to analyze any substance.

The first step is the compilation of a list of candidate laboratories. Laboratories entered on this list would be those that use methods recommended by EPA or other federal or state regulatory agencies. Also important are such factors as prior firsthand experience with a laboratory, recommendation by a university or some other impartial authority, accessibility with respect to sample delivery, turnaround time, analytical capacity, and, of course, costs of analysis. From this list, perhaps five or six laboratories would be selected for more detailed evaluation.

The next step involves a visit to the laboratory premises and interviews with laboratory personnel. This can be carried out by a technically qualified person representing the laboratory's potential client or by a consultant engaged by the prospective client. This person's observations are set forth on a very detailed questionnaire containing general information as well as information about personnel, space and facilities, analytical methods, laboratory equipment, and quality controls.

Answers are ranked according to a point system with a score of "5" denoting complete adequacy of equipment, practice, and the like; a "3" for some degree of laxity or diminished adequacy; and a "1" for poor facilities or performance. Sometimes, a score of "1\*" may be assigned; the asterisk indicates that this judgment of "poor" must be resolved to the satisfaction of the evaluator before a final score is calculated.

## Project-specific samples

Of the five or six laboratories visited, perhaps the two ranking highest on the interview and questionnaire would be asked to analyze project-specific samples. A specially prepared or pur-

### Laboratory evaluation questionnaire

The evaluator seeks answers to 50 questions concerning a candidate laboratory. Five questions address general information (organization, strength of management, and the like); six consider personnel; 10 deal with space; three look at analytical methods and equipment; and 21 examine quality control. Scores are computed with weighting factors for the six categories of 10, 13, 21, 3, 3, and 44%, respectively. For example, in the quality control category, here is how "inter-laboratory checks—precision and accuracy" would be assessed:

Best description of laboratory	Score
• Laboratory has a well-organized program to check the validity of data it produces.	5
• Incomplete information is available on precision and accuracy of the tests in use.	3
• Laboratory has no plan to check validity of its data.	1

Source: Paper presented to WPCF by Roy Ball

chased reference standard sample is submitted by the prospective client or by the consultant to a laboratory for analysis, along with samples exhibiting characteristics pertinent to components expected to be found. Examples of analytes could include BOD<sub>5</sub>, priority pollutants, or other substances.

Ball calls the latter type of sample a project-specific sample. He says that a minimum of four or five such samples should be analyzed to provide "a statistically valid basis for determining the relative performance of laboratories." The project-specific sample would be physically blended with the reference material for some of the analysis exercises that the candidate laboratories must carry out at this stage of the competition.

On the other hand, William Horwitz of the U.S. Food and Drug Administration (FDA), and one of the elder statesmen of the Association of Official Analytical Chemists (AOAC), advocates a minimum of 30 "data points" (analyses) from any laboratory comparison exercise. He notes that this rule is used by AOAC members for the evaluation of laboratory capabilities. This approach calls for the number of laboratories being compared times the number of samples to equal 30. If there are six candidate laboratories, each would be required to analyze five samples; three candidates would each analyze 10 samples, and so on.

### Indexing

Evaluation of the laboratory's performance at this stage would be based on a correlation coefficient for analytical results. For example, the laboratory coming in with a correlation coefficient probability of <1% might

be rated "5"; that at 1-5% would be put at "3"; while that >5% would score "1."

The last step in the laboratory selection process is indexing. Ball said that indexing is perhaps best explained with an example of the selection procedure he and his associates actually used. From the list of candidate laboratories they examined, they found that six were worth visiting for an on-site inspection and interviews with personnel. These laboratories were designated as A-F. Next, those laboratories scoring less than 80 on the questionnaire were eliminated; that left only laboratories A and E in the running (they scored 82 and 85, respectively).

These two laboratories were then called upon to analyze reference samples and reference and project-specific sample mixtures. Samples were so prepared that they could not be considered replicates. Therefore, results between the two laboratories could not be expected to agree.

The results themselves were analyzed statistically through linear regression. That operation obtained correlation coefficients ( $r$ ) for the chemical analyses of the samples. A rating of "5" was given for  $r \geq 0.99$ ; "3" for  $r \geq 0.95$  but  $< 0.99$ ; and "1" for  $r < 0.95$ . On the basis of the analyses, laboratory A tallied 77, while laboratory E achieved 80. Averaging these scores with those from the visits and interviews gave A an index of 80 and E an index of 83, so E was awarded the contract.

Ball says that other factors can come into play in the final choice of laboratories. Potential conflict of interest is one. Changes in personnel, management, equipment, and other areas are another. This is why Ball recommends close contact with the laboratory chosen for the award of a contract, and, if necessary, reevaluation and reselection of a laboratory.

### Round-robin tests

Even the most exemplary laboratories probably have little or no control over the reliability of identification and quantitation that decreases *exponentially* as the concentration decreases. Horwitz estimates that at present "the practical limit of measurement is in the low parts-per-billion [ppb]," and gives aflatoxin contamination of food as an example. He defined an interlaboratory coefficient of variation (CV) as an expression of interlaboratory precision, and warned that at a low-ppb level, the CV for quantitation could be as great as  $\pm 30\%$ . It may be much greater at

lower concentrations.

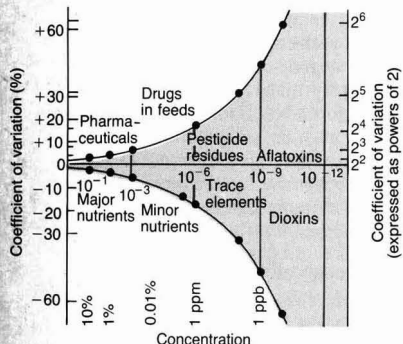
When a discharger of wastewater is limited by NPDES permit terms to a daily maximum effluent of 225 ppb for 1,2,4-trichlorobenzene, a priority pollutant, the compound may be analyzed by gas chromatography according to EPA Method 612 for chlorinated hydrocarbons. However, James Norris of Ciba-Geigy Corporation (McIntosh, Ala.), who is also chairman of the Environmental Monitoring Task Group of the Chemical Manufacturers Association, pointed out that an EPA-conducted 20-laboratory round-robin test using this method has shown that readings varying from 0-580 ppb can be expected, at the 95% confidence level, even if the true value is 225 ppb. This situation could force a discharger to report violations, and make him liable to adverse government action, when the problem may actually be the lower reliability of quantitation, brought about by the broad 95% confidence range in the determination of a given analyte—in this case, 1,2,4-trichlorobenzene.

Norris gave similar examples of quantitative variability for other priority pollutants also analyzed by EPA-approved methods. He pointed out that the laboratories participating in the study were "experienced veterans" whose quality assurance and control were "unprecedented," and that the EPA methods "are good methods. The problem is that these good methods are being pushed to the extremes of analytical applicability with attempts to quantitate results at levels that approach limits of detection. When this is done, great variability in the numbers generated can always be expected." He added that while those methods would most likely be required for NPDES permit compliance, "there have not been any comments or peer reviews solicited for them by EPA or any other agency."

So those who must furnish independently evaluated monitoring and analytical data under the various environmental laws and regulations and others who need data assessed by qualified third parties could encounter problems in locating reliable laboratory facilities. Moreover, pending further—perhaps *very* expensive—advances in the analytical chemistry state of the art, data documenting compliance with low-ppb limitations, for instance, might be clouded by analytical variability. That could occur regardless of how unimpeachable the equipment and performance of the analyzing laboratory may be.

—Julian Josephson

Variability of interlaboratory results increases with decreasing concentration



Source: Horwitz, W. Anal. Chem. 1982, 54, 67 A.

## RCRA reauthorization



**Richard M. Dowd**

In November 1983, the House of Representatives voted to reauthorize the Resource Conservation and Recovery Act with a new title, the "Hazardous Waste Control and Enforcement Act of 1983" (H.R. 2867). The House expressed concern about the distribution and disposal of toxic pollutants and about methods of control for reducing long-term environmental and health damage, while still encouraging recycling and reuse. The act is rather long; in this review, only a few sections are discussed.

In H.R. 2867, Congress is seeking more definitive action by EPA. The House passed a bill that is far more specific in many ways than the previous legislation and far more restrictive on the disposal of wastes. Clearly, the intent of this legislation is to substantially reduce, if not eliminate, land disposal as a way of managing untreated hazardous wastes.

One item that has been widely noted is a change in the exemption for generators of small volumes of hazardous wastes. The House reduced the exemption for generators of hazardous waste from 1000 kg to 100 kg or less per month. Representative James Florio (D-N.J.) estimates that an additional 4 million metric tons of waste (a 10% increase in the volume already regulated) will be covered by this provision. EPA informally estimates that the number of regulated generators could increase from the present 30 000–40 000 to 150 000.

The bill discusses the current practice of disposing of hazardous wastes in, on, and under land. As proposed, the underground injection of hazardous wastes would be forbidden where they are injected into a geologic formation containing drinking water supplies (within a quarter mile or above such a formation). In addition, specified liquid hazardous wastes and halogenated organics must be reviewed within 32 months of the bill's enactment, to determine whether their disposal via underground injection poses the risk of damage to human health or the environment.

H.R. 2867 establishes very stringent criteria for the EPA administrator to determine which land disposal technique may be used for specific wastes. Certain techniques "... must be protective of human health and the environment for as long as the waste remains hazardous, taking into account the long-term uncertainties associated with land disposal ... the persistence, toxicity, mobility, and propensity to bioaccumulate of such hazardous wastes and their toxic constituents."

### Liquid wastes in landfills

Liquids in landfills also are covered in detail. Effective six months after enactment, placing bulk or noncontainerized liquid hazardous wastes in any landfill would be prohibited.

Within one year, the placement of any liquids (even if they are not hazardous) in hazardous waste landfills would be eliminated unless there are no alternative methods for disposal. Landfilling of certain liquid hazardous wastes containing specific concentrations of arsenic, cadmium, chromium, lead, mercury, nickel, selenium, thallium, PCBs, and halogenated organic compounds would also be prohibited, unless the administrator determined that the prohibition of one or more methods of land disposal was not re-

quired to protect human health. If the administrator failed to determine whether a disposal method for specific waste poses health or environmental risks, that method would automatically be prohibited.

In addition to those hazardous wastes not covered by any of the sections discussed above, the administrator is to study all of the wastes listed in 40 CFR 261.31 and 261.32 and promulgate regulations on their disposal in landfills. He or she must promulgate regulations for a third of the listed wastes within 32 months, an additional third within 42 months, and the remainder by 52 months after enactment of the House bill.

H.R. 2867 also requires the administrator to promulgate regulations for monitoring and controlling air emissions from hazardous waste storage, treatment, and disposal facilities as needed.

In this broad context, Congress is encouraging resource recovery, production process changes to reduce the amount of hazardous wastes generated, and the use of alternative disposal techniques, such as incineration and chemical fixation. This policy is likely to raise more problems—witness recent public reaction to the siting and use of incinerators and incinerator ships to dispose of hazardous wastes. The stringency of criteria and the waste-specific determinations required in H.R. 2867 create the need for a large volume of information that is not presently available.

The Senate, of course, has yet to finalize its own legislation; however, it is reasonable to believe that the broad outlines presented by the House bill are going to be favored in some way.

*Richard M. Dowd, PhD, manages the Washington, D.C., office of Environmental Research & Technology, Inc.*



# Health risks from light-duty diesel vehicles

*Low risk of lung cancer from exposure to diesel exhaust is projected from laboratory and epidemiologic data*

**Richard G. Cuddihy  
 William C. Griffith  
 Roger O. McClellan**

*Inhalation Toxicology Research  
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Increasing numbers of automobiles and light-duty trucks are likely to be equipped with diesel engines in the future because they have higher fuel efficiencies than gasoline engines and because diesel fuel traditionally has cost less than gasoline. Interest in diesel engines also was stimulated by the Federal Corporate Average Fuel Economy Requirement for 1985 (1). By then, manufacturers of light-duty vehicles must attain an overall fleet average of 27.5 miles per gallon (mpg) (11.7 km/L) of fuel. Introducing more fuel-efficient diesel-powered vehicles is one approach to meeting the fuel economy average while minimizing the need to reduce vehicle size.

Current diesel-powered vehicles emit more visible smoke and odors than gasoline-powered vehicles, and this has led to concern about their possible effects on human health and the environment. In November 1977, the EPA issued a precautionary notice reporting that organic solvent extracts of diesel exhaust particles were mutagenic in bacteria cell assays. Because chemical mutagens and carcinogens may alter genetic material in cells from different organisms in similar ways,

evidence that a chemical causes genetic damage in bacteria is reason for concern that it may cause cancer in people. Thus, the EPA and the Department of Energy developed major research programs to determine the potential health and environmental effects of increasing the use of diesel engines in light-duty vehicles in the U.S. (2). The EPA also requested that the National Research Council conduct a study of the potential health effects and the public policy issues related to diesel vehicle emissions to inform government bodies, automotive industries, and the public about our current state of knowledge (3).

## Future use

Light-duty vehicles include automobiles and trucks with gross weights less than 3850 kg (4). Currently, there are about 130 million light-duty vehicles in the U.S. Of these, about 2% are powered by diesel engines. Within 20 years, the total number of light-duty vehicles is expected to reach 165 million, but the portion that will have diesel engines will depend on many factors. These include the availability and cost of diesel fuel, government regulations that may be enacted to limit their emissions, and customer satisfaction with diesel vehicle cost, performance, and maintenance.

Because of past market demands, petroleum refineries in the U.S. have generally been designed to produce gasoline most efficiently. In terms of fuel volume, the average ratio of gasoline to middle-distillate fuel produced

in the U.S. is about 16:10 (5). (The middle-distillate fraction includes diesel fuel, kerosene, jet fuel, and heating oil.) The fuel product ratio could be reduced to about 7:10 by producing more diesel fuel, but beyond this point, production of diesel fuel becomes less practical because there is no economical way to use the lighter by-products from the process. In addition to this practical limit on diesel fuel production, increased demands for the other middle-distillate products in the future could further raise the price of diesel fuel relative to gasoline.

Diesel-powered vehicles now achieve 20-40% more distance per unit volume of fuel than gasoline-powered vehicles because of their higher fuel efficiencies and because diesel fuel contains about 15% more energy than an equal volume of gasoline (6). If vehicle fuel consumption rates are corrected for the higher specific energy content of diesel fuel and only similar model vehicles are compared, then diesel vehicles are about 20% more efficient than equivalent gasoline-powered vehicles. The gasoline engine vehicles used for this comparison burn lead-free gasoline and are equipped with emission control devices. Between 1965 and 1975, pollution control technology reduced fuel efficiencies of gasoline-powered vehicles by about 25% (7). If similar reductions in fuel efficiency occur with diesel vehicles when emission controls are added, then both types of vehicle may operate with similar efficiencies.

A comparison between regulated

**TABLE 1**  
**Typical vehicle emissions**

Vehicle type	Grams/km			
	Particles	Nitrogen oxides	Carbon monoxide	Hydrocarbons
Light-duty diesel	0.1-0.4	0.5-2	0.5-3	0.05-0.8
Light-duty gasoline	0.001-0.004	0.2-1	1-3	0.08-0.5
Heavy-duty diesel	0.5-4	3-20	5-50	0.9-6
Heavy-duty gasoline	0.004-0.2	1-11	10-200	2-20
<b>Diesel engine models <sup>a</sup></b>				
Oldsmobile Cutlass Diesel	0.6	0.7	1.1	0.4
Volkswagen Rabbit Diesel	0.2	0.6	0.4	0.1
Oldsmobile D-88	—	1.6	1.4	0.4
Mercedes 300-D	0.3	1.7	1.2	0.3
Audi 5000	—	1.9	2.9	0.9
Peugot 504D	—	1.5	0.8	0.3
<b>Proposed emissions standards</b>				
EPA—1985	0.12	0.6	2	0.25

<sup>a</sup> Federal test procedures hot start.  
Source: Reference 8.

emissions from gasoline- and diesel-powered vehicles along with proposed standards for 1985 is given in Table 1. Diesel vehicles appear likely to have difficulty meeting the proposed particle standard, but the EPA may allow manufacturers to average particle emission rates over families of engine types (9). This could permit future diesel vehicles to have particle emission rates similar to those of current models. Because of these regulatory uncertainties, our discussion of the potential effects of light-duty diesel-powered vehicles considers only current emission rates. However, the projected magnitudes of most effects can be scaled higher or lower in direct proportion to the pollutant emission rates that actually occur.

Substantial economic gains could be achieved by using more diesel engines in future light-duty vehicles. For example, if we could obtain 20% more fuel efficiency with 20% of our light-duty vehicle fleet, this would save approximately 100 million barrels of crude oil per year—or 2% of the total amount of petroleum refined in the U.S. Our assumption that 20% of light-duty vehicles eventually will be powered by diesel engines is consistent with reports prepared by the EPA, the Department of Transportation (DOT), and the AMOCO Oil Company (8). It is also consistent with the amount of diesel fuel that can easily be produced in the future.

#### Vehicle particle emissions

Although substantial engineering efforts have been made to reduce diesel

**TABLE 2**  
**Atmospheric emissions in U.S. during 1977 <sup>a</sup>**

Source	Thousand metric tons/y			
	Particles	Nitrogen oxides	Carbon monoxide	Hydrocarbons
<b>Stationary</b>				
Electric generation	4 000	8 000	300	80
Mining and metals	6 000	200	2 000	100
Petroleum supply	80	400	2 000	3 000
Other industries	2 000	6 000	5 000	10 000
Fires	700	100	5 000	8 000
Other	1 000	3 000	11 000	6 000
<b>Mobile</b>				
Light-duty gasoline	680	5 000	68 000	9 000
	(7)	(800)	(5 000)	(600)
Light-duty diesel	(60)	(400)	(600)	(200)
Heavy-duty gasoline	80	700	13 000	1 300
Heavy-duty diesel	160	1 500	1 300	200
Tobacco smokers	20	0.2	10	0.6

<sup>a</sup> Values in parentheses are projected for future years assuming that 20% of the light-duty vehicles are diesels.  
Source: References 8, 15.

exhaust particles, they are probably an innate product of the diesel combustion process. They differ in chemical composition from particles found in gasoline engine exhaust because of differences in the compositions of diesel fuel and gasoline and in the combustion processes. In gasoline engines, fuel is usually mixed with air in the carburetor, and the vaporized fuel is supplied to the cylinders, compressed, and ignited by a spark. In diesel engines, fuel droplets are injected directly into the cylinders or

adjacent mixing chambers. Injection begins during the last part of the compression stroke and continues through about 20% of the piston downstroke. The temperature rise resulting from air compression in the cylinders is sufficient to ignite the fuel almost immediately.

The composition of particles emitted by gasoline-powered vehicles has changed markedly with the transition from regular to unleaded fuel (4). Regular gasoline contains about 0.2 g/L of tetraethyl lead. The lead

vaporizes during combustion, but it recondenses upon cooling in the exhaust train to form chain aggregates of small microspheres. About 95% of the lead is exhausted in fine particles that have aerodynamic diameters  $<0.5 \mu\text{m}$  (10). Emissions from gasoline engines that use catalytic converters and unleaded fuel contain  $<2\%$  of the particle concentrations found in exhaust from gasoline engines that use regular fuel. Exhaust particles from engines powered by unleaded fuel are also chain aggregates of smaller microspheres, but they are composed mainly of carbon and trace metal impurities present in the fuel.

Exhaust particles form in diesel engines because combustion begins in the cylinders before the fuel completely mixes with air (11). As the fuel droplets begin to burn, the region nearest each droplet is oxygen poor and the region farther away is oxygen rich. Rapid oxidation probably begins in the oxygen-rich region and proceeds inward. Since the fuel droplet is oxygen poor when first heated, it may pyrolyze and form an inert carbon particle. The particle may be eliminated by further oxidation, or it may remain and grow by adsorption of vapor-phase hydrocarbons. Studies have shown that most particles in the exhaust are formed late in the combustion cycle and that a portion of the adsorbed hydrocarbons may originate from crankcase oil (12).

Diesel exhaust particles consist of chain aggregates of carbon microspheres coated with a variety of organic compounds that comprise 15–65% of the total particle mass. Individual microspheres are about 35 nm in diameter, and the aggregate particles have a mean volume diameter of about  $0.16 \mu\text{m}$ . Several hundred organic compounds have been identified in solvent extracts of diesel exhaust particles (13), some of which have been shown to initiate skin tumors in mice when applied in milligram quantities (14).

#### Ambient levels of diesel exhaust

Exhaust from diesel vehicles does not contain unique atmospheric pollutants, and it is not likely to be the largest source of regulated pollutants in the future (Table 2). If 20% of the light-duty vehicles are diesel-powered, their emissions of particles, carbon monoxide, and hydrocarbons are projected to contribute less than 1% of the current total emissions of these pollutants in the U.S. For nitrogen oxides, future diesel vehicle emissions could amount to 1–2% of the current total

emissions. Although diesel vehicles are not a large source of these pollutants, their emissions generally occur close to where people live and work. In contrast, other large industrial sources generally emit pollutants from the tops of tall stacks located away from the most densely populated centers. For this reason, the following exposure and health risk analyses specifically focus on evaluating the effects of light-duty diesel-powered vehicles in congested urban areas.

To predict how ambient concentrations of diesel particles may increase over large urban areas in future years, we developed a computer simulation model (8). In this model, the air over cities was represented by a matrix of cells. The concentrations of particles within the cells were increased or decreased by the projected local emissions from vehicles, by exchange with neighboring cells, and by particle deposition. Traffic density patterns were changed to simulate higher emissions in city centers, which were located in different positions with respect to the geographic boundaries of a city. The model output included estimates of diesel particle concentrations in air at different points within a city, the citywide average levels, and the population-weighted average levels.

From the results of these simulations, average population distributions and vehicle operating conditions were selected to project future ambient concentrations of diesel exhaust particles in different U.S. cities. We assumed that 40% of urban populations and diesel vehicles would be concentrated in city centers occupying 5% of the total metropolitan areas, that this population distribution would exist for one-half of each day and five days per week, and that populations and diesel vehicles would be distributed uniformly throughout cities at other times. The projected population-weighted ambient concentrations using these assumptions were twice as high as those calculated when using uniform distributions of vehicles and people, but only one-half as large as those calculated assuming a more extreme condition—that 70% of the urban populations would be concentrated in city centers during normal business hours.

This model, together with current urban area and population density information and projections of diesel fuel consumption rates—based on 1975 gasoline consumption rates—was used to predict future ambient concentrations of diesel exhaust particles in major U.S. cities (Figure 1). Assuming

the average diesel particle emission rate will be  $0.3 \text{ g/km}$ , the mean ambient concentration was predicted to be  $0.5 \mu\text{g/m}^3$ , but the most densely populated cities could experience levels between 1 and  $5 \mu\text{g/m}^3$ .

To predict future urban ambient concentrations of gaseous emissions from light-duty diesel vehicles requires complex mathematical models that incorporate photochemical reactions, detailed weather information, and complete information about local pollution sources. These analyses are costly, and they cannot be performed for many metropolitan centers because the necessary pollution models are not available.

One modeling study representing the San Francisco Bay area was done in parallel with this analysis (8). It indicates that urban concentrations of diesel-powered-vehicle gaseous pollutants and their photochemical reaction products are not likely to change significantly. This is because diesel- and gasoline-powered vehicles currently have similar levels of gaseous emissions and other large sources of these pollutants are located in major metropolitan centers. Thus, further urban modeling studies of photochemical pollutants were not done for other cities, and our analyses focused on human exposures that will occur in close proximity to congested urban streets. These exposures will be dominated by nearby vehicle emissions, and they will be the highest exposures to diesel vehicle emissions encountered by the public.

To estimate future ambient levels of diesel emissions in congested areas, we used empirical relationships between measured concentrations of carbon monoxide and distance from or above the streets (4). Carbon monoxide reacts very slowly in urban air. Therefore, it is a good tracer for vehicle emissions with reaction times in the atmosphere that are longer than the period of time that the pollutants remain near the site of interest. This period lasts only a few minutes in most weather conditions.

The relationships use pollutant concentration indexes calculated by dividing the measured ambient levels of the pollutant at a given location by its emission rate from all of the vehicles using the street. The emission rate is defined as the number of vehicles passing the location each hour multiplied by the emission rate of an average vehicle. Most of the data used to develop the relationships between ambient concentrations of pollutants and their sources were derived from studies

FIGURE 1  
Projected diesel particle concentrations for U.S. cities

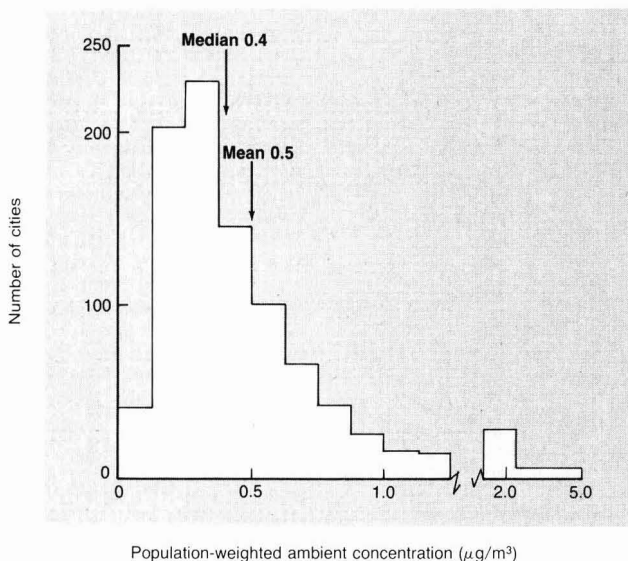
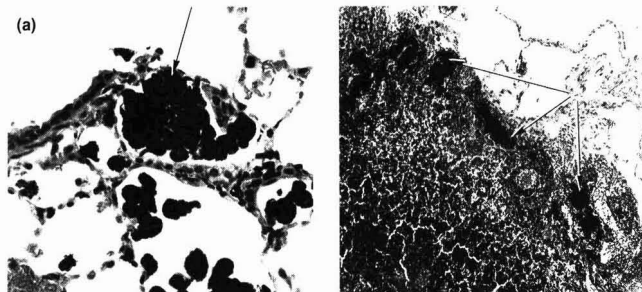
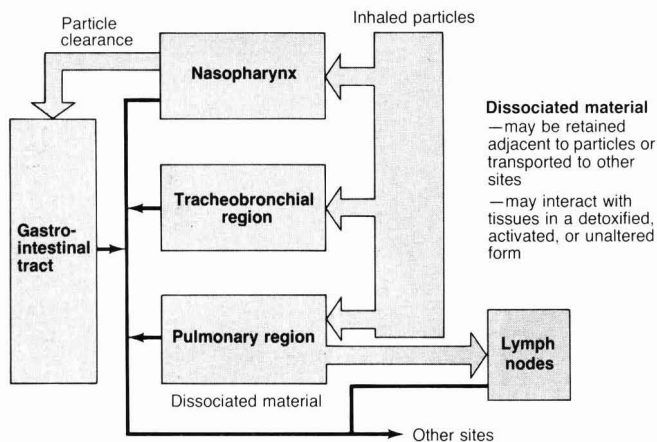


FIGURE 2  
Model of diesel particle retention



Photomicrographs of tissues from rats that were chronically exposed to diesel exhaust show the accumulation of particles in lung macrophages (a) and in lymph nodes (b).



Source: McClellan et al. (14)

in St. Louis, San Jose, and Nashville, where the tallest buildings near the sampling sites were only 40 m high. However, measurements made 1.5 m above street level in a Manhattan street canyon over a 4-y period are only about 50% higher than the curves obtained for the more shallow street canyons.

Brief, high ambient concentrations of diesel vehicle exhaust also may occur in urban parking garages and other enclosed structures. Mathematical models, such as simple box models, can be used to calculate these pollutant levels by taking into account the volume of a garage, its rate of ventilation, the number of vehicles running at one time, and the vehicle emission rates (4).

Typical ambient concentrations of diesel and gasoline engine vehicle emissions in congested urban areas were calculated for a time when 20% of the light-duty vehicles may be diesel powered (Table 3). Diesel vehicles are expected to add significantly to the ambient levels of particles, but they are not likely to increase the levels of nitrogen oxides and vapor phase hydrocarbons by more than 25%. Carbon monoxide levels in congested urban areas are not expected to rise because emissions of this pollutant from diesel and gasoline engines are similar.

#### Exposures to diesel exhaust

Concerns about the potential health effects of exposures to light-duty diesel vehicle exhaust have focused mainly on particle emissions. Diesel exhaust particles are small, and they readily deposit in the respiratory tract when inhaled (Figure 2) (16). Particles that deposit in the upper airways remain there for only a brief period of time because they are rapidly cleared from these regions to the gastrointestinal tract. In contrast, particles that deposit in the lower pulmonary region may be retained for several hundred days after inhalation.

Particles also are transported to the pulmonary lymph nodes by macrophages where they are retained for a long time. The fate of organic compounds associated with the particles is of special concern because these compounds are similar to organic compounds associated with cigarette smoke, coke oven emissions, and roofing tar vapors, which are known to cause lung cancer in humans (2). The organic compounds may dissociate from the particles and be transported to other tissues where they can be metabolized and excreted or cause additional damage to health.

**TABLE 3**  
**Projected ambient concentrations of emissions from light-duty vehicles if 20% of them are diesel powered<sup>a</sup>**

Location	Ambient concentration in $\mu\text{g}/\text{m}^3$			
	Particles	Nitrogen oxides	Carbon monoxide	Hydrocarbons
Typical street canyon (2000 vehicles/h)	10	100 (20) <sup>b</sup>	150	40
Manhattan street canyon <sup>c</sup> (2000 vehicles/h)	30	230 (45)	250	90
Expressway (10 000 vehicles/h)				
at roadside	35	350 (70)	500	90
at 100 meters	6	60 (10)	100	15
Parking garage (8-h average)	80	400 (70)	2000	800
U.S. cities (annual average)	0.5	—	—	—
Rural areas (annual average)	0.05	—	—	—

<sup>a</sup> Estimates include emissions from both diesel- and gasoline-powered vehicles.

<sup>b</sup> Values in parentheses are for nitrogen dioxide.

<sup>c</sup> Assumed emissions are for the New York City driving cycle.

Prolonged human exposure to high levels of atmospheric pollutants has also been shown to cause changes in respiratory function and may contribute to long-term development of respiratory diseases other than cancer (17). Irritant particles and gases produce toxic effects through chemical reactions with cells lining the respiratory airways. This leads to functional and morphological alterations of pulmonary defense mechanisms, causing increased susceptibility to infection.

Because many different pollutants are always present in the atmosphere, it has not been possible to identify specific pollutants that may be responsible for causing damage to health. The EPA has derived standards for total suspended particles based on mass, irrespective of their chemical composition. This approach assumes that the total mass of particles can be used as an index of noncancer risks and that by controlling emissions of particles in general, the ambient concentrations of toxic compounds that may be associated with the particles will be held within appropriate limits. In addition, nitrogen oxides and sulfur oxides emitted from both diesel- and gasoline-powered vehicles are toxic gases that may contribute to health risks.

### Lung cancer risk

To date, inhaled diesel engine exhaust has not been shown to cause lung cancer in humans. The most significant epidemiologic study was done with London transit workers who were exposed to diesel bus exhaust between 1930 and 1974 (18). Although this

study did not detect an increase in lung cancer risk even in bus garage workers, the group with the highest exposure, there were important deficiencies in the information available for analysis. The worker groups were highly variable in ethnic composition, and many workers were born and had lived outside of Great Britain; the workers were not followed up after they left employment; and smoking histories and age information were not available.

Harris (19) analyzed the London transit worker study statistically to

answer the question: How high could the lung cancer risks have been in the exposed workers and yet not have been detected? Taking the large uncertainties of the original study into account, Harris estimated that worker lifetime risk could have increased by 0.05% for each year of exposure to diesel exhaust particles at a level of  $1 \mu\text{g}/\text{m}^3$  calculated as an average over all of the air breathed. This was estimated to be the 95% upper confidence limit of the increased lung cancer risk. Thus, people who would be exposed to an average ambient concentration of  $2 \mu\text{g}/\text{m}^3$  for 70 y could have their normal lung cancer risk increased by as much as 7% ( $2 \mu\text{g}/\text{m}^3 \times 70 \text{ y} \times 0.05\%$ ). Because this upper confidence limit may represent a larger involuntary risk than many people would readily accept, more information is needed to better define this risk.

Additional perspective can be gained by reviewing measured cancer incidence rates in other groups of people who have been exposed to similar hydrocarbon combustion products. These include cigarette smokers, coke oven workers, roofers, and people exposed to ambient pollution. Their annual lung cancer rates are shown in Figure 3 in relation to the calculated daily average ambient concentrations of particles that they breathe. Groups of people who inhale higher average particle concentrations also have higher lung cancer risks, but smokers develop fewer cancers per unit con-

**FIGURE 3**  
**Measured lung cancer risks in human populations compared to projected risk for diesel exhaust**

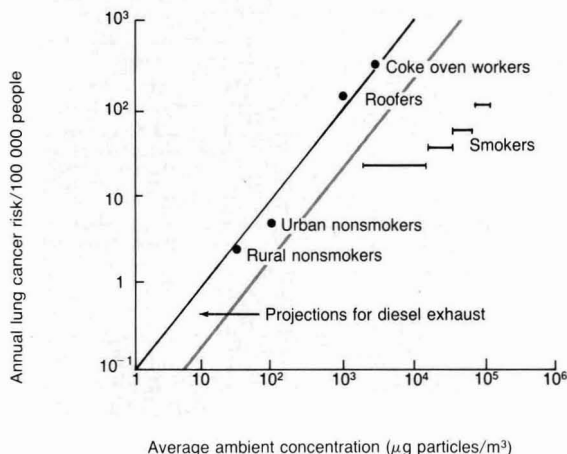


TABLE 4

**Summary of results from short-term mutagenesis and carcinogenesis tests using organic extracts of particle emission samples**

Assay	Slopes of the reported dose-effect relationships <sup>a</sup>							
	Diesel				Gasoline (Mustang)	Cigarette smoke	Coke oven emissions	Roofing tar vapors
	Caterpillar	Oldsmobile	Volkswagen	Nissan				
Ames mutagenesis (20)								
TA98 +MA <sup>b</sup>	0.6	3	3	14	3	1	3	1
-MA	0.7	6	4	12	1	0	2	0
TA100 +MA	1	2	4	9	2	NA <sup>c</sup>	3	4
-MA	2	2	6	13	2	0	3	0
Mouse lymphoma cell (21)								
+MA	0.08	1	2	3	2	0.5	10	30
-MA	0.2	0.7	3	4	0.4	0.5	0.9	0.4
Balb C/3T3 mutagenesis (22)								
+MA	0.2	0.5	NA	2	4	NA	NA	2
-MA	0.2	0.5	NA	1	4	NA	8	3
CHO mutagenesis (23) <sup>e</sup>	0	0	0.01	0.03	0.01	0	0.02	0
(24)	NA	0.2	NA	NA	0.6 <sup>d</sup>	0.06	6	6
SCE in CHO cells (21) <sup>e</sup>								
+MA	0	0.02	0.03	0.07	NA	0.02	0.05	0.2
-MA	0.01	0.02	0.07	0.3	0.8	0.1	0.4	0.1
SHE viral enhancement (23) <sup>f</sup>	0.04	0.06	0.1	0.6	0.2	0.5	0.7	2
Skin tumor initiation (25)	0	0.3	0.2	0.6	0.2	NA	2	0.4

<sup>a</sup> The slope is the cell mutation or transformation frequency per unit concentration of extract applied or, for skin tumor initiation, the number of papillomas per mouse at 1 mg of dose.

<sup>b</sup> Indicates whether or not metabolic activation was used for the assay.

<sup>c</sup> Results not available.

<sup>d</sup> Chevrolet Citation.

<sup>e</sup> SCE, sister chromatid exchange; CHO, Chinese hamster ovary cells.

<sup>f</sup> SHE, Syrian hamster embryo.

centration of particles breathed than all of the other groups. This is consistent with the hypothesis that exposure to polycyclic aromatic hydrocarbons (PAHs) is a major factor increasing lung cancer risk because chemical analyses have shown that cigarette smoke condensate contains only about 1-10% of the levels of many PAHs found in urban soot, gasoline engine exhaust, and diesel engine exhaust (8).

For the past several years, EPA has supported a major research program to compare the mutagenic and carcinogenic potencies of organic extracts of diesel and gasoline engine exhaust particles, cigarette smoke condensate, roofing tar vapors, and coke oven emissions (2). Many biological test systems were used, including mutagenesis assays with bacteria and mammalian cells, DNA damage assays with hamster ovary cells, and carcinogenesis assays using hamster embryo cells and mouse skin painting. Results from these different assays indicate that in comparison with the other combustion products, extracts of diesel exhaust particles could be more, less, or equally potent in causing genetic transformations (Table 4). Rather than reflecting the total cancer risk, the relative carcinogenic potencies

derived from the results of individual test systems seemed to depend more on the unique sensitivities of each test to specific chemical compounds (26). Thus, it is difficult to know how to combine the varied results of these studies and derive appropriate numerical values to express the relative carcinogenic potencies of these combustion products. The fact that diesel particle extracts do not appear to be significantly more potent than the other mixtures may be the most important finding.

Also, it may not be necessary to argue that diesel particles are somewhat more or less potent than the other products on the basis of the short-term bioassay results because the actual exposures of people to these substances range over several orders of magnitude. Smokers inhale hundreds of grams of cigarette smoke each year; coke oven workers and roofers inhale a few grams of emissions each year; but people exposed to diesel particles will inhale only milligram amounts annually. For diesel exhaust to represent a similar hazard to people as the other combustion products, diesel particles would have to be several orders of magnitude more potent in causing lung cancer. This is clearly not the case.

For this analysis, we assumed that lung cancer risk from exposure to diesel exhaust is not likely to result in more than 0.1 lung cancer deaths each year in a population of 100 000 people per  $\mu\text{g}/\text{m}^3$  of particles breathed over their lifetimes. This level of risk is represented by the solid upper line in Figure 3. Albert et al. used results of the short-term bioassay studies with the different combustion products to mathematically derive a lifetime cancer risk of  $0.3 \times 10^{-4}$  per  $\mu\text{g}/\text{m}^3$  average ambient concentration of particles breathed (27). If the average lifespan in a population is 70 y, then this risk would be equivalent to 0.05 lung cancer deaths each year per 100 000 people per  $\mu\text{g}/\text{m}^3$  average concentration of particles breathed. This level of risk is indicated by the blue line in Figure 3.

In a second analysis of the short-term bioassay information, Harris (19) derived a lung cancer risk factor about twice that indicated by Albert et al. (27). Harris used a relative risk model suggesting that the increased risk for members of a population would be proportional to the lung cancer risk that they would incur without being exposed to diesel exhaust. This implies that the increased lung cancer risk would be much more likely to affect

smokers and other people who already have a high risk of developing lung cancer. About 110 000 lung cancer deaths now occur each year in the U.S., and about 90% of these occur in smokers. Therefore, the risk model used by Harris would predict that about 90% of the increased risk from exposure to diesel engine exhaust would also occur in smokers.

Using the lung cancer risk factor described above (0.1 cancer deaths per year in a population of 100 000 per  $\mu\text{g}/\text{m}^3$  average concentration of particles) and the projected ambient levels of particles in urban areas (Table 3), we calculated the potential lung cancer risks from future light-duty diesel-powered vehicles (Table 5). The current average annual lung cancer risk for nonsmokers is about 7 per 100 000 people; for smokers, it is about 80 per 100 000. Results of the analysis described here indicate that about 200 additional lung cancer deaths might occur in the U.S. each year if 20% of the light-duty vehicles were diesels. Most of this increased risk is expected to be incurred by people living near congested expressways or working near congested urban streets. Uncertainties in these calculations are discussed in detail elsewhere (8).

#### Respiratory functional diseases

Health specialists often use linear mathematical relationships to estimate cancer risk from exposures to different levels of chemicals or physical agents. These relationships are used to estimate risk, even at very low exposure levels, although the validity of the estimates at low levels of exposure cannot be proven. For noncancer health effects, such as changes in respiratory function and decreased resistance to infection, damage to the respiratory system may not be apparent below threshold exposure levels, but it may increase sharply above those levels. The National Ambient Air Quality Standards are thought to represent exposure levels that are below health effects thresholds for different atmospheric pollutants (17).

Because diesel-powered vehicles are not the only sources of particles, nitrogen dioxide, and other pollutants in urban air, we cannot estimate their noncancer health risks independently. By themselves, diesel vehicles are not expected to cause levels of pollutants in urban areas that would exceed air quality standards. But combined with pollutants from other sources, the total could exceed air quality standards and contribute to development of long-term damage to respiratory health. A

TABLE 5

#### Projected lung cancer risk from diesel vehicle exhaust

Population	Particle exposure ( $\mu\text{g}/\text{m}^3$ )	Added annual lung cancer risk <sup>a</sup>
Resident of major U.S. city	0.05–5	0.005–0.5
Urban resident living 100 m from expressway	0.06–6	0.006–0.6
Worker on urban expressway	4–35	0.4–3.5
Worker in urban street canyon	1–30	0.1–3

<sup>a</sup> Cancers per 100 000 people.

primary concern is for the increased frequency of respiratory symptoms and decreased pulmonary function observed in children exposed to  $>200 \mu\text{g}/\text{m}^3$  of particles and sulfur dioxide. These levels have also decreased lung function in adults (17). Chronic exposure to  $\text{NO}_2 >30\text{--}100 \mu\text{g}/\text{m}^3$  has also been observed to increase respiratory illness and may cause small changes in pulmonary function in children under two years of age (28); it also has been reported to cause increased respiratory symptoms in children between the ages of six and 11.

Currently, the primary air quality standard for total suspended particles is  $75 \mu\text{g}/\text{m}^3$  for the annual average and  $260 \mu\text{g}/\text{m}^3$  for the highest daily average. If future particle emissions from light-duty diesels average  $0.3 \text{ g}/\text{km}$ , then ambient concentrations of these exhaust particles in congested urban areas could reach  $35 \mu\text{g}/\text{m}^3$ —a 30–80% increase over current levels in these areas. Future air quality standards may be based on size-selective particle sampling that would include only respirable particles smaller than  $10 \mu\text{m}$  in aerodynamic diameter (17). In this event, diesel particles will contribute a larger share of the samples than if all particle sizes were collected because diesel particles are smaller than  $1 \mu\text{m}$  in diameter.

The current air quality standard for nitrogen dioxide is  $100 \mu\text{g}/\text{m}^3$ . The mean annual concentration in urban areas of the U.S. between 1977 and 1979 was  $50 \mu\text{g}/\text{m}^3$ , but 5% of the reporting sites, mainly congested urban areas, exceeded  $100 \mu\text{g}/\text{m}^3$  (28). Nitrogen dioxide emissions from gasoline-powered vehicles have been reduced in recent years, mainly with exhaust gas recirculation and catalytic converters. Current model diesel-powered vehicles emit levels of nitrogen oxides similar to those of gasoline-powered vehicles manufactured in the mid-1970s, but twice as much as those of current models of similar size. Therefore, increasing our use of diesel

vehicles in the future may not alter ambient concentrations of nitrogen dioxide.

#### Other potential effects

A complete assessment of the potential effects of light-duty diesel-powered vehicles requires consideration of several topics that have not yet been addressed. First, diesel exhaust has a distinctive odor that many people find unpleasant. Based on the results of odor tests (29) and projections of future concentrations of diesel exhaust at congested urban sites, Forrest et al. concluded that diesel exhaust would not, on the average, lead to a significant deterioration of these atmospheres (4). However, it is likely that some people who are very close to congested traffic areas with higher-than-average numbers of diesel vehicles may find the odors unpleasant or even unbearable over short periods of time. This will be similar to the experience that people encounter in passing directly through the exhaust plume of diesel vehicles.

Second, diesel exhaust will add to the total ambient concentrations of particles in urban and rural areas. This may reduce visibility and increase soiling. The effect is expected to be small in most areas, but near expressways and in urban street canyons, diesel exhaust particles may comprise 30% or more of the total particulate pollution and contribute a proportionate amount to nearby urban soiling. The potential for this requires further evaluation.

Third, increased use of diesel-powered vehicles may affect overall highway safety (30). Use of diesel engines provides a means of obtaining improved fuel economy without reducing vehicle size. When involved in collisions, passengers in larger vehicles have been noted to experience fewer serious injuries and deaths than passengers in smaller vehicles. Although this may lead to improved safety for passengers in large vehicles, it may lead to higher risks for passengers in

small vehicles. Also, diesel fuel is less combustible than gasoline and might decrease the risk of fire. Because of such offsetting safety factors, it is still uncertain whether increased use of diesel-powered vehicles will alter the overall risk to motorists.

### Summary and conclusions

Particle emissions from diesel-powered vehicles are significantly higher than those from gasoline-powered vehicles that use unleaded fuel. There are two concerns related to inhaling high concentrations of particles. First, they may cause respiratory functional changes and increased susceptibility to infections because of their toxic properties. Second, they may increase our risk of developing respiratory tract cancers because they contain mutagenic and carcinogenic chemical compounds.

Because concentrations of particles from diesel vehicles will not exceed about 40  $\mu\text{g}/\text{m}^3$ , even in very congested urban areas, they should not by themselves cause symptoms of respiratory disease. However, combined with particle emissions from other sources, diesel vehicles could contribute substantially to the total particulate pollution levels in urban areas. In consequence, ambient levels in these areas may then exceed air quality standards, and cause a concomitant rise in respiratory disorders.

Lung cancer risks from inhaling diesel exhaust particles were estimated by comparing their carcinogenic potencies with other substances that have been shown to cause cancer in humans. We estimate that the expected levels of exposure in congested urban areas could increase a person's lung cancer risk by a few percent, but that the overwhelming cause of lung cancer in a population will continue to be cigarette smoking. Overall, diesel-powered vehicles are expected to cause less than about 200 lung cancers per year in the U.S. population. However, the information currently available is insufficient to exclude the possibility that no lung cancer cases can be attributed to the emissions from light-duty diesel vehicles.

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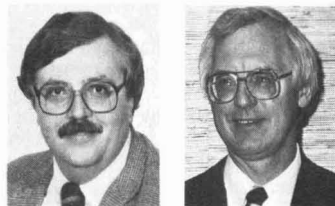
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# PCB contamination in and around New Bedford, Mass.

*Although higher levels exist elsewhere in North America, the cumulative exposure involving aquatic life and humans in this locality is said to be unique*

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As home port to those vessels that ply the rich offshore waters of Georges Bank, New Bedford is the largest revenue-producing fishing port on the U.S. Atlantic seaboard. Bounded by the Acushnet River estuary, New Bedford Harbor, and Buzzards Bay, this community of 100 000 has weathered wave after wave of changing economic fortunes—first as the world's largest whaling port and later as a major textile center.

Since the end of World War II, the city has struggled to broaden its economic base through the development of an industrial park as well as other incentives designed to encourage the movement of new industry to the area. Two of the mainstays of New Bedford's recently diversified economy are electronic capacitor manufacturers located in old textile mill houses situated on the banks of the Acushnet River estuary.

The past use of polychlorinated biphenyls (PCBs) in southeastern Massachusetts by these capacitor manufacturers has left a lasting impact on New Bedford's vibrant port. PCBs are industrial chemical compounds that were commercially manufactured and marketed in the U.S. from 1929 to 1977. The Monsanto Corporation of St. Louis, Mo., the former industrial producer of PCBs in the U.S., marketed PCB blends and mixtures under the trade name Aroclor. The total national production of PCBs during the approximately 50 years of their manufacture is believed to have totaled

600 million kg.

The chemically stable, nonflammable nature of PCBs, together with their high boiling point, low solubility, and nonconductive nature makes these chemical compounds nearly ideal for many industrial applications, including capacitors and transformers. Unfortunately, these same properties cause PCBs to persist in the environment and bioconcentrate, creating potential hazards to affected biota.

The four-digit number following the trade name Aroclor was used to characterize the blend of polychlorinated biphenyls. Except for Aroclor 1016, which was not named according to protocol, the first two digits were assigned to represent 12 carbon atoms (thereby identifying the biphenyl structure) while the final two digits were used to represent the approximate percentage of chlorine by weight in the PCB blend.

The physical characteristics of PCBs vary according to the mixture. As the chlorine content increases, the Aroclors change from a colorless oil, to a sticky resin, to a white powder, and their persistence in the environment generally increases.

Even very small concentrations of PCBs can be detrimental. The U.S. EPA has recommended a marine water quality standard of 0.03 ppb to protect marine life. Marine and freshwater organisms have been found to concentrate PCBs in their bodies to levels 100 000 to one million times or higher than those levels present in ambient waters.

The U.S. Food and Drug Administration (FDA) has established regulatory limits for PCBs in various foods (Table 1). The limit for fish and shellfish is 5 ppm wet weight in the edible portions of these foodstuffs.

(Biotic concentrations are given as wet weight; all other solid-phase data are reported as dry weight. Solid fraction PCB concentrations of mg/L are considered equivalent to ppm.)

At this time there are no federal standards for PCBs in drinking water or ambient air. The Occupational Safety and Health Administration (OSHA) has set a workplace standard of 1 mg/m<sup>3</sup> for Aroclor 1254. The National Institute for Occupational Safety and Health (NIOSH) recommended a more stringent workplace standard of 1 µg/m<sup>3</sup> total PCBs; however, the OSHA standard remains in effect.

Wastewater discharges of PCBs are regulated by EPA in accordance with Code of Federal Regulations, 40 CFR 129.105. This regulation is implemented through the National Pollution Discharge Elimination System (NPDES) permitting program. PCBs are severely limited in discharges from electrical capacitor manufacturers.

Localized PCB spills have contaminated surface sediments in a number of widespread locations across North America. A number of sites including the Hudson River (N.Y.), Lake Michigan's Waukegan Harbor (Ill.), and the municipal wastewater treatment facility in Bloomington, Ind., have been contaminated by PCBs. Nonetheless, the recently completed Remedial Action Master Plan states that New Bedford "is one of the most extensive cases of environmental contamination by polychlorinated biphenyls. . . ." Although the concentration of PCBs in water, sediment, and air has occasionally been found to exist elsewhere at levels greater than that observed in the New Bedford area, the cumulative environmental exposure affecting New Bedford's

biota (including portions of the human population) is said to be unique.

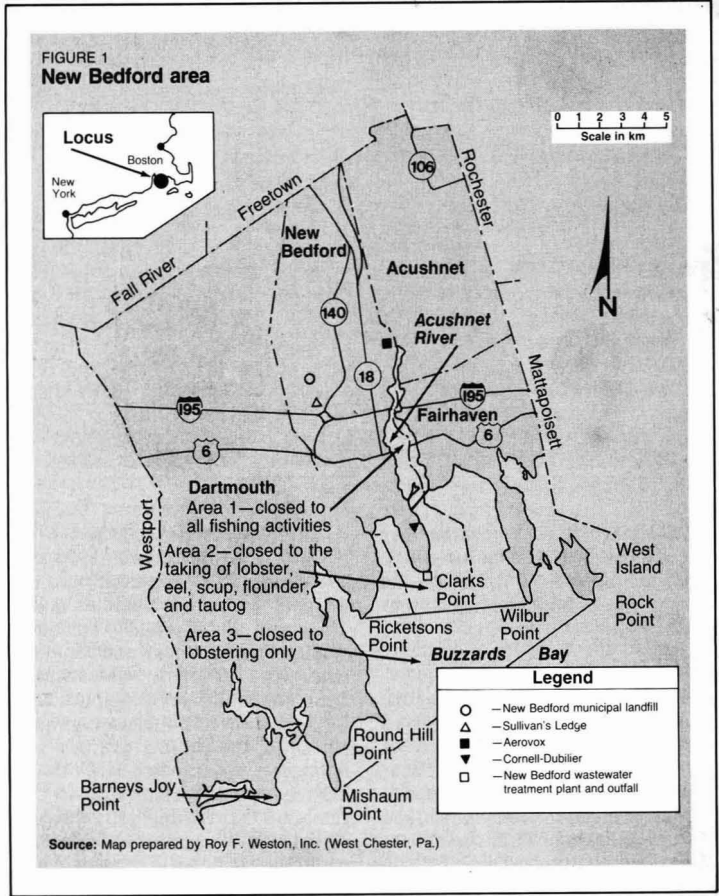
### Other contaminated areas

**Hudson River.** The most widely publicized PCB contamination of an American waterway—more than 250 000 kg were discharged over 25 years from two capacitor manufacturing plants—is that which exists in New York State's Hudson River near Fort Edward. In 1975, PCB levels in some fish were found to exceed the FDA's tolerance level of 5 ppm. As a result, the New York State Department of Environmental Conservation (NYSDEC), with the advice of the Department of Health, instituted a ban on fishing in the upper Hudson River from the Troy Dam to Fort Edward. In the lower Hudson River, commercial fishing was restricted, and recreational fishermen were advised to restrict fish consumption to one meal per week (American eel excluded).

In 1976, after lengthy hearings, the state and the General Electric Company, the principal PCB discharger, sharing the responsibility, agreed to seek ways to remove PCBs from the river. The two parties established a \$7-million fund for research and engineering studies, which were carried out by consultants, universities, and federal and state agencies in one of the most comprehensive investigations of a hazardous waste problem ever undertaken in the U.S. These studies found that the PCB-contaminated sediments in the upper Hudson River act as a source to the entire downstream river system. According to 1979 U.S. Geological Survey readings at the Troy Dam, approximately 3200 kg of the chemical moved downstream of the dam annually.

Much of the Hudson's contamination is concentrated in a relatively small area. Forty "hot spots" have been located by the NYSDEC in the upper reach where PCB concentration is equal to or greater than 50 ppm. Removal of these hot spots from the river would greatly reduce the amount of PCBs available to the ecosystem, according to the study.

**Waukegan, Ill.** Another documented case of the contamination of a navigable waterway by PCBs exists in Lake Michigan's Waukegan Harbor. The area of contamination encompasses a 15-hectare (ha) shipping port, an adjacent upland industrial area, and a lengthy drainage ditch. PCB concentrations up to 250 000 ppm, or 25% by weight, have been observed in areas of upland and submerged sediments in the vicinity of the Outboard Marine



Corporation's Johnson Motors facility. Fish containing PCBs at levels exceeding 100 ppm have been captured within the harbor, while immediately outside Waukegan Harbor fish exhibit PCB levels characteristic of Lake Michigan fish (averaging, and occasionally exceeding, 2–5 ppm).

**Bloomington, Ind.** PCB contamination of the city's Winston Thomas wastewater treatment plant has resulted in the stockpiling of six years' accumulation of residual sludges amounting to approximately 25 000 m<sup>3</sup> of material with a PCB concentration averaging 100–300 ppm.

### New Bedford PCBs

Contamination of New Bedford Harbor was first documented in 1976 when EPA conducted a New England PCB survey and found elevated levels of the material in various harbor locations. Testing revealed that two industrial operations were discharging wastewaters containing PCBs. Both the direct discharge of contaminated waters to the Acushnet River estuary and PCB contamination of the New

Bedford municipal wastewater treatment facility were identified.

Since this initial survey of the New Bedford area, a much better, although not yet complete, understanding of the extent of PCB contamination has been gained. The direct discharge of PCB-contaminated wastewater from all industrial operations has been significantly reduced. The discharge of PCBs from the city wastewater treatment plant, however, remains significant. Recent studies have documented that 90–300 kg of PCBs continue to be discharged annually in this manner.

The sediments underlying the entire 440-ha New Bedford Harbor contain elevated levels of PCBs. Concentrations range from a few parts per million to well over 100 000 ppm. Portions of Buzzards Bay are also contaminated with concentrations occasionally exceeding 50 ppm. The water column in New Bedford Harbor has been found to contain PCBs in the parts-per-billion range, well in excess of EPA's 0.001-ppb guideline. (Liquid fraction PCB concentrations of  $\mu\text{g/L}$  are considered equivalent to ppb.) EPA, ac-

TABLE 1  
**FDA limits on PCB concentrations in foodstuffs**

Foodstuff	PCB limit (mg/L wet weight)
Fish and shellfish	5.0 <sup>a</sup> (edible portion)
Milk and manufactured dairy products	1.5 (fat basis)
Poultry	3.0 (fat basis)
Red meat	3.0 (fat basis)—action level
Eggs	0.3
Infant and junior foods	0.2
Paper food package in direct contact with foodstuff	10.0—action level
Animal feed components of animal origin	2.0
Feed for food-producing animals	0.2 (except concentrates, supplements, and premixes)

<sup>a</sup> FDA recommended lowering this standard to 2.0 mg/L in 1977; however, challenges by the seafood industry resulted in the courts ordering a temporary stay on any changes.

knowledging this contamination, has placed New Bedford Harbor on the expanded Superfund listing of the nation's most imminently hazardous sites.

#### Closed fishing grounds

Widespread contamination of the Acushnet River estuary and environs has resulted in the accumulation of PCBs in many marine species. Thousands of hectares have been closed to the harvesting of shellfish, finfish, and lobsters because of PCB contamination.

The fisheries closure established by the Massachusetts Department of Public Health on Sept. 25, 1979, is divided into three areas as shown in Figure 1. Area 1, New Bedford Harbor, is closed to the taking of all finfish, shellfish, and lobsters. Area 2 is closed to the harvesting of lobster and bottom-feeding finfish (eel, scup, flounder, and tautog). Area 3 is closed to the taking of lobsters. Since the FDA has determined that the affected fishery resources are not marketed as interstate products, the enforcement of these closures is entrusted to the Massachusetts Division of Law Enforcement.

Although the median PCB levels in five finfish species have been found to exceed the 5-ppm standard (see Table 2), lobster contamination concerns area residents the most. The closing of the bountiful lobstering grounds of Buzzards Bay has resulted in lawsuits being filed against both the Commonwealth of Massachusetts and the former manufacturers of PCB-impregnated capacitors. These lawsuits call on the industries to remedy the pollution and on the state to reopen the prized lobstering grounds.

Of 183 lobsters collected from Areas 1, 2, and 3 between 1976 and 1980, a median PCB concentration of 4.9 ppm was found in edible tissues. The mean value was 8.7 ppm, the maximum was 84 ppm, and the minimum was 0.1 ppm. Subsequently, lobster data have been compiled only for Area 3. In this, the most seaward portion of the closure area, the following results were observed: Of the 66 lobsters sampled from April to December 1982, the highest value observed was 8.8 ppm; the lowest recorded was 0.7 ppm. The median was found to be 4.1 ppm and the mean 4.4 ppm. In 1982, in the interest of economy, two lobsters were collected per sampling station and analyzed as composites. Therefore, the PCB concentrations reported above for these 66 lobsters are defined by 33 sampling results.

#### Industrial properties

Two areas known to contain substantial quantities of PCB wastes are the industrial properties of the capacitor manufacturers. Landfilling at these sites has taken place in recent years, and some of the materials used as fill were apparently contaminated with PCBs. Even today, capacitors containing concentrations of PCBs in the thousands of parts per million litter the New Bedford Harbor foreshore behind one factory. Upland sediments in the vicinity of another contain up to 99 000 ppm PCBs.

Other sites in New Bedford may contain substantial quantities of PCBs. One suspected area to the north is Sullivan's Ledge (Figure 1). Located near the municipal landfill, this site is now a vacant lot owned by the city of New Bedford, and was, until recently,

to be developed into a commuter parking lot. Sullivan's Ledge was filled when the city used the area as a dumpsite for brush, rubble, and demolition and industrial wastes.

Waste oils containing PCBs were used by New Bedford and possibly other area public works departments in the oiling of local roadways. In summary, past activities in New Bedford have resulted in the presence of PCBs in diverse areas throughout the community.

The few New Bedford area residents who have been studied have been found to contain elevated levels of PCBs in their blood. Recently, two small-scale epidemiology studies were conducted by the Massachusetts Department of Public Health, Harvard's School of Public Health, and the Centers for Disease Control in Atlanta, Ga. Consumers of large quantities of fish and occupationally exposed individuals were selected for study. The results of these studies indicate that the 51 residents tested possessed blood serum PCB concentrations ranging from 2 to 343 ppb (measured as Aroclor 1260). The mean concentration of Aroclor 1260 observed was 36 ppb, and the median was 15 ppb.

#### Industrial PCB practices

PCBs were used in the manufacture of electronic capacitors during the years 1947-78 in buildings presently occupied by Aerovox Inc., a subsidiary of R.T.E. Corp. (Figure 1). Capacitors were produced for a wide range of electrical applications ranging from ballasts used in fluorescent light fixtures to components used in atomic research. Their size ranged from approximately 15 cm<sup>3</sup> to nearly 1 m<sup>3</sup>.

PCB Aroclor 1242 was purchased from Monsanto for use in capacitor manufacture until 1972 when Aroclor 1016 completely replaced Aroclor 1242 as the impregnation fluid. Lesser quantities of Aroclors 1254 and 1252 were also used by Aerovox. At the peak of production, Aerovox used approximately 500 000 kg/y of PCBs. All use of PCBs stopped in 1978 when dioctyl phthalate (DOP) was substituted in the manufacture of capacitors.

To determine the extent, if any, of PCB contamination of Aerovox's sanitary waste discharges, the Massachusetts Department of Environmental Quality Engineering (DEQE) retrieved two wastewater grab samples in 1981. No PCBs were found. In 1976, when PCBs were still being used, EPA sampling detected PCB levels ranging from 73 to 400 ppb in the

wastewater.

Open channels parallel the northern and southern exterior walls of the factory, terminating at the Acushnet River. At one time, the troughs conveyed cooling waters. Today, a closed-cycle cooling system has eliminated the need for anything other than an occasional discharge. An EPA sampling effort in June 1981 led to the detection of the presence of contamination in the sediments in the bottom of the external troughs. After the findings of 40–22 000 ppm were reported to the company, Aerovox removed the contaminated sediments and disposed of them in accordance with state and federal laws.

All analyzed soil and sediment samples collected on the Aerovox property have been found to contain elevated levels of PCBs. Soils inside the chain link fence surrounding the property contain up to 24 000 ppm. Seaward of the fence, sediment sampling revealed levels of 190–190 000 ppm. These values were found in upland, intertidal, and subtidal sediment samples collected from a widespread area of several hectares.

NIOSH performed an extensive industrial hygiene survey of the Aerovox facility in March 1977 when PCBs were still being used in the manufacture of capacitors. As part of this survey both "personal" and "area" air samples were collected throughout the facility and analyzed for PCB content. Results indicated that the 29 personal and 25 area air samples that had been collected and analyzed for PCBs ranged from 0.17 to 1.26 mg/m<sup>3</sup>. At-

mospheric sampling has begun only recently.

Cornell-Dubilier Electronics Corporation (Figure 1) is also engaged in the manufacture and sale of capacitors for use in consumer products. Cornell-Dubilier is a wholly owned subsidiary of Federal Pacific Electric which is, in turn, wholly owned by Reliance Electronics, itself a wholly owned subsidiary of Exxon. Located across New Bedford from Aerovox, Cornell-Dubilier manufactured PCB-impregnated capacitors from 1941 to 1977.

Most of the capacitors manufactured prior to mid-1977 contained PCBs. A relatively small number, however, were produced using mineral oil and no PCBs. Aroclor 1016 was in use from 1971 to 1977; Aroclor 1242 was used prior to 1971. From 1971 to 1975, Cornell-Dubilier used over 1.4 million kg of Aroclor 1016 and approximately 10 000 kg of Aroclor 1254. PCB-containing capacitors are no longer manufactured.

Industrial wastewaters are discharged to the municipal wastewater treatment plant via sanitary sewers. A direct discharge of process water via a city storm sewer is received by the Acushnet River estuary. Cornell-Dubilier's direct discharge permit, NPDES No. MA0003930, allows limited discharges of PCBs to Buzzards Bay. Monitoring conducted by the corporation and by the Massachusetts Division of Water Pollution Control (DWPC) reveals that less than 250 g/y of PCBs are discharged in this manner. Although EPA sampling in

1976 found up to 110 ppb PCBs in this discharge, the PCB concentration is now generally maintained at or below 5 ppb.

Cornell-Dubilier's discharge to the municipal sewer system has proven somewhat difficult to monitor. The presence of combined sewer overflows in the municipal collection system allows seawater to enter during high tide, confusing sampling efforts. Nonetheless, EPA sampling in 1976 located one discharge containing up to 2900 ppb PCBs. Three grab samples taken by the Commonwealth of Massachusetts in 1981 indicate that the wastewater in the municipal sewer line downstream of the factory contained as much as 118 ppb. Sediments removed from the city of New Bedford sewer at this location were recently found to contain 660 ppm PCBs.

Soils collected from the factory grounds during a June 1981 EPA inspection contained from 4400 to 99 000 ppm. A playground area immediately west of Cornell-Dubilier was filled with dredge spoils during the construction of a nearby hurricane barrier in the mid-1960s. Sediment samples taken by the state in 1981 revealed that the soils contain PCBs at concentrations consistently below 5 ppm, and the playground has remained open. September 1978 air monitoring conducted at several sites in New Bedford showed atmospheric PCB levels in the vicinity of Cornell-Dubilier to be 767–862 ng/m<sup>3</sup>.

### Sewage treatment plant

Located at the southern terminus of Clark's Point, the New Bedford wastewater treatment plant (Figure 1) discharges a daily average of 10<sup>8</sup> L (26.5 million gal) of primary treated wastewater to Buzzards Bay. Influent and effluent PCB concentrations are typically in the range of 1–6 ppb, and no decrease in PCB level is evident following treatment. Recent monitoring by the city's consultant and the Commonwealth of Massachusetts reveals that the facility releases from 90 to 300 kg/y of PCBs.

Wastewater entering the facility passes through coarse screens to remove bottles, cans, sticks, and rags. These screenings are raked, collected, and transported to the municipal landfill for disposal. The wastewater next flows through a grit chamber where gravel and coarse sand are removed. This grit is also trucked to the city landfill for disposal. Following this, the wastewater is pumped to sedimentation tanks where settling of the heavier solids occurs. The liquid

TABLE 2  
PCB concentrations in New Bedford area finfish (1978–80)

Species	PCB concentration (mg/L wet weight, edible portion)			Number Sampled
	Mean	Median	Range	
American eel	131	24	11–730	32
Cunner	38	—	20–57	2
Summer flounder	9.3	7.4	0.2–22	10
Windowpane	8.8	5.5	3.1–14.3	30
Winter flounder	6.4	6.8	0–22	44
Silver hake	3.5	—	0.7–6.4	2
Scup	2.1	2.3	0–11.4	50
Bluefish	2.1	0.3	0.2–18.5	11
Tautog	1.7	0.9	0.1–11.0	17
Striped bass	1.2	0.9	0.1–3.0	8
Fourspot flounder	0.8	—	—	1
Butterfish	0.5	0.5	<0.1–0.9	4
Black sea bass	0.4	—	—	1
Dogfish	0.2	—	—	1
Red hake	<0.1	—	—	1

effluent from these tanks is chlorinated and discharged to Buzzards Bay via a 1000-m-long outfall pipe.

The sludge that settles to the bottom of these basins is thickened and pumped to centrifuges for dewatering. The dewatered sludge is incinerated on the premises in a multiple-hearth incinerator, and the residual ash is taken to the municipal landfill where it is dumped with the screenings and grit.

Even though the reduction of PCBs in the wastewater as it passes through the treatment facility is too small to be accurately quantified, wastewater residuals have been found to contain elevated levels of PCBs. During the past two years of sampling, the concentration in the sludge has generally fluctuated between 0.5 and 20 ppm. Levels in ash, however, are typically less than 0.1 ppm.

In 1977, EPA contracted with an environmental consultant to study the atmospheric release of PCBs during sludge incineration. The consultant concluded that approximately 50% of the PCBs fed into the New Bedford incinerator were destroyed during combustion. Other EPA sampling efforts found atmospheric PCB levels in the area of the incinerator to range from 13 to 240 ng/m<sup>3</sup> during March 1977 and January 1978.

Although the level of contamination is generally below EPA hazardous waste criteria, wastewater, sludges, and other residuals contain PCB levels much higher than those encountered at most municipal treatment facilities. For example, a 1974 survey of 33 Canadian wastewater treatment plant effluents revealed values typically in the range of a 0.1-ppb detection limit. Local, state, and federal entities are presently allocating funds to design and implement changes to improve the New Bedford treatment facility.

The wastewater collection system contains approximately 30 combined sewer overflows, and these overflows may, during periods of wet weather, release PCB-contaminated wastewaters. Monitoring of these sewer overflows for PCBs in future studies will lead to a better understanding of this situation. An evaluation of industrial discharges and the level of industrial pretreatment needed to protect the municipal facilities and the waters of Buzzards Bay will also be undertaken in the near future by the city's consultant.

#### **New Bedford landfill**

The New Bedford municipal landfill has been used as a repository for domestic, commercial, and industrial

wastes since the early 1920s. The landfill includes 16 ha of marshland, 10 of which (as of 1978) were filled with refuse and cover material. The geology of the area consists of a layer of freshwater peat varying from 2 to 3 m thick, underlain by a thin layer of silty fine sand. Under this are layers of stratified silts and clayey silts with thin layers of silty clay. These sand and silt layers vary from 2 to 11 m in depth.

Originally operated as an open dump, the site is now maintained as a sanitary landfill in accordance with state and federal requirements. For decades, reject capacitors and other PCB-contaminated wastes, including sludges, ash, and grit from the sewage treatment plant, were disposed of at this site; over 200 000 kg of PCBs have been deposited in the municipal landfill. Before 1972, Aroclor 1242 was the predominant PCB material disposed. From 1972 to 1978, Aroclor 1016 replaced Aroclor 1242 as the PCB most commonly used in the local production of capacitors, and presumably in the waste products disposed of at the landfill.

Monitoring for PCBs has not revealed the presence of any significant groundwater contamination problems in the area of the landfill. The release of PCBs to the atmosphere may, however, be significant. Data compiled by EPA in 1978 revealed that the summertime atmospheric level of PCBs exceeded the NIOSH recommended workplace exposure limit of 1 µg/m<sup>3</sup>. No atmospheric monitoring has been conducted since 1978; air sampling of the area will be conducted in the near future. Lately there has been some concern over the placement of monitoring wells at the landfill, and the results of the 1978 groundwater leachate study are now being reassessed.

#### **Widespread contamination**

In addition to the direct discharges of PCB-containing wastewaters from the municipal wastewater treatment facility and by the capacitor manufacturers, other as yet unidentified discharges of PCB-contaminated fluids may be entering New Bedford Harbor and Buzzards Bay. Numerous combined sewer overflows and storm sewer outfalls discharge into the estuary. It is very likely that during storms PCBs are discharged from those sewer overflows immediately downstream from the capacitor manufacturers. Other combined sewer overflows may contribute to the PCB contamination; however, no information has been gathered on PCB levels in any storm or

combined sewer discharges.

Urban storm drains in the communities of New Bedford, Acushnet, and Fairhaven may carry measurable levels of PCBs into the harbor. The source of PCBs, if present, could be atmospheric fallout or residual PCBs remaining on the roadways from what is believed to have been a common practice in the past—the oiling of municipal streets with PCB-contaminated waste oils. Urban runoff from industrial properties may contain PCBs as may runoff from railroad sidings where PCBs were transferred from rail cars to tank trucks for delivery to the factories.

A site in northern New Bedford known as Sullivan's Ledge may contain large quantities of PCBs. Originally Sullivan's Ledge was operated as a quarry. Later, after it filled with water, it became a popular neighborhood swimming hole.

Today, this approximately 5-ha site is completely filled to a nearly level grade. Rubble, brush, and other demolition materials are evident. A brook flows along the southern and eastern boundaries of the property, through a municipal golf course and into the Appongansett Swamp in the vicinity of the New Bedford municipal landfill.

Although it is not presently used as a dumpsite, in years past the city of New Bedford used Sullivan's Ledge as an industrial dump. Rubber tires were the primary waste product disposed of, but industrial waste oils, sludges, and other materials were also disposed of there. According to landfill operators and one local official, PCBs were deposited at the site. Random piles of electronic capacitors are evident at various locations at Sullivan's Ledge today. The quantity of PCBs disposed of is unknown but may be substantial. EPA has identified this area as a Superfund site and is currently exploring the extent of contamination.

Only two PCB samples have been collected at Sullivan's Ledge. No detectable level of PCB was identified in the one water sample obtained from the brook adjoining the property in 1978. A grab sample of the sediment underlying this brook was found to contain 0.288 ppm PCBs. No air monitoring has been conducted to date; however, EPA plans to establish an atmospheric sampling station at Sullivan's Ledge in the near future.

In the mid-1970s, a report documenting the historical solid waste disposal practices in New Bedford, Acushnet, Fairhaven, and Dartmouth was prepared. In addition to the New

Bedford municipal landfill and Sullivan's Ledge, several sites were discussed. Any number of these locales may contain PCBs. Although there exists no evidence to support the belief that area scrap dealers may have inadvertently contaminated their properties by accepting PCB-containing materials for metal recycling, this situation was found to exist in the upper Hudson River Valley. Thus, areas adjacent to the capacitor manufacturers that received fill while these companies were using PCBs should be considered contaminated until shown otherwise. Sediments dredged from New Bedford Harbor anytime during the past 30-40 years possibly contained PCBs.

#### Pollution abatement

Before concluding this report on PCB contamination in New Bedford, it is appropriate to list those abatement procedures that have been implemented. By 1972 both Aerovox and Cornell-Dubilier ceased using Aroclor 1242 and substituted Aroclor 1016, which was considered much less harmful environmentally. Whether Aroclor 1016 is more or less hazardous is now a matter of scientific debate, but at the time of its introduction, the lower percentage of chlorine in 1016 was believed to render it relatively innocuous. In 1978, all use of PCBs at the New Bedford capacitor manufacturing facilities ceased.

Early in 1982, both capacitor manufacturers reached agreements with EPA and the Massachusetts DEQE in which the companies accepted the final obligation of implementing limited cleanup measures. The corporations have cleaned and replaced contaminated sewer pipes, installed monitoring wells, and applied asphaltic coverings over all exposed soils on their properties. In addition, cleanup efforts, such as sediment removal and containment, have been performed.

New Bedford's wastewater treatment plant is currently operating well below its design efficiency. Suspended solids and biochemical oxygen demand (BOD<sub>5</sub>) removal efficiencies often approach zero, and NPDES discharge permit levels are exceeded on a daily basis. City administrators applied for a waiver of the secondary wastewater treatment requirement in accordance with Section 301(h) of the Clean Water Act. The application was made in 1978 and denied by EPA in 1982. The city must now embark on the construction of a secondary, or biological, wastewater treatment facility to supplement the existing primary

treatment plant.

The fate of the extensive harbor contamination is unknown. A state-funded study prepared in 1981 concluded that 90% of the PCBs could be dredged from the harbor at a cost of \$140 million. New findings regarding the extent of the harbor contamination will undoubtedly surface as EPA's Superfund study progresses, and these findings will, in all probability, change this figure.

#### Acknowledgment

I am grateful to James Okun of GZA (Newton, Mass.), Charles Bering of EPA Region I, Steve Bliven of the Massachusetts Coastal Zone Management program, and Martha Weaver of the U.S. Geological Survey (Hartford, Conn.) for their technical support and advice.

Before publication, this article was reviewed for suitability as an *ES&T* feature by Gil Addis, Electric Power Research Institute, Palo Alto, Calif. 94303.

#### Additional reading

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- Roy F. Weston, Inc. "New Bedford Remedial Action Master Plan"; for EPA Region I, Boston, Mass., July 1983.
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For any queries concerning further references, the reader is invited to contact the author at P.O. Box 1008, Norwich, Conn. 06360; (203) 887-2555.



*Grant Weaver is the manager of Water and Sewer for the Norwich, Conn., Department of Public Utilities. His work on PCB contamination in New Bedford was conducted during his previous employment as staff environmental engineer for the Massachusetts Coastal Zone Management program. Weaver holds a BS in biology from Kansas State University, an MS in environmental engineering from Oklahoma State University, and has completed postgraduate studies in environmental toxicology at the Massachusetts Institute of Technology. He is a registered professional engineer and a licensed wastewater treatment plant operator.*

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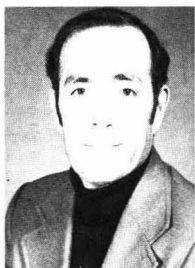
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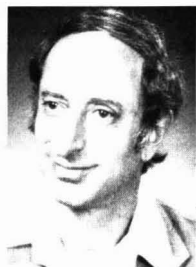
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**Capillary columns.** *Supelco Reporter* (Vol. II, No. 5) features bonded capillary columns and explains how to monitor the pesticide chlordane accurately. Supelco **151**

**Water analysis.** Catalog lists water test kits using colorimetry and disposable ampoules sealed under vacuum with premeasured reagents. About 72 tests are available in various concentration ranges for different species. CHEMetrics **152**

**Hazardous substances training.** Listing of training and reference materials concerning prevention and control of hazardous substances and oil spills and control and cleanup of toxic and hazardous wastes is available. Seminar Publishers **153**

**Laboratory accessories.** Catalog features timers, pipettors, balances, cells, and other items pertinent to all facets of laboratory operation. Lux Scientific Instrument **154**

**Uranium analysis.** Application Note 48 tells how to determine uranium as  $UO_2^{2+}$ . The key is ion chromatography. Applications can be in mining, wastewater analysis, and nuclear power. Dionex **155**

**Air sampling.** Brochure, "Air Sampling Equipment & Supplies," lists the firm's product line with emphasis on the detection of toxic substances in ambient air. Gilian Instrument **156**

**FGD system upgrading.** Environmental improvement folder has brochures explaining how to upgrade the performance of flue gas desulfurization (FGD) systems and electrostatic precipitators and how to reduce operating costs. Babcock & Wilcox **157**

**Breathing apparatus.** Mark 2 SCBA information brochure describes self-contained breathing apparatus, which provides respiratory protection in hazardous environments. Survivair **158**

**CO monitor.** Brochure describes carbon monoxide monitor, Model 8000,

for monitoring this pollutant in situ. Ranges can be 0-400, 0-1000, or 0-2000 ppm CO, with 1% repeatability and 3% or  $\pm 20$  ppm accuracy. Land Combustion **159**

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**Environmental consulting.** Brochure lists services of this analytical and consulting firm, stressing the "total program" approach to problems and issues and the company's 13 years of experience. Controls for Environmental Pollution **161**

**Acid stream neutralization.** Brochure explains why magnesium hydroxide has advantages over lime, soda ash, and sodium hydroxide for acid waste stream neutralization. Dow Chemical U.S.A. **162**

**Groundwater contaminant removal.** Brochure tells how to remove volatile organic compounds such as vinyl chloride, trichloroethylene, and tetrachloroethylene, from groundwater. Two methods are compared. Hydro Group **163**

**Air filters.** Brochure 12-103 discusses the use of the High-Capacity Absolute 2000 product line, which has guaranteed efficiency levels of 99.97-99.99%, is leak-free, and is designed to run at 2000 cfm. Cambridge Filter **164**

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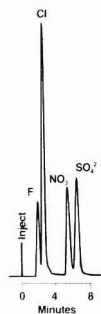
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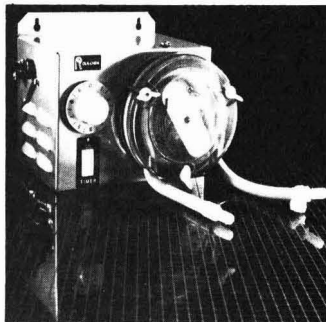
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Air purification equipment  
M:67 L:68 S:69

Water monitors & samplers  
M:70 L:71 S:72

Water purification equip.  
M:73 L:74 S:75

Waste disposal equipment  
M:76 L:77 S:78

Water treatment chemicals  
M:79 L:80 S:81

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M:82 L:83 S:84

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29	30	31	32	33	34	35	36	37	38	39
40	41	42	43	44	45	46	47	48	49	50
51	52	53	54	55	56	57	58	59	60	61
62	63	64	65	66	67	68	69	70	71	72
73	74	75	76	77	78	79	80	81	82	83
84	85	86	87	88	89	90	91	92	93	94

NEW PRODUCTS:																					
101	102	103	104	105	106	107	108	109	110												
111	112	113	114	115	116	117	118	119	120	121	122	123	124	125	126	127	128	129	130		
131	132	133	134	135	136	137	138	139	140	141	142	143	144	145	146	147	148	149	150	151	
152	153	154	155	156	157	158	159	160	161	162	163	164	165	166	167	168	169	170	171	172	173
174	175	176	177	178	179	180	181	182	183	184	185	186	187	188	189	190	191	192	193	194	195

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- H. Soaps/Cleaners
- I. Paint/Coating/Ink
- J. Agrichemicals
- K. Stone/Glass/Cement
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121	122	123	124	125	126	127	128	129	130
131	132	133	134	135	136	137	138	139	140
141	142	143	144	145	146	147	148	149	150
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161	162	163	164	165	166	167	168	169	170
171	172	173	174	175	176	177	178	179	180
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- E. Food/Beverages
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- H. Soaps/Cleaners
- I. Paint/Coating/Ink
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## Bioregeneration of Activated Carbon Saturated with Phenol<sup>†</sup>

Wayne A. Chudyk\* and Vernon L. Snoeyink

Department of Civil Engineering, University of Illinois, Urbana, Illinois 61801

■ Bioregeneration of granular activated carbon (GAC), under conditions typical of water treatment plant operation, is demonstrated conclusively for the first time in the literature. An increase in adsorptive capacity, resulting from bacterial removal of material adsorbed on carbon, was shown to occur in bench-scale GAC columns presaturated with phenol. Influent was composed of a pH 7.5 mineral medium and 2 mg/L phenol, while the influent level of dissolved oxygen (DO) was at air saturation (9 mg/L). No bioregeneration was found when influent DO was 4 mg/L. In a transient loading test, a column saturated with phenol at 0.8 mg/L was seeded and operated for a period of time with an influent DO of 9 mg/L and phenol of 0.8 mg/L at pH 7.5. The bioregeneration occurring was sufficient to significantly lower the effluent concentration resulting from a pulse of phenol (150 mg/L, 1 h) compared to a similar pulse through the column under nonseeded conditions.

### Introduction

Bioregeneration of granular activated carbon (GAC), under conditions typical of water treatment plant operation, has not been conclusively demonstrated in the literature (1, 2), although the fact that organisms are ubiquitous in GAC beds used to treat drinking water is well-recognized (3-10). Bioregeneration is defined here as an increase in adsorptive capacity resulting from bacterial removal of material adsorbed on carbon. Biodegradation of compounds in bioactive GAC columns may occur even though the compounds have not been adsorbed, and this too may increase the useful life of the column. The term bioregeneration has often erroneously been used to describe this phenomenon as well. Typically, there has been no attempt to identify the fraction of the amount of material biodegraded that has previously been adsorbed (6, 8, 11).

A major objective of this study was to determine and prove if regeneration of the carbon surface could occur under conditions typical of water treatment. It was shown by this study that both effects of biological activity occur: bioregeneration of the carbon surface can occur under certain conditions, while biodegradation of material in the influent stream can also occur. Parallel operation of bioactive and nonbioactive GAC columns were useful in

Table I. Composition of Mineral Medium at pH 7.5

g/L	component	source
0.5	K <sub>2</sub> HPO <sub>4</sub>	Mallinckrodt
0.005	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	Baker & Adamson
0.007	CaCl <sub>2</sub> ·2H <sub>2</sub> O	Mallinckrodt
0.02	MgCl <sub>2</sub> ·6H <sub>2</sub> O	Mallinckrodt
0.005	NaCl	J. T. Baker
0.001	FeCl <sub>3</sub>	Matheson

accounting for the amount of oxygen that reacted with the GAC and the amount used to oxidize the phenol. Transient influent phenol loading experiments showed the beneficial effect of bioregeneration.

### Materials and Methods

**Materials and Analytical Procedures.** Phenol (Gilt Label, Mallinckrodt, Inc.) was used as the model compound and was measured by the 4-aminoantipyrine direct photometric method (12). The activated carbon (F-400, Calgon Corp.) was sieved, washed with deionized water to eliminate fines, and dried at 100 °C prior to use. Dissolved oxygen (DO) levels in the column influent and effluent were measured by using a continuous flow cell, an oxygen and temperature probe, and a carefully calibrated DO meter (Yellow Springs Instrument Co.). Bacteria were enumerated by using the standard plate count (SPC) (12).

**Activated Carbon Columns.** The experimental system is shown in Figure 1. In order to minimize wall effects in a 22 × 1.5 cm diameter column, 30 by 40 mesh (U.S. Standard) size (0.42-0.59 mm) was used (13). Sterile granular activated carbon (GAC) that had been presaturated with phenol was placed in the column by using a sterile technique. The carbon was prepared by autoclaving, adding phenol crystals and sterile deionized distilled water to the carbon by using a sterile technique, and equilibrating for 14 days in sealed, head space free bottles. Any bottles showing a SPC other than zero per milliliter were discarded.

The organisms used to seed the columns were originally taken from an enrichment prepared by inoculation of an aliquot of the mineral medium listed in Table I, which was supplemented with 2 mg/L phenol, with 1.0 mL of water taken from a creek downstream from a wastewater treatment plant discharge. Phenol-degrading organisms were concentrated by filtration (sterile Millipore 0.45-μm filters) and flushed onto the carbon slurry used to pack the first seeded column. After the column test, the carbon was stored at 1 °C; subsequent seeded columns were prepared by addition of 0.2 g of this carbon to the influent end of

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<sup>†</sup>Portions of this paper were presented at the AIChE Annual Meeting, New Orleans, LA, Nov 8-12, 1981.

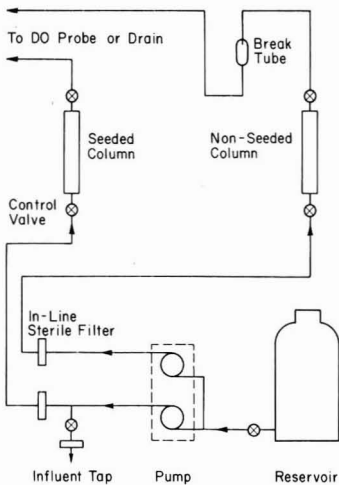


Figure 1. Column setup.

the column. Nonseeded columns were shielded from contamination via use of an effluent line break tube and an influent line filter with Nuclepore 4.7 cm, 0.2  $\mu\text{m}$  nitrocellulose filters and type P40 prefilters, in accordance with the procedures of others (3).

Twelve-liter reservoirs were used with connectors such that the solution contacted only glass, Teflon, and stainless steel, except for a 30-cm length of Tygon tubing through the Buchler peristaltic pump. The DO concentration was controlled by regulation of the atmosphere over the influent solution, which contained phenol and the mineral medium shown in Table I. Air was used for the 9 mg/L solution, while an  $\text{O}_2\text{-N}_2$  mixture was used for the 4 mg/L solution.

**Column Operation: Varied Influent DO Experiments.** Ten grams of sterile granular activated carbon preequilibrated with approximately 2 mg/L phenol was used in the columns for this series of experiments. Columns were operated upflow at 2 mL/min (0.68 m/h, 0.28 gal/(min-ft<sup>2</sup>)), giving an empty bed contact time of 14 min. After being assembled with sterile technique, both columns were operated under sterile conditions for 12 h in order to check effluent phenol concentrations and operating systems. One of the two parallel columns (see Figure 1) was then seeded as outlined above. These parallel seeded and nonseeded columns were monitored over the length of the experiment in order to follow oxygen depletion in both columns and phenol uptake by the seeded column. In this manner, adsorption of oxygen by the carbon early in the experiment could be monitored and accounted for.

**Column Operation: Varied Influent Phenol Experiments.** A total of 3.1 g of sterile granular activated carbon preequilibrated with 0.8 mg/L phenol was used in the columns for this series of experiments. The flow rate used was 10 mL/min (3.4 m/h, 1.4 gal/(min-ft<sup>2</sup>)). A single, initially nonseeded column was used in a continuous sequential series of experiments, which involved initial sterile operations followed by seeded operations and finally by inhibition of bacterial activity by lowered pH. Two influent pulses of phenol were applied under sterile conditions, the first after approximately 1000 bed volumes and the second after about 7500 bed volumes; then (after 13500 bed volumes) the column was seeded with bacteria as above; two more influent phenol pulses (similar in size to the sterile pulses) then were sent through the seeded column at about 17000 and 20000 bed volumes. These

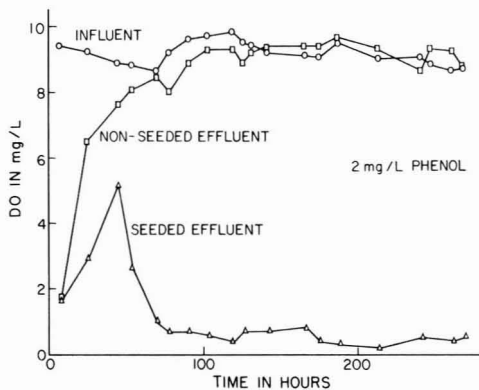


Figure 2. Dissolved oxygen data for the 9 mg/L experiment.

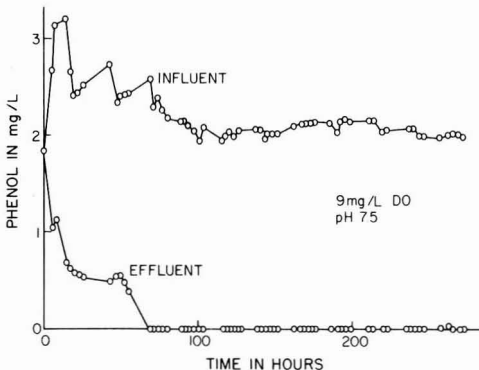


Figure 3. Phenol data for the 9 mg/L experiment.

were called "seeded pulses" since they passed through the column during its bioactive phase. Later (after about 26000 bed volumes) the influent pH was dropped to 3, and a fifth phenol pulse pulse was sent through the column. At all times the phenol influent was a sterile solution: the only differences among the pulses were due to conditions in the column.

### Results and Discussion

**Effect of Dissolved Oxygen Concentration on Extent of Bioregeneration.** The first series of experiments was conducted to determine whether significant amounts of adsorbed phenol could be biodegraded, thus making adsorption sites available to incoming molecules, and also to determine the effect of oxygen concentration on this process. Two levels of DO were studied: 4 and 9 mg/L. The DO data and the phenol data for the 9 mg/L experiment are shown in Figures 2 and 3, respectively, while the data for the 4 mg/L concentration are presented in Figures 4 and 5. The initial portions of these experiments were repeated to ensure reproducibility.

Figure 2 shows that the DO in both the seeded and nonseeded column effluents was initially significantly less than the influent. Chemisorption of  $\text{O}_2$  from solution onto carbon has been well-documented (14) and is expected in both columns. The DO in the nonseeded column effluent approaches that in the influent after a period of time, as expected if only chemisorption is taking place. This was confirmed by SPC's. Monitoring of the SPC's in the nonseeded column effluent showed that they never exceeded a few hundred per milliliter and were usually less than 100 per milliliter. By contrast, the SPC's in the

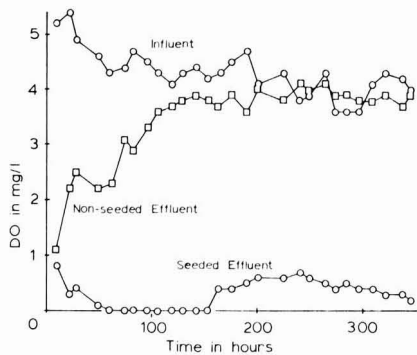


Figure 4. Dissolved oxygen data for the 4 mg/L experiment.

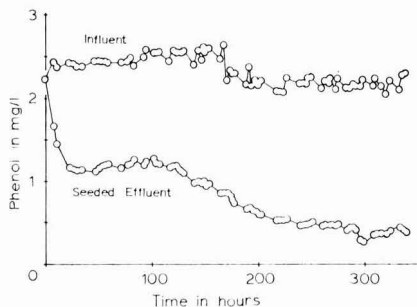


Figure 5. Phenol data for the 4 mg/L experiment.

seeded column effluent increased to a steady-state value of  $10^5$ – $10^6$  per milliliter typical of those found in carbon bed effluents at drinking water treatment plants (15). No oxygen was removed by the nonseeded column after the chemisorption demand was satisfied, and phenol concentration in the effluent was equal to that in the influent. Thus, it was assumed that no biodegradation was taking place. The difference in DO concentration between the seeded column effluent and the nonseeded column effluent was taken as the amount of oxygen used in the biodegradation reaction.

Comparison of Figures 2 and 3 shows that during the first 60–80 h of the run, both chemisorption of  $O_2$  and biodegradation were occurring. Before seeding, the effluent concentration of phenol from each column was equal to that in the influent because the carbon was presaturated with phenol prior to beginning the run. The decrease in phenol concentration after seeding one of the columns is thus indicative of biodegradation. After chemisorption of  $O_2$  was approximately complete, the phenol concentration continued to decrease to zero, but all DO was not utilized.

The amount of biodegradation which occurred was calculated by using the data for the amount of oxygen utilized. Complete oxidation of phenol would follow the equation



If complete oxidation to  $CO_2$  and water occurs, 7 mol of  $O_2$  are required per mol of phenol, or 1 mg of  $O_2$ /0.42 mg of phenol. Bacterial oxidation may well stop short of completion (16), in which event less oxygen per unit phenol would be required. Thus, the amount of biodegradation calculated by using the above relation is by definition a *minimum* value. If less than complete oxidation were achieved, products such as catechol, *cis,cis*-musconic acid, and/or 2-hydroxymuconic acid would be expected, but

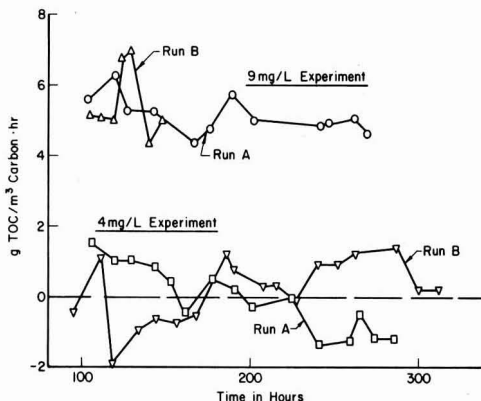


Figure 6. Minimum bioregeneration rates vs. time.

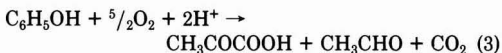
these were not found on the carbon or in the effluent. Similarly, the measured TOC and suspended solids in the effluent could not be used to account for significant conversions of phenol to something other than  $CO_2$  (17).

The *minimum* rate of bioregeneration was calculated by using the following equation:

$$M = [0.420(DO_{in} - DO_{out}) - (\text{phenol}_{in} - \text{phenol}_{out})] \left( \frac{0.68 \text{ m/h}}{0.161 \text{ m}} \right) \left( \frac{0.766 \text{ g of TOC}}{\text{g of phenol}} \right) \quad (2)$$

Here  $M$  is the amount of adsorbed phenol that is biodegraded, in grams of TOC per meter cubed of carbon per hour,  $(\text{phenol}_{in} - \text{phenol}_{out})$  is the amount of influent phenol removed by biodegradation, phenol and DO are in units of grams per meter cubed ( $=\text{mg/L}$ ), 0.68 m/h is the flow velocity in the carbon, and 0.161 m is the column length.  $M$  vs. time is plotted in Figure 6 for two separate experiments at each of the DO concentrations. In each case, "run A" corresponds to the same experiments shown in Figures 2–5. This figure shows that negligible bioregeneration took place when influent DO was 4 mg/L, apparently because all of this amount of oxygen was needed to degrade the phenol in the influent. Increasing the DO to 9 mg/L resulted in oxygen penetration through the entire bed and in removal of approximately 5.0 g of TOC/ $m^3$  of carbon-h. Degradation rates achieved in pilot studies have been reported to be in the range of 1–4 g of TOC/ $m^3$  of carbon-h (18).

Figure 6 shows *minimum* phenol biogenerated with time. These numbers are by definition lower boundary values and are based on the amount of oxygen used in the columns. This lower boundary value assumes complete conversion of phenol to carbon dioxide, an assumption which was not supported by plate count data, for example, which indicated bacterial growth had occurred. If any of the phenol was converted to biomass, for example, through the intermediates pyruvic acid and acetaldehyde with coproduction of carbon dioxide (19), fewer than seven molecules of oxygen would be needed per molecule of phenol:



In any such case where metabolites other than carbon dioxide are produced, fewer than seven molecules of oxygen will be used per molecule of phenol, and the amount of bioregeneration will be greater than that shown in Figure 1. The oxygen used would represent that required for a



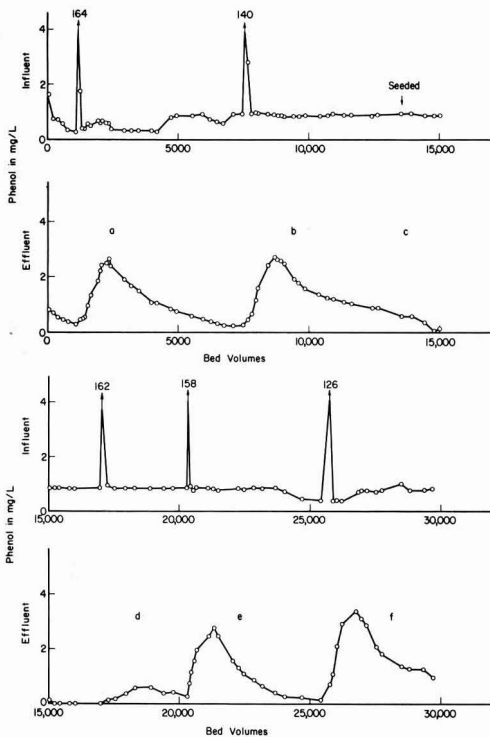


Figure 7. Transient loading experiments.

variety of simultaneous biodegradation reactions, all involving phenol and oxygen.

**Effect of Bioregeneration on GAC Column Response to Transient Loadings.** A series of experiments was conducted to show the response of bioregenerated carbon of columns to transient loadings, in comparison to nonbioregenerated columns. The history of the column that was used is shown in Figure 7. Figure 7 shows the influent and effluent phenol concentrations during the entire column run. The influent was constant except for spike loadings at the times shown in the figure. Influent DO and pH were maintained at approximately 9 mg/L and 7.5, respectively, and influent phenol concentration was approximately 0.8 mg/L, except when the phenol pulses (each about 150 mg/L for 1 h) were introduced.

The effluent concentration data following the first and second sterile pulses are shown in Figure 7 at points a and b, respectively. These pulses, under similar conditions, are virtually identical. They indicate that the experimental system is reproducible in its attenuation of high transient peak influent phenol concentrations in the absence of biological activity. Also, they can be used as a basis of reference for later operations of the column when it is bioactive.

In Figure 7 at point c, the column was seeded, but no other parameters were changed. As the bacterial population became established, following a pattern similar to that in Figures 2 and 3, the effluent phenol concentration decreased to zero. It was possible to calculate, via mass balances on phenol and oxygen, the *minimum* amount of bioregeneration which occurred during this time.

Figure 7 at points d and e shows effluent phenol concentrations for two pulses that were introduced after a minimum of 50 mg of the 175 mg of adsorbed phenol had

been removed by bioregeneration. The only differences between these pulses and the initial "sterile pulses" are the presence of bacteria on the column and the time of input. For the first of these two pulses to the seeded column, bioregeneration had removed enough adsorbed phenol so that carbon capacity was great enough to contain almost the entire influent phenol pulse. This dramatic effect of bioregeneration can be seen by comparing the effluent profile at point d with either of the effluent profiles at point a or b. It is clear from this part of the experiment that bioregeneration can increase carbon capacity for phenol. Following this first pulse to the bioactive column, the effluent phenol concentration was near that in the influent, indicating that the amount of phenol adsorbed was near the amount on the carbon before seeding.

The effluent concentration after the second pulse to the seeded column, shown at point e in Figure 7, is closer in shape and size to those after the sterile pulses at points a and b than to that resulting from the first seeded pulse at point d. This effluent profile is consistent with the observation that the adsorption sites that were made available by bioregeneration were occupied with phenol when the previous pulse was applied and that there was insufficient time for a significant amount of bioregeneration to take place between pulses d and e. It is also likely that biodegradation of the phenol in the influent solution, after application of the pulse, had some effect on the shape of the effluent profile curve.

After the second pulse, to the bioactive column, the influent pH was reduced to 3 to stop biological activity, and a new pulse was introduced (point f, Figure 7). An effluent pattern similar to that seen under sterile conditions at points a and b is evident. Concentrations are slightly higher in the effluent, as expected, because the capacity of carbon for phenol is slightly less at pH 3 than at pH 7.5 (17, 20). This observation shows that the bacteria in the column had a minor effect, if any, on effluent phenol concentration when they were biologically inactivated. This is probably due to the low surface coverage of bacteria expected under such influent carbon loadings (3, 21).

### Conclusions

(1) Bioregeneration of activated carbon occurs in bench-scale columns when carbon presaturated with phenol is fed an influent composed of a pH 7.5 mineral medium and 2 mg/L phenol, and the influent DO is at air saturation (9 mg/L). No bioregeneration was found when influent DO was 4 mg/L, but the phenol in the influent solution was biodegraded.

(2) The bioregeneration that took place when a column saturated with phenol at a solution concentration of 0.8 mg/L was seeded and operated for a period of time with an influent DO of 9 mg/L, and phenol of 0.8 mg/L at pH 7.5, was sufficient to significantly lower the effluent concentration resulting from a pulse of phenol (150 mg/L, 1 h). Thus, a biologically active column, with DO in excess of that needed to biodegrade compounds in the influent, will be better able to adsorb surges in concentration of these same compounds. Further, because of the bioregeneration, adsorption sites may be made available for nonbiodegradable compounds.

(3) Further research is needed in order to fully understand the processes involved in biologically active carbon columns. The effects of changing bacterial varieties on biodegradation rates, the exact nature of degradation products under different column conditions, and the effects of a mixture of organic compounds in the influent on effluent profiles need to be investigated.

Registry No. O<sub>2</sub>, 7782-44-7; phenol, 108-95-2.

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## Decomposition of Organic Matter in Lake Sediments

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■ The decreases with depth of organic carbon, nitrogen, and total phosphorus in sediments from 64 lakes, reservoirs, and estuaries across the U.S. were analyzed. The ages of the sediments were determined with <sup>137</sup>Cs. The decreases in concentrations of C, N, and P were found to be in good agreement with a first-order kinetic model. The average rate coefficients for C, N, and P were 24 × 10<sup>-3</sup>, 21 × 10<sup>-3</sup>, and 5 × 10<sup>-3</sup> year<sup>-1</sup>, respectively. The corresponding modes of the rate coefficients were 4 × 10<sup>-3</sup>, 5 × 10<sup>-3</sup>, and 4 × 10<sup>-3</sup> year<sup>-1</sup>, respectively, for C, N, and P. The constants for C and N are closely related and reflect the microbial decomposition of these components. The P decay coefficient is probably related to the decomposition of organic P and subsequent upward P diffusion. The C decay coefficient is very similar to other data reported or derived from reports on lakes and shallow marine sediments. The decay coefficients derived here may be used as a general first approximation to the rates of organic matter diagenesis in sediments.

### Introduction

Cycling of organic matter in aquatic systems is one of the most important processes determining chemical and

biological properties of a given impoundment. Rate and extent of organic matter cycling are dominant factors determining oxygen, carbon dioxide, and redox potential levels in both sediment and water columns. Solubilities of phosphorus, iron, and manganese compounds are controlled through the resulting redox potential. Biological activities are controlled and limited by the concentration gradients of oxidizing and reducing components. Decomposition of organic matter is also the main route of nutrient regeneration.

Most of the organic cycling in impoundments occurs on and within the sediments. About 50% of the photosynthesized organic carbon settles to the sediment (1, 2). Most of the allochthonous organic matter, introduced to lakes as particulate organic carbon, accumulates in the sediment.

The amounts of organic and related components in the sediments are, in most cases, considerably above the equivalent quantities in the water column. For example, organic carbon in the water is usually in the range of 10<sup>-3</sup>-10<sup>-2</sup> g/L (see ref 2, pp 541-543), while its concentration in the sediment is in the order of 10 g/L; i.e., a 1 cm deep sediment layer contains as much organic carbon as 10-100 m high water column. Similar ratios hold for other components such as ammonium, organic nitrogen, and phosphorus. Thus, even a sediment layer of only a few centimeters depth contains, in shallow lakes, more organic components and nutrients than the contents of the water column.

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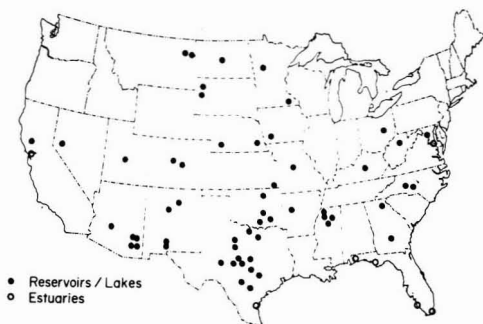


Figure 1. Location of sampling sites.

As a consequence, the microbial community found on and within the sediment is denser than that found in the water (see ref 2, pp 593-596). The substrate utilized by most of these organisms is the sedimentary organic matter, and the final result of their activity is the decomposition and the diminution in quantity of the deposited organic materials. The decrease of the organic matter below the sediment surface is generally recognized (e.g., 3-5), yet, only a few attempts had been made to assess the quantitative rate and extent of this process. In addition, most of these attempts are related to specific sites. Since the experimental assessment of such data is difficult, the availability of a quantitative framework to be used in different lakes is very limited. Quantitative assessments of the rate of degradation can be obtained either through the analysis of the organic carbon concentration profile in sediments or indirectly through the measurement of the fluxes of carbonaceous materials from the sediment into the water column. The decrease of organic C with depth from the surface (4) is attributed to the degradation of the organic C (6-8). If the age of the sediments can be determined, then the decrease in the organic carbon can be related to the time since the deposition of the organic C; first-order kinetics are assumed (6, 7), and the decomposition rate coefficient can be calculated. This approach was used for the calculation of the decomposition rate of organic C in lake sediments (9) and in marine sediments (6, 8). A different approach is based on the measurement and computation of the flux of the decomposition products from the sediment up to the water sediment interface (10-12). The important components are  $\text{CH}_4$ ,  $\text{CO}_2$ , and dissolved organic carbon.

Sediment profiles were sampled during 1970-1972 by McHenry, Ritchie and others, in some 70 lakes, reservoirs, and impoundments across the continental U.S.A. (13-15). Data collected included radiochemical, chemical, and physical characteristics of the sediments. This data base is used here for the calculation of the decomposition rates for organic components in those sediments.

#### Data Base and Calculation

The impoundments sampled (Figure 1) are mostly man-made lakes, but a few natural lakes are also included. Seven sites are actually estuaries, and 13 sites represent lakes that are dry during the dry season or filled with sediment and not covered by a water column. A list of the impoundments and some of their characteristics is given in Table I.

The sediment sampling and analysis have been described previously (14). Sediment cores were collected in 5-10-cm layers through the depth of recent sediment, at three or more locations within each lake. At each location,

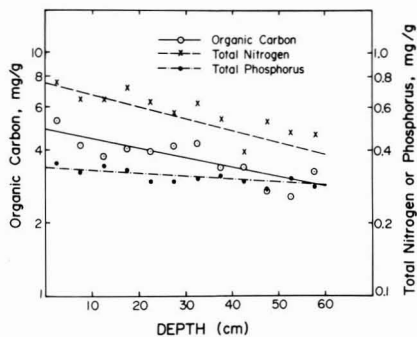


Figure 2. Organic carbon, total nitrogen, and total phosphorus profiles in Murphy Pond (MS) sediment.

eight sediment cores were sampled and composited. The data used in this work included organic C, total N, total P,  $^{137}\text{Cs}$ , and clay concentrations as well as the sediment densities.

Data from 64 lakes comprising 172 profiles with each profile containing 4-20 subsamples were used in this study. All sites included in the data base were used in the analyses indiscriminately, except a few having less than three subsamples in sediment cores.

The first-order rate equation describing organic carbon decomposition is

$$dC/dt = -K_1C \quad (1)$$

where  $C$  is the organic carbon content (mg/g),  $t$  is the time (years) from onset of deposition, and  $K_1$  is the rate coefficient.

Upon integration and solution for the integration coefficient, we obtain

$$\ln C = \ln C_0 - K_1t \quad (2)$$

where  $C_0$  is the organic matter content at  $t = 0$  which is the time of deposition. The time since deposition of a given sediment layer and its depth below the surface ( $d$ ) are related through the deposition rate (DR, cm/year):

$$d = t \times \text{DR} \quad (3)$$

Equation 2 can accordingly be given by using depth or time as the independent variable:

$$\ln C = \ln C_0 - K_2d \quad (4)$$

where  $K_2 = K_1/\text{DR}$ .

The correlation coefficients, the rate coefficient, and initial concentrations were computed for each profile, according to eq 4. The deposition rate was obtained through the location of the  $^{137}\text{Cs}$  peaks along the profile, considering the peaks of atmospheric  $^{137}\text{Cs}$  during the year 1958 and 1964 (16). A sedimentation rate of 0.7 cm/year, the limit of the method's sensitivity for the given conditions, was attributed to all cases when  $^{137}\text{Cs}$  was found only at the top layer of the sediment. By use of the values for sedimentation rates for each profile, the depth-dependent eq 4 was transformed into the time-dependent eq 2.

#### Results

A representative plot of organic C, total N, and total P concentration data from Murphy Pond, a small lake in northern Mississippi vs. depth is given in Figure 2. The concentrations of these three components decrease with depth, the decrease being steepest for the organic carbon and very slight for the phosphorus concentration. The logarithms of the three-component concentrations are

Table I. First-Order Decay Coefficients for Organic Carbon, Total Nitrogen, and Total Phosphorus ( $K_c$ ,  $K_n$ , and  $K_p$ , Respectively), the Computed Organic Carbon and Total Nitrogen Contents at the Onset of the Decomposition Process ( $C_o$  and  $N_o$ , Respectively), and Some Characteristics of the Studied Impoundments

site name	state	type <sup>a</sup>	$K_c$ , $\times 10^{-3}$ year <sup>-1</sup>	$r$	$K_n$ , $\times 10^{-3}$ year <sup>-1</sup>	$K_p$ , $\times 10^{-3}$ year <sup>-1</sup>	$C_o$ , mg g <sup>-1</sup>	$N_o$ , mg g <sup>-1</sup>	clay, %	DR, cm year <sup>-1</sup>
Ashland	MO	R	-38	0.472	60	1	13	0.9	21.7	12.5
Lake Frank	MD	R	-27	0.748	-27	42	10	0.7	8.8	13.0
Mill Canyon	UT	R, D	-23	0.590	23	-6	20	1.2	22.1	1.7
Highland	CA	R	-16	0.625	57	-23	18.4	0.9	19.2	5.0
Deep Creek no. 3	TX	R	-10	0.479	5	12	26.3	1.6	59.7	5.1
Petalina	CA	E	-6	0.655	-2	0	9	0.8	43.9	0.7
Cow Bayou no. 4	TX	R	-3	0.342	11	0	40	1.0	68.2	7.0
Gallenta Tank	AZ	R	-2	0.793	25	16	14	0.8	15.5	0.8
Tviet Pond	MT	R, D	-1	0.107	0	2	35	2.7	37.6	6.3
Salem Fork no. 11A	WV	R	-1	0.635	34	4	16	1.7	34.4	2.2
Dawson City	TX	R	0	0.270	2	1	23	0.9	75.9	3.5
Card Sound	FL	E	0	0.553	3	4	90	4.5	14.4	0.7
Nuecus Bay	TX	E	0	0.367	25	-13	12	0.4	48.1	3.0
Hafner Pond	SD	R	1	0.220	11	-4	9	1.1	73	2.5
Swan Lake	MN	L	1	0.273	3	4	134	10.9	34.2	0.7
Scheetz Pond	MT	R	3	0.127	5	4	30	4.0	42.7	7.6
Thousand Is.	FL	E	3	0.460	5	3	75	2.8	21.9	0.7
Taghorn Pond	ND	R	3	0.842	4	1	35	2.9	56.8	0.7
East Willow Creek	MN	R	3	0.764	2	6	29	2.2	31.3	0.7
Apalachicola	FL	E	4	0.577	16	1	14	0.8	28.4	1.7
Deep Creek no. 8	TX	R	4	0.415	7	10	19	1.6	64.0	2.6
Treece Pond	KS	R	4	0.617	9	-2	3	3.0	32.7	0.7
Patuxent	MD	E	5	0.665	4	0	21	1.4	28.8	0.7
Walnut Gulch no. 7	AZ	R	5	0.716	5	3	36	1.0	21.0	0.7
Smeenk Pond	SD	R	5	0.73	10	2	17	1.1	33.0	22.0
North Ford Broad no. 14	GA	R	6	0.694	7	6	14	0.8	30.6	0.7
Durant no. 12	OK	R	6	0.880	17	6	63	2.9	46.5	0.7
Honey Creek no. 12	TX	R	7	0.305	14	4	39	1.4	71.2	9.9
Mule Creek B	IA	R, D	8	0.160	5	0	16	1.3	30.8	11.8
Double Creek no. 5	OK	R	10	0.513	7	1	18	1.5	31.5	5.1
Escambia Bay	FL	E	14	0.660	2	11	101	1.6	31.2	0.7
Clear Fork no. 10	TX	R	14	0.719	20	16	13	0.8	27.8	0.7
Santa Cruz no. 6	NM	R, D	14	0.472	133	12	7	0.1	10.2	25.0
Sulphur Creek no. 3	TX	R	17	0.633	29	-37	53	2.2	52.7	3.2
LT-14-A	MS	R	17	0.788	15	12	17	1.1	23.8	0.7
Powerline	MS	R	19	0.749	12	10	6	0.5	38.5	0.7
Upper Peavine	NV	R, D	20	0.308	28	11	7	0.5	34.3	2.3
Third Creek no. 21	NC	R	23	0.976	30	24	24	1.9	31.4	0.7
Clear Fork no. 7	TX	R	24	0.605	-9	-20	6	0.4	55.4	8.5
Cummins Creek no. 6	TX	R	25	0.819	32	26	17	1.3	26.5	2.0
Plum Creek no. 4	KY	R	26	0.761	27	-5	22	1.9	29.2	2.9
Sardis A	MS	R	30	0.581	-13	-15	11	0.6	27.7	3.3
Durant no. 1A	OK	R	34	0.851	36	38	37	2.9	24.2	0.7
Dry Creek no. 2A	NE	R, D	35	0.509	30	8	17	1.4	49.2	3.6
Third Creek no. 7A	NC	R	38	0.808	43	87	29	2.0	27.8	2.2
Lake Mary	GA	L	38	0.954	49	1	26	0.9	5.0	0.7
Ferry 64	MS	F	41	0.464	62	6	6	0.6	15.4	3.8
Brownell no. 1	NE	R	44	0.864	51	28	25	1.8	38.6	4.2
Smith Pond	MS	R	45	0.798	27	14	7	0.7	39.6	4.8
Murphy Pond	MS	R	47	0.837	23	14	6	0.6	33.8	4.2
Kiowa no. 79	CO	R	48	0.847	41	39	46	2.7	20.5	1.0
Fry Creek	AZ	R, D	51	0.769	32	10	14	0.7	20.3	1.5
Lowry Draw no. 11	TX	R, D	57	0.936	53	22	33	2.4	55.0	0.7
Bernalillo no. 1	NM	R, D	60	0.703	69	-2	22	1.2	15.6	2.2
Freeman	AZ	R, D	61	0.707	45	20	14	0.5	36.9	6.1
Escondido Creek no. 1	TX	R	63	0.862	67	2	23	1.5	56.5	5.1
Six-Mile Creek	AR	R	63	0.829	27	62	11	1.1	21.0	2.8
Tortugas Arroyo no. 1	NM	R, D	65	0.224	48	15	11	0.5	12.9	9.0
Ferry 66	MS	F	73	0.816	83	2	9	0.9	15.1	4.0
Dona Ana NF	NM	R, D	79	0.715	66	47	25	1.5	18.7	3.8
Creighton	AZ	R, D	81	0.643	78	19	12	1.0	20.4	14.0
Elm Creek no.11B	TX	R	81	0.843	92	52	29	2.4	59.8	3.2
Durant 1B	OK	R	84	0.920	69	67	20	2.0	63.5	2.0
Upper Hocking no. 1	OH	R	92	0.670	7	-15	29	1.4	27.1	5.6

<sup>a</sup> L = lake, R = reservoir, D = dry during part of the year, E = estuary, and F = flood plan deposition.

linear functions of depth in agreement with eq 4.

The values derived for all 64 lakes studied here by using first-order kinetic eq 2 and 4 and the decay with depth of the organic C, total N, and total P are given in Table I. Decay rates for all the lakes are given, even in cases when

the correlation coefficients are low or when the scatter of the data points seemed to be erratic. The sites are listed in this table according to increasing magnitude of the organic carbon decomposition constants. The distribution of the values for the organic C decomposition rate coef-

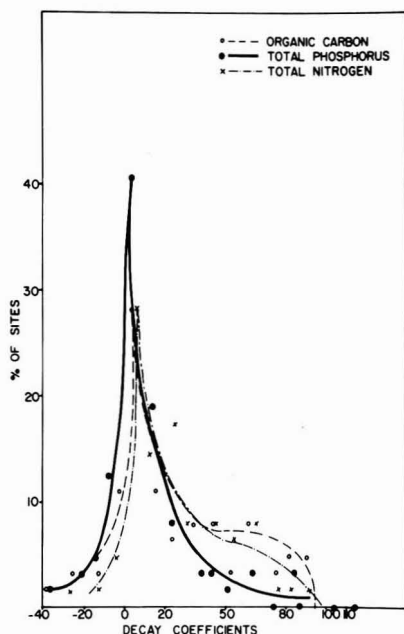


Figure 3. Frequency distribution of organic carbon, total nitrogen, and total phosphorus decay Coefficients ( $\times 10^{-3}$  year $^{-1}$ ).

Table II. Correlation Matrices for Decomposition Coefficients

de- pendent variable	inde- pendent variable	A	B	F	r
$K_c$	% clay	28.8	-0.14	0.521	0.06
$K_c$	DR	26.7	-0.71	0.776	0.07
$K_c$	$C_o$	23.5	-0.02	0.003	0.01
$K_n$	$K_c$	3.2	1.68	192.5	0.73
$K_n$	% clay	24.6	-0.12	0.363	0.05
$K_n$	DR	26.0	-1.45	3.17	0.136
$K_n$	$N_o$	19.3	0.62	0.43	0.05
$K_p$	$K_c$	3.9	0.76	59.4	0.510
$K_p$	% clay	13.4	-0.04	0.124	0.03
$K_p$	DR	14.0	-0.60	1.33	0.08
% clay	DR	33.8	-0.12	0.36	0.03
$C_o$	% clay	22.7	0.04	0.84	0.02

coefficients is given in Figure 3. The values are spread throughout a relatively narrow range with 70% of the rate coefficients ranging between  $-1 \times 10^{-3}$  and  $60 \times 10^{-3}$  year $^{-1}$ , the average value is  $24 \pm 44$ , and the mode is  $4.10^{-3} \times 10^{-3}$  year $^{-1}$ . The distribution diagram is somewhat asymmetrical, skewed toward the high range. No statistically significant dependence is found between the organic C decomposition rate and either clay contents, deposition rate, or the initial organic C contents (Table II).

Decomposition rates of nitrogen, presented in Table I, are similar to those of the organic carbon. The average rate is  $(21 \pm 43) \times 10^{-3}$  year $^{-1}$ , and the mode is  $5 \times 10^{-3}$  year $^{-1}$ . The nitrogen decomposition rate,  $K_n$ , is related to that of organic carbon:

$$K_n = 1.35 + 0.727K_c \quad r = 0.730^{xxx} \quad (5)$$

where xxx denotes significance at  $p = 0.01$ .

The dependence of nitrogen decomposition rate on the deposition rate and clay contents is statistically nonsignificant, tending to decrease with the increase of these variables. The frequency distribution of the nitrogen

decomposition rates (Figure 3) is very similar to that of the organic carbon, having some skewness toward the higher values.

The rate coefficients derived for the phosphorus concentration profile,  $K_p$ , have an average value of  $(5 \pm 8) \times 10^{-3}$  and a mode of  $4 \times 10^{-3}$  year $^{-1}$ . They are related to the rate coefficients of the organic carbon decomposition through

$$K_p = 1.70 + 0.327K_c \quad r = 0.510^{xxx} \quad (6)$$

The slope of this relationship, 0.327, indicates a slower average decay of P compared to organic C. The frequency distribution curve of the phosphorus decomposition rates (Figure 3) is symmetrical and does not indicate any skewness. The dependence of the phosphorus decomposition rate on the sediment clay contents, initial P contents, and deposition rates is nonsignificant.

### Discussion

The present work deals with the calculation of the rate of degradation of organic components in lake sediments. The calculation is based upon the change in concentration with depth of these components in cores collected in 64 lakes and impoundments in a wide geographical region. Lakes considered here are located from Minnesota to Florida and from Maryland to California. All are relatively small and shallow, most of them having a rather high sediment deposition rate.

The calculations of the decomposition rate coefficients are based on the assumption that the composition of the sediment added yearly has been roughly the same during the period involved in the buildup of the sediment examined. The time span involved in most of the cores studied here is relatively short, ca. 20 years. No known significant changes had taken place during this period in the hydrological or other conditions in the watersheds involved, and we believe that the assumption involved is reasonable. According to this assumption, the decrease with depth in the concentration of the components studied here is due to a series of degradation processes.

An intrinsic problem involved in the analysis and presentation of such work based on sampling from heterogeneous media has to do with a possible selection of data. Sediment profiles are heterogeneous due to different sedimentation patterns, physical and biological mixing, and other local variations. Sampling and analytical errors also add to the variability. It is possible, as done by several investigators (e.g., ref 8), to use only those profiles or sites selected to a given criterion. Since this work is based upon a vast amount of data, it was decided to use all available data without any selection process (except for the omission of profiles having three or less samples). The spread of the computed decay coefficients is, accordingly, the one expected for such a variable system, and the significance of the findings is attributed to average properties and not to a single profile or site. The correlation coefficients associated with the computation of the organic carbon decay as given in Table I indicate in several cases insignificant statistical dependence of the organic carbon on depth. In addition, negative decay coefficients found for several sites are most probably erroneous.

The organic carbon decay coefficients for all lakes involved have an arithmetic average of 24 and a mode of  $4 \times 10^{-3}$  year $^{-1}$ . The deviation from the average value is rather small considering the heterogeneity in any given sediment, errors in sampling and analysis, and errors involved in the estimation of the deposition rate. Moreover, the deviation between the averages for all the sites is similar to the deviation among profiles within the same

Table III. First-Order Decay Rates for Total Organic Carbon (TOC) and Fatty Acids in Sediments: Data or Decay Rates Compiled from Literature

site	water depth, m	deposition rate, mm year <sup>-1</sup>	component	decay coefficient, × 10 <sup>-3</sup> year <sup>-1</sup>	ref
Lake Superior	50-260	0.4-2	TOC	8.6	8
Lake Kinneret (Israel)	20-40	1	TOC	15	17 <sup>a</sup>
Saanich Inlet, B.C.	250	10	TOC	13	6 <sup>b</sup>
Buzzards Bay, MA	17	3	TOC	3.6	18
Buzzards Bay, MA	17	3	fatty acids	3.3	18
North Philippine Sea	2000	0.2-1.2	TOC	0.001	7
Santa Barbara Basin	570	4	TOC	0.013-0.047	9
North Pacific	5000-6000	0.01-6	TOC	0.03-0.22	9

<sup>a</sup> Calculated from data given in the paper. <sup>b</sup> The authors give decay rates relative to metabolizable carbon. Original data were used to convert this to total organic carbon decay coefficients.

Table IV. First-Order Decay Coefficients for Organic Components in Sediments (Calculated from Kemp and Johnston (19))

depth range, cm	amino acids, × 10 <sup>-3</sup> year <sup>-1</sup>	carbohydrate C, × 10 <sup>-3</sup> year <sup>-1</sup>	amino sugars, C, × 10 <sup>-3</sup> year <sup>-1</sup>	lipid C, × 10 <sup>-3</sup> year <sup>-1</sup>	humic C, × 10 <sup>-3</sup> year <sup>-1</sup>
(a) Lake Ontario (sedimentation rate 0.75 mm year <sup>-1</sup> )					
0-749	0.3	0.2	0.3	0.08	0.2
0-17.5	5.3	2.4	4.5	3.7	3.9
(b) Lake Erie (sedimentation rate 3 mm year <sup>-1</sup> )					
0-90	3.7	1.9	3.4	3.1	2.8
0-17.5	18.7	3.3	14.5	12.1	14.0
(c) Lake Huron (sedimentation rate 0.7 mm year <sup>-1</sup> )					
0-88	0.3	0.2	0.7	-0.2	0.2
0-12.5	1.6	0.03	0.4	-0.9	1.0

site. (The average coefficient of variation within a site, calculated for three sites having seven or more profiles each, was 56%, compared to 181% for the coefficient of variation among all sites). The mode, the peak value of the frequency distribution, seems to be the more suitable measure of the central location, due to the skewness of the frequency distribution curve (Figure 2).

The rate constant found in this work is similar to others reported in the literature or derived from reported data. Compiled data for several lakes and marine sediments is given in Table III. It can be seen that decay coefficients obtained in other lakes or shallow marine sediments are very similar to those found in this work. Organic carbon decay coefficients for deep marine sediments are appreciably lower. Kemp and Johnston (19) have presented very detailed concentration profiles for several organic fraction in Lakes Ontario, Erie, and Huron sediments. The first-order coefficients for these fractions were calculated and are presented in Table IV. The decay coefficients calculated for the whole profile (representing time spans of up to 1000 years) are lower than those found in this work. Yet, the decay coefficients calculated by using the topmost four layers (representing a 12.5-17.5-cm depth and a 60-240-year time span) are similar to the decay coefficients found in the present studies. Moreover, it seems that the decay coefficients of all components studied in that work, amino acids, amino sugars, carbohydrates, lipids, and humic compounds, are within this range.

The rate coefficients of organic carbon decomposition are not affected by the concentration of organic carbon in the sediment (Table II), as expected for a first-order rate reaction. The rate constant is reduced, though insignificantly, with an increase of either clay or deposition rate. Both factors would diminish fluxes of oxygen into the sediment or metabolites out of the sediments. The effects of these factors would at best explain just a few percents

change of the rate coefficients.

An interesting feature revealed through the frequency distribution diagram (Figure 3) is the skewness of the distribution curve of  $K_c$  values. The distribution curve is not symmetrical, and a bias toward the higher values is observed. Similar asymmetry can be seen in Table I, where the lakes in which the sediment is exposed during the dry season tend to have a higher decay constant. Fifty percent of the exposed sediments have decay coefficients higher than twice the average value, compared to 12% for the continuously flooded sediments. It seems that the decomposition rate increases to some extent when the sediment is aerated and that the skewness of the distribution curve is due to some extent to the presence of drained lake sediments in the population studied here. The mode, the peak value of the frequency distribution, seems to be the more suitable measure of the central location as an estimate for continuously flooded sediments.

An important feature related to the present analysis is that the substrate considered is the total organic carbon. Some investigators (6, 20) have related the decomposition rates to the available fraction of the organic carbon. Possible use of both substrates in kinetic models indicates that the fraction of available organic carbon within the total organic carbon is probably similar for different sediments of shallow water bodies and that the two substrates are thus related.

Nitrogen decay coefficients were derived from the decrease, with depth, of the total nitrogen in the sediment. The organic nitrogen is usually the dominant fraction of total nitrogen in rapidly depositing sediments (2). Thus, the total N is a good estimate of the organic N.

Nitrogen decay coefficients are practically identical with those of the organic carbon. (The average values are 21 and 24 and the modes are  $5 \times 10^{-3}$  and  $4 \times 10^{-3}$  year<sup>-1</sup> for the nitrogen and the carbon, respectively.) This is expected, both due to the fact that both are part of the organic matrix composing soil or sediment organic matter and as a condition to maintenance of a constant C:N ratio. The C:N ratios in the 10-20 range were practically constant along all profiles studied. Carbon and nitrogen mineralizations represent different viewpoints of the same overall reaction.

The decrease in total P concentration with depth is not obvious. A significant fraction of the total P is inorganic and does not undergo decomposition. In addition, even though a large fraction of P in sediments is organic, or associated with the organic matter (see ref 2, pp 216-227), its mineralization does not lead, in contrast with that of C and N, to volatile or highly soluble products. Seemingly, any conversion of organic P to inorganic P should not change the amount of P at any given layer. The decrease in P with depth is probably due to the upward migration of P from reduced sediment layers onto the more oxidized

water sediment interface (21). The decomposition of organic P under anaerobic conditions leads to the release of a relatively soluble form of P that diffuses upward (22). A finding strengthening this hypothesis is the symmetrical frequency distribution curve of the P decay coefficients, unlike the asymmetrical C and N curves. The asymmetry of the C and N curves seems to stem from the higher decay rates in cases where the sediment is partially exposed to the air. Under such oxidized conditions, even if phosphorus mineralization is higher, its upward mobility is slow. The total P decay rate is lower than those of the C and N, probably due to reasons mentioned above (presence of inorganic P and incomplete removal of the mineralized fraction). This difference in decay rate leads to a decrease in C:P and N:P ratios with increasing depth or with the age of a given sediment layer.

An interesting finding of this study is the similarity of the decay rates for organic C, N, and P in lakes located in different climatic and geographic regions. Equivalent processes in terrestrial systems, processes leading to the accumulation and decomposition of organic matter, have markedly different rates in different environments. The dominant factors leading to this variability in terrestrial systems are the seasonal distribution of water in the soil, the soil temperature, and the soil aeration (23). As suggested recently (24), soil organic matter degradation can be formulated through a universal equation containing adjustable parameters to account for the effects of moisture and temperature regimes. The factors mentioned above are almost constant in aquatic sediments. Water contents are constant and temperature variations are limited in lake sediments (from a minimal value of 4 °C up to about 20 °C as the high limit). In addition, oxygen is absent from most sediments below the topmost few millimeters (25). Thus, since the dominant environmental factors are fairly constant, the important factor determining the rate of the decomposition is the substrate concentration; i.e., decomposition can be described as a first-order reaction with rate coefficient of similar magnitude in different sediments. This conclusion may, of course, be untrue for extreme cases such as arctic lakes, extreme pH values in sediments, etc., but is a useful first approximation.

In addition to the effects of the decomposition rate, an intrinsic difference exists between terrestrial systems and aquatic sediments as to the turnover of organic components in these systems. Jenny's work (23) dealt with the top layer of the soil, the root zone. A steady-state situation exists in this layer, having organic matter decomposition on one hand and an addition of decaying roots and roots excretion all along this profile on the other. The situation in sediments is different: Organic matter is being added only to the topmost layer of the sediment, and except for the limited effect of burrowing organisms, only decomposition takes place in the deeper layers, thus preventing an establishment of a steady-state situation. The organic carbon contents of the sediments seem to depend on the supply of organic carbon from the watershed and on the primary production by algae and macrophytes within the lake, both factors that cannot be readily generalized for given regional conditions.

Berner (20) has suggested a multiple first-order model for the decomposition of organic matter in Long Island Sound sediments. According to this model the organic carbon is composed of several fractions markedly differing in their decomposition rates. The most available fraction, derived mainly from algal blooms and amounting to about 10% of the deposited organic matter, decomposes with a rate constant of 0.6 year<sup>-1</sup>. The decomposition of this

fraction takes place within the topmost few centimeters of the sediments. (This fraction may be less significant in lakes or estuaries, deriving most of their organic matter from eroded terrestrial material). The analysis given in our work is not relevant to this fraction. The sectioning procedure (5–10-cm increments) ignores processes occurring at the surface of the sediment.

A second fraction suggested by Berner (20) decomposes further down in the sediment and is described by a first-order coefficient of  $1.2 \times 10^{-3}$  year<sup>-1</sup> which is similar to the coefficient found in the present work. The decomposition process dealt with in this work is accordingly the process following the rapid decomposition during and shortly after the deposition of the organic particles.

As suggested by Berner (20) it is possible that below a certain level the decay reactions will be modified. In the present study, we do not have any indication as to the time or concentration limits for which the derived kinetic equations are applicable. The analysis of the data reported by Kemp and Johnston (19) presented here (Table IV) indicates that the decomposition rate for old sediment is appreciably lower than that occurring during the first stages of diagenesis. The slow decomposition rate in deep ocean sediments could be due to the fact that the organic components reach these sediments after a very long sedimentation period. The first stages of diagenesis occur in these systems while the organic particles are suspended in the water column. The half-lives for the organic carbon, nitrogen, and phosphorus dealt with in this work and by using the appropriate modes of the decay coefficients are 173, 139, and 193 years, respectively.

The reasonably narrow distribution of the decomposition rate coefficients justifies a description and analysis of an "average" or typical lake sediment, as an approximation for real systems. This sediment contains, at the onset of deposition, 24 mg of C/g, the deposition rate is 3.8 cm/year, its density is 0.96 g/cm<sup>3</sup> (average density for sediment studied here was  $0.962 \pm 0.214$ ), and its decomposition rate coefficients are the average values obtained in this work. The concentration of any of the components with depth in the sediment can be calculated by using eq 7.

$$C = C_0 e^{-Kt} \quad (7)$$

The calculated cumulative carbon and nitrogen fluxes for the sediment down to 100 cm (deposited along a 26-year period) are given in Figure 4. The lines defining the cumulative fluxes have only a very slight curvature, due to the fact that the period considered is only about 15% of the calculated half-lives of the components considered here. In addition, the fluxes were computed by assuming that the decay coefficients considered here control the decay all along the profile. This, as mentioned before, is probably an unrealistic assumption. After a given duration of decay, the process is probably controlled by slower decay reactions. We make a somewhat arbitrary assumption that a 100 cm deep sediment layer is contributing carbon and nitrogen to the overlying water. (This layer represents, in the "typical" sediment considered here, a layer accumulated during about 26 years.) The carbon flux from this layer is, according to Figure 4, 87 g m<sup>-2</sup> year<sup>-1</sup>, and the nitrogen flux is 8.4 g m<sup>-2</sup> year<sup>-1</sup>. The assumed typical carbon flux is of the same magnitude as values reported for fluxes of CH<sub>4</sub> or CH<sub>4</sub> + CO<sub>2</sub> from sediments. Martens et al. (26) reported, for Cape Lookout Bight, NC, a combined flux of 410 g of C m<sup>-2</sup> year<sup>-1</sup> Crill and Martens (27) measured methane evolution from sediments in the same location. Averaging their values for the whole year, a flux of about 50 of C m<sup>-2</sup> year<sup>-1</sup> is obtained. Kelly and Chynoweth (10) reported CH<sub>4</sub> evolution of 147 and 24 g of C

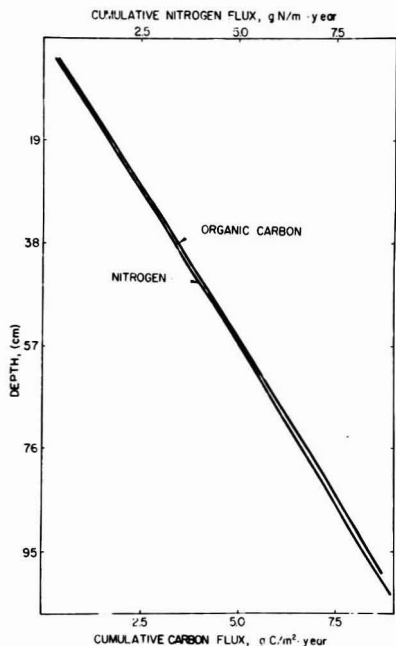


Figure 4. Calculated flux of carbon from a typical sediment (deposition rate  $3.8 \text{ cm year}^{-1}$ ).

$\text{m}^{-2} \text{ year}^{-1}$  for Frain lake and Third Sister Lake, respectively. These values are in good agreement with those calculated herein.

Zeitzchel (28) reviewed studies on the release of nutrients from marine sediments. The average reported nitrogen release from shallow sediments (maximal depth 30 m) is  $9.35 \pm 14.7 \text{ g m}^{-2} \text{ year}^{-1}$  compared to our calculated flux of  $8.4 \text{ g m}^{-2} \text{ year}^{-1}$ .

The consistency of the data included in this work and the agreement of these data with different types of similar works elsewhere support the use of the decay coefficients reported here as a general first approximation for the evaluation of a wide range of reactions related to organic components in aquatic sediments.

**Registry No.** Carbon, 7440-44-0; nitrogen, 7727-37-9; phosphorus, 7723-14-0.

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# Elemental Partitioning in Ash Depositories and Material Balances for a Coal Burning Facility by Spark Source Mass Spectrometry

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■ Spark source mass spectrometry (SSMS) is shown to be an excellent analytical tool for determining enrichment factors and a useful tool for measuring material balances for a coal burning facility. Enrichment and material balance are measured for 62 elements in an Iowa and a Colorado coal by using SSMS as the sole analytical technique. Copper was used as an internal reference. The elements As, Cd, Ga, Ge, Pb, Sn, Tl, and Zn were found to be highly partitioned in the various ash depositories and Bi, Cs, Cu, I, Mo, Na, Se, Ta, and W were partially partitioned. The halogens, Hg, S, and Se were found to be lost to the stack. One-third of the elements studied for material balance gave an influent/effluent ratio agreeing within 30% of unity. Systematic errors are noted in relative sensitivity coefficients, used for instrument calibration, for some of the elements and between coal and ash samples.

## Introduction

Certain elements are known to concentrate in various ash depositories in coal burning facilities (1-3). The current trend toward the burning of coal containing significant levels of inorganic constituents presents the opportunity for using these ash depositories as sources of some strategically important elements. In searching for such opportunities an analytical technique is needed which possesses high sensitivity and broad elemental coverage. Spark source mass spectrometry (SSMS) possesses both of these attributes. However, it has reputed limited reproducibility and accuracy (3-6) unless combined with isotope dilution (7) which also limits its elemental range and complicates sample preparation. When special sample fusion techniques are used to improve homogeneity (8), spectral interferences increase, contamination of the samples is likely, and the time required for the analysis increases. When electrical means for recording SSMS results (9) are used to reduce the measuring uncertainties, the mass resolution is limited.

Measurements of elemental material balances (MB) at coal burning facilities are made usually by using a combination of analytical techniques (1, 10, 11). Here, MB as well as elemental partitioning were studied solely by SSMS by using minimal sample preparation, but with legitimate sampling, for a broad array of elements. The purpose of the MB measurements were to study sources of random variations such as sample inhomogeneity and to identify systematic errors due to instrument calibration by using coal and ash reference standards. Results cited summarize work from a more detailed study (12).

## Experimental Section

The coal burning facility used in this study is located on the Iowa State University campus. It produces power and steam for operating the university and normally burns a blend of high sulfur Iowa coal and low sulfur Colorado coal in order to meet environmental sulfur emission standards. A schematic illustration of the ash recovery

sites and distribution of ash from the particular boiler used in this study is given in Figure 1. The boiler is a spreader-stoker unit where ~60% of the ash falls below the boiler grates as bottom ash (BA), ~34% is recovered in a primary mechanical collector (PMC) which is ~85% efficient, and the remaining ash is collected in an electrostatic precipitator (ESP) which is ~97% efficient. For this study the plant burned only the Iowa coal mined near Lovilla, IA, during August of 1979 and only the Colorado coal mined near Craig, CO, during September of 1979 in this particular boiler. In mid-August and -September 12 samples of the influent coal and 12 samples at each of the ash recovery sites were collected during a 3-day period by using American Society for Testing and Materials (ASTM) standard methods (12, 13). These samples were crushed, mixed, riffled, and then low-temperature ashed (LTA) (12) prior to analysis by spark mass spectrometry. All of the samples (coal, ash, and reference standards) were subjected to identical LTA (<200 °C) procedures since organic material in samples analyzed by SSMS can adversely affect the analytical results (14). Portions of the LTA samples were subjected to high-temperature ashing (HTA) at 750 °C in an open muffle furnace for 4 h prior to wet chemical determination of copper which provided the primary reference element for the SSMS analyses (12).

Eleven standard coal samples were acquired from sources identified in Table I. These samples were selected because they represent different and diverse geographical areas and their trace elemental concentrations cover a broad range. One standard ash sample (SRM 1633) was acquired from the National Bureau of Standards (NBS). Equal weights of the standard sample (selected in random sequence) and spectroscopically pure graphite (National Carbon Co., New York, NY, grade SP-1) were mixed on a vibrating mixer/mill. Electrodes were formed from the sample-graphite mixture into conical shapes by compression under 40000 psi in polyethylene molds onto pure silver wires which support the cones as well as provide high conductivity into the pellet and flexible mounting into the sample holders of the SSMS. This electrode arrangement, illustrated in Figure 2, makes handling of the samples easy but is not considered critical to the results being cited.

The instrument used for these studies was a Model GRAF 2.2 (Nuclide Corp., State College, PA) spark source mass spectrograph. The instrument was modified previously for automatic control of the spark and ion illumination angle (15) and for computer control of the spectrograph (16). Ilford Q2 (Ilford Ltd., Manchester, U.K.) photographic plates were used to record the mass spectra. The emulsions were calibrated by using a computer adaptation of the Franzen-Maurer-Schuy formula (12) with additional corrections for emulsion response due to ion mass. The transmission of the mass spectral lines was determined with a microphotometer manufactured by Jarrell-Ash Co., Newtonville, MA, Model 2100, which was modified here for computer measurement of line areas and deconvolution of multiplets using a microprocessor computer system (16).

Table I. Standard Coal Samples

source	sample no.	origin	location
National Bureau of Standards	SRM1632-coal SRM1635-subbit. coal		
Illinois State Geological Survey	C13464 C16030 C16408	Herrin 6 Herrin 6 Chapel 8	Williamson County, IL
United States Geological Survey	PAS16 PAS47 D160984 D165578 D165762 D165766	Upper Freeport Bed Pittsburgh Bed Wyodak Anderson Bed Beulah Bed Pust Bed Pust Bed	Westmoreland County, PA Washington County, PA Campbell County, WY Mercer County, ND Richland County, MT Richland County, MT

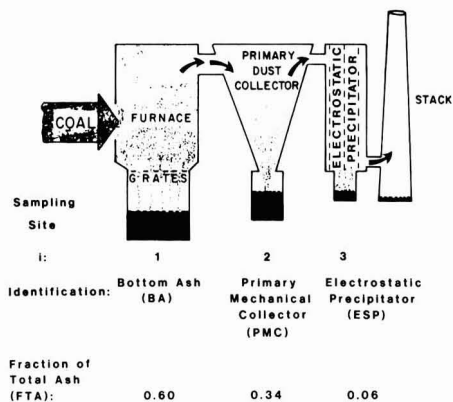


Figure 1. Illustration of ash recovery sites.

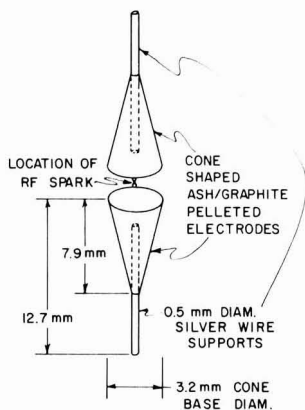


Figure 2. Electrode shape and configuration for SSMS analysis of ash samples.

**Enrichment Factor.** The enrichment factor ( $R_{ji}$ ) used by others (1), with aluminum as the normalizing element, was computed according to

$$R_{ji} = \frac{M_{j,i}/M_{Al,i}}{\sum_{i=1}^3 M_{j,i}/\sum_{i=1}^3 M_{Al,i}} \quad (1)$$

where  $M_{j,i}$  is the mass flow for element  $j$  at recovery site  $i$  or

$$M_{j,i} = CA_{j,i} \times FTA_i \quad (2)$$

where  $CA_{j,i}$  is the concentration of element  $j$  at site  $i$  and  $FTA_i$  is the fraction of total ash recovered at site  $i$ . Table II lists the computed factors and uncertainties in order of

relative enrichment at the ESP site. The uncertainties are computed as the expected error due to the statistical combination of the random variations in the 12 determinations for each data population used in eq 1 and 2 and the estimated uncertainties in the  $FTA_i$ .

**Material Balance.** The sensitivity of the SSMS method of analysis is not the same for all of the elements. This difference in sensitivity is corrected by applying a sensitivity coefficient in which the elemental values of the coefficients are calculated relative to that of an internal reference element (copper in this case) which is given a coefficient of 1.0. The elemental relative sensitivity coefficients (RSC) are calculated by

$$RSC_i = \frac{(ppma_i)(ATWT_i)(ppmw_R)}{(ppma_R)(ATWT_R)(ppmw_i)} \quad (3)$$

where the subscripts  $i$  and  $R$  refer to a specific element,  $i$ , and to the reference,  $R$ ,  $ppma$ 's are the SSMS observed atomic signal levels in parts per million,  $ATWT$ 's are the atomic weights, and  $ppmw$ 's are the concentrations in the standard samples. Relative sensitivity coefficients,  $RSC$ , were computed separately for the coal and for the ash standards, and the mean values are listed in Table III along with the standard deviation from the mean.

The elemental levels in the coal and ash samples were computed as parts per million by weight by using

$$ppmw_i = \frac{(ppma_i)(ATWT_i)(ppmw_R)}{(ppma_R)(ATWT_R)(RSC_i)} \quad (4)$$

where the notations are as above. Here  $ppmw_R$  is the copper level determined by wet chemical techniques for each sampling. For the elements in Table III not having an  $RSC$  from the coal standards, the  $RSC$  from the ash standard was used for both the coal and the ash measurements. The concentration levels and standard deviations for each of the 62 elements determined in the two coals for each of the four measured data populations is given elsewhere (12).

The MB were computed for each element in each of the coals as the ratio  $R/C$  of the amount recovered,  $R$ , at the ash sites to the amount in the influent coal,  $C$ . Ideally  $R/C = 1$ :

$$\left(\frac{R}{C}\right)_j = \frac{[\sum(CA_{i,j} \times FTA_i)]PAF_c}{CIN_j} \quad (5)$$

where  $j$  refers to the element of interest,  $CA_{i,j}$  is the concentration of element  $j$  at site  $i$ ,  $FTA_i$  is the weight fraction of the total ash recovered at site  $i$ , given in Figure 1,  $CIN_j$  is the concentration of element  $j$  in the influent coal, and  $PAF_c$  is the plant ash factor for coal type  $c$  obtained from the ratio of the total weight of effluent ash to the total weight of influent coal:  $PAF_{Iowa} = 0.183$ ;  $PAF_{Colorado} = 0.096$ . The MB for the 62 elements are given in bar graphs

Table II. Enrichment Factors<sup>a</sup> by SSMS in Three Ash Depositories<sup>b</sup> for an Iowa Coal and a Colorado Coal

Iowa coal				Colorado coal					
no.	Sy	BA	PMC	ESP	no.	Sy	BA	PMC	ESP
1	Cd	0.28 ± 0.10	0.77 ± 0.21	9.99 ± 2.71	1	Pb	0.17 ± 0.06	0.33 ± 0.11	18.13 ± 5.79
2	Pb	0.27 ± 0.08	0.96 ± 0.24	9.27 ± 2.33	2	Tl	0.21 ± 0.07	0.42 ± 0.13	16.75 ± 4.91
3	Sb	0.34 ± 0.09	0.83 ± 0.21	9.04 ± 2.25	3	Cd	0.08 ± 0.03	0.73 ± 0.23	16.36 ± 4.68
4	Tl	0.37 ± 0.14	1.06 ± 0.26	7.87 ± 1.95	4	Sn	0.33 ± 0.10	0.55 ± 0.15	14.09 ± 3.67
5	Ga	0.52 ± 0.14	0.85 ± 0.20	6.92 ± 1.57	5	Sb	0.24 ± 0.07	0.77 ± 0.21	13.70 ± 3.51
6	As	0.34 ± 0.09	1.39 ± 0.32	6.79 ± 1.58	6	Ge	0.26 ± 0.07	0.78 ± 0.21	13.35 ± 3.35
7	Zn	0.51 ± 0.17	0.95 ± 0.26	6.64 ± 1.58	7	As	0.14 ± 0.04	1.25 ± 0.42	11.66 ± 2.95
8	Ge	0.49 ± 0.12	1.08 ± 0.23	6.34 ± 1.36	8	Zn	0.49 ± 0.19	0.63 ± 0.19	11.24 ± 3.29
9	Sn	0.88 ± 0.23	0.78 ± 0.17	3.19 ± 0.72	9	Ga	0.56 ± 0.14	0.78 ± 0.17	9.10 ± 1.94
10	Mo	0.77 ± 0.19	1.19 ± 0.25	2.84 ± 0.59	10	Bi	≤ 0.74	≤ 0.61	≥ 7.9
11	Cu	0.88 ± 0.20	0.89 ± 0.18	2.78 ± 0.55	11	I	0.27 ± 0.07	1.89 ± 0.44	4.87 ± 0.99
12	Bi	≤ 0.85	≤ 1.01	≥ 2.67	12	Hf	0.74 ± 0.24	1.00 ± 0.28	4.70 ± 3.99
13	Cs	0.79 ± 0.21	1.19 ± 0.33	2.54 ± 0.62	13	Na	0.79 ± 0.21	0.94 ± 0.20	4.56 ± 0.95
14	I	0.57 ± 0.15	1.88 ± 0.41	2.25 ± 0.47	14	Mo	0.87 ± 0.20	0.83 ± 0.18	4.15 ± 0.81
15	Co	0.80 ± 0.18	1.27 ± 0.25	2.15 ± 0.42	15	F	0.55 ± 0.14	1.48 ± 0.37	3.94 ± 0.87
16	V	0.84 ± 0.19	1.20 ± 0.25	1.95 ± 0.40	16	Cl	0.75 ± 0.19	1.15 ± 0.27	3.50 ± 0.96
17	Se	1.05 ± 0.27	0.65 ± 0.15	1.89 ± 0.41	17	Dy	0.69 ± 0.19	1.31 ± 0.35	3.25 ± 0.69
18	Ta	0.96 ± 0.21	0.89 ± 0.20	1.84 ± 0.49	18	Ta	1.04 ± 0.33	0.63 ± 0.17	3.19 ± 0.95
19	Na	1.04 ± 0.25	0.70 ± 0.15	1.78 ± 0.46	19	Cu	1.05 ± 0.24	0.61 ± 0.13	3.15 ± 0.61
20	Nd	0.85 ± 0.20	1.24 ± 0.25	1.70 ± 0.34	20	Cs	0.90 ± 0.26	0.93 ± 0.25	2.91 ± 0.73
21	U	0.84 ± 0.21	1.28 ± 0.27	1.67 ± 0.34	21	Er	0.73 ± 0.19	1.27 ± 0.31	2.89 ± 0.61
22	Ni	0.97 ± 0.24	0.91 ± 0.20	1.65 ± 0.36	22	Se	1.05 ± 0.25	0.66 ± 0.15	2.84 ± 0.57
23	W	0.90 ± 0.36	1.12 ± 0.34	1.64 ± 0.48	23	W	1.05 ± 0.32	0.66 ± 0.18	2.80 ± 0.67
24	Yb	0.81 ± 0.19	1.39 ± 0.35	1.62 ± 0.35	24	U	0.67 ± 0.16	1.41 ± 0.29	2.76 ± 0.55
25	Sm	0.85 ± 0.23	1.28 ± 0.30	1.60 ± 0.34	25	Sm	0.71 ± 0.20	1.35 ± 0.34	2.67 ± 0.54
26	Ce	0.85 ± 0.20	1.28 ± 0.27	1.55 ± 0.34	26	Zr	0.87 ± 0.21	1.04 ± 0.21	2.59 ± 0.50
27	Dy	0.89 ± 0.29	1.17 ± 0.29	1.52 ± 0.37	27	Hg	0.99 ± 0.29	0.81 ± 0.32	2.56 ± 0.68
28	Er	0.85 ± 0.22	1.30 ± 0.28	1.50 ± 0.36	28	Gd	0.75 ± 0.20	1.29 ± 0.32	2.50 ± 0.51
29	Cl	0.73 ± 0.18	1.66 ± 0.42	1.45 ± 0.40	29	Sr	0.71 ± 0.20	1.37 ± 0.32	2.45 ± 0.50
30	Pr	0.93 ± 0.23	1.10 ± 0.25	1.44 ± 0.31	30	B	0.67 ± 0.19	1.45 ± 0.55	2.38 ± 0.58
31	F	0.83 ± 0.28	1.38 ± 0.40	1.41 ± 0.38	31	Ho	0.83 ± 0.18	1.15 ± 0.24	2.36 ± 0.47
32	Y	0.96 ± 0.21	1.02 ± 0.21	1.41 ± 0.29	32	Nd	0.89 ± 0.22	1.04 ± 0.24	2.28 ± 0.45
33	Mg	1.01 ± 0.24	0.87 ± 0.18	1.39 ± 0.28	33	Rb	0.98 ± 0.26	0.87 ± 0.22	2.28 ± 0.50
34	Gd	0.84 ± 0.23	1.36 ± 0.30	1.36 ± 0.30	34	Co	1.02 ± 0.23	0.81 ± 0.17	2.22 ± 0.43
35	Sr	1.01 ± 0.26	0.88 ± 0.19	1.34 ± 0.30	35	Yb	0.72 ± 0.19	1.40 ± 0.38	2.13 ± 0.51
36	Ba	1.01 ± 0.26	0.89 ± 0.19	1.29 ± 0.29	36	Tb	0.79 ± 0.18	1.28 ± 0.28	1.99 ± 0.40
37	La	0.91 ± 0.23	1.18 ± 0.26	1.27 ± 0.27	37	Eu	0.79 ± 0.19	1.27 ± 0.30	1.98 ± 0.39
38	Sc	0.93 ± 0.24	1.13 ± 0.24	1.26 ± 0.28	38	Tm	0.86 ± 0.22	1.16 ± 0.26	1.94 ± 0.48
39	S	1.16 ± 0.38	0.50 ± 0.14	1.25 ± 0.39	39	Ba	0.69 ± 0.19	1.48 ± 0.40	1.93 ± 0.51
40	Ti	0.86 ± 0.19	1.35 ± 0.26	1.20 ± 0.24	40	Cr	0.91 ± 0.23	1.04 ± 0.22	1.93 ± 0.43
41	Tm	0.89 ± 0.31	1.27 ± 0.38	1.15 ± 0.30	41	Ni	1.00 ± 0.23	0.89 ± 0.19	1.91 ± 0.39
42	Rb	0.90 ± 0.22	1.26 ± 0.31	1.07 ± 0.24	42	Ce	0.81 ± 0.19	1.24 ± 0.34	1.88 ± 0.38
43	Zr	0.91 ± 0.21	1.24 ± 0.25	1.07 ± 0.22	43	La	0.85 ± 0.22	1.20 ± 0.27	1.73 ± 0.36
44	Al	1.00 ± 0.26	1.00 ± 0.22	1.00 ± 0.21	44	V	0.91 ± 0.23	1.07 ± 0.25	1.73 ± 0.35
45	Hf	0.78 ± 0.22	1.61 ± 0.46	1.00 ± 0.27	45	Br	1.08 ± 0.36	0.75 ± 0.20	1.70 ± 0.50
46	P	0.95 ± 0.22	1.16 ± 0.25	0.96 ± 0.20	46	Pr	0.89 ± 0.21	1.14 ± 0.30	1.58 ± 0.34
47	Lu	0.93 ± 0.31	1.20 ± 0.31	0.95 ± 0.23	47	Lu	0.55 ± 0.19	1.80 ± 0.43	1.58 ± 0.40
48	Cr	0.92 ± 0.22	1.26 ± 0.27	0.92 ± 0.19	48	P	1.06 ± 0.27	0.82 ± 0.18	1.56 ± 0.32
49	Li	0.92 ± 0.27	1.26 ± 0.40	0.88 ± 0.27	49	Ti	1.15 ± 0.28	0.63 ± 0.14	1.56 ± 0.31
50	K	0.84 ± 0.19	1.47 ± 0.30	0.87 ± 0.17	50	Li	1.04 ± 0.33	0.86 ± 0.30	1.45 ± 0.38
51	B	0.96 ± 0.28	1.15 ± 0.29	0.84 ± 0.20	51	Mg	1.03 ± 0.24	0.88 ± 0.19	1.42 ± 0.28
52	Hg	1.15 ± 0.39	0.62 ± 0.37	0.82 ± 0.24	52	S	1.37 ± 0.43	0.23 ± 0.06	1.41 ± 0.42
53	Be	1.09 ± 0.46	0.78 ± 0.38	0.82 ± 0.39	53	Sc	0.96 ± 0.24	1.04 ± 0.24	1.33 ± 0.28
54	Ho	0.89 ± 0.22	1.37 ± 0.29	0.81 ± 0.18	54	K	1.03 ± 0.26	0.89 ± 0.21	1.33 ± 0.30
55	Eu	0.95 ± 0.26	1.20 ± 0.27	0.79 ± 0.19	55	Y	0.89 ± 0.22	1.18 ± 0.24	1.23 ± 0.25
56	Th	1.02 ± 0.26	1.00 ± 0.22	0.75 ± 0.17	56	Ca	1.08 ± 0.27	0.83 ± 0.18	1.14 ± 0.23
57	Tb	0.89 ± 0.22	1.38 ± 0.29	0.68 ± 0.14	57	Al	1.00 ± 0.26	1.00 ± 0.22	1.00 ± 0.20
58	Br	1.01 ± 0.34	1.07 ± 0.27	0.61 ± 0.16	58	Si	0.96 ± 0.22	1.08 ± 0.22	0.96 ± 0.18
59	Si	0.89 ± 0.20	1.45 ± 0.28	0.47 ± 0.09	59	Th	0.96 ± 0.24	1.09 ± 0.23	0.91 ± 0.19
60	Fe	1.14 ± 0.27	0.76 ± 0.16	0.45 ± 0.09	60	Mn	1.02 ± 0.25	0.99 ± 0.21	0.74 ± 0.15
61	Ca	1.11 ± 0.26	0.87 ± 0.18	0.32 ± 0.07	61	Be	1.34 ± 0.44	0.40 ± 0.14	0.62 ± 0.26
62	Mn	1.11 ± 0.26	0.90 ± 0.19	0.14 ± 0.03	62	Fe	1.15 ± 0.26	0.80 ± 0.17	0.29 ± 0.06

<sup>a</sup> Elements are listed in order of enrichment factor at the ESP site for each coal. <sup>b</sup> Ash depositories as defined in Figure 1.

in Figure 3 to permit easy identification of errors and trends. Table IV contains the tabulated results with accumulated errors which are computed from random variations observed in the SSMS results for the means of the six different data populations used in the MB computations (RSC<sub>coal</sub>, RSC<sub>ash</sub>, CIN, CA<sub>BA</sub>, CA<sub>PMC</sub>, and CA<sub>ESA</sub>). These accumulated errors represent the variation from unity that R/C can be expected to have due simply to

random variations in the measurements. They do not include systematic errors which may occur in FTA nor PAF. The columns labeled "bias" and "comments" are discussed below.

#### Discussion

**Enrichment Factors.** Klein et al. (2) in a study of partitioning of 38 elements in a coal-fired power plant

R/C for COLORADO COAL

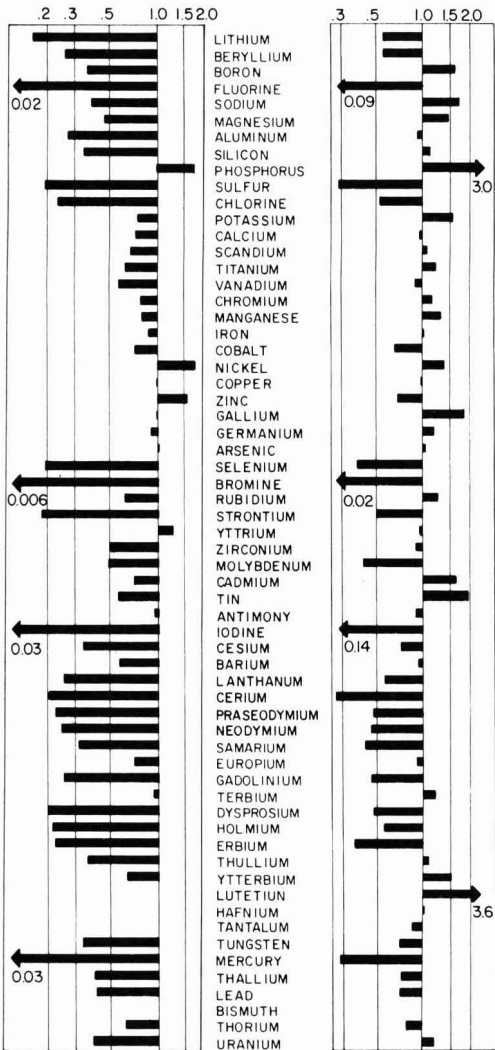


Figure 3. Mass balances by SSMS in ratio (R/C) of mass recovered/mass in influent coal.

classified the elements according to the following: *class I*, 20 elements, Al, Ba, Ca, Ce, Co, Eu, Fe, Hf, K, La, Mg, Mn, Rb, Sc, Si, Sm, Sr, Ta, Th, and Ti, have no tendency to concentrate in or on the fly ash; *class II*, 9 elements, As, Cd, Cu, Ga, Mo, Pb, Sb, Se, and Zn, tend to concentrate in or on the fines and are depleted in the slag; *class III*, 3 elements, Hg, Cl, and Br, remain completely in the gas phase throughout the plant and may be lost to the stack. The 6 remaining elements, Cr, Cs, Na, Ni, U, and V, were intermediate between classes I and II.

Natusch et al. (17) found As, Cd, Cr, Ni, Pb, Sb, Se, and Zn concentrated in or on smaller particulate matter and that Al, Ca, Co, Cu, Fe, K, Mg, Mn, Si, Ti, and V had no tendency to partition according to particle size.

Kaakinen et al. (1) report that Cu, Zn, As, Mo, Sb, Pb, Se, and Po partition in a coal burning plant and are concentrated in or on the smaller ash particles. They found Zn to be depleted from the smaller particles and Al, Fe,

R/C for IOWA COAL

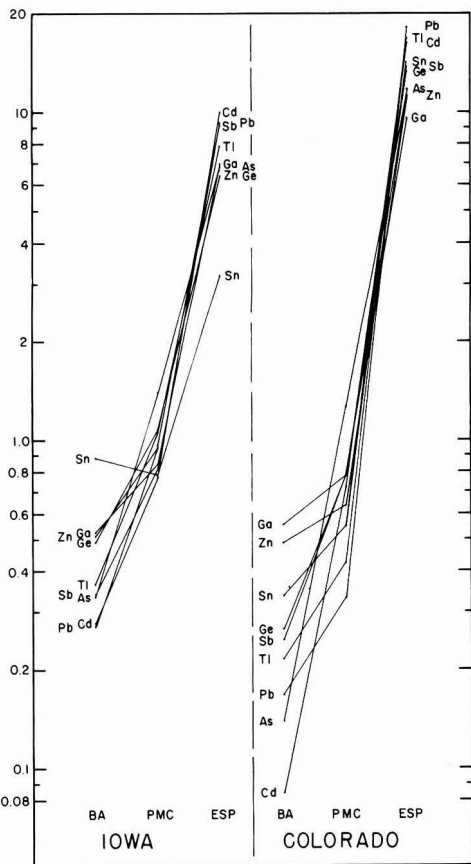


Figure 4. Plot of enrichment factors for elements partitioned in the ashes.

Rb, Sr, Y, and Nb to be unpartitioned. Semiquantitative data indicated Ga and Sn were also partitioned and K, Ca, and Mn were unpartitioned.

We use the same classification defined by Klein et al. (2). Our data show excellent agreement in the tendency of elements to partition within the plant (class II) for both coals. Indeed the enrichment of nine elements, As, Cd, Ga, Ge, Pb, Sb, Sn, Tl, and Zn, is highest in the ESP, and these same nine elements concentrate there for both coals. A plot of the computed enrichment factors for the class II elements is given in Figure 4 to show the similar behavior among this group of elements although Pb and Cd have the greatest range of partitioning for both coals and Sn is significantly less partitioned in the ash from the Iowa coal. In general, partitioning is greater for the Colorado coal which may be expected since this coal produces smaller diameter ash particles than does the Iowa coal (12).

Our data indicate a partitioning intermediate between class I and class II for 10 elements, Bi, Cs, Cu, I, Mo, Na, Se, Ta, and W (Bi detected only in the ESP and the enrichment factor based on upper limits in the BA and PMC). Here agreement with others is found for all of these elements except Ta. The data for Cu are particularly significant since it is used as an internal reference for the SSMS analyses (12, 18). Our Cu results agree very well with the arguments of Kaakinen et al. (1) that Cu behaves in a manner intermediate between the class I and class II elements.

Table III. Relative Sensitivity Coefficients from Analysis of Coal and Ash Standards

	coal	ash	coal	ash	coal	ash
Li	2.2 ± 0.6	11.0 ± 4.0	Ni	1.6 ± 0.4	Ce	0.75 ± 0.04
Be	11.0 ± 4.0	40.0 ± 10.0	Cu	≅1.00	Pr	0.43 ± 0.10
B	0.71 ± 0.07	1.6 ± 0.3	Zn	1.7 ± 0.1	Nd	0.34 ± 0.11
F	0.25 ± 0.06	1.8 ± 0.2	Ga	1.9 ± 0.2	Sm	0.45 ± 0.10
Na	1.5 ± 0.2	2.0 ± 0.2	Ge	2.8 ± 1.0	Eu	1.4 ± 0.3
Mg	0.55 ± 0.03	0.84 ± 0.05	As	1.9 ± 0.2	Tb	1.4 ± 0.2
Al	0.44 ± 0.9	0.94 ± 0.16	Se	1.4 ± 0.3	Dy	0.53 ± 0.2
Si	0.57 ± 0.03	0.91 ± 0.07	Br	0.022 ± 0.0004	Ho	1.4 ± 0.3
P	0.89 ± 0.22	0.44 ± 0.06	Rb	1.4 ± 0.3	Er	0.45 ± 0.10
S		0.88 ± 0.10	Sr	0.22 ± 0.02	Tm	1.4 ± 0.3
Cl		1.9 ± 0.20	Y	0.73 ± 0.04	Yb	1.4 ± 0.3
K	1.5 ± 0.1	1.8 ± 0.2	Zr	0.28 ± 0.04	Lu	1.2 ± 0.6
Ca	1.5 ± 0.07	2.0 ± 0.2	Mo	0.66 ± 0.14	Hf	0.95 ± 0.25
Sc	1.1 ± 0.07	1.1 ± 0.09	Cd	1.9 ± 0.2	Ta	0.50 ± 0.09
Ti	0.52 ± 0.07	0.57 ± 0.07	Sn		W	1.2 ± 0.3
V	0.73 ± 0.09	1.0 ± 0.08	Sb	1.4 ± 0.2	Hg	1.3 ± 0.2
Cr	1.5 ± 0.3	1.4 ± 0.08	I	0.77 ± 0.19	Tl	3.0 ± 0.5
Mn	1.8 ± 0.2	2.0 ± 0.2	Cs	2.0 ± 0.3	Pb	0.71 ± 0.09
Fe	0.59 ± 0.08	0.78 ± 0.04	Ba	0.35 ± 0.04	Bi	1.0 ± 0.1
Co	0.68 ± 0.04	1.0 ± 0.05	La	0.17 ± 0.03	Th	0.83 ± 0.16
					U	1.4 ± 0.2
						2.2 ± 0.2

Most of the elements studied here fall into the class I category showing no partitioning within the experimental uncertainties associated with the analyses. However, there are clear indications of small depletions at the ESP site for Mn, Ca, Fe, and Si for the Iowa coal and Fe for the Colorado coal.

The computed enrichment factors for elements in the PMC are close to unity for all the elements indicating no significant enrichments at this site and with only small depletions for S (0.50) in the Iowa coal and Pb (0.33), Tl (0.42), Sn (0.55), and Be (0.40) in the Colorado coal. The bottom ash likewise shows no enrichments, but it has depletions for all the class II elements and for iodine from both of the coals. The observation that class III elements are not highly partitioned in the BA, PMC, and ESP, with only small enrichments in the ESP, may be due to the fact that the portion that is not lost to the stack exists as a stable aluminosilicate or other nonvolatile compound and therefore tends toward a uniform distribution.

**Material Balance.** cursory consideration of Figure 3 identifies some obvious trends. The Iowa MB have a reasonably random  $R/C$  ratio fluctuating about unity as should be expected unless elements are lost to the stack. The Colorado MB are biased toward lower  $R/C$ 's. This bias was computed except for elements obviously lost to the stack as the ratio of the Colorado MB to the Iowa MB and is given in Table IV. The bias is consistent with a mean value of 0.59. More careful inspection of Figure 3 and Table IV reveals some trends common to both coals. A low  $R/C$  indicates loss of the element to the stack. In spite of the difficulty with SSMS determination of volatile elements (3) the MB for the halogens, Hg, S, and Se agree with the assumption (2) that these elements are lost to the stack. For each of the 62 elements the computed errors are of the same magnitude, indicating similar causes for fluctuation in measurements for each coal. The only significant differences involve Zn, which was observed to be inhomogeneously distributed by visual examination of the raw data (12), and for Cd, Ba, and Tm. The cause for the high variations observed for Li and Be may be due to the high background levels on the photographic plates in the low mass region of the recorded mass spectra and to high volatility of these elements which is known to affect spark spectra (4).

The column of comments in Table IV gives systematic trends: "S" indicates loss of the element to the stack; "BD"

indicates a high uncertainty due to the element being barely detected. "RSC" refers to indications of systematic errors in the relative sensitivity coefficients used to compute the concentrations. For Sr, Mo, and most of the rare earths the  $R/C$ 's are lower than expected for both coals. Indeed the magnitude of the RSC's, listed in Table III, for these elements from the coal standards are very low compared to elements of similar physical and chemical properties (4) and to the RSC's for these elements from the ash standard. The elements, P, Ni, and Ga have systematically high  $R/C$ 's, and these are the only elements (except for Ge) with RSC's significantly higher for the coal standards than for the ash standards.

The presence of possible systematic errors can be revealed by examining the data in Tables II and IV. The errors given in Table II indicate the reproducibility of SSMS in analyzing standard samples. However, the magnitude of the RSC and the results of their use in the computation of the MB indicate a matrix effect is present. The differences in the RSC's between the coal and ash standards show most elements are enhanced in sensitivity in the ash samples relative to copper which was used as the normalizing element. The MB for the Iowa coal indicates the RSC's in Table II are correct since the coal and ash RSC's used in the computations appear to be close to unity with some discrepancies for a few elements noted earlier. However, the MB for the Colorado coal has a bias which can be explained on the basis of an absence of a matrix effect between RSC's in ash and coal which has been noted elsewhere (18). If the sensitivities (RSC's) for the Colorado coal were the same as for the ash samples, then the same RSC is used in computing the ppmw for both the coal and the ash. The results of such a computation on the MB for the Colorado coal are given in Table V. Now the  $R/C$ 's for all the elements are remarkably close to unity with the exception of Zn, noted previously to be inhomogeneous, and the elements lost to the stack.

This study indicates that SSMS analyses of ashes provide reliable enrichment factors as well as maintain its other attributes of minimal sample preparation, high sensitivity, and broad elemental coverage. The results of the study agree with and extend the results of others in showing that the ESP is a potential commercial source for the class II elements.

Relative analytical precision on the order of 10-30% can be attained for most of the elements by using straight-

Table IV. Material Balances as Amount Recovered/Amount Influent for Iowa and Colorado Coals

	Iowa coal, R/C <sup>a</sup> ± error <sup>b</sup>	Colorado coal, R/C <sup>a</sup> ± error <sup>b</sup>	bias <sup>c</sup> CO/IA	comment <sup>c,d</sup>
Li	0.56 ± 0.46	0.16 ± 0.47	0.28	
Be	0.56 ± 0.57	0.26 ± 0.63	0.46	
B	1.62 ± 0.25	0.36 ± 0.27	0.22	
F	0.09 ± 0.30	0.02 ± 0.28		S
Na	1.72 ± 0.17	0.38 ± 0.18	0.22	
Mg	1.48 ± 0.11	0.44 ± 0.12	0.30	
Al	0.95 ± 0.25	0.27 ± 0.25	0.28	
Si	1.11 ± 0.09	0.34 ± 0.11	0.31	
P	2.98 ± 0.28	1.73 ± 0.28	0.58	RSC
S	0.29 ± 0.29	0.19 ± 0.26	0.66	S
Cl	0.53 ± 0.17	0.23 ± 0.20		S
K	1.59 ± 0.15	0.75 ± 0.17	0.47	
Ca	0.93 ± 0.12	0.72 ± 0.14	0.77	
Sc	1.04 ± 0.13	0.67 ± 0.15	0.64	
Ti	1.22 ± 0.16	0.62 ± 0.17	0.51	
V	0.91 ± 0.15	0.56 ± 0.18	0.61	
Cr	1.17 ± 0.23	0.78 ± 0.26	0.67	
Mn	1.31 ± 0.15	0.79 ± 0.18	0.60	
Fe	1.02 ± 0.15	0.88 ± 0.15	0.86	
Co	0.68 ± 0.10	0.71 ± 0.09	1.04	
Ni	1.39 ± 0.27	1.76 ± 0.26	1.27	RSC
Cu	1.00 ± 0.07	1.00 ± 0.08	1.00	
Zn	0.69 ± 0.30	1.56 ± 0.20		inhomo
Ga	1.86 ± 0.16	0.99 ± 0.15	0.53	RSC
Ge	1.19 ± 0.35	0.90 ± 0.36	0.76	
As	1.05 ± 0.15	1.02 ± 0.18	0.97	
Se	0.38 ± 0.24	0.19 ± 0.25	0.50	S
Br	0.02 ± 0.19	0.01 ± 0.22		S
Rb	1.27 ± 0.28	0.61 ± 0.31	0.48	
Sr	0.51 ± 0.18	0.18 ± 0.15	0.35	RSC
Y	0.95 ± 0.10	1.23 ± 0.13	1.29	
Zr	0.90 ± 0.17	0.49 ± 0.18	0.54	
Mo	0.41 ± 0.25	0.48 ± 0.24	1.17	RSC
Cd	1.66 ± 0.21	0.69 ± 0.13	0.42	
Sn	1.95 ± 0.21	0.55 ± 0.19	0.28	
Sb	0.90 ± 0.18	0.94 ± 0.16	1.04	
I	0.14 ± 0.27	0.03 ± 0.30		S
Cs	0.72 ± 0.22	0.33 ± 0.23	0.46	
Ba	0.95 ± 0.19	0.56 ± 0.26	0.59	
La	0.57 ± 0.24	0.25 ± 0.26	0.44	RSC
Ce	0.28 ± 0.29	0.20 ± 0.29	0.71	RSC
Pr	0.48 ± 0.30	0.22 ± 0.30	0.46	RSC
Nd	0.47 ± 0.36	0.24 ± 0.35	0.51	RSC
Sm	0.43 ± 0.28	0.31 ± 0.29	0.72	RSC
Eu	0.92 ± 0.26	0.70 ± 0.26	0.76	RSC
Tb	1.22 ± 0.23	0.93 ± 0.19	0.76	
Dy	0.49 ± 0.38	0.20 ± 0.37	0.41	RSC
Ho	0.58 ± 0.30	0.21 ± 0.30	0.36	RSC
Er	0.37 ± 0.28	0.22 ± 0.29	0.59	RSC
Tm	1.11 ± 0.30	0.35 ± 0.64	0.32	BD
Yb	1.55 ± 0.31	0.63 ± 0.32	0.41	BD
Lu	3.57 ± 0.40			BD
Hf	1.04 ± 0.44			BD
Ta	0.87 ± 0.88			BD
W	0.72 ± 0.40	0.33 ± 0.41	0.46	BD
Hg	0.30 ± 0.37	0.03 ± 0.37		S
Tl	0.74 ± 0.25	0.39 ± 0.26	0.53	
Pb	0.73 ± 0.16	0.41 ± 0.18	0.56	
Bi		0.23 ± 0.21		BD
Th	0.80 ± 0.24	0.62 ± 0.24	0.78	
U	1.21 ± 0.20	0.38 ± 0.15	0.31	

<sup>a</sup> For complete recovery R/C = 1. <sup>b</sup> Error = computed accumulated error due to random variations. <sup>c</sup> Bias = (R/C for Colorado)/(R/C for Iowa). <sup>d</sup> See text for definitions.

forward sample preparation. The work indicates systematic errors can be identified and that accuracies approaching these precisions can also be expected. The systematic errors shown here include variations in the weight fraction of total ash at the three sites in the power plant. Some of the errors may be due to inadvertent inhomogeneities in sampling. Certain of the low recoveries

Table V. Materials Balance for Colorado Coal Using Equal RSC's for Coal and Ash Determinations

	R/C <sup>a</sup>		R/C <sup>a</sup>		R/C <sup>a</sup>		R/C <sup>a</sup>	
Li	0.80	Ti	0.68	Rb	0.91	Nd	0.70	
Be	0.93	V	0.77	Sr	0.69	Sm	0.88	
B	0.82	Cr	0.71	Y	1.37	Eu	1.35	
F	0.14 <sup>b</sup>	Mn	0.88	Zr	1.09	Tb	0.80	
Na	0.51	Fe	1.16	Mo	0.94	Dy	0.61	
Mg	0.68	Co	1.04	Cd	0.98	Ho	0.54	
Al	0.57	Ni	0.84	Sn	0.55	Er	0.69	
Si	0.54	Cu	±1.00	Sb	1.15	Tm	0.40	
P	0.86	Zn	3.9	I	0.08 <sup>b</sup>	Yb	0.52	
S	0.19 <sup>b</sup>	Ga	0.76	Cs	0.58	Hg	0.15 <sup>b</sup>	
Cl	0.23 <sup>b</sup>	Ge	0.69	Ba	1.12	Tl	0.56	
K	0.90	As	0.93	La	0.80	Pb	1.20	
Ca	0.96	Se	0.38 <sup>b</sup>	Ce	0.95	Th	1.48	
Sc	0.67	Br	0.35 <sup>b</sup>	Pr	0.67	U	0.59	

<sup>a</sup> R/C computed by using equal RSC for coal and ash.

<sup>b</sup> Elements known to be lost to stack.

pertinent to the MB may in fact have actually occurred. The observations indicating possible matrix effects between coal and ash samples should not be alarming. It is encouraging that systematic effects can be identified while accessing partitioning and MB in an actual power plant by a single analytical technique for such a large number of elements.

Although greater effort in applying SSMS techniques to the analysis of coal and its effluent products could result in improving the precision and accuracy of the determinations, the data cited here are satisfying and useful for assessing material balances and reliable for measuring enrichment factors.

#### Acknowledgments

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**Registry No.** As, 7440-38-2; Cd, 7440-43-9; Ga, 7440-55-3; Ge, 7440-56-4; Pb, 7439-92-1; Sn, 7440-31-5; Tl, 7440-28-0; Zn, 7440-66-6; Bi, 7440-69-9; Cs, 7440-46-2; Cu, 7440-50-8; W, 7440-33-7; Mo, 7439-98-7; Na, 7440-23-5; Ta, 7440-25-7; S, 7704-34-9; Se, 7782-49-2; F<sub>2</sub>, 7782-41-4; Cl<sub>2</sub>, 7782-50-5; Br<sub>2</sub>, 7726-95-6; Hg, 7439-97-6; I<sub>2</sub>, 7553-56-2; Li, 7439-93-2; Be, 7440-41-7; B, 7440-42-8; Mg, 7439-95-4; Al, 7429-90-5; Si, 7440-21-3; P, 7723-14-0; K, 7440-09-7; Ca, 7440-70-2; Sc, 7440-20-2; Ti, 7440-32-6; V, 7440-62-2; Cr, 7440-47-3; Mn, 7439-96-5; Fe, 7439-89-6; Co, 7440-48-4; Ni, 7440-02-0; Rb, 7440-17-7; Sr, 7440-24-6; Y, 7440-65-5; Zr, 7440-67-7; Sb, 7440-36-0; Ba, 7440-39-3; La, 7439-91-0; Ce, 7440-45-1; Pr, 7440-10-0; Nd, 7440-00-8; Sm, 7440-19-9; Eu, 7440-53-1; Gd, 7440-54-2; Tb, 7440-27-9; Dy, 7429-91-6; Ho, 7440-60-0; Er, 7440-52-0; Tm, 7440-30-4; Yb, 7440-64-4; Lu, 7439-94-3; Hf, 7440-58-6; Th, 7440-29-1; U, 7440-61-1.

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## Physicochemical Properties Controlling Polychlorinated Biphenyl (PCB) Concentrations in Aquatic Organisms

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■ The uptake and bioaccumulation of PCB's by mullet and polychaetes have been shown to be influenced by two factors: (i) partition behavior, quantitatively measured by the partition coefficient between 1-octanol and water ( $p$ ), and (ii) the adsorption characteristics of the PCB's onto a surface, estimated by chromatographic elution time on carbon and also by application of coefficients for chlorines in different substitution patterns giving a steric effect coefficient (SEC). The combination of these two factors, as  $\log p \times$  elution time or  $\log p \times$  SEC, gives a measure which is highly correlated with bioaccumulation. The results show that adsorption of PCB molecules onto a surface is influenced principally by their stereochemistry. Planar molecules are most efficiently adsorbed, and adsorption decreases as the molecule becomes less planar.

### Introduction

Polychlorinated biphenyls (PCB's) are widespread and persistent contaminants of aquatic ecosystems (1). However, the factors controlling the occurrence of these substances in aquatic organisms are not well understood (e.g., ref 2 and 3). Unexpectedly large differences in the bioconcentration of closely related PCB isomers by aquatic organisms have been well documented (e.g., ref 4). These differences have been attributed to variations in  $\log p$  values ( $p$  is the 1-octanol/water partition coefficient), which are measures of the lipophilicity of the compounds (5-8). However, several authors have found significant deviations from the  $\log$  bioconcentration factor (BCF)- $\log p$  relationship for certain PCB's (9-11).

In previous work (12, 13) we have shown that the concentration of individual PCB's in aquatic organisms is related to steric effects as well as  $\log p$ . The steric effects result from different substitution patterns of chlorine in the PCB molecule, and an empirically developed factor (the steric effect coefficient, SEC) provided a reasonable quantitative expression of this. Within groups of isomers the SEC was found to be directly related to the relative uptake although a weaker relationship occurred with all compounds together (12). However, in later work (13) relative uptake of all individual PCB's were shown to be directly related to the corresponding products of  $\log p$  and SEC.

This paper presents the results of investigations into the relationship of quantitative measures of steric factors and  $\log p$  to the uptake and bioaccumulation of PCB's and the mechanism whereby molecular stereochemistry influences this process.

### Experimental Section

The PCB standards, Monsanto Arochlors, were obtained from the U.S. Environmental Protection Agency, Research Triangle Park, NC, at a nominated purity of 100%. Solvents used for high-performance liquid chromatography were special HPLC grade. All solvents were distilled in an all glass fractional distillation apparatus with an efficiency of about 10 theoretical plates. Solid-liquid chromatography adsorbents were purified by heating at 600 °C for 4 h followed by solvent washing to remove organic impurities. Celite and charcoal for use in HPLC packings were solvent washed, and the charcoal was activated at 110 °C.

**Sample Collection.** Juvenile sea mullet (*Mugil cephalus*; length 7-10 cm) were collected at a PCB-free site in the Logan River estuary by using a monofilament bait net (2.5-cm diagonal mesh) and transported to the laboratory in 20-L containers aerated with pure oxygen. Polychaetes (*Capitella capitata*) were collected by manual methods in an intertidal marine area shown to be PCB free.

**Bioaccumulation Experiments.** (1) **Polychaetes.** The polychaetes, approximately 28 individuals giving a total mass of approximately 100 g per aquaria, were held in all glass aquariums (40 × 23 × 23 cm) to which a mixture of sand, silt, and crushed shell from the collection area and clean filtered seawater (10 L) was added. This static system was vigorously aerated and maintained at 25 °C. The polychaetes were acclimated for 1 week in the aquariums before the addition of PCB's. The PCB's (Arochlors 1242, 1254, and 1260) were prepared as 1000 mg/L solutions in acetone from the authentic standards. The PCB solutions, in calculated quantities, were incorporated separately into the sediments by thorough mixing before the addition of the water layer, to give concentrations of 0.5, 1, 2, 2.5, and 7.5 mg/kg. Subsamples of polychaetes were removed for gas chromatographic analysis at appropriate time intervals. The bioaccumulation of the

PCB's was followed by plotting organism concentration against time, and at equilibrium the slope of the line of best fit was zero.

(2) **Fish.** The bioaccumulation experiment was performed by static bioassay in glass aquariums (90 × 45 × 45 cm) containing clean filtered seawater (20 L). A calculated quantity of acetone solution (1000 mg/L) of the PCB's as a mixture of Arochlors (1260/1254/1242, 2/2/1) was added to give a concentration of 0.5 mg/L. After thorough mixing and standing for 1 week, an equilibrium concentration was reached (0.19 mg/L) and fish (58 individuals of approximately 300 g total mass) were added. Fish (four to six) and water samples were removed from the system for gas chromatographic analysis at appropriate time intervals.

The bioaccumulation of the PCB's was followed by plotting organism concentration against time, and at equilibrium the slope of the line of best fit was zero.

**Sample Preparation.** Samples were composited and homogenized, and subsamples (25 g) were extracted by blending with sodium sulfate (50 g) and hexane (150 mL) followed by 2 × 100-mL aliquots. All hexane extracts were combined, and solvent was removed on a stream bath. The resultant lipid samples were cleaned up by solid-liquid chromatography with a 50/50 mixture of 5% deactivated silica gel and alumina (50 g). PCB's are eluted from the column with 50 mL of hexane.

**Gas-Liquid Chromatography (GLC).** A Hewlett-Packard 5830A gas chromatograph fitted with a <sup>63</sup>Ni linear electron capture detector was used for analysis. The column used was 3% Apiezon-L on 100/200 mesh Gas Chrom Q operated at 220 °C. The injector detector temperatures were 240 and 300 °C, respectively. The gas (argon/methane 95/5) flow was 46 mL/min.

**High-Performance Liquid Chromatography (HPLC).** The operating conditions for partition coefficient determination have been described previously (12).

HPLC chromatography with a carbon stationary phase was performed on a Varian Model 5000 HPLC with a Varicom variable wavelength UV detector operated at 254 nm. The column used had dimensions of 30 cm × 4 mm i.d., packed with 20/80 activated charcoal/Celite (seived 5–20 μm) packed by using a Waters stirred slurry packing apparatus with methanol as the slurry solvent. The mobile phase was isooctane at a flow rate of 1.8 mL/min.

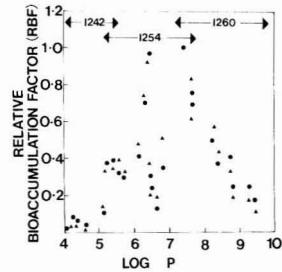
**Identification Technique.** Identification of PCB isomers involved comparison of GLC retention times with published data. The PCB mixtures were simplified by fractionation on reverse-phase HPLC. The techniques are described previously (12).

**Partition Coefficients.** The 1-octanol to water partition coefficients (*p*) were measured by the method described by Veith et al. (6).

## Results and Discussion

**General Characteristics of PCB Bioaccumulation.** The bioconcentration of lipophilic compounds is considered to be the result of competitive uptake and depuration processes which follow first-order kinetics. At equilibrium, when uptake and depuration are equivalent, the total bioconcentration should be directly related to the partition coefficient, *p* (6).

In this work the relative bioaccumulation factor (RBF, referred to in previous work, (12, 13) as the "relative uptake") for an individual PCB was measured as the ratio between its concentration in the PCB mixture in the water and sediments at the sampling time and its concentration in the PCB mixture which was bioaccumulated by the organism. Concentrations were determined from peak



**Figure 1.** Relative bioaccumulation factors of PCB's, exhibited by polychaetes (●) and mullet (▲) in aquariums, as related to log *p* at equilibrium between water and organism. The range of components of Arochlors 1242, 1254 and 1260 are indicated.

areas produced by gas chromatography (see Experimental Section). To enable comparisons to be made between different sets of results, the RBF's were standardized by calculating all ratios in a given chromatogram as relative to 2',3,4,4',5'-pentachlorobiphenyl as unity. This substance was selected because it was readily accumulated by organisms. The RBF's were calculated, as outlined above, for the mullet at equilibrium (12 weeks), but with polychaetes the concentrations at equilibrium (12 weeks), resulting from the various experiments at different starting concentrations, were averaged. During the experiment with mullet a substantial decrease in PCB water concentration was observed, but this decrease had no significant effect on the RBF values which remained constant throughout the uptake period.

If the bioaccumulation of lipophilic compounds by aquatic organisms was directly related to lipophilicity alone, a plot of log *p* vs. log bioaccumulation should yield a straight line (e.g., ref 6). The RBF provides a quantitative measure of bioaccumulation and thus should behave similarly. In this work we have plotted the RBF rather than log RBF to accentuate deviations from a regular relationship.

Figure 1 shows a plot of RBF against log *p* for individual PCB's containing from three to eight chlorines, i.e., Arochlors 1242, 1254, and 1260. In aquarium experiments this general pattern was consistently exhibited for polychaetes and sea mullet at a variety of concentrations as shown in previous work (13). The same general pattern was also found with isolates from the same organisms collected in the field from PCB-contaminated areas. There is a systematic, but not linear, distribution of the points which exhibit a maximum bioaccumulation for Arochlor 1254 containing mainly pentachlorobiphenyls with some hexachlorobiphenyls (13).

Uptake and bioaccumulation involve the movement of a lipophilic molecule through an external membrane to the organism interior. Internal organism structure is complex, and the molecule would have to be partitioned between polar, aqueous, and nonpolar phases in the uptake and movement process. Accordingly Hansch and Fujita (14) have stated that it will be more complex than simple partitioning since accompanying it will be many adsorption-desorption steps at surfaces.

Thus, it is suggested that the log *p* function is a measure of partition between polar and nonpolar phases and is a representation of lipophilicity alone. But uptake and bioaccumulation of PCB molecules are influenced by characteristics related to adsorption-desorption processes as well as lipophilicity. As outlined below the former characteristic leads to the deviations from linearity shown in Figure 1.



TABLE I. Revised Coefficients for Different Chlorine Substitution Patterns Used To Calculate the Steric Effect Coefficient (SEC)

description	structure	coefficient
three chlorines in the 2-, 2', 6-positions		0.80
four chlorines in the 2-, 2', 6-, 6'-positions		0.60
two chlorines in the 2-, 6- or 2', 6'-positions		0.85
four chlorines adjacent		0.80 (1 ring) 0.60 (2 rings)
three chlorines adjacent		0.95 (1 ring) 0.90 (2 rings)
chlorines in 3- or 5-positions if adjacent to chlorine in 2- or 6-position		0.95 (1 in molecule) 0.90 (2 in molecule) 0.85 (3 in molecule) 0.80 (4 in molecule)
chlorines in 3- or 5-positions not adjacent to chlorine		subtract 0.02 from SEC for each chlorine in this configuration
no chlorines in the 2-, 2', 6-, 6'-positions		SEC is 1 irrespective of substitution pattern

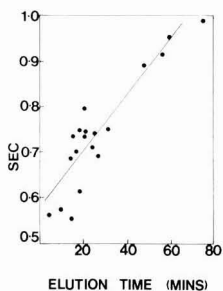
**Influence of PCB Stereochemistry on Uptake and Bioaccumulation.** The deviation from linearity of plots of log BCF vs. log  $p$  has been noted before. Tulp and Hutzinger (9) have stated that there is apparently an optimal steric configuration and molecular size for processes such as membrane passage. They have suggested several parameters which may be suitable to measure these factors: molar volume, molar refractivity, and parachor. In fact, a linear correlation has been found to exist between BCF and parachor for eight compounds with widely differing structures (9). We have found, however, that parachor places too much emphasis on the number of chlorine substituents on the biphenyl rings and gives too little weight to the position of the chlorine atoms. Kenaga (15) has developed equations relating log BCF to log  $p$  but has stated that these equations may be invalid for compounds that do not penetrate well through tissues.

Matsuo (16, 17) has related accumulation of organic chemicals by fish to interactions between the chemical and fish tissue involving hydrogen bonding and van der Waals forces. The bioaccumulation is determined by the affinities of the compound to fish and to water. Matsuo (16, 17) has developed  $\sum i$  and  $\sum o$  parameters to quantitatively describe the amount of superimposition between a compound and fish tissue by a consideration of the polar and nonpolar areas of the molecule. He has found that some PCB's deviate from the relationship because of twisting out of plane of the biphenyl rings causing less interaction with tissue surface. It would be expected that this out of plane twisting would reduce adsorption at a surface. Matsuo (18) has also found that in determining bioaccumulation of chlorinated benzenes, hexachlorobenzene is accumulated to a comparatively low extent. This was ascribed to the interaction of the six chlorines which force the ring into a nonplanar configuration and prevent the molecule from efficient interaction with fish tissue.

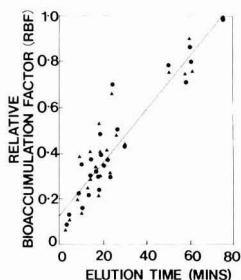
In previous work (12, 13) we developed a steric effect coefficient (SEC) as a measure of the influence of steric

factors on uptake and bioaccumulation of PCB's. It is obtained by using an empirically estimated set of coefficients representing different patterns of chlorine substitution (see Table I). The SEC for a compound is calculated by multiplying together the coefficients corresponding to those substitution patterns which appear in the molecule. For example, 2,2',3,3',4,5,5',6'-octachlorobiphenyl has an SEC of  $0.8 \times 0.8 \times 0.85$ , i.e., 0.54 (see Table I). The SEC had a linear relationship to the relative uptake (referred to here as the RBF) within groups of PCB isomers. But with all PCB's the product of log  $p$  and the SEC provided a more satisfactory measure of bioaccumulation except for the tri- and tetrachloro compounds which had a lower RBF than that predicted. With all of these substances an SEC of unity was calculated, but in fact, the degree of chlorination has an effect on adsorption properties with adsorption generally decreasing with decreasing chlorination (19). Nevertheless, these results and those from previous work (13) indicate that stereochemistry is a significant factor influencing bioaccumulation but do not give a clear indication of its function in the bioaccumulation process.

**Adsorption Characteristics of PCB's.** Chromatography using activated carbon has the capacity to separate chlorinated aromatic hydrocarbons on the basis of molecular planarity and to some extent the degree of chlorination and can provide a direct measurement of the degree of surface adsorption and these compounds. This method has been used previously to separate PCB's into classes depending on the amount of twisting out of plane of the biphenyl rings (20, 21). In addition, polychlorinated dibenzodioxins are separated according to degree of planarity (19). In contrast Huckins et al. (21) found that Florisil and silica gel were not successful for the separation of aromatic hydrocarbons exhibiting different degrees of planarity because these separations depend primarily on solute polarity rather than strength of adsorption to the chromatographic adsorbent.



**Figure 2.** Relationship between SEC and elution time of PCB's on charcoal. Equation to the line of best fit:  $SEC = 0.0062 \times \text{elution time} + 0.58$ , significant at the 0.001 level.



**Figure 3.** Relationship between relative bioaccumulation factors and elution times of PCB's on charcoal for polychaetes (●) and mullet (▲) in aquarium experiments. Equation to the line of best fit:  $RBF = 0.012 \times \text{elution time} + 0.13$ .

The relationship between elution time by HPLC on charcoal and our empirically developed steric effect coefficient (SEC) was evaluated. A strong correlation (significant at the 0.01 level) was found. However, five gas chromatographic peaks due to 2,2',5', 2,2',4', 2',3,4', 2,4,4', 2',3,3', and 2,2',3'-trichlorobiphenyl and 2,3',4',5-tetrachlorobiphenyl, individually or in mixtures, had elution times of about 15 min and SEC's of about 0.95. These did not fit the correlation well, probably due to the difficulties in calculating accurate relationships with mixtures, further factors not accounted for in the SEC calculation, or other factors. Figure 2 shows the relationship between elution time and SEC without the five points mentioned above. This relationship is significant at the 0.001 level. This suggests that the SEC is in fact an estimation of adsorption strength on the charcoal surface.

Figure 3 shows the relationship between RBF's of PCB's with mullet and polychaetes and corresponding retention times on the charcoal column (significant at the 0.001 level), demonstrating that adsorption characteristics alone have a significant effect on bioaccumulation. The SEC provides an approximate evaluation of adsorption based on structural characteristics but has some limitations, particularly with tri- and tetrachloro compounds as outlined previously.

**Relationship between Adsorption, Stereochemistry, Bioaccumulation, and Uptake.** The RBF's are considered to result from competitive uptake and depuration processes. However, the RBF's with polychaetes and mullet were constant during the exposure period when considerable variation in relative rates of uptake and depuration would be expected. Since the major depuration processes of metabolism and excretion are very slow in fish (12), depuration was not considered to be a significant influence on the RBF's. Accordingly these would be expected to reflect uptake factors.

During uptake the adsorption process is caused by hydrogen bonding and specific van der Waals forces operating between the molecule and adsorbent surface (22). For maximum interaction a close spatial relationship is required. This interaction and consequently adsorption will be diminished if the groups involved are held apart by distortion out of plane of the PCB molecule. In addition the distribution of electrons and hence the resonance of the molecule are affected by positional placement of the electron-withdrawing chlorine atoms on the biphenyl rings, thus affecting van der Waals attractions between PCB molecules and adsorbent surfaces.

The SEC was based on the assumption that uptake, and consequently bioaccumulation, was hindered by three structural features of the PCB molecules, namely, (a) the presence of three or four chlorine atoms in ortho positions, (b) the presence of three or four chlorine atoms adjacent on a phenyl ring, and (c) chlorine atoms in the three- and five-positions. The magnitude of the effects is in the order  $a > b > c$ .

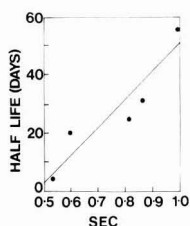
It is well-known (19, 20, 23) that increasing ortho chlorine substitution in PCB's increases the angle of twist between rings, thus reducing the planarity of the PCB's. The angle of twist for 2,2',4,4',6,6'-hexachlorobiphenyl was found to be 87.3°.

Substitution of biphenyls with electron-withdrawing substituents such as chlorine reduces the resonance of the structure, thus weakening the phenyl-phenyl bond (25). The distortion of individual phenyl rings is also likely in a situation where three, four, or more chlorine atoms are adjacent. Matsuo (8) has observed the distortion of the aromatic ring in the more highly chlorinated benzenes, resulting in decreased bioaccumulation. The positioning of chlorine atoms in the three- and/or five-positions promotes a "buttressing" effect if adjacent to chlorine atoms in the 2- and 6-positions (26). This reduces the extent to which ortho substituents can bend back at the equilibrium position; thus the dihedral angle between the rings is greater than if the 3- and 5-positions are not substituted.

It has been previously shown in this work that the adsorption characteristics influencing uptake can be measured by chromatographic behavior on charcoal. Thus, analysis of the stereochemical features influencing this behavior was carried out. In addition to the three structural features outlined above, it was recognized that the presence of two ortho chlorines on the same phenyl ring is significant in causing reduced adsorption. In this case it is believed that the long molecular axis running through the phenyl-phenyl bond is bent out of plane because of reduced phenyl-phenyl bond strength caused by a reduction in resonance between the phenyl rings due to the electron-withdrawal effect of the ortho chlorine atoms (27). The coefficients previously developed for the SEC (12) were revised in accord with the discussion above and are shown in Table I.

Studies by other workers with related compounds also indicate that the planarity of the molecules affects uptake. Matsuo (18) found that hexachlorobenzene uptake by guppies was less than expected and suggested that this was due to nonplanarity of the benzene ring caused by the six adjacent chlorines. Jan and Josipovic (28) found that the order of uptake of chlorinated biphenyls from the Aroclor 5640 mixture is para > meta > ortho. Spectral evidence showed that the ortho-substituted isomers exist in a twisted conformation, causing decreased resonance between the rings.

The half-lives of some hexachlorobiphenyls in mice (29) correlate well with the revised SEC ( $r = 0.95$ ) shown in



**Figure 4.** Relationship of the half-lives of hexachlorobiphenyl in mice to the SEC using half-life data from Mizutani et al. (29). The equation to the line of best fit is  $\text{half-life} = 96 \times \text{SEC} - 45$ .

Figure 4. It was suggested that the half-lives are determined by the rate of release from body fat mass rather than metabolism except for 3,4,5,3',4',5'-hexachlorobiphenyl which is unusual in that it has no ortho chlorine. In this instance no buttressing effect occurs as the chlorine atoms in the 3- and 5-positions cause no increase in dihedral angle due to the lack of chlorine in the 2- and 6-positions.

**Influence of Partition Coefficient and Adsorption on Uptake.** The 1-octanol/water partition coefficient ( $p$ ) is an operational representation of what is termed "hydrophobic bonding". When an organic molecule is in solution, a loose envelope of water molecules forms around it (30). In partitioning from an aqueous phase into a nonpolar phase, the orderly shell of water molecules disintegrates, resulting in exchange of entropy which forms the driving force for the partition (18). Thus, the  $\log p$  term gives a measure of the capacity of a molecule to pass from aqueous to nonpolar phase.

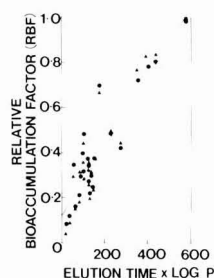
In organisms this process involves passage through a membrane separating the phases. Thus, to obtain a more accurate representation of uptake by organisms, the two factors mentioned above need to be taken into account.

The SEC (see Table I) can be used to derive an evaluation of membrane adsorption and passage characteristics from chlorine substitution patterns, and the product of SEC and  $\log p$  provides a measure of relative uptake and bioaccumulation of the PCB's. The equation to the line of best fit between these characteristics is  $\text{RBF} = 0.25(\log p \times \text{SEC}) - 0.75$  with a correlation coefficient  $r = 0.86$  (0.001 significance). However, a more accurate measure of RBF can be obtained from the elution behavior on carbon. A graph of the RBF's against corresponding products of elution time by  $\log p$  is shown in Figure 5 and exhibits a correlation coefficient of  $r = 0.97$  (significant at the 0.001 level).

The bioaccumulation pattern shown in Figure 1 is clarified by this information. In organisms, although steric factors enhance uptake, the concentrations of the PCB's containing two to five chlorine atoms are low due to comparatively unfavorable partition coefficients. Thus, compounds containing five to seven chlorines have partition characteristics favorable to uptake, and many, but not all, have suitable adsorption behavior. Those with chlorine numbers between 7 and 10 have suitable partition coefficients but are generally inhibited from uptake by unfavorable stereochemistry and adsorption characteristics. Therefore, these substances produce lower uptake and bioaccumulation characteristics than those predicted from the partition coefficients.

### Conclusions

Uptake and bioaccumulation of PCB's involve not only partition between lipids in the organism and the surrounding water but also surface adsorption on and passage



**Figure 5.** Relationship of relative bioaccumulation factor to the product of elution time and  $\log p$  exhibited by polychaetes (●) and mullet (▲) in aquariums.

through membranes. The SEC provides a measure of the strength of surface adsorption.

The SEC's developed in previous work (12, 13) were found to be related to the planarity of the PCB molecules as measured by chromatographic adsorption behavior on carbon. In fact, the elution times on charcoal were believed to provide a measure of the capacity of the molecules to be adsorbed on and pass through membranes. This measure alone gives a good correlation with the uptake and bioaccumulation of the PCB's by mullet and polychaetes. By use of data from the carbon chromatography, the SEC coefficients were revised, which now allows accurate evaluation of the stereochemical effects of different chlorine substitution patterns on uptake and bioaccumulation.

When the elution times on carbon and  $\log p$  were used, an accurate measure of the RBF's of the various PCB's was obtained. Optimum PCB uptake and bioaccumulation were observed with PCB's having from five to seven chlorine atoms. Those with less chlorines had less favorable partition coefficients while those with higher chlorines had unfavorable SEC values.

These results provide an explanation for the unexpectedly low uptake and bioaccumulation of PCB's with comparatively high numbers of chlorine substituents and indicate that PCB stereochemistry is an important factor in uptake by organisms. The results suggest that membrane passage, not previously quantitatively considered, may be an important uptake process. However, this latter conclusion requires future confirmatory work.

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## Retrospective Analysis of the Response of Saginaw Bay, Lake Huron, to Reductions in Phosphorus Loadings<sup>†</sup>

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■ A retrospective analysis was conducted of the response of Saginaw Bay, Lake Huron, to a substantial reduction in external phosphorus loadings over the study period 1974-1980. Loadings to Saginaw Bay from the Saginaw River for total phosphorus and dissolved ortho phosphorus were 55% and 72% lower, respectively, in 1980 than in 1974. In the most seriously degraded area of the bay, spring and fall total phosphorus concentrations decreased by 1% and 14%, respectively, while chlorophyll *a* concentrations decreased by 53% and 61% in the same seasons. The corresponding decreases for inverse Secchi depth were 0% and 17%. Sediment resuspension due to wind-induced wave action was the probable cause for the anomalous relationship between chlorophyll *a* and total phosphorus concentrations, and the lack of response of inverse Secchi depth. A substantial decrease in threshold odor observed in the municipal water supply during the study period was correlated with a decrease in blue-green dry weight biomass concentration. This change, however, was poorly correlated with blue-green cell number, total phytoplankton dry weight biomass, or chlorophyll *a* concentrations.

### Introduction

Control of phosphorus inputs to lakes is one of the principal means for attempting to reverse the symptoms

of cultural eutrophication. Cultural eutrophication, here defined as overproduction of phytoplankton biomass caused by increased anthropogenic nutrient inputs, may lead to increased turbidity, aesthetic nuisances, and dissolved oxygen depletion in hypolimnetic waters. It may also lead to filter-clogging, taste, and odor problems in water supplies.

The Federal Water Pollution Control Act Amendments of 1972 (P.L. 92-500) provided the impetus on a national scale for improved phosphorus control from municipal point sources. Within the Great Lakes Basin, the 1972 Water Quality Agreement (WQA) between the United States and Canada contained the provision for a 1 mg/L total phosphorus concentration limit on all point sources discharging greater than 1 million gal/day (3800 m<sup>3</sup>/day) in the Lake Erie and Ontario basins. The 1978 WQA extended this provision to include the entire Great Lakes Basin and, in addition, contained provisions for diffuse source phosphorus control for Lakes Erie and Ontario and for Saginaw Bay, Lake Huron.

The implementation of phosphorus controls is sufficiently advanced in a number of areas that it is now possible to assess its effects. Such studies are important because large sums of money have been spent to upgrade existing wastewater treatment plants and to construct new plants. Since 1972, the U.S. and Canada have spent or committed more than \$6.65 billion for municipal wastewater treatment plants in the Great Lakes Basin alone (1). From a management perspective, it is important to determine if phosphorus control strategies are effective and if they produce the expected benefits. From a research perspective, it is important to understand the relationship between changes in phosphorus inputs and observed lake responses.

Results from prior retrospective studies of lake responses to phosphorus load reductions have been mixed. In general, for lakes where substantial reductions in total external

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loads were attained, and where no significant internal sources existed, results indicated substantial improvements over the course of several hydraulic detention times (2-4). In other cases, either lakes did not respond or the responses were varied (5-9). In these cases, it was generally found that substantial reductions in point source phosphorus loads resulted in only small decreases in total phosphorus loads or that internal phosphorus sources were important, especially during late summer. Indeed, Gakstatter et al. (10) pointed out that an effluent concentration standard of 1 mg/L for total phosphorus, by itself, may have only a limited impact on eutrophication problems because of the relatively high proportion of nonpoint source loadings to many lakes.

In the Great Lakes, responses to reductions in phosphorus loads are difficult to determine because of the large spatial and temporal scales involved. The problem of natural variability which occurs in all lake systems is compounded by the difficulty and cost of obtaining a sufficient number of measurements to identify trends. Lake Ontario appears to have shown the most substantial response on a whole lake scale in terms of spring total phosphorus concentration (11). In Lake Erie, total phosphorus concentrations appear to have declined in the western and central basins, but not in the eastern basin (1). Chlorophyll *a* concentrations, however, do not appear to have declined in any of the three basins. In contrast to the whole lake scale, real and substantial improvements in water quality have occurred in certain nearshore areas in both lakes (12, 13).

The purpose of this paper is to describe the observed responses of Saginaw Bay, Lake Huron, to a substantial reduction in external phosphorus loadings over the period 1974-1980. During the study period, measurements of loadings and responses were sufficiently intensive to provide a basis for identification of trends. Phosphorus loadings were analyzed in terms of changes due to point source controls, as well as to variations in tributary flow rates. Responses were analyzed in terms of phosphorus and chlorophyll *a* concentrations, inverse Secchi depth, and threshold odor in the principal municipal water supply. Attempts were also made to relate threshold odor to various measures of phytoplankton abundance, including chlorophyll *a*, and phytoplankton cell number and dry weight biomass concentrations.

### Background

Saginaw Bay is a broad, shallow extension of the western shore of Lake Huron (Figure 1). The bay is oriented in a southwestward direction and is approximately 85 km long and 42 km wide, and the total area of the Saginaw Bay watershed is approximately 21 000 km<sup>2</sup>. The Saginaw River is the major tributary, accounting for over 90% of the total tributary inflow to the bay. The principal land use categories in the watershed are agriculture and forest. The total population of the watershed is slightly over 1.2 million, most of it concentrated into four major urban-industrial centers in the State of Michigan: Bay City, Midland, Saginaw, and Flint. These centers are all situated along the Saginaw River or its major tributaries.

The principal water uses in Saginaw Bay include municipal and industrial water supply, waterborne transportation, recreation, commercial fishing, and waste assimilation. These have been severely impacted by waste discharges and runoff inputs, and the bay has consequently been identified by the International Joint Commission (IJC) as one of the Great Lakes Areas of Concern (1).

The principal results of eutrophication in Saginaw Bay were adverse taste and odor and filter-clogging problems

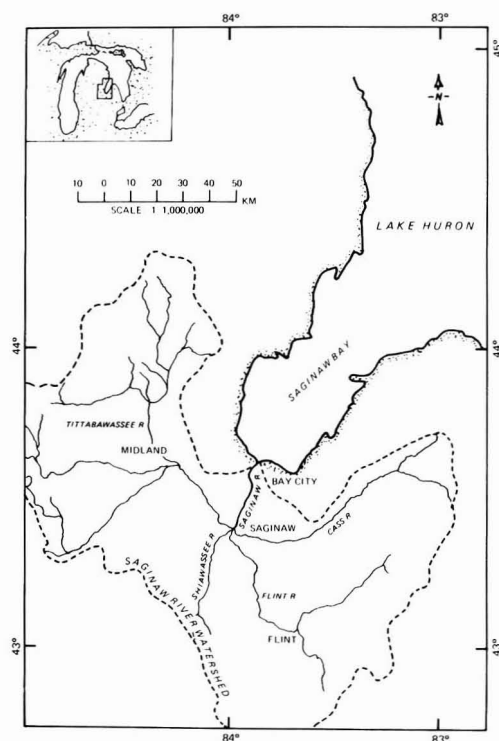


Figure 1. Saginaw Bay and the Saginaw River river system.

experienced by municipal water treatment plants. On the basis of daily measurements at the Saginaw-Midland water supply system (14), 42% of the threshold odor values in 1974 were found to be equal to or greater than the U.S. Public Health Service (USPHS) standard. Threshold odor is defined as the ratio by which a sample needs to be diluted so that taste and odor are just detectable (15). Statistical analyses of these data (16) revealed a strong correlation between threshold odor number and phytoplankton cell number concentration in the raw water supply, particularly for the blue-green component of the total crop.

Comprehensive base-line surveys were conducted on Saginaw Bay in 1974 and 1975 as part of the Upper Lakes Reference Study sponsored by the IJC, and less intensive monitoring studies were conducted during 1976-1979. When it became apparent that there had been a substantial reduction in phosphorus loadings to the bay, a comprehensive resurvey was conducted in 1980. The objectives of the resurvey were to assess the effects of the loading reduction and to provide a data base for testing predictions of several mathematical models used to develop the target phosphorus load to the bay for the 1978 WQA (17).

### Data Base

During 1974-1980, an extensive data base was acquired on Saginaw Bay for a large number of physical, chemical, and biological parameters. A total of 62 sampling stations was established in the bay proper and in the lower Saginaw River. A total of 93 sampling cruises was conducted during the study period at intervals of 2-3 weeks between April and December of each year. This effort was coordinated by the Large Lakes Research Station of the U.S. Environmental Protection Agency and involved close cooper-

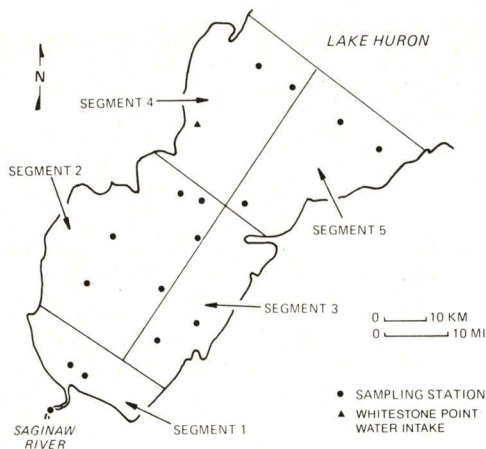


Figure 2. Location of sampling stations used for analysis of 1974–1980 trends.

ation among several different institutions and organizations.

Cranbrook Institute of Science was the lead organization for sample collections and for conducting water chemistry and chlorophyll analyses. A complete discussion of methods and results for the intensive surveys in 1974 and 1975 is given by Smith et al. (18). Phytoplankton samples were collected and analyzed by the Great Lakes Research Division, University of Michigan (19). This work was conducted only during 1974–1976 and again in 1980. Analyses included determination of cell number and cell volume concentrations. Canada Centre for Inland Waters conducted analyses for nutrients and chlorophyll in 1980, and Ohio State University conducted analyses for total phosphorus in 1978–1979. Other principal sources of data included the U.S. Geological Survey for tributary flow rates, the Michigan Department of Natural Resources for supplemental tributary monitoring and information on municipal point sources, and the Saginaw–Midland water supply system for daily records of threshold odor during the study period.

Total phosphorus loading from the Saginaw River was determined by linear interpolation of the available daily average loading rate data. Flow rate measurements were available on a daily basis, and concentration measurements for total phosphorus were usually available 5 days/week. The exception was 1977, when total phosphorus concentrations were available only twice monthly. Concentration measurements for dissolved ortho phosphorus were available only approximately 15 days/year, from April to December, for 1974–1976 and 1980. The dissolved ortho phosphorus loads for each year, and the total phosphorus load for 1977, were determined by using the stratified ratio estimator technique given by Dolan et al. (20).

A 15-station subset of the complete 62-station network was used to conduct analyses of responses to loading reductions (Figure 2). This subset contained the largest number of stations in the bay that was sampled continuously over the study period. It also constituted a representative group of stations in terms of assessing water quality. The bay was divided into five spatial segments (Figure 2) on the basis of observed gradients in water quality. Segments 1–3 constitute the inner portion of the bay, and segments 4 and 5 constitute the outer portion. Although these portions are approximately equal in surface area, only 30% of the total water volume is contained in

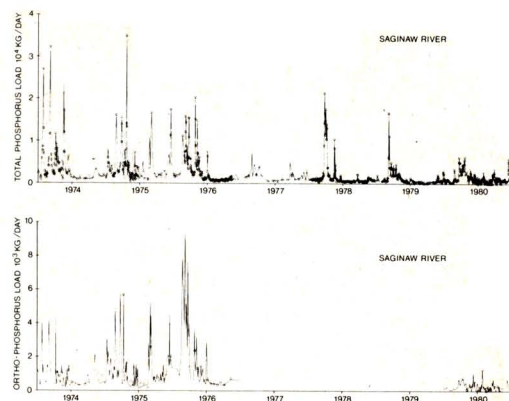


Figure 3. Saginaw River phosphorus loads for the period 1974–1980.

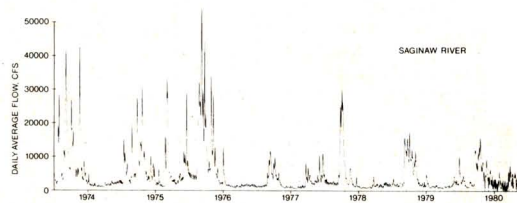


Figure 4. Saginaw River flow rates for the period 1974–1980.

Table I. Total Phosphorus Loads and Flow Rates for Saginaw River, 1974–1980

year	total phosphorus load, mta	annual average flow, m <sup>3</sup> /s	proportion of historical average flow
1974	1044	165	1.45
1975	1267	191	1.67
1976	937	191	1.67
1977	511	81	0.71
1978	595	94	0.82
1979	409	97	0.85
1980	472	104	0.91

the inner portion because of differences in depths. Average depths of the inner and outer portions are approximately 6 and 15 m, respectively.

#### Trends in Phosphorus Loadings

Interpretation of trends in Saginaw River phosphorus loadings during the study period was confounded by the simultaneous effects of wastewater treatment plant upgrades, variations in annual flow rates, and the imposition of a detergent phosphorus ban in the State of Michigan in Oct 1977. On examination of the loading time series for total phosphorus and dissolved ortho phosphorus (Figure 3), it is apparent that a substantial loading decrease actually occurred. Consideration of the corresponding Saginaw River flow rates (Figure 4) indicated that reductions in phosphorus loadings from diffuse sources were probably responsible for a large proportion of the total reduction. Because no control measures were taken on diffuse sources in the basin, phosphorus loadings from these sources could be expected to depend on the magnitude and timing of the Saginaw River flow rates. During the study period, the annual average Saginaw River flow rate varied from a high of 67% above historical average to a low of 29% below historical average. Table I contains a summary of phosphorus loads and flow rates for each

year of the study. Loads for total phosphorus and dissolved ortho phosphorus in 1980 were 55% and 72% lower, respectively, than in 1974.

To confirm that the Saginaw River phosphorus loadings decreased significantly, independent of flow effects, a multiple regression analysis of loading trends was conducted. Daily average total phosphorus loads were regressed against daily average flow rates and time. A total of 953 pairs of concentration and flow measurements was used. Measurements for days on which flow rates were greater than 425 m<sup>3</sup>/s were not included in the regression because they corresponded to storm events which would have distorted the flow-time relationship.

The following regression equation was obtained:

$$\text{load} = 771 + (0.135 \times 10^{-3})\text{flow} - (0.345)\text{time} \quad r^2 = 0.88 \quad (1)$$

where load = daily average total phosphorus load (kg/day), flow = daily average flow rate (m<sup>3</sup>/day), and time = number of days from Jan 1, 1974. Loading was found to be significantly related to flow ( $p < 0.01$ ). With flow in the equation, however, loading was also found to be significantly related to time at the same probability level. Higher order terms in flow and time were subsequently included in the regression; however, they were not found to be significant, and an examination of residuals did not reveal any noticeable pattern.

The estimated time coefficient of 0.345 in eq 1 can be interpreted to mean that phosphorus loadings decreased over the 7-year period at an average rate of 0.345 kg/day each day. This corresponds to an overall reduction of 881 kg/day (0.345 kg day<sup>-1</sup> day<sup>-1</sup> × 2555 days) or a reduction of 322 metric tons per annum (mta) over the entire period. Because the loading reductions explained by flow were accounted for by the flow term in eq 1, 322 mta represents the decrease in phosphorus loadings attributable to point source controls. This decrease accounted for 56% of the total decrease in annual loading between 1974 and 1980.

Attempts to separate point source phosphorus loading reductions into components due to wastewater treatment plant upgrades and the detergent phosphorus ban were unsuccessful. Using flow and concentration measurements from 58 major plants in Michigan, Hartig and Horvath (21) compared pre- and postban conditions and concluded that the ban resulted in an average decrease of 24% in total phosphorus effluent rates. Unfortunately, data for the Flint wastewater treatment plant, the largest single point source in the Saginaw River watershed, were not available for their study. Our multiple regression analysis of the Saginaw River loadings failed to reveal a significant change in the time coefficient at Oct 1977. Accordingly, the effect of the detergent phosphorus ban could not be identified in the river mouth loading data.

#### *Trends in Water Column Response Parameters*

The response of Saginaw Bay to phosphorus load reductions was analyzed in terms of total phosphorus and chlorophyll *a* concentrations and inverse Secchi depth. Phosphorus and chlorophyll are the most widely used indicators of trophic state in lakes. Inverse Secchi depth can also be useful because it is directly proportional to light extinction in the water column (22, 23), which is related to turbidity due to dissolved organic materials, chlorophyll, and other suspended particulate materials. Dissolved oxygen was not considered as a response parameter because the bay remained aerobic during the entire study period.

Analysis and interpretation of trends in water quality data can be confounded by many different factors. All

three of the response parameters can be influenced by physical, chemical, and biological processes, independent of changes in phosphorus loadings. Another important consideration is the identification of appropriate space and time scales. With regard to spatial scale, the present analyses were conducted separately for the inner and outer portions of the bay. This segmentation was used because these portions were dominated by different processes, and their water quality characteristics were somewhat distinct. The inner bay was directly influenced by loading from the Saginaw River and contained the most seriously degraded water in the bay. The outer bay was more strongly influenced by exchanges with the oligotrophic waters of Lake Huron.

The data were aggregated into operationally defined spring (April-June) and fall (August-October) seasons, which were consistent with the characteristic hydrological and productivity cycles observed in the bay. The spring data tended to reflect the consequences of high and variable input loadings due to snowmelt and peak runoff and colder temperatures, while fall data tended to reflect the consequences of lower and reasonably stable input loadings and higher temperatures. These two seasons tended to be uncoupled in the bay because they were generally separated by a period of very rapid hydraulic flushing in late June, prior to establishment of a stable summer-fall circulation pattern (24).

In our analysis, data from the individual sampling stations were aggregated over space and/or time by using the median as the primary measure of central tendency, instead of the arithmetic mean. This more robust measure was found to be necessary because the data were not always normally distributed. The reason for nonnormality was not clear but perhaps was related to the exponential character of biological growth processes.

As a first approach, median values for the three response parameters were calculated for each sampling cruise for the inner bay (Figure 5). A downward trend over the period appeared likely for chlorophyll *a* but was not obvious for total phosphorus or inverse Secchi depth. The 1980 values for total phosphorus appeared to be lower than the 1974 values; however, there appeared to be a slight increase in the middle years 1976-1978. Chlorophyll *a* concentrations appeared to decrease substantially over the period for both the spring and fall, but there was no apparent trend in inverse Secchi depth. For all three parameters, variability in the data was sufficiently great that graphical techniques alone were not sufficient to clearly identify trends.

The first statistical approach used to identify trends was a two-way ANOVA, in which time and sampling station were treated as independent variables in order to identify possible trends in time by removing variability associated with stations. This analysis was conducted separately for both the inner and outer portions of the bay. Results of the analysis indicated statistically significant differences among stations, as well as over time. However, a linear decrease was found only for chlorophyll *a* concentration over the study period. This trend was significant ( $p < 0.01$ ) for both seasons, and in both spatial segments. No such linear decreases were found for total phosphorus concentration or inverse Secchi depth.

Seasonal average values for the three response parameters in the inner bay are contained in Table II. These values represent seasonal averages of the individual station medians for the given season. It is clear that chlorophyll *a* concentration decreased substantially. Total phosphorus concentration and inverse Secchi depth both increased

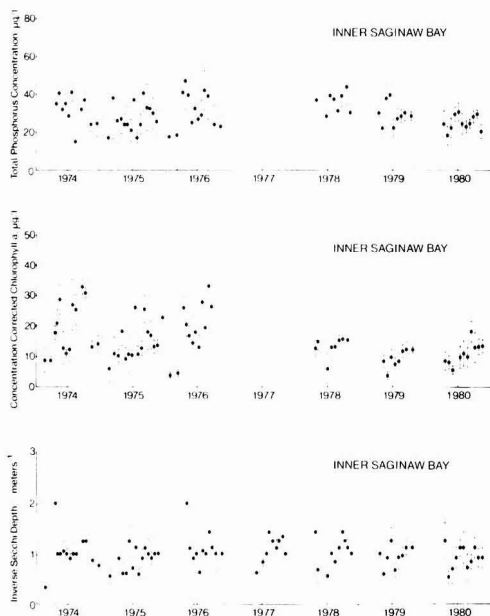


Figure 5. Saginaw Bay responses in terms of total phosphorus and chlorophyll *a* concentrations, and inverse Secchi depth, for the period 1974–1980.

Table II. Seasonal Average Water Quality Parameters for Inner Saginaw Bay, 1974–1980

year	total phosphorus concn, µg/L		chlorophyll <i>a</i> concn, µg/L		inverse Secchi depth, m <sup>-1</sup>	
	spring	fall	spring	fall	spring	fall
1974	30.5	29.3	20.6	29.1	0.92	1.05
1975	35.4	27.3	19.5	19.9	0.77	0.89
1976	41.2	40.9	18.6	26.4	1.28	1.19
1977					0.72	1.28
1978	47.3	34.8	14.0	14.1	1.02	1.07
1979	37.3	27.7	8.1	12.4	0.92	1.05
1980	26.8	24.8	12.2	12.2	0.86	0.86

during the middle years and then declined to values in 1980 that were somewhat lower than the 1974 values. Seasonal average values for total phosphorus and chlorophyll *a* concentrations were never less than 24 and 8 µg/L, respectively.

Results of all trend analyses for phosphorus loads and the three response parameters in both the inner and outer bay are summarized in Table III. Results are expressed in terms of percent decreases in each quantity over the study period, as determined from the respective regressions. The most notable feature of the results was the disproportionate response of total phosphorus and chlorophyll *a* concentrations in the inner bay. Over the period 1974–1980, spring and fall total phosphorus concentrations decreased by 1% and 14%, respectively, while chlorophyll *a* concentrations decreased by 53% and 61% in the same seasons. The corresponding decreases for inverse Secchi depth were 0% and 17% during the study period. It appeared that the reduction in external phosphorus loadings resulted in a decrease in chlorophyll *a* concentrations in the inner bay but had little effect on total phosphorus concentrations or inverse Secchi depth.

In the outer bay, spring total phosphorus concentrations decreased by 51%, but fall total phosphorus did not de-

Table III. Percent Decreases<sup>a</sup> in Selected Water Quality Parameters in Saginaw Bay, 1974–1980

parameter <sup>b</sup>	spring	fall
total phosphorus concentration		
inner bay	1	14
outer bay	51	0
chlorophyll <i>a</i> concentration		
inner bay	53	61
outer bay	53	0
inverse Secchi depth		
inner bay	0	17
outer bay	26	0

<sup>a</sup> Determined from the respective regression equations.

<sup>b</sup> Decrease in annual total phosphorus load = 56%.  
Decrease in annual dissolved ortho phosphorus load = 72%.

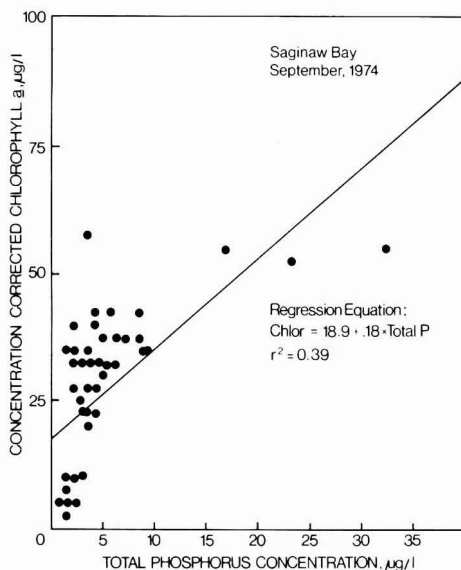


Figure 6. Results for linear regression of chlorophyll *a* concentrations vs. total phosphorus concentrations for Sept 1974.

crease. Similarly, spring chlorophyll *a* concentrations decreased by 53%, but fall values did not decrease. The response of inverse Secchi depth was intermediate between the responses of total phosphorus and chlorophyll *a*. The general lack of response in the fall may have been due to the typical high spring distribution of the Saginaw River input loadings and the influence of water exchange with Lake Huron.

The apparent uncoupling of total phosphorus and chlorophyll *a* concentrations prompted an attempt to determine the degree to which these variables were correlated in the bay. Two different approaches were used for aggregating the data in time: first, maximum fall chlorophyll *a* concentrations were regressed against spring cruise median total phosphorus concentrations; second, all possible combinations and permutations of fall cruise median chlorophyll *a* concentrations and spring and fall cruise median total phosphorus concentrations were regressed. All existing pairs of chlorophyll *a*–total phosphorus concentrations from each sampling station during the 1974 intensive survey were used.

The regression analysis with the highest correlation coefficient ( $r^2 = 0.39$ ) was obtained by using data from the Sept 1974 sampling cruise (Figure 6). Only 39% of the



Table IV. Seasonal Phytoplankton Concentrations in Segment 2, Inner Saginaw Bay

parameter	concentration, mg of dry weight/L							
	1974		1975		1976		1980	
	spring	fall	spring	fall	spring	fall	spring	fall
peak total algal concentration	8.00	2.47	9.87	4.42	19.6	3.32	0.630	1.39
peak diatom concentration	7.62	0.921	9.64	3.66	19.1	1.97	0.541	1.30
peak total blue-green concentration	0.217	1.29	0.387	0.863	0.066	0.59	0.043	0.027
percent blue-greens during blue-green peak	15.0	63.4	25.4	27.9	0.49	19.2	8.04	5.46
ratio of blue-green peak to total algal peak, %	2.71	52.2	3.93	19.5	0.34	17.7	6.82	1.94
no. of annual odor days (odor >3)	56		22		9		0	
maximum odor value	9		6		4		3	

variance in chlorophyll *a* concentration was explained by total phosphorus concentration. Since it appeared that this result was strongly influenced by the four data points corresponding to chlorophyll *a* concentrations greater than 50 µg/L, the regression analysis was repeated with these data points removed. The new regression indicated a higher correlation coefficient ( $r^2 = 0.51$ ). Although both of these regressions were statistically significant ( $p < 0.01$ ), the stronger of them explained only 51% of the variance in chlorophyll *a* concentration.

#### Taste and Odor in the Municipal Water Supply

One of the principal water quality issues on Saginaw Bay was adverse taste and odor in the Saginaw-Midland water supply system. Taste and odor are direct perceptions of water quality by the public and often lead to increased treatment costs required to remove them. Water from this system constitutes approximately 85% of the water drawn from Saginaw Bay for human use. The intake site is located at Whitestone Point in segment 4 of the outer bay (Figure 2).

We have attempted to determine whether the relationship between threshold odor and blue-green phytoplankton established earlier (16) could be extended from the raw water supply to blue-green phytoplankton concentrations in the bay itself. Paul (25) has shown that blue-green phytoplankton at the intake site originated from the inner bay and was transported to the site by episodic storm events. All of the available data for threshold odor and blue-green phytoplankton are shown in Figure 7. Threshold odor is presented as biweekly averages calculated from daily measurements, and blue-green phytoplankton represents cruise average concentrations for segment 2 in the inner bay. These data are presented in terms of cell number and by dry weight biomass concentrations calculated from cell volume measurements. We assumed that dry weight was 25% of wet weight and that cellular specific gravity was unity (26-29).

Our results indicated a decrease in threshold odor over the study period. Threshold odor exceeded the USPHS standard of 3 for an extended period during 1974 but did not exceed the standard at all in 1980. Peak values were confined to the fall season of each year. The available phytoplankton data indicated that blue-green concentrations were substantially lower in 1980 than in 1974. During 1974-1976, there appeared to be a decreasing trend in blue-green biomass concentration and an increasing trend in blue-green cell number concentration. This probably reflected a shift toward species with smaller individual cell volumes. The data suggested that threshold odor was more related to blue-green biomass than to blue-green cell numbers.

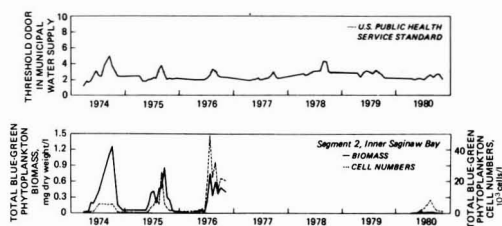


Figure 7. Comparison of threshold odor in municipal water supply and blue-green phytoplankton concentrations for the period 1974-1980.

A more detailed assessment of the relationship between threshold odor and phytoplankton concentration can be made by using the data contained in Table IV. During 1974-1976, annual peak total phytoplankton concentrations occurred during spring and consisted primarily of diatoms. Fall peak concentrations were much lower than spring peaks; however, they consisted of higher concentrations and higher relative proportions of blue-greens. In 1980, all phytoplankton concentrations were much lower in spring and fall. Both the concentration and the relative proportion of blue-greens were much lower in the fall of 1980 than in the fall of 1974. The number of days on which threshold odor exceeded the USPHS standard decreased from 56 in 1974 to 0 in 1980, and the annual maximum value decreased from 9 to 3. The apparent trends in both magnitude and timing suggested a relationship between threshold odor in the raw water supply and the concentration of blue-green phytoplankton in the bay.

To further investigate this relationship, a series of correlation analyses was conducted. Regressions of threshold odor number against 5 different measures of phytoplankton abundance for each of three different time periods were conducted. In each case, biweekly average threshold odor values were regressed against cruise average phytoplankton concentrations.

Results indicated that regressions of threshold odor against total phytoplankton concentration in terms of dry weight biomass and cell number were not significant ( $p > 0.05$ ) (Table V). Two of the three regressions involving chlorophyll *a* concentrations were statistically significant; however, the stronger of them was only able to explain 33% of the variability in threshold odor. In contrast, all of the regressions involving blue-green phytoplankton concentrations in terms of dry weight biomass and cell number were statistically significant. All three regressions involving dry weight biomass were able to explain greater than 50% of the variability in threshold odor. In the strongest of these, the 1974 blue-green dry weight biomass concentrations were able to explain 71% of the variability in threshold odor.

Table V. Results for Linear Regressions between Threshold Odor in Municipal Water Supply and Phytoplankton Concentrations in Segment 2, Inner Saginaw Bay

phytoplankton concentration parameter	time period	intercept, $B_0$	slope, $B_1$	(standard error of slope)	$r^2$	standard error of regression
total phytoplankton dry weight	1974	2.96	-0.14	(0.140)	0.084 <sup>a</sup>	1.03
	1974-1976	2.62	-0.044	(0.032)	0.050 <sup>a</sup>	0.72
	1974-1980	2.50	-0.028	(0.026)	0.024 <sup>a</sup>	0.66
cell number	1974	2.10	0.000077	(0.00008)	0.071 <sup>a</sup>	1.04
	1974-1976	2.32	0.000008	(0.00001)	0.023 <sup>a</sup>	0.73
	1974-1980	2.25	0.000010	(0.00001)	0.038 <sup>a</sup>	0.65
chlorophyll <i>a</i>	1974	1.33	0.079	(0.034)	0.326	0.89
	1974-1976	1.55	0.055	(0.019)	0.201	0.68
	1974-1980	2.21	0.026	(0.014)	0.056 <sup>a</sup>	0.67
blue-greens dry weight	1974	1.86	1.82	(0.035)	0.713	0.58
	1974-1976	1.92	1.64	(0.23)	0.587	0.48
	1974-1980	2.04	1.47	(0.20)	0.534	0.46
cell number	1974	2.13	0.00015	(0.00007)	0.296	0.91
	1974-1976	2.29	0.000022	(0.00001)	0.107	0.70
	1974-1980	2.27	0.000023	(0.00001)	0.118	0.63

<sup>a</sup> Regression not significant at  $\alpha = 0.05$ .

In general, the regressions which indicated the strongest correlations were those involving 1974 data. Each of these correlations tended to become weaker as data from other years were added to the regressions, because the range of additional threshold odor values became progressively more narrow, and the values themselves became smaller as water quality improved in the bay. In spite of this tendency, no statistically significant differences were found among the regressions of threshold odor against blue-green dry weight biomass concentrations for the three different time aggregations of the data. These results tended to confirm that blue-green biomass concentration in the inner bay was a good indicator for threshold odor in the municipal water supply.

### Discussion

Total phosphorus loadings to Saginaw Bay from the Saginaw River were 55% lower in 1980 than in 1974. Of this decrease, 56% was estimated to be due to reductions in point sources and 44% was due to reductions in tributary flow rates. These findings raise the possibility that phosphorus loadings could increase in the future if tributary flow rates increase, even if point sources remain under control. If such a loading increase occurs, it will probably lead to increased phytoplankton abundance in the bay. However, because nonpoint sources generally contain lower proportions of available phosphorus than municipal point sources (30), the magnitude of such an increase would be difficult to estimate. If flow rates increase in the future to the high levels observed in 1974-1976, the corresponding loading rates of available phosphorus would probably be lower than during this earlier period, provided that the present level of point source control is maintained.

Total phosphorus and chlorophyll *a* concentrations in Saginaw Bay were poorly correlated, compared with results for many other lakes (31-35). It might have been possible to obtain better correlations by aggregating the data differently in space or time and/or by including data from years other than 1974. Either of these approaches, however, would have resulted in using smaller ranges for the values of chlorophyll *a* concentration than the range used; consequently results of such regressions would have less meaning and potential utility. In any case, the purpose of the present analyses was not to exhaust all possible space-time aggregations of the data in a search for meaningful regression equations. The point is that processes

which occur in Saginaw Bay are sufficiently complex that simple analyses might not be as appropriate here as in other systems.

The anomalous relationship between chlorophyll *a* and total phosphorus concentrations suggested the existence of an unaccounted source of phosphorus loading. Further, it suggested that this source was not as available for phytoplankton growth as the Saginaw River phosphorus loadings. Circumstantial evidence indicated that particulate phosphorus due to sediment resuspension was responsible for confounding the chlorophyll *a*-total phosphorus relationship and that the sediment resuspension itself resulted in the lack of response of inverse Secchi depth. The principal depositional zone in Saginaw Bay is confined to the inner portion, primarily segment 2, and consists of fine grain silt-clay material (36). On the basis of correlations between turbidity and wind speed (25), wind-driven resuspension of particulate material was found to be a frequent occurrence. Dolan et al. (37) applied a dynamic mass balance model for total phosphorus to the data for 1974-1978 and compared the effects of two different mechanisms for sediment-water column exchanges. They concluded that a wind-dependent resuspension mechanism was required to successfully describe total phosphorus concentration in the water column. Particulate phosphorus from resuspended sediment is not in a form which is immediately available for phytoplankton growth (38). Apparently, the flux of this phosphorus from the sediment was sufficiently great to influence the water column concentration, but the average residence time in the water column was not sufficient for conversion of a substantial amount to an available form.

We have attempted in this study to describe the causal chain from reductions in phosphorus loadings, through reductions in blue-green phytoplankton biomass, to reductions in threshold odor in the municipal water supply. The precise nature of the causal linkage between blue-green phytoplankton and threshold odor is not well understood. Bratzel et al. (39) suggested that high threshold odor numbers appeared to be caused by the products of blue-green biomass decomposition by actinomycetes (aquatic fungi) and by the biomass itself. This was consistent with the present finding that threshold odor was better correlated with dry weight biomass concentration than with cell number concentration. Apparently, any species shifts that might have occurred in the bay as water

quality improved, either within the blue-green group or in any of the other groups, did not significantly change the relationship found between threshold odor and blue-green dry weight biomass. This result provides a basis for investigating similar relationships in other lakes.

The response of Saginaw Bay to phosphorus loading reductions which we report here was consistent with the rationale and objectives developed in support of the target phosphorus load to the bay for the 1978 WQA (17). The primary water quality criterion used in developing the target load was threshold odor at the Whitestone Point intake of the Saginaw-Midland water supply system. A secondary criterion was the degree of degradation of the inner bay ecosystem, as indicated by total phosphorus concentration. It was originally concluded that a total phosphorus load of 620 mta would result in minimal compliance (threshold odor  $\leq 3$ ) with the USPHS standard and in a total phosphorus concentration of 20  $\mu\text{g/L}$  in the inner bay. It was further concluded that a total phosphorus load of 440 mta would result in threshold odor values less than 3 and in a total phosphorus concentration of 15  $\mu\text{g/L}$ . The value of 440 mta was recommended as the target phosphorus load.

The total phosphorus load to the inner bay in 1980 was 569 mta. This included 472 mta from the Saginaw River (Table I) and 97 mta from minor tributaries and atmospheric sources (40). In 1980, threshold odor did not exceed a value of 3 (Table IV), and total phosphorus concentration in the inner bay was approximately 26  $\mu\text{g/L}$  (Table II). Thus, responses were consistent with the primary water quality objective involving threshold odor but fell short of the total phosphorus concentration objective. This may have been a consequence of the fact that none of the mathematical models used to develop the target load contained explicit wind-dependent mechanisms for describing sediment resuspension. On the basis of the present analysis, however, it is not clear that resuspended phosphorus is a valid indicator of ecosystem degradation because it is not readily available for phytoplankton production.

### Conclusions

Loadings to Saginaw Bay from the Saginaw River for total phosphorus and dissolved ortho phosphorus were 55% and 72% lower, respectively, in 1980 than in 1974. It was estimated that 56% of the total phosphorus loading decrease was due to point source controls and 44% was due to decreases in tributary flow rates. Attempts to separate point source loading reductions into components due to wastewater treatment plant upgrades and the detergent phosphorus ban were unsuccessful.

Total phosphorus and chlorophyll *a* concentrations in Saginaw Bay were found to be poorly correlated. Circumstantial evidence indicated that particulate phosphorus due to sediment resuspension was responsible for confounding the chlorophyll *a*-total phosphorus relationship and that the sediment resuspension itself resulted in the lack of response of inverse Secchi depth. Particulate phosphorus from the resuspended sediment was probably not in a form immediately available for phytoplankton growth. Apparently, the flux of this phosphorus from the sediment was sufficiently great to influence the water column concentration, but the average residence time in the water column was not sufficient for conversion of a substantial amount to an available form.

A substantial decrease in threshold odor in the municipal water supply occurred over the study period. This decrease was found to be well correlated with a decrease in blue-green dry weight biomass concentration. This

change, however, was poorly correlated with blue-green cell number, total phytoplankton dry weight biomass, or chlorophyll *a* concentrations.

The fact that significant improvements in water quality were not reflected in water column concentrations of total phosphorus implied that this parameter was not a meaningful water quality indicator in Saginaw Bay. The most critical causative factor in the response of the bay appeared to be the decrease in supply rate of available phosphorus to the water column. This conclusion may have similar implications for other lake systems in which sediment resuspension constitutes a substantial source of phosphorus loading to the water column.

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Registry No. P, 7723-14-0; chlorophyll *a*, 479-61-8.

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## Fish/Sediment Concentration Ratios for Organic Compounds

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■ The concentration ratio of chlorinated or polynuclear aromatic hydrocarbons in fish to the sediments from their habitat increases with hydraulic retention time of the basin. Fish/sediment ratios for chlorinated hydrocarbons are about 3 orders of magnitude higher than for aromatic hydrocarbons with the same octanol-water partition coefficient. Normalizing for sediment concentrations and animal concentrations of chlorinated aromatic hydrocarbons, the body burdens of polynuclear aromatic hydrocarbons in different phyletic groups are consistent with the inverse of their mixed-function oxygenase activity; the order for concentrations is mollusks > polychaetes = crustaceans > fish.

### Introduction

Heightened public concern about potential groundwater contamination and air pollution has brought increasing demands to use coastal waters for waste disposal. Consequently, increasing demands are being made of environmental scientists to predict the amount of wastes which can be safely discharged into the oceans. One aspect of such safety concerns is protecting the health of people who consume fish and shellfish. Fish and shellfish are known for their capacity to accumulate toxic organic compounds at thousands of times their concentration in the surrounding medium.

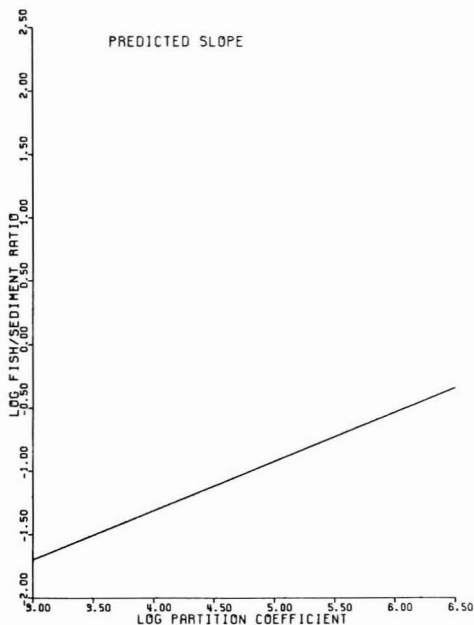
To estimate these risks, we would like to know the relationship between the amount of wastes dumped and the concentration of pollutants in fish. Several authors have suggested that 1-octanol-water partition coefficients may

be used to predict the extent to which hydrophobic organic contaminants will be concentrated from water by fish and shellfish (1-5). Their data show a log-log correlation between the octanol-water partition coefficient and the bioconcentration factor from 96-h bioassay experiments in laboratory aquariums. This bioconcentration factor is defined as the ratio of the concentration of a chemical in the biota as compared to its concentration in the surrounding medium.

Such a model assumes that equilibrium exists between water and the lipid tissues of fish. Yet, bioconcentration values depend not only on equilibrium partitioning and uptake but also on loss through metabolism and excretion (6). Considering the complexity of biological processes, the correlation between the 96-h bioconcentration factor and the octanol-water partition coefficient is impressive in the extent to which these biological processes may apparently be ignored.

However, the oceans are more complex than the laboratory, and blind extrapolation of 96-h test data to the marine environment has been criticized (7). One major concern is that temporal and spatial variations in water concentrations of various xenobiotics in lakes and estuaries make it difficult to compare laboratory estimates with field monitoring results (7).

Given these considerations, in this paper I explore whether sediments are a more appropriate environmental compartment to compare to concentrations of contaminants in fish flesh. Sediments change more slowly than the water column, which makes it easier to collect representative sediment data. There is less concern about



**Figure 1.** Predicted relationship between fish/sediment concentration ratio and the octanol-water partition coefficient for a sediment organic carbon content of 1%.

sampling during different hours of the day or seasons of the year. Conversely, the sediments must be sampled carefully so that only the surface sediments for the time period of concern are analyzed to prevent dilution with uncontaminated sediments. In addition, the sediments may serve as a storage compartment for long-term release, reflecting the history of discharges to an area. Both PCBs and DDT deposited in the sediments have been a source of contamination in the following years (8) as the contaminant is released by biogeochemical processes (9).

There is some dispute whether compounds sorbed to sediment particles are available to fish for uptake, but an equilibrium model assumes that fish and sediments will be in equilibrium through their individual equilibria with the water. If so, we can predict the logarithmic relationship of the fish/sediment concentration ratio as a function of octanol-water partition coefficient. As described above, the bioconcentration factor (BCF) is a function of the octanol-water partition coefficient ( $K_{ow}$ ). The sediment partition coefficient ( $K_{sed}$ ) is equal to  $K_{oc}$  multiplied by the percentage organic content. The soil sorption capacity ( $K_{oc}$ ) is a function of the soil's organic content and can also be predicted by using octanol-water partition coefficients. Kenaga and Goring (4) have developed a series of regression equations describing these relationships:

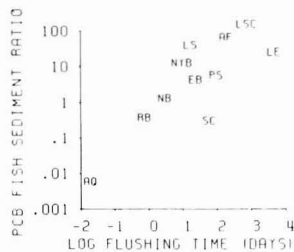
$$\log BCF = -1.495 + 0.935 \log K_{ow} \quad (1)$$

$$\log K_{oc} = 1.377 + 0.544 \log K_{ow} \quad (2)$$

By subtraction and substitution of  $K_{sed}$  for  $K_{oc}$ , we can derive

$$\log BCF/K_{sed} = -2.872 + 0.391 \log K_{ow} + \log (\% \text{ organic content}) \quad (3)$$

Figure 1 shows a plot of eq 3 for sediments containing 100% organic carbon. For sediments with less organic carbon, the slope of this line would remain constant, but



**Figure 2.** Fish/sediment PCB concentration ratios for benthic fish species as a function of flushing time. Symbols: AQ, lab aquariums containing Dover sole (21); SC, Southern California Bight Dover sole liver data transformed to muscle data by dividing 25 (16, 22); NB, New Bedford bottom fish (23, 24); NYB, New York Bight flounder (10, 25); RB, Raritan Bay flounder (10, 26); EB, Escambia Bay, FL, assuming sediment dry weight is 50% of wet weight (27, 28); PS, Puget Sound sole and sculpin (11, 29); LS, Lake Seminole, FL, flushing time calculation from average monthly flow and volume reported by the Army Corps of Engineers, Mobile, AL, personal communication (30); AF, American Falls Reservoir, ID, suckers (31), reservoir turnover time from Bureau of Reclamation, Boise, ID, personal communication; LSC, Lake St. Clair, MI, channel catfish (20, 32); LE, Lake Erie channel catfish (20, 32), lake turnover times estimated by R. J. Hesselberg, Great Lakes Fishery Lab, personal communication.

the y intercept would decrease by log (% organic content).

#### Data Analysis

A computer search located those studies reporting pollutant concentrations in sediments and the fish which live over those sediments. While there are a number of papers comparing animal and sediment concentrations of single compounds or a class of compounds, there are only two studies surveying a broad array of organics in both fish and sediments (10, 11). Generally, less than five replicates per station are analyzed, and the coefficients of variation were often large, averaging almost 100%. Fish and sediments were matched by sampling station or by lake basin, and fish/sediment ratios calculated by dividing the average concentration of organic compounds in wet fish tissue by an average concentration in dry sediments to obtain the fish/sediment ratio—the standard way such concentration data are reported. Most of the fish data were from whole animal analysis, though some results were reported for muscle filets or livers. All the sediment samples in the studies were "surface sediments", either as the top 2 cm in cores or from sediment "grabs". In most of these studies, the fish are bottom fishes with a fairly limited home range though the extent of the home range in relation to the sediments samples is not well-known in most of these reports. Unfortunately, organic carbon content of the sediment was not reported in any of the studies.

Flushing time was summarized from residence time calculations reported for many of the regions from several sources. There could be variations due to the assumptions and methods used by the different authors—for instance, we might expect Southern California Bight to flush more quickly than New York Bight. Despite these limitations, when the various data were analyzed for a broad array of chemicals and fish species from different habitats, consistent patterns emerged.

#### Results and Discussion

**Areal Differences.** When the fish/sediment ratios for the same compound from different areas are compared, there is a correlation between the residence time of water in the area and the fish/sediment ratio (Figure 2). Lakes have higher ratios than poorly flushed coastal areas, which, in turn, have higher ratios than well-flushed coastal areas.

Flow-through aquariums with a complete water exchange 4 times per hour had the lowest fish/sediment concentration ratio. This relationship to flushing holds within the areas as well. Ratios in New Bedford Harbor decline by a factor of 8 from confined to open waters. In Puget Sound, enclosed bays (Case Inlet and Budd Inlet) have ratios 3–14 times higher for a suite of compounds than more open bays (Elliot and Commencement Bays).

The dependence of this bioconcentration measure on flushing time could indicate that surface sediments are not in equilibrium with fish lipid pools. While water and sediments shaken in the laboratory reach equilibrium within hours, achieving equilibrium between surface sediments and the water column is a much slower process. In addition, it takes several weeks for fish lipid pools to reach equilibrium with water concentrations in laboratory bioaccumulation tests (12). Equilibrium between animals and sediments, then, should be a slow process. In fact, polychaetes reach equilibrium with their sediment habitat after 12 weeks (13).

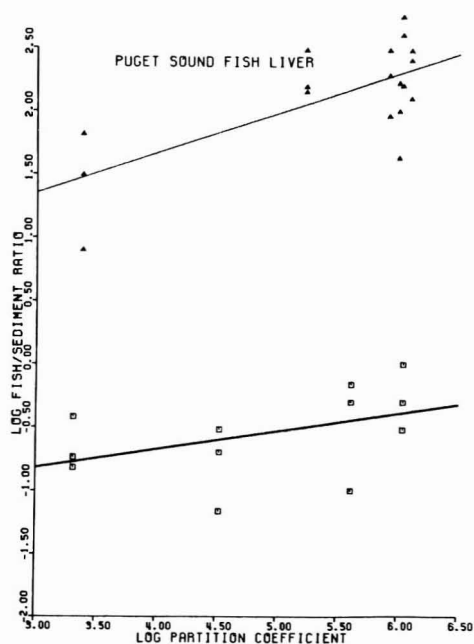
In shallow coastal waters, sediment particle adsorption accounts for the major portion of lipophilic xenobiotics. Under the assumption of equivalent rates of desorption, areas more rapidly flushed by relatively unpolluted waters would therefore have lower water and thus fish concentrations of these lipophilic compounds. The limited data presented here indicate that the fish/sediment ratio may reach a plateau at flushing times greater than 100 days, suggesting that the time necessary for fish–sediment equilibrium in the field may be of the same order indicated by the laboratory studies cited above.

Some part of the differences between these ratios probably results from the higher organic carbon content of sediments in low energy environments. Poorly flushed environments could accumulate organic carbon which would increase the sediment concentration of organic contaminants. But organic content of all sediments considered probably varies by less than 2 orders of magnitude while the animal/sediment ratios vary over 4 orders of magnitude. For instance, sediments used in flow-through aquariums were collected near the Los Angeles sewage outfall, yet the fish/sediment ratio was 10–20 times higher in the ocean than in the more rapidly flushed aquariums.

**Compound Class Differences.** Different classes of organic compounds with the same octanol–water partition coefficient show quite different fish/sediment concentration ratios (Figure 3). For example, chlorinated aromatic hydrocarbons (CAH) show much higher fish/sediment ratios than polynuclear aromatic hydrocarbons (PAH).

This difference is consistent with observations of fish metabolism. Complex organic compounds are metabolized by the mixed-function oxygenase (MFO) system in fish. Polynuclear aromatic hydrocarbons are much more easily metabolized by this system than are chlorinated hydrocarbons (14). Differential metabolism, therefore, causes levels of PAH in fish to be several hundred times lower than what would be predicted from sediment concentrations and partition coefficients alone.

Within the compound classes of PAH and CAH, there is a log–log correlation between the fish/sediment concentration ratio and octanol–water partition coefficient (Figure 3). The slopes of these regression lines are shallow (CAH, 0.34; PAH, 0.14) when compared to the slope of the 96-h bioconcentration factor as a function of the partition coefficient which is about one (for a recent discussion, see ref 3). These shallow slopes indicate the high affinity of both fish tissue and sediment organic matter for these organic compounds.



**Figure 3.** Relationship between the fish liver/sediment concentration ratios of selected hydrocarbons and chlorinated hydrocarbons and the 1-octanol–water partition coefficient. Triangles represent the chlorinated aromatic hydrocarbons (CAH) (dichlorobenzene, hexachlorobenzene, DDT, chlordane, PCBs, and nonachlor), squares, the polynuclear aromatic hydrocarbons (PAH) (naphthalene, phenanthrene, benz[*a*]anthracene, and benzo[*a*]pyrene). Regression lines are drawn for the CAHs (light) and PAHs (heavy).  $r^2 = 0.50$  (CAH) and 0.20 (PAH). Raw data from ref 11.

While the slopes of these field samples are consistent with the predicted slope from eq 3 (0.39; compare Figure 2 to Figure 3), each of the individual ratios is 3–5 orders of magnitude higher than predicted by assuming an organic content of 1% carbon, a reasonable concentration for these shallow marine sediments in Puget Sound (15). The 25-fold concentration factor by fish liver (16) accounts for only a part of the difference. From eq 3 we see that fish/sediment ratios greater than about 0.01 are higher than could be predicted. As shown in Figure 1, such ratios are generally reported. Pollutant concentrations in fish and sediments are related in these equations by their concentration in the water column. Perhaps fish equilibrate more quickly with water concentrations than do sediments.

Besides indicating the differences in lipophilicity between fish and sediments, the slope of the fish/sediment ratio as a function of the partition coefficient reflects the different rates of xenobiotic metabolism between fish and sediments. Within compound classes, the smaller, less lipophilic compounds are often metabolized more quickly. For instance, fish metabolize naphthalene which has a low partition coefficient ( $\log K_{ow} = 3.31$ ) much more quickly than benzo[*a*]pyrene which has a high partition coefficient ( $\log K_{ow} = 6.04$ ) (6). Interpreting the slope of these lines, then, is complicated because they represent a combination of the differential partitioning of these compounds within the body, as well as differential metabolism throughout the body.

**Phyletic Differences.** One can also compare the difference in metabolism of these pollutants among different phyletic groups. Cytochrome P-450 mediated mixed-

Table I. Ratio of Animal/Sediment Ratios for Chlorinated Aromatic Hydrocarbons (CAH)/Polynuclear Aromatic Hydrocarbons (PAH) and Mixed Function Oxygenase (MFO) Activity for Various Phyla in Puget Sound (PS) and the New York Bight (NYB)<sup>a</sup>

animal (no. of samples)	CAH/PAH ratio		MFO activity, pmol min <sup>-1</sup> mg <sup>-1</sup>
	me-dian	range	
fish			
winter flounder			213 ± 15
NYB winter flounder liver (1)	3400		
NYB flounder flesh (4)	800	120-2000	
PS sole liver (6)	2200	790-3300	
polychaetes			
sand worm			89 ± 24
NYB polychaetes (1)	210		
PS "worms" (4)	25	6-45	
crustaceans			
blue crab hepatopancreas			42 ± 15
PS crab hepatopancreas (5)	1300	450-2900	
NYB lobster digestive gland (1)	590		
NYB lobster flesh (3)	100	95-120	
NYB grass shrimp (1)	28		
PS shrimp (6)	19		
mollusks			
oyster			8 ± 2
mussel digestive gland			3 ± 1
NYB sea scallops (3)	48	10-76	
NYB mussels (2)	50	32-65	
PS clams (7)	12	1-49	

<sup>a</sup> Raw concentration data from MacLeod et al. (10) and Malins et al. (11) grouped by station. The geometric mean of the animal/sediment ratios for each PAH and CAH compound was used to calculate an overall CAH/PAH ratio. MFO data from Stegeman (17) and Lee (18).

function oxygenase (MFO) systems metabolize foreign compounds in marine fish and invertebrates. Because MFO activity is generally higher in the liver (17), one would expect lower concentrations of PAHs relative of CAHs in the liver as compared to whole body concentrations. Table I shows that the ratio of CAH animal/sediment ratios of PAH animal/sediment ratios is approximately 4 times higher in fish livers than in whole fish and 6 times higher in lobster digestive gland than in flesh.

MFO activity levels within individual species can vary over 2 orders of magnitude due to enzymatic induction (18), which serves to mask differences across phyla. One can examine phyletic trends in these data by comparing CAH/PAH animal/sediment ratios for different organisms to their MFO activity (Table I). In general, fish have slightly higher MFO activity than crustaceans or polychaetes while MFO activity in mollusks is only one-tenth to one-hundredth that of fish (17, 18). As a result the CAH/PAH ratio in fish is between 1 and 2 orders of magnitude higher than that of mollusks and generally less than 10 times higher than the ratio for various crustaceans and polychaetes.

### Conclusions

Applying a bioconcentration factor directly to predict the potential for the contamination of fish by toxic organic compounds may be insufficient in the field. Partition coefficients make accurate predictions of contamination in short-term laboratory tests, but in the environment, biological and physical factors play an important role. In this collection of data from field monitoring studies, I have shown that the concentration of organic contaminants in

bottom fish is correlated with the sediment concentration of those compounds depending on the area's physical flushing capacity (residence time of water in a basin) and the biological flushing capacity of the organisms (metabolism by the MFO system).

Modeling fish concentrations as a function of sediment concentrations has a number of advantages besides the temporal and spatial averaging of inputs mentioned earlier. Fish tend to bioconcentrate lipophilic compounds of low water solubility. Because of their low solubilities, these compounds will often be adsorbed to organic-rich particles rather than existing free in solution. Since the chemistry of these contaminants is so particle oriented, it probably makes more sense to follow the particles rather than following the water column. Sewage particle dispersion, at least, has been amenable to prediction (19). Such models could predict the extent of the impacted area and eliminate the need for modeling the much larger area encompassed by a hydrographic boundary.

The consistent behavior of classes of compounds allows extrapolation from data for individual compounds to a variety of pollutants in aquatic environments where the flushing capacity has been determined. Extending the analysis to fish that do not live on the bottom will increase the variation by about a factor of 10 (for example, see ref 20). Much of this variation is inherent to any attempt at field predictions due to the importance of fish age, sex, and trophic position. The processes that make sediment contaminants available to fish (bioturbation, tidal pumping, resuspension, particle ingestion, etc.) are still being elucidated. In the meantime, computing fish/sediment ratios is a useful step beyond laboratory bioassays in predicting the aquatic fates of pollutants.

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## Characterization of Individual Particles in the Phoenix Urban Aerosol Using Electron-Beam Instruments

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■ More than 8000 individual particles from the Phoenix aerosol were analyzed by using an analytical scanning electron microscope. The compositions of the aerosol were similar at the three sampling locations. Approximately 75% of the coarse particle fraction (>1 μm) is crustal material, i.e., clays, quartz, feldspars, calcite, etc. The remaining coarse particles consist mainly of biological material, S compounds, Pb salts from automobiles, and other anthropogenic particles. S-bearing particles comprise an estimated 60-80% of the submicron aerosol fraction. Presumably, the most abundant S species is (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>; however, many of the S-bearing particles contain various amounts of other elements such as Zn, Pb, Cu, Na, Ca, As, and K. The remainder of the submicron fraction is composed largely of automobile Pb halides and particles from a variety of anthropogenic sources. Some of the anthropogenic particles have been pinpointed to specific sources, but in most cases to date only possible sources are suggested.

### Introduction

The impacts that atmospheric particles have on health and materials ultimately depend on the chemical compositions of the particles. Detailed knowledge about the composition of an aerosol also allows, in some cases, identification of the sources of specific particles. Consequently, in recent years much work has been concerned with identification of chemical species in urban and non-

urban aerosols. Most of these studies employ a variety of techniques to determine average bulk compositions of samples. A critical limitation of such bulk analytical methods is that the speciation and distribution of the elements in the aerosol are largely undetermined. For example, bulk composition data will normally not reveal whether an element occurs as a major component in a few particles or in trace concentrations in many particles. It is also not possible to obtain from bulk methods definitive information about surface coatings, elemental associations, agglomeration, or detailed variation of composition with particle size. These types of information can only be obtained by examining and analyzing individual aerosol particles.

Analysis of individual particles is the method of choice for source identification of aerosols. If particles from major point sources are characterized by individual particle methods, it is commonly possible to identify particles from those sources in ambient aerosol samples. Conversely, detailed knowledge of the compositions of particles from the aerosol can lead to recognition of previously unknown sources.

Until recently, little work on atmospheric aerosols has included the study of individual particles, primarily because the necessary analytical techniques were not available. The application of electron-beam instruments to the study of atmospheric particles, however, has added a new dimension to aerosol science; it is now feasible by using the electron microprobe, analytical scanning electron microscope (SEM), transmission electron microscope (TEM), or scanning transmission electron microscope (STEM) to perform rapid qualitative and, commonly,

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quantitative analyses of many atmospheric particles.

For the past several years our laboratory has been using electron beam instruments to study atmospheric particles in general and, specifically, those from the Phoenix urban aerosol (1-7). In this paper we present some of the preliminary results of our attempts to characterize the major particle types in the Phoenix urban aerosol.

Prior to the work described here, the only extensive study of individual particles in an urban aerosol was conducted by Russell and Ruud (8) for Denver, CO. They used an SEM equipped with an energy dispersive spectrometer (EDS) to analyze qualitatively a relatively limited number of particles, most of which were in the coarse ( $>1 \mu\text{m}$ ) size fraction. We have utilized both qualitative and quantitative EDS analysis to examine more than 8000 particles, ranging in size from about 0.1 to 30  $\mu\text{m}$ , thus making this the most comprehensive study of individual particles in an urban aerosol reported to date.

### Phoenix

Relatively little detailed work has been done on the urban aerosols over cities in the southwestern desert of the United States. Because of its isolated location in an arid region and the high total suspended particulate (TSP) levels experienced in the city, Phoenix is well suited for the type of study discussed here. In addition, the absence of numerous, large industrial sources of particles gives rise, perhaps, to a less complex aerosol (and therefore one more easily studied) than is found over the large industrial cities in the East or Midwest. At the same time, however, the climate and geography provide a unique urban setting, with air pollution problems that differ from cities in other areas.

Phoenix is a typical western community with a relatively low population density; its sprawling nature is responsible for a large automobile-dependent commuter population. Because of its location in a desert area, Phoenix is naturally dusty. Sparse vegetation, dry soil, and strong winds result in substantial amounts of dust being introduced into the air. The natural dust, combined with particle emissions from several anthropogenic sources, gives Phoenix one of the highest average TSP levels of any city in the United States (9). Graf et al. (10) concluded that approximately 90% of the Phoenix TSP load is crustal material that is entrained either naturally or anthropogenically (primarily from road traffic, agriculture, and quarrying operations). Suck et al. (11) concluded that the majority of particles in the Phoenix air are produced locally; very little material is transported laterally from the surrounding desert.

Although Phoenix is not characterized by extensive heavy industry, it does have a variety of anthropogenic sources of atmospheric particles, including oil-burning and natural gas-burning power plants, secondary iron foundries, an aluminum foundry, brass and bronze foundries, several small incinerators, electronics plants, chemical industries, and automobiles. Also, approximately 150 km SE of Phoenix are several major copper smelters, which are sources of large quantities of  $\text{SO}_2$ . The magnitude of the impact of the smelters on the Phoenix aerosol is not known; however, a recent study (12), comparing  $\text{SO}_4^{2-}$  concentrations over Phoenix during periods when the smelters were operating and shut down, suggests that the smelters contribute significant amounts of  $\text{SO}_4^{2-}$  and  $\text{SO}_2$  to the Phoenix aerosol.

### Experimental Section

**Sample Collection and Preparation.** The majority of samples examined in this study were collected during two days (Sunday, Feb 9, and Monday, Feb 10, 1980) at

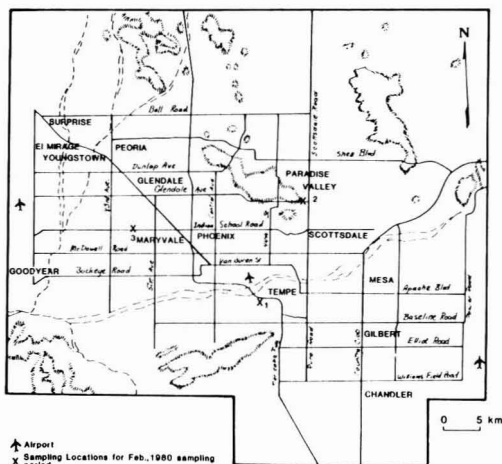


Figure 1. Map of Phoenix metropolitan area showing locations of the three sampling sites used to collect particle samples.

three sites triangulating the Phoenix area (Figure 1): (1) the U.S. Water Conservation Laboratory (USWCL) in southeastern Phoenix, (2) a private residence in Paradise Valley (northeast of Phoenix), and (3) a private residence in Maryvale (west of Phoenix). A detailed description of the sampling locations is given by Post (13). None of the sampling locations is near ( $<5 \text{ km}$ ) known major point sources of particles; therefore, we assume that the samples are, to a first approximation, representative of the average Phoenix urban aerosol.

The samples were collected on stacked sequences of 47-mm diameter Nuclepore filters, having nominal pore sizes of 12, 3, and 0.4  $\mu\text{m}$ . Filters were changed every 3 h; such samples provided a sufficient number of particles for study without problems of agglomeration and filter clogging. The filter holders were connected to Anderson pumps operating at a flow rate of about  $15 \text{ L min}^{-1}$  ( $\sim 12 \text{ cm}^2 \text{ s}^{-1}$  face velocity), which is comparable to the respirable rate. At each site, pertinent meteorological data were monitored, including wind speed and direction, temperature, relative humidity, and barometric pressure. The weather during the sampling period was generally clear and cool ( $3-20^\circ \text{C}$ ) with maximum wind velocities of about  $6 \text{ km h}^{-1}$ . High volume ( $1200 \text{ L min}^{-1}$ ) samples collected at the USWCL yielded an average TSP level measurement for the 2 days of  $35 \mu\text{g m}^{-3}$ , corresponding to relatively clean air days for Phoenix.

Nuclepore filters are chemically pure (14) and have uniformly smooth surfaces, making them excellent substrates for SEM examination and analysis of individual particles. Consequently, particles can be studied in situ on the filter, with little sample handling and minimal possibility of contamination or alteration. For individual particle analyses, two 1-cm squares were cut from the centers of the Nuclepore filters and mounted with a thin film of colloidal C paint directly onto a smooth C planchette. One square from each filter was coated with Au-Pd for imaging in the SEM, and the second square was C coated ( $\sim 200 \text{ \AA}$ ) for X-ray analysis.

**Particle Analyses.** The primary instrument used in this study was an analytical SEM (JEOL JSM-35) that has been modified specifically for the analysis of small particles by the addition of an energy dispersive spectrometer (EDS), wavelength dispersive spectrometer (WDS), and annular back-scattered electron detector. Quantitative

EDS analyses were performed by using the correction procedures of Aden (15) and Aden and Buseck (16), which are outgrowths of the work of Armstrong and Buseck (2). Relative errors are typically less than about  $\pm 10\%$  for particles larger than  $0.1 \mu\text{m}$ .

Quantitative EDS analyses were normally performed at an accelerating voltage of 15 keV and a beam current of 0.2 nA with the detector 30 mm from the sample. These conditions are suitable for good X-ray analysis and allow reasonable secondary electron imaging. The takeoff angle for the EDS detector is fixed at  $35^\circ$ , and polished thick-flat sections of appropriate oxides, sulfides, and silicates were used as standards. Count rates for  $1\text{-}\mu\text{m}$  diameter particles were typically 800–1000 cps and counts were collected for 200–400 s (depending on particle size and composition).

Quantitative EDS analyses of individual particles were used to identify a variety of chemical compounds in the Phoenix aerosol; however, quantitative analyses of small particles must be carefully interpreted. The complexity of the aerosol combined with limitations in the analytical method can, in some cases, give rise to misleading results. Standard EDS analyses can only be performed for elements with  $Z \geq 11$  and normally provide no information about the presence (or absence) of light elements ( $Z < 11$ ). Also, the oxidation state for each element in the particle being analyzed must be known. In most common minerals, elements occur as oxides, and oxidation states are well documented. However, in complex aerosols where particles originate from a variety of sources, it is commonly not possible to make assumptions about the chemical states or the presence of light elements.

In conventional microprobe analysis, information about light elements and oxidation states can, in some cases, be deduced from the value of the summation for the analysis. However, this is not possible for particle analyses because the correction program normalizes all summations to 100%. In some cases, light elements (e.g., N, O, C) can be detected by electron energy loss spectroscopy (EELS), WDS, or EDS by using ultrathin windows. However, none of these techniques are routine for most particle work, and they are not applicable for analysis of large numbers of different particles. Also, many particles (e.g., most atmospheric sulfates) are not stable at the high electron beam currents required for WDS analysis.

The correction program of Aden and Buseck (16) requires input of the particle thickness, in the direction of the electron beam. Accurate measurements for non-spherical particles can only be obtained by tilting the sample stage and measuring the thickness from the SEM screen. It is quicker but less accurate to estimate thickness from the projected area diameter and particle shape. We generally used the latter method and hence may have introduced errors into the analyses, especially for particles less than  $1 \mu\text{m}$  thick.

Finally, even if an accurate analysis is obtained, it is necessary to determine whether the particle is homogeneous or, as is common, composed of more than one phase. In many cases, SEM images and knowledge of the particle source will help to interpret correctly an analysis.

It is apparent that it can be extremely difficult, and sometimes impossible, to perform accurate quantitative analyses on small particles of unknown composition and origin. If several complementary techniques are employed, good quantitative analyses can be obtained for many atmospheric particles. However, the time required to properly perform such analyses makes it impossible to analyze quantitatively a large number of aerosol particles in a reasonable amount of time. Rather, quantitative

Table I. Composition of the Coarse Particle Fraction in the Phoenix Aerosol<sup>a</sup>

particle type	total number of coarse mode particles, <sup>b</sup> %		
	site 1	site 2	site 3
mineral-type particles	69.8	74.7	67.1
Pb-bearing particles from automobiles	5.4	2.2	8.3
S-bearing particles <sup>c</sup>	8.6	13.6	11.4
miscellaneous particles	16.2	9.5	13.2

<sup>a</sup> Particles from  $3\text{-}\mu\text{m}$  pore diameter filters. <sup>b</sup> Results based on 803, 854, and 1589 particles from sites 1, 2, and 3, respectively. <sup>c</sup> Particles having S as the major element in EDS spectra.

particle analysis is best applied to the detailed study of specific particle types in an aerosol and for characterization of source emission.

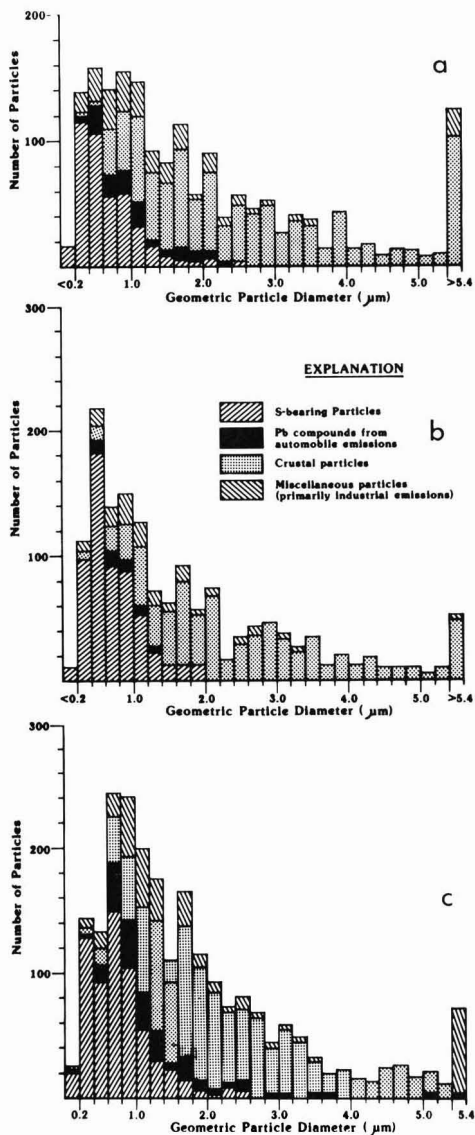
In order to analyze as many particles as possible in a reasonable time period, we employed a combination of quantitative and qualitative EDS particle analyses. Quantitative analyses were initially performed on a large number of aerosol particles to allow subsequent identification of similar types by qualitative analysis alone; this was particularly useful for mineral particles. Normally, qualitative analyses were performed on the first 200 or 300 particles encountered on a filter. The qualitative analyses were carried out with the aid of a computer program [QKQUAL (13)] that performed a background subtraction on the EDS spectrum, searched for and identified peaks, and printed uncorrected intensities for each element encountered. Each spectrum was also checked by the operator for peaks that were not identified by the computer program. Qualitative analyses were typically counted for 30 s at an accelerating voltage of 25 keV and beam current of 0.2 nA. The projected area diameter of each analyzed particle was measured from the SEM screen. The majority of particles analyzed are on  $3\text{-}\mu\text{m}$  Nucleopore filters and are  $0.4\text{--}5 \mu\text{m}$  in diameter. To provide as comprehensive a study as possible, however, particles on several  $0.4\text{-}$  and  $12\text{-}\mu\text{m}$  filters were also analyzed.

Whenever unusual or complex particles were encountered, spectra were collected for quantitative analyses. After the initial group of particles on each filter was analyzed, the filter was searched by using secondary and back-scattered electron imaging for different or unusual looking particles. Back-scattered electron imaging is especially useful for locating particles containing elements with high atomic numbers such as the heavy metals. Also, sketches or photographs were made of particles that appeared in SEM images to contain several phases. We then attempted to analyze each of the separate phases. In cases where they were too small to be resolved by EDS analysis, notes to this effect were made and later used in interpreting the bulk particle analysis.

### Results and Discussion

The particles analyzed are here separated into coarse ( $\geq 1 \mu\text{m}$ ) and fine ( $< 1 \mu\text{m}$ ) size fractions. These size categories approximately correspond to the coarse and accumulation modes, respectively (17).

Figure 2 shows the distribution of major particle types according to size for the particles examined. As expected from previous studies of urban aerosols (17), almost all particles having mineral-like compositions are larger than  $1 \mu\text{m}$ , and S-bearing particles are generally smaller than  $1 \mu\text{m}$ . Pb-containing particles and miscellaneous particles (primarily from anthropogenic sources) are concentrated



**Figure 2.** Distribution of major particle types vs. diameter for particles collected at (a) site 1, (b) site 2, and (c) site 3. Particle types included in the figure are S-bearing particles, Pb compounds from automobile emissions, crustal particles, and miscellaneous (primarily industrial emissions) particles.

in the 0.4–1.5- $\mu\text{m}$  size range.

The coarse particle mode is similar at all three sampling locations (Table I), with mineral-type particles comprising about 75% of the total number. The remainder of the coarse mode consists of about 8–14% particles with S as the major element and 2–8% Pb halides from automobile emissions, and 9–16% are miscellaneous particles.

At all three sampling sites, S-bearing particles are the most abundant submicron particles. It is estimated that 60–80% of the particles in the 0.1–1- $\mu\text{m}$  size range are S-bearing particles—presumably sulfates. This is consistent with observations made in other urban areas (18, 19). The remaining major submicron particle types are Pb compounds and other anthropogenic particles.

**Table II.** Mineral Particles in the Phoenix Aerosol<sup>a</sup>

mineral	total number of mineral particles, <sup>b</sup> %		
	site 1	site 2	site 3
clay minerals	47.2	44.3	44.7
quartz	13.7	10.2	13.3
orthoclase	7.5	8.5	6.2
albite	5.3	9.4	4.3
calcite	10.0	13.0	8.2
miscellaneous minerals	16.2	14.7	23.3

<sup>a</sup> Particles on 3- $\mu\text{m}$  pore diameter filter. <sup>b</sup> Calculated for 561, 639, and 1066 particles from sites 1, 2, and 3, respectively.

**Mineral Particles.** The compositions of most of the particles larger than 1  $\mu\text{m}$  in the Phoenix aerosol correspond to minerals common in the local rocks and soils. Metamorphic and acidic igneous rocks are predominant in the Phoenix area, and soils consist mainly of weathered clay minerals, sand, and caliche (20). It is not surprising, then, that the major mineral species observed in this study are clays, quartz, feldspars (albite and orthoclase, with some Ca plagioclases), micas, iron oxides (magnetite, limonite, etc.), calcite, and gypsum. Also, several accessory minerals common in igneous and metamorphic rocks were identified, including pyroxenes, hornblende, monazite, apatite, and ilmenite.

The most abundant minerals in the Phoenix aerosol are clays (Table II), comprising 40–50% of the total number of crustal particles. Chemical analyses reveal that the most prevalent clay minerals are illites, commonly mixed with montmorillonite and kaolinite. Many of the clay particles contain minor concentrations of elements typically not found in clay minerals, e.g., Cl, S, Zn, and Cu; presumably these elements occur as surface coatings of sulfates or chlorides.

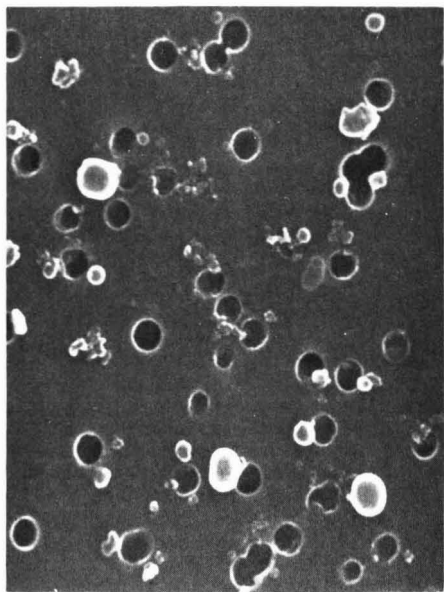
Particles showing only Ca in EDS spectra, or Ca with small amounts of Si, Al, S, Mg, or Fe, are assumed to be primarily calcite or dolomite, probably derived from local rocks and soils. Particles produced by cement plants or traffic on concrete roads also are rich in Ca, and many have compositions similar to natural limestones. Certain cements, however, including Portland cement, have higher Si contents than found in most limestones; thus, in some cases it was possible to distinguish between natural calcite and cement.

**Sulfates. (1) Sources and Physical Characteristics.**

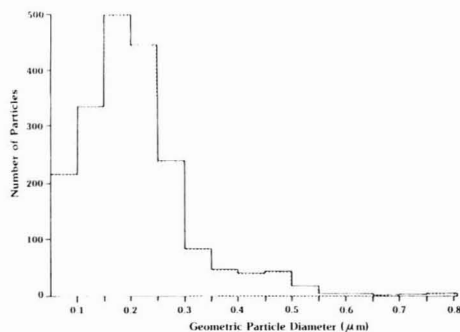
As mentioned above, the most abundant particle type in the Phoenix aerosol is composed of S-rich compounds, the majority of which are probably sulfates. Other studies have concluded that atmospheric sulfates either can be emitted directly as primary particles or, more commonly, are the result of gas to particle conversion reactions in the atmosphere (21). Sulfates can undergo numerous reactions in the atmosphere to form a great variety of complex compounds. In the Phoenix area, the major anthropogenic sources of S compounds, either as primary sulfates or gases, include oil-burning power plants, automobile emissions, foundries, incinerators, gypsum-use industries, and the copper smelters located southeast of the city.

The sulfate particles in the Phoenix aerosol typically appear smooth, rounded, and spherical, ellipsoidal, or bean shaped (Figure 3); this is consistent with sulfates observed in rural and other urban aerosols (22, 23). Some of the sulfates were observed to occur as rounded prisms or as agglomerates.

The physical appearances of the S-bearing particles differ in samples collected at different times of the day.



**Figure 3.** SEM photograph of S-bearing particles from the Phoenix aerosol. The filter pores are  $\sim 0.3 \mu\text{m}$  in diameter.



**Figure 4.** Size distribution of  $\sim 2000$  sulfate particles in the Phoenix aerosol as determined from SEM images of several 0.4- and 3- $\mu\text{m}$  filters, collected at site 3 on Feb 11, 1980 (1200–1600 h). The average diameter of the sulfate particles is between 0.15 and 0.25  $\mu\text{m}$ .

This change of appearance correlates with change in relative humidity, which ranged from about 16 to 98% during the sampling days. In the afternoon and early evening, when humidity was lowest, the S-bearing particles are rounded and distinct; in early morning, however, when the humidity was greatest, the hygroscopic acid sulfates take on water and appear irregularly shaped and blobby on the Nuclepore filters.

The approximate size distribution of 2000 S-bearing particles from SEM images of several 0.4- and 3- $\mu\text{m}$  filters is shown in Figure 4. The distribution is non-Gaussian and has a maximum at about 0.15–0.25  $\mu\text{m}$ ; the mass median diameter is about 0.3  $\mu\text{m}$ . This is in general agreement with observations for other urban areas and with laboratory experiments that give an average size of 0.2–0.3  $\mu\text{m}$  (aerodynamic diameter) for sulfate aerosols (24).

Hygroscopic sulfates may undergo dehydration in the vacuum of the SEM. The blobby appearance of sulfates collected at times of high humidity might be the result of

such effects. We did not, however, notice any other evidence of particle modification in the SEM.

**(2) Chemical Analyses of S-Bearing Aerosols.** Bulk chemical analyses of size-fractionated aerosols from various urban areas generally show nearly equal concentrations of  $\text{SO}_4^{2-}$  and of  $\text{NH}_4^+ + \text{H}^+$ ; thus, it is commonly assumed that the prevalent S compounds are  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NH}_4\text{HSO}_4$ , and  $\text{H}_2\text{SO}_4$  (25, 26). EDS spectra of most S-bearing particles collected in Phoenix show only S, or S with minor amounts of other elements. All of the acid sulfate compounds thought to be common in aerosols show only S in EDS spectra; thus, it is not normally possible to identify or distinguish among these compounds by EDS analysis alone.

Successful chemical analysis of atmospheric sulfates can only be accomplished by techniques capable of detecting light elements, e.g., WDS, thin-window EDS, and EELS. In this study, attempts to analyze aerosol sulfate particles using WDS and thin-window EDS yielded generally unsatisfactory results. The S-bearing particles decompose rapidly at the high electron beam currents (15 nA) needed for WDS work, and in all cases the particles were completely destroyed before analyses could be completed. Thin-window EDS analyses showed S and O, but N was not detected in aerosol sulfates or reagent  $(\text{NH}_4)_2\text{SO}_4$ . The thin-window EDS analyses were only preliminary attempts to apply this technique to aerosol sulfates; it is likely that a more comprehensive study, including analyses under various instrumental conditions, might provide important information.

We have also attempted to identify atmospheric sulfate compounds using selected area electron diffraction. Of the several dozen particles examined, only a few showed any diffraction spots, all of which faded within a few seconds. Similar results were reported by Russell (27) for aerosol S-bearing particles collected in Denver, CO. Bradley (28) attempted to obtain electron diffraction spots from S-bearing particles using a scanning transmission electron microscope equipped with a movie camera to record even fleeting diffraction patterns. He concluded that although spots were observed in some cases, most of the particles appeared amorphous.

Approximately 10% of the S-bearing particles from the Phoenix aerosol contain one or more elements in addition to S, e.g., Na, Ca, K, Sr, Fe, Cu, Zn, Pb, As, Mg, Al, Si, and Cl. Quantitative analyses of these particles indicate that some are stoichiometric sulfate compounds such as  $\text{Na}_2\text{SO}_4$ ,  $\text{K}_2\text{SO}_4$ ,  $\text{CaSO}_4$ ,  $\text{SrSO}_4$ ,  $\text{Fe}_2(\text{SO}_4)_3$ ,  $\text{CuSO}_4$ , and  $\text{ZnSO}_4$ ; however, in most cases these other elements occur as minor constituents. Presumably, most of these particles are mixtures of two or more sulfates (e.g.,  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{Na}_2\text{SO}_4$ ) or sulfates and nonsulfates. Several of the S-bearing particles seem to contain nuclei or central cores. In some cases, these cores contain primarily Al and Si (probably clays), and in other cases no elements were detected in the EDS spectra, indicating that the cores are probably soot. These particles may have formed when  $\text{H}_2\text{SO}_4$  or some other S-bearing compound condensed onto or reacted with existing particles.

The element that we most commonly found associated with S-bearing particles in Phoenix is Na. Quantitative analyses of these particles yield Na/S ratios ranging from nearly zero to greater than two ( $\text{Na}/\text{S} = 2$  in  $\text{Na}_2\text{SO}_4$ ); many particles have compositions consistent with  $\text{Na}_2\text{SO}_4$ . Particles with  $\text{Na}/\text{S} < 2$  are possibly mixtures of  $\text{Na}_2\text{SO}_4$  and other sulfates, such as  $\text{NaHSO}_4$ ,  $(\text{NH}_4)_2\text{SO}_4$ , and  $\text{H}_2\text{SO}_4$ . The abundance of Na in the submicron particles is somewhat surprising; previous studies of urban aerosols

have not shown  $\text{Na}_2\text{SO}_4$  to be an abundant species. Although we find it to be relatively abundant in submicron sulfate particles, the total weight percent of Na in a bulk aerosol sample is probably small.

The most likely sources of atmospheric Na in the Phoenix area include oil and gas combustion (29), secondary iron foundries (30), local playa and salt deposits (31), and possibly sea salt transported from the West Coast. Aden and Buseck (32) also observed significant quantities of  $\text{Na}_2\text{SO}_4$  in emissions from a coal-burning power plant. Although there are no coal-burning operations in Phoenix, several large plants are located in the northern part of Arizona and may contribute Na to the Phoenix urban aerosol.

Several particles of  $\text{SrSO}_4$  or  $(\text{Sr,Ca})\text{SO}_4$  were observed in samples from all three sampling locations. The particles range in size from 1 to 5  $\mu\text{m}$  and, in most cases, appear as euhedral crystals. The source of the  $\text{SrSO}_4$  is not known, although natural  $\text{SrSO}_4$  (celestite) does occur in sedimentary rocks and tuffs in Maricopa County (33).

$\text{CaSO}_4$  particles in the Phoenix aerosol appear to be of two types: (1) euhedral crystals larger than 1  $\mu\text{m}$ , probably derived from gypsum deposits or from industries that use gypsum, and (2) spherical or rounded particles, usually smaller than 1  $\mu\text{m}$ , suggesting a high-temperature origin. The source(s) of the second type of  $\text{CaSO}_4$  particles is (are) not known; however,  $\text{CaSO}_4$  spheres have been found in emissions from Cu smelters in southeastern Arizona (15). Also, particles consisting of NaCl and  $\text{CaSO}_4$  were observed by us in abundance near an oil-burning power plant in Phoenix.

**Pb Halide Compounds.** Pb compounds emitted from automobiles burning leaded gasoline constitute one of the major particle types in the Phoenix aerosol. Generally the Pb is associated with Cl and Br, but lead phosphate and particles showing only Pb in EDS spectra (presumably  $\text{PbCO}_3$ ,  $\text{Pb}(\text{OH})_2$ , or  $\text{PbO}$ ) are also observed. Quantitative analyses of several hundred Pb-bearing particles indicate that the major Pb halide compounds in the Phoenix urban aerosol are probably  $\text{NH}_4\text{Cl}\cdot 2\text{PbBrCl}$ ,  $(\text{PbO})_2\text{PbBrCl}$ , and  $\text{PbBrCl}$ . Particles containing mixtures of  $\text{PbBrCl}$  and  $\text{Pb}_3(\text{PO}_4)_2$  also are common. A large number of other Pb-bearing particles show a range of compositions and are probably mixtures of several compounds. Very few Br-rich Pb halides, and no  $\text{PbBr}_2$  particles, were observed; apparently, these compounds, if they are emitted from automobiles, are unstable in the air, losing Br to form  $\text{Pb}(\text{OH})_2$ ,  $\text{PbO}$ , or  $\text{PbCO}_3$ . Pb compounds having Cl/Br ratios greater than about 1 (and Br/Pb molar ratios less than 1) seem to be stable in the atmosphere. A detailed discussion of Pb halide particles in the Phoenix aerosol is presented in Post and Buseck (34).

It is interesting that we did not observe  $\text{PbSO}_4$  to be a major species in the Phoenix aerosol, although it has been reported, on the basis of X-ray diffraction studies, to be abundant in other urban areas (35). One possible explanation is the difficulty of resolving the Pb  $M\alpha$  and S  $K\alpha$  lines in EDS spectra. We found, however, relatively few particles that show only Pb in EDS spectra, thus suggesting that, even considering the overlap problem,  $\text{PbSO}_4$  is not common in the particle size fraction examined in this study.

**Miscellaneous Particles.** Approximately 10–15% of the particles that we examined from the Phoenix aerosol are not minerals, S-bearing particles, or Pb compounds from automobiles, and these are here grouped as miscellaneous aerosol particles. Included are compounds emitted from a variety of anthropogenic sources and particles that

do not show elements in EDS spectra such as soot, organic, and biological particles, e.g., spores, pollen, and other plant material. Most of the nonbiological particles are smaller than 2  $\mu\text{m}$  and are characteristic of anthropogenic sources near where the samples were collected. In some cases, the sources of specific particle types have been identified by considering wind directions during sampling and by comparing ambient particles with those collected near suspected sources, e.g., emissions from two secondary iron foundries southeast of Phoenix. In most cases, however, only possible sources of a given particle are suggested, based on studies by other researchers or knowledge of the types of processes that produce certain particles.

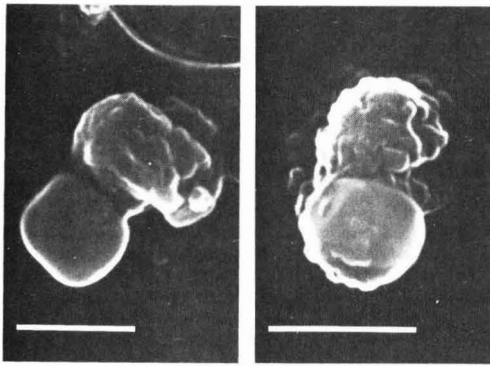
We present here a description of only the most common or interesting anthropogenic particles observed in this study; for a more complete listing and description see Post (13).

**Site 1.** The most prevalent anthropogenic particles observed at site 1 (USWCL) are from two secondary iron foundries located approximately 6 km SE of the sampling location. In some samples, more than half of all miscellaneous particles apparently originated from these foundries. Identifications of ambient particles as foundry emissions were based on detailed studies of particles from the two foundries by Armstrong and Buseck (36) and Post and Buseck (30). The ambient foundry particles are typically smaller than 2  $\mu\text{m}$ , with an average size of 0.8  $\mu\text{m}$ . The two main types of foundry particles observed are (1) oxides of Fe and Zn, usually with smaller amounts of Pb, Mn, Cl, Al, Si, Ca, K, or Cr, and (2) salts of Na, Mg, Cl, Ca, S, and K.

Other anthropogenic particles common in samples from site 1 include Al, Si fly-ash spheres. Many particles, ranging from 0.5 to 3  $\mu\text{m}$  in diameter, contain S and Cl with minor amounts of other elements and give relatively low X-ray count rates; they probably are organic material or partially burned wood, paper, or plastic from incinerators or other burning operations (37).

**Site 2.** The samples collected at site 2 (Paradise Valley) show the fewest number of miscellaneous particles; this is not surprising since the area is mainly residential. All of the samples contain Al, Si fly-ash spheres, with the greatest abundance in the samples collected between 9:00 a.m. and 6:00 p.m. on both days. The fly ash suggests a fuel oil or coal combustion process, probably a power plant; the exact source, however, has not been pinpointed. Three particles containing W (one with minor S) were found in the sample collected from midnight to 3:00 a.m. on Sunday morning, but no similar particles were observed in other samples. The W particles are about 0.5  $\mu\text{m}$  in diameter, and their source is unknown. Several Fe and Zn oxide particles identical with emissions from the secondary iron foundries in Tempe were found in samples from site 2, collected between midnight and 3:00 a.m. on Sunday and between 6:00 p.m. and midnight on Monday. The winds at this time were from the south-southeast; thus, it is likely that these particles were emitted by the Tempe foundries.

**Site 3.** The most prevalent miscellaneous particle type (ranging from a few percent to >50% by number) in the samples collected at site 3 (west of Phoenix) contains Na, Cl, Ca, S, and Si with minor amounts of Mg, K, and Fe. SEM images show that the particles consist of two distinct phases (Figure 5). One phase appears smooth and rounded, and quantitative analyses show it to be NaCl; the second phase is rough and irregularly shaped and is primarily  $\text{CaSO}_4$ , with some Si, Al, Fe, Mg, K, and Cl. The proportion of NaCl to  $\text{CaSO}_4$  differs from particle to particle. These biphasic particles range from about 0.5 to



**Figure 5.** SEM images of biphasic particles collected at site 3 between 2100 and 00 h on Feb 10, 1980. The smooth, rounded portion of each particle is NaCl; the remainder of each particle is primarily CaSO<sub>4</sub>, commonly with minor amounts of Mg, Si, Al, Fe, and/or K. The source of these particles is not known positively but might be an oil-burning power plant, located ~5 km N of site 3. The scale bars represent 1  $\mu$ m.

4  $\mu$ m in diameter and have an average diameter of about 1.4  $\mu$ m. They were observed in all of the samples from site 3 but are most prevalent in the sample collected between 9:00 p.m. and midnight on Sunday. In this sample over two-thirds of the miscellaneous particles are NaCl-CaSO<sub>4</sub> particles.

The large quantity of NaCl-CaSO<sub>4</sub> particles in the site 3 samples suggests that they are emitted nearby; the most likely source is a large aluminum foundry located about 6 km SE or an oil-burning power plant 5 km N of the sampling location. The wind direction previous to and during collection of the sample showing the highest abundance of biphasic particles was variable, ranging from northeast to southeast; thus, emissions from either the aluminum foundry or power plant could have been carried in the direction of the sampler.

The aluminum foundry uses a mixture of Cl<sub>2</sub> and N<sub>2</sub> gases as a flux during melting of the Al metal. According to plant officials, most of the Cl<sub>2</sub> that does not react in the melt escapes into the atmosphere; thus, the foundry is a major source of Cl in the west Phoenix aerosol. The only other likely particle emissions from the foundry are Al, Al<sub>2</sub>O<sub>3</sub>, and AlCl<sub>3</sub>; therefore, apparently the aluminum foundry is not the source of the Ca, Na, and S in the NaCl-CaSO<sub>4</sub> aerosol particles.

Emissions from the oil-burning power plants in Phoenix have not been studied. Studies of similar power plants in other areas indicate that, depending on the type of fuel burned, emissions may be enriched in Na, S, Ca, Mg, and several other elements (29). Thus, it is possible that oil-burning power plants are the sources of the NaCl-CaSO<sub>4</sub> biphasic particles observed in the Phoenix aerosol. One of the many projects that remain is characterization of the emission from the aluminum foundry and oil-burning power plants. Another possibility is that these biphasic particles originate from playa deposits west of Phoenix (31); however, their size and morphology are more consistent with a high-temperature source.

Several Fe oxide spheres and other typical Fe foundry particles were encountered in the west Phoenix samples; most were chemically identical with the particles from the foundries south of Tempe and probably originated from these or similar industries. Several particles containing Cu, Fe, Cl, and S were found in many of the west Phoenix samples. The origin of these particles is not known;

however, several small brass or bronze foundries in the area are likely sources.

**Carbonaceous Particles.** Approximately 10% of the particles examined in this study showed no elements in the EDS spectra. Usually these particles resemble published photographs of soot particles (37). It is assumed that most of these particles are primarily carbonaceous soot, although some may be organic or biological materials. Because EDS analyses cannot provide information on light elements, no information other than morphology could be obtained for the soot particles. Some of the sootlike particles were collected onto Cu TEM grids and were examined with a TEM. High-resolution images of at least one of the particles show it to be graphitic in nature. Commonly, sooty appearing particles contain small amounts of S, Cl, Si, and other elements. These elements probably originate as residues in the material that is burned or occur as volatile species adsorbed onto the surfaces of soot particles. The major sources of soot particles in Phoenix are automobiles, aircraft, oil-fired power plants, and incinerators.

### Conclusions and Summary

Different and changing sources, combined with complex atmospheric reactions and interactions, theoretically can produce an almost infinite variety of particles in the aerosol. However, we observed a relatively limited number of different anthropogenic particle types in the aerosol, presumably because Phoenix has few heavy industries, no large municipal incinerators, no coal-burning power plants, and in general a limited number of major sources of anthropogenic particles. Because of the large number of particles analyzed, we are confident that the major particle types in the Phoenix aerosol have been identified. For each group of samples, the primary anthropogenic particles observed reflect sources in the vicinity of the sampling sites. Examination of additional particles from existing samples, as well as from samples collected in other areas, will undoubtedly reveal different anthropogenic particle types than have been described or listed here.

Although it was possible to pinpoint likely sources for many of the particles studied, a large fraction are from unknown sources. If only one or two particles of a certain composition are encountered, it is extremely difficult to determine a specific source. Also, particles in the sub-micron size range can agglomerate or take part in chemical reactions and thus not have the same compositions as when they were emitted from their sources. In most cases, source determination depends upon detailed characterization of known or suspected sources. In this work, only emissions from the secondary iron foundries were examined in detail; as a result, particles from these foundries were recognized in samples from all three sites. The sources of many more of the particles described here will probably be pinpointed as additional studies of individual source emissions are conducted.

The work described here is a step toward a comprehensive characterization of the aerosol of a major urban community. It has been the primary goal of this aspect of the study to compile an inventory of particles in the Phoenix urban aerosol. Also, this work has provided an opportunity to evaluate critically the particle analysis procedures used and to define more clearly the problems and benefits of analyzing individual aerosol particles.

More than 8000 aerosol particles, collected over a 2-day period at three sites in Phoenix, were examined and analyzed with an analytical SEM. As expected, when considering that Phoenix is located in a desert region, about 75% of the total number of particles larger than 1  $\mu$ m in

diameter (coarse mode) consist mainly of clay minerals, quartz, feldspars, calcite, and micas. The remaining coarse particles are sulfates, Pb compounds emitted from automobiles, and other anthropogenic particles (e.g., soot, foundry emissions, fly ash, etc.).

The most abundant submicron particle types in the Phoenix aerosol are S-bearing particles (probably sulfates); it is estimated from this study that 60–80% of all submicron particles larger than 0.1  $\mu$ m are sulfates. It is widely assumed, based on bulk analyses, that the most prevalent species are  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NH}_4\text{HSO}_4$ , and  $\text{H}_2\text{SO}_4$ . Some sulfate compounds that were specifically identified in the Phoenix aerosol include  $\text{Na}_2\text{SO}_4$ ,  $\text{K}_2\text{SO}_4$ ,  $\text{SrSO}_4$ , and  $\text{CaSO}_4$ . However, the majority of the sulfate particles contain only minor amounts of elements other than S (e.g., Zn, Cu, Pb, Fe, As, Na, Ca, K, Mg, etc.). It is of concern that potentially toxic elements, e.g., Pb, Cu, Zn, and As, occur in the tiny sulfate particles; studies have shown that certain metals, e.g., Zn, Mn, and Pb, aggravate the adverse health effects of sulfates (38).

Most of the remaining submicron particles also have anthropogenic sources. The most common anthropogenic particles are Pb compounds from automobile exhaust, emissions from secondary iron foundries, fly ash, biphasic particles of NaCl and  $\text{CaSO}_4$ , and soot.

It is obvious that a major limitation of the type of study described here is the time required to analyze a representative number of aerosol particles. As a step to partially alleviate this problem we have recently outfitted our analytical SEM with automation and image analysis capabilities. Also, we will be using individual particle analyses methods to supplement bulk analyses, thereby enabling a more representative and detailed study of this urban aerosol.

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**Registry No.** Ca, 7440-70-2; K, 7440-09-7; Sr, 7440-24-6; Fe, 7439-89-6; Cu, 7440-50-8; Zn, 7440-66-6; Pb, 7439-92-1; As, 7440-38-2; Mg, 7439-95-4; Al, 7429-90-5; Si, 7440-21-3; Cl, 7782-50-5; Na, 7440-23-5;  $\text{CaSO}_4$ , 7778-18-9; S, 7704-34-9; quartz, 14808-60-7; orthoclase, 61076-95-7; albite, 12244-10-9; calcite, 13397-26-7.

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# Nonreversible Sorption of Phenolic Compounds by Sediment Fractions: The Role of Sediment Organic Matter

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■ The sorption and desorption of phenol, 2-chlorophenol, and 2,4-dichlorophenol by a fine and coarse sediment fraction were measured in a continuous flow stirred cell. Sorption was extensive (up to 0.3 mmol/g of sorbent) and was not due solely to hydrophobic interactions. Desorption was slower than sorption, and in some cases up to 90% of the sorbate was irreversibly held. Sorption of the three phenols by the two sediment fractions was also compared with sorption by the same sediment fractions with organic matter partially removed. The penetrability and accessibility of organic matter associated with sediment are proposed to exert a major influence in the sorption of compounds which take part in extensive hydrogen-bond interactions.

## Introduction

The environmental fate of many organic chemicals will be determined largely by their sorption interactions with soils or sediments (1-6) or with soluble humic compounds (7). The organic matter content of these natural sorbents has been shown to be an important factor in determining their sorption properties. This behavior has been summarized in terms of a mechanism involving solute partitioning between aqueous solution and the sorbent organic matter (2-12), in which the partition coefficient is influenced by the hydrophobicity of solute rather than by the makeup of the organic matter itself. However, the apparent uniformity of the sorbent character of organic matter may be partially the result of "averaging" which is inherent in observations of such complex material. The early formulation of an index for soil sorption equilibria (8) required the postulation of a "corrected" organic matter content, or "active fraction" of organic matter, in order to obtain the best indexing results. Also, different linear relationships have been observed between the organic carbon contents of extracted humic and fulvic fractions and the sediment content of chlorinated hydrocarbons (2). More generally, the observed partition coefficient for a whole sediment has been shown to be the weighted sum of a series of partition coefficients applicable to different particle size fractions within a whole sediment (11).

The treatment of organic matter as a "solvent" for organic molecules implies a uniform penetrability of the macromolecular organic matter which is itself present primarily as the adsorbed phase in organomineral particles. Humic components are commonly associated with clay-size particles (13-15), and a lower proportion of these components are extractable with alkali (13), than from the total humic content of the sediment. Some low molecular weight organic matter can even be present in clay interlamellar spaces (16). The association of organic matter with mineral particles can alter the surface charge characteristics of the particles (17). The effect on the organic matter itself may be to apply some constraint to conformational changes that can otherwise occur freely when humic particles are present in true solution (18). It is important to see if such constraints have a significant influence on the sorption properties of organic matter.

The treatment of sorption as a distribution process also assumes that the mechanism is reversible, but where it has

been studied the results are varied. Carbonyl and parathion sorption by homoionic soil organic matter preparations is completely reversible (9), whereas PCB sorbed by lake sediment material consists of both a reversible and a nonreversible fraction (19). Halobenzene and haloalkane sorption by aquifer sorbents is reversible in terms of material balance over complete sorption-desorption cycles, but differences may exist in the kinetics of sorption and desorption (6).

The aim of this study was to examine the sorption and desorption of phenol, 2-chlorophenol, and 2,4-dichlorophenol by lake sediment material. These compounds were chosen as representatives of widely used organic chemicals, or of possible organic degradation products (20). In addition, they have the potential for interaction by hydrogen-bond mechanisms, which contribute a significant part of the inter- and intramolecular forces governing the conformational structure of humic compounds (21). The interactions of the phenols with the sediment-associated organic matter are investigated in order to examine the sensitivity of sorption and desorption to organic matter structure and "penetrability".

## Experimental Section

The terms sorptive, sorbate, and sorbent are used to refer to the free solute in solution, solute sorbed by sediment material, and the sediment material, respectively.

**Sorptives.** Phenol, 2-chlorophenol, and 2,4-dichlorophenol were obtained from commercial sources and used without further purification.

**Sorbents.** Surface sediment from Lake Zoar, CT, was sampled, by using an Eckman dredge and was stored in glass containers at 4 °C. Subsamples were separated into two particle size fractions, coarse (>2 μm) and fine (<2 μm), by standard methods of suspension and sedimentation without the use of dispersants. Labile organic matter was removed from another subsample of whole sediment by treatment with hydrogen peroxide (22), and this treated sample was also separated into coarse and fine fractions. "Untreated" and "treated" fractions are therefore those with and without labile organic matter associated with the inorganic substrates. Organic carbon contents of treated and untreated fractions were estimated by loss-on-ignition (23), after preelution with distilled water in the sorption apparatus (see below). The organic carbon contents obtained from three replicates were the following: fine fraction, untreated (10.2 ± 0.2%); fine fraction, treated (3.3 ± 0.2%); coarse fraction, untreated (4.2 ± 0.2%); coarse fraction, treated (0.7 ± 0.1%). Sorbent suspensions were not dried prior to sorption and desorption experiments unless otherwise stated.

**Sorption and Desorption.** Sorption and desorption isotherms were obtained by using a thermostated continuous flow stirred cell (CFSC) apparatus (24). This system consists of a suspension of sorbent contained by two hydrophilic membranes (one 0.45 μm and one 0.22 μm; Millipore) in a glass cell (~100 cm<sup>3</sup>) with entry and outlet ports. Eluent solutions were drawn through the CFSC cell from a reservoir containing a known concentration of sorptive (sorption) or containing distilled water (desorption) and then through the flow cell of a spectrophotometer



Table I. Sorption Capacity<sup>a</sup> ± s of Sediment Fractions and Percentage of Sorbate<sup>b</sup> Irreversibly Sorbed

sorbative	sediment fraction							
	fine				coarse			
	untreated		treated		untreated		treated	
	a	b	a	b	a	b	a	b
phenol	0.18 ± 0.008	(17)	<0.02 ± 0.02	(0)	0.08 ± 0.006	(13)	<0.02 ± 0.02	(0)
2-chlorophenol	0.30 ± 0.017	(90)	0.19 ± 0.013	(74)	0.10 ± 0.017	(60)	0.10 ± 0.019	(40)
2,4-dichlorophenol	0.27 ± 0.012	(50)	0.11 ± 0.010	(30)	0.07 ± 0.011	(35)	0.04 ± 0.005	(15)

<sup>a</sup> Sorption capacity expressed as millimoles per gram of sorbent;  $s = a/(n - 1)^{1/2}$ ,  $n = 3$ . <sup>b</sup> Amount of irreversibly held sorbate as percentage of total sorbate.

(Bausch & Lomb Spectronic 21 UVD) by using a peristaltic pump at a known flow rate. The flow rates were in the range 0.03–1.00 cm<sup>3</sup>/min giving mean residence times of 3000–100 min. The amount of sorptive sorbed at any given time in this system can be calculated by obtaining the mass balance around the cell, which can be calculated knowing the volume of reservoir solution input, and the concentration profile of the eluted solution (24). Sorptive concentration in the eluate was measured by continuous monitoring of absorbance (at 268 nm for phenol, 274 nm for 2-chlorophenol, or 284 nm for 2,4-dichlorophenol) in the spectrophotometer flow cell. Linear calibration curves of concentration vs. absorbance were obtained for each sorptive, over the range of eluent concentrations used. The absorbance method was checked against quantitation by gas chromatography using a 0.1% SP-1000 6 ft × 2 mm column in a Hewlett-Packard 5840A gas chromatograph. Selected eluate fractions were also chromatographed to identify any degradation products formed during the course of interaction, and none were found.

All sorbent suspensions were preeluted with distilled water to remove material capable of passing through the end-of-cell membranes. Only the untreated fine fraction showed any measurable absorbance in the eluate, which was ascribed primarily to release of soluble organic matter from this fraction. The amount lost was estimated by drying to be less than 0.5% of the initial sorbent weight.

Blank sorption and desorption experiments were performed for each of the three sorptives, in the absence of sorbent, to verify that there was no interaction with the CFSC system. Teflon tubing was used for all connections between the different elements of the apparatus, except in the peristaltic pump where Elkay flexible tubing was used.

### Results

**Sorption.** The sorption data could only be described by linear isotherm models over the more dilute sorptive concentrations examined (less than 0.5 mmol/dm<sup>3</sup>), after which sorption became a limiting process and the isotherm slopes decreased significantly, indicating that the sediment has a limited sorption capacity for each phenol (Figure 1 and Table I). All the isotherms reported here are derived from the mean results of three experiments at the same flow rate. The CFSC method showed that sorption was a function of the mean residence time of sorptive in the cell (Figure 2). However, sorption by undried sediment approached a "limiting" isotherm when the residence time exceeded about 900 min, and it is these limiting isotherms which are reported here. "Isotherms" obtained at rates above the limiting flow, that is, under nonequilibrium conditions, gave lower final sorption capacities than the limiting isotherm and were less reproducible.

The sorption capacities included in Table I were primarily a function of the organic carbon content of both particle size fractions (Figure 3) (11). The nonlinearity of

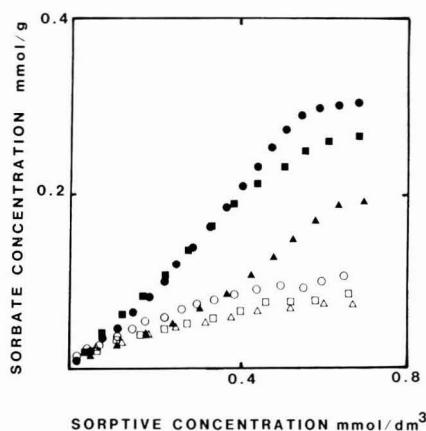


Figure 1. Sorption of phenol (▲, △), 2-chlorophenol (●, ○) and 2,4-dichlorophenol (■, □) by fine sediment fraction (full symbols) and by coarse sediment fraction (open symbols).

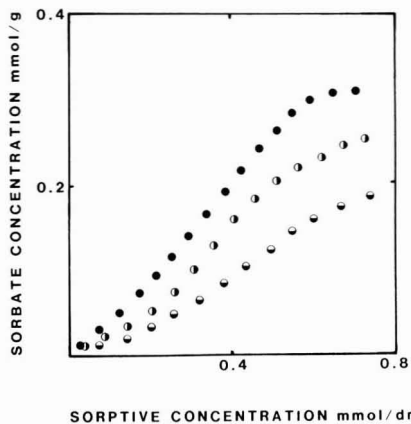


Figure 2. Sorption of 2-chlorophenol by fine sediment fractions at eluent flow rates of 0.08 (●), 0.50 (○), and 1.0 (◐) cm<sup>3</sup>/min.

the sorption isotherms shows that partition coefficients are not independent of sorptive concentration. Coefficients calculated at 0.6 mmol/dm<sup>3</sup> sorptive concentration show that their values are closely related to the organic carbon content of the sorbent (Table II). The sorption capacities of the treated fractions were smaller per gram of sediment (Figure 4 and Table I), but much greater per gram of residual organic matter (Figure 5), than for the untreated sorbents. Sorption of unsubstituted phenol by the treated fractions was poorly reproducible.

The isotherms observed fall into two categories, which have been called L type and S type (25). The L-type

Table II. Partition Coefficients<sup>a</sup> ( $K_{oc} \pm s$ ) Calculated on the Basis of Sediment Organic Carbon Content

sorbptive	sediment fraction			
	fine		coarse	
	untreated	treated <sup>b</sup>	untreated	treated <sup>b</sup>
phenol	2.90 ± 0.19		3.10 ± 0.35	
2-chlorophenol	4.89 ± 0.38	9.57 ± 1.11	3.99 ± 0.83	23.15 ± 6.71
2,4-dichlorophenol	3.99 ± 0.18	5.11 ± 0.71	3.13 ± 0.63	9.60 ± 2.16

<sup>a</sup>  $K_{oc} = K_p/f_{oc}$  ( $\text{dm}^3/\text{g}$ ), and  $S = K_p C$ , where  $K_{oc}$  = partition coefficient on organic carbon basis,  $f_{oc}$  = fraction of organic matter,  $S$  = concentration in solid phase, and  $C$  = concentration in solution phase. All  $K_{oc}$  values should be multiplied by  $10^3$ .  $s = \sigma/(n-1)^{1/2}$ ,  $n = 3$ . <sup>b</sup> Treated with hydrogen peroxide to remove labile organic matter.

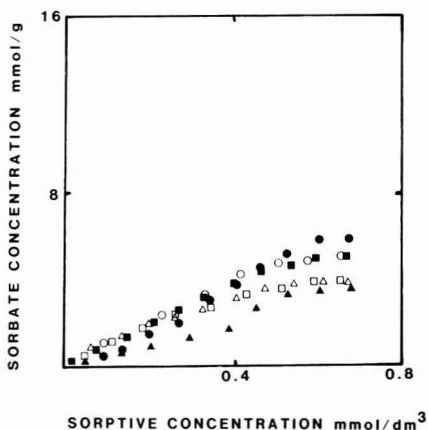


Figure 3. Sorption of phenol ( $\blacktriangle$ ,  $\triangle$ ), 2-chlorophenol ( $\bullet$ ,  $\circ$ ), and 2,4-dichlorophenol ( $\blacksquare$ ,  $\square$ ) by fine sediment fraction (full symbols) and by coarse sediment fraction (open symbols), with sorbate concentrations calculated per gram of sediment fraction organic matter.

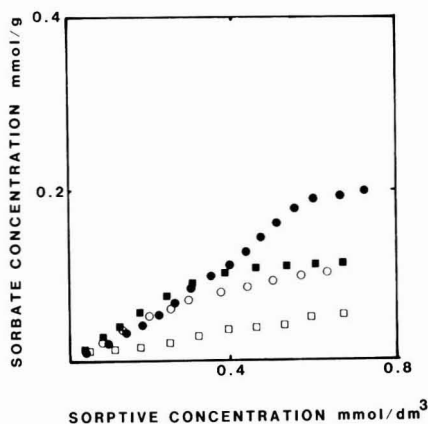


Figure 4. Sorption of 2-chlorophenol ( $\bullet$ ,  $\circ$ ) and 2,4-dichlorophenol ( $\blacksquare$ ,  $\square$ ) by treated fine sediment fraction (full symbols) and by treated coarse sediment fraction (open symbols).

isotherm (e.g., Figure 1 (O)) is common to many sorption systems, although these frequently deviate from the ideals for which the Langmuir equation has been derived. The S-type isotherm (e.g., Figure 1 ( $\blacktriangle$ )) is less common and implies that successive sorbate molecules cooperate strongly in the sorption of further sorbate.

The variations in isotherm shape and in sorption capacities did not follow trends consistent with either the sorptive or sorbent characteristics. The isotherms for sorption of phenol and 2-chlorophenol by the fine fractions

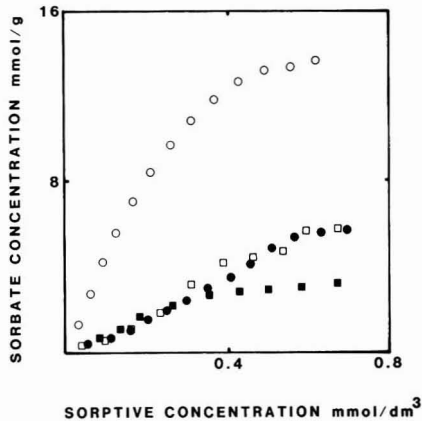


Figure 5. Sorption of 2-chlorophenol ( $\bullet$ ,  $\circ$ ) and 2,4-dichlorophenol ( $\blacksquare$ ,  $\square$ ) by treated fine sediment fraction (full symbols) and by treated coarse sediment fraction (open symbols), with sorbate concentrations calculated per gram of sediment fraction organic matter.

tended to be S type (Figures 1 and 4 ( $\bullet$ ,  $\blacktriangle$ )) and this shape was accentuated in isotherms calculated on the basis of organic carbon content (Figures 3 and 5 ( $\bullet$ ,  $\blacktriangle$ )). L-type isotherms were observed for the interactions of these sorptives with the coarse fraction (Figures 1 and 3-5: (O,  $\Delta$ )). However, the sorption of 2,4-dichlorophenol by the untreated fine fraction gave a less S-type isotherm, while the untreated coarse sediment had a moderate S character (Figure 1 ( $\blacksquare$ ,  $\square$ )).

The treated fine fraction sorbed less of the phenols (on a whole sediment basis) than its untreated counterpart, while the treated and untreated coarse fractions sorbed very similar amounts of 2-chlorophenol but not of unsubstituted phenol or 2,4-dichlorophenol (Table I).

Sorption isotherms calculated on the basis of organic carbon content show that those for the untreated fractions and the two treated fractions (Figures 3 and 5, respectively) were grouped in different areas. The isotherm for 2-chlorophenol sorption by the treated sediment deviated sharply from the other isotherms.

Partition coefficients calculated from sorption capacities on the organic carbon basis (Table II) were larger for 2-chlorophenol than for 2,4-dichlorophenol or unsubstituted phenol, and these were increased substantially in the treated fine and coarse fractions. This enhancement in the treated fractions was not so great for 2,4-dichlorophenol.

Samples of the untreated fine and coarse fractions were oven-dried at 110 °C, and this treatment was found to reduce their sorption capacities greatly. The isotherms obtained were all distinctly S type, and the sorption capacities were much less than for the undried sorbents. The situation was complicated, however, because a decrease in

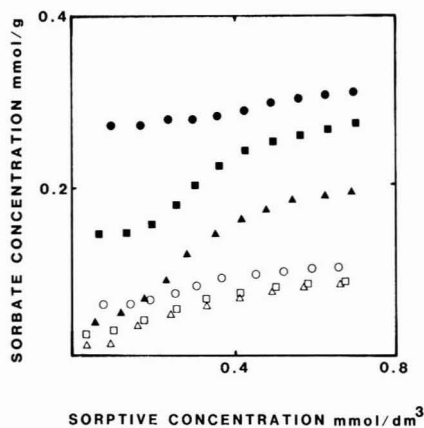


Figure 6. Desorption of phenol ( $\Delta$ ,  $\triangle$ ), 2-chlorophenol ( $\bullet$ ,  $\circ$ ), and 2,4-dichlorophenol ( $\blacksquare$ ,  $\square$ ) from fine sediment fraction (full symbols) and from coarse sediment fraction (open symbols).

eluent flow rate steadily increased the amount of sorbate that could be bound, and the indications were that maximum sorption ability was not being observed at the lowest flow rate used ( $0.03 \text{ cm}^3/\text{min}$ ).

**Desorption.** Considerable hysteresis occurred for most of the sorbent-sorptive combinations (Figure 6), in that the isotherms computed from desorption data deviated from their corresponding sorption isotherms. This deviation extended as far as zero sorptive concentration, corresponding to a fraction of sorbate being irreversibly held (Table I). The term "isotherm" is invalid in these cases, because of the dependence of desorption upon the route of prior sorption, but it is used for convenience. It has been mentioned that the sorption data were found to be a function of eluent flow rate until the mean residence time exceeded about 900 min, after which limiting isotherms were obtained. By contrast, the observed desorption "isotherms" showed significant, if small, changes as far as the lowest practical limit of eluent flow rate, which corresponded to a mean residence time of 3000 min. Desorption was therefore a slower process than sorption in most cases, and the data were obtained under nonequilibrium conditions. Nevertheless, it is considered that the hysteresis and irreversibility of sorption observed would have occurred even under equilibrium conditions, because the changes in desorption behavior were very small at the slowest flow rates examined. The desorption "isotherms" in Figure 6 were obtained at the same eluent flow rate which gave maximum interaction (limiting isotherm) at the sorption stage.

The extent of deviation of the sorption and desorption isotherms over most of the sorptive concentration range was less for the coarse fractions than the fine fractions. The fraction of sorbate irreversibly held was greater in the untreated fractions than in the treated ones. Hysteresis between the sorption and desorption isotherms over the whole sorptive concentration range was greatest for 2-chlorophenol sorption. The amounts of irreversibly held sorbate were also highest for this sorptive (Table I), showing that this compound was both more strongly and more extensively sorbed than the other two sorptives.

### Discussion

Sediments are capable of sorbing considerable amounts of the three phenolic compounds, and some of the sorbate was irreversibly held in each case. The extensive hysteresis

between sorption and desorption shows that the desorption process is affected by the previous sorption.

The sorption capacities of the untreated sediment (on a per gram organic carbon basis) are of the same order of magnitude as those observed for 4-chlorophenol and 4-toluenesulfonate sorption by activated charcoal (26), which was itself found to sorb more than various polymeric and carbonaceous sorbents. The organic matter associated with sediment is therefore of comparable efficiency with charcoal.

The strong affinity of the sorptives for the organic matter can also be seen in the very high values (2900-4900) of the partition coefficients calculated on an organic matter basis (Table II). These values greatly exceed those predicted on the basis of sorption controlled solely by hydrophobic forces. The contribution of such forces has been described by semiempirical equations relating partition coefficients to the water solubility or to the octanol-water partition coefficient of various sorptives (12). Partition coefficients predicted on this basis for phenol, 2-chlorophenol, and 2,4-dichlorophenol are 7.3, 16.5, and 57.6, respectively. The difference between the observed and predicted values implies a substantial contribution to sorption by more specific sorbate-sorbent interactions than by general hydrophobic forces. The mechanism of sorption is likely, therefore, to involve extensive hydrogen-bond formation between the sorbate phenolic hydroxyl groups and hydrogen-bonding sites on the sediment organic matter. At the same time, hydrogen-bonding forces will also be important in solvent-sorptive interactions that will tend to oppose the sorption process. The complexity of the balance between factors influencing sorption is illustrated by the variation of the observed partition coefficients and sorption capacities between sorptives and between sorbents (Tables I and II). The observed values are not consistent with the decrease in water solubility of the sorptives, although the two chlorophenols were sorbed more extensively by the fine fraction than the unsubstituted compound. Nor was a consistent trend obvious in terms of the potential of the sorptive for hydrogen-bond formation and of the steric effect of ortho substitution which can hinder hydrogen-bond formation.

The three sorptives are weak organic acids, the general behavior of which has been shown to be strongly pH dependent in their sorption by inorganic hydrous oxide and clay materials (17). The pH of eluent was not monitored continuously in the experiments reported here, but the difference in pH between suspensions of the uninteracted sediments and the suspensions at maximum sorptive concentration was found to be an increase of about 0.2 unit (0.07 to 0.26 unit). Such an increase may be due to complex formation between sediment surface hydroxyl groups and the acidic phenolic hydroxyl groups. The pHs of uninteracted sediment suspensions were in the range 6.21-6.35, so that an increase of the order of 0.2 unit will have increased the degree of dissociation of 2,4-dichlorophenol ( $\text{p}K_a = 7.7$  (20)) to a slightly greater extent than of 2-chlorophenol or phenol ( $\text{p}K_a = 8.5$  and 9.8, respectively). An increase in the degree of dissociation of the sorptive species would tend to decrease its hydrophobicity and increase its effective size by increasing the extent of its hydration. However, an increase in pH would also tend to increase the dissociation of weakly acidic functional groups on the sediment organic matter, which would result in increased intramolecular repulsion between dissociated groups in the macromolecular structure. This in turn could cause some "opening out" of the structure of the sediment-associated organic matter and an increased avail-

bility of access to some sorption sites. The role of pH in organic molecule-sediment organic matter interactions is likely to be complex and merits detailed investigation.

Although initial sorption of the phenols on organic matter surfaces will be influenced largely by their aqueous solubilities, as material moves into the bulk of sediment organic matter, the environment it encounters becomes less aqueous. The results show that sorption is also affected by the nature of the sediment fraction, and hence partly by its associated organic matter.

All of the observed partition coefficient values are greater than those reported for the sorption of the same phenols on a clay loam soil (4), illustrating again the complex relationship between the behavior of soils and sediments (1). The lower partition coefficient values for soils which were air-dried may also be related to the effects on sorption of sediment drying observed here.

The source of differences in the sorption behavior of sediment-associated organic matter may lie in small differences in the overall structure of such material in different particle size fractions and in the ease of penetration of sorptive into the bulk of the organic matter. Inter- and intramolecular hydrogen bonds are of basic importance to the structure and conformation of humic macromolecules (21), and they will also contribute to the forces that hold such molecules on the surfaces of inorganic particles (15). The entry of sorptive molecules that will be sorbed by means of strong hydrogen-bond interactions into such macromolecules may necessitate considerable disruption and reordering of the overall structure of the humic compounds. Such reordering can occur easily for humic molecules in solution (at high pH), where they have a flexible, randomly coiled structure (18), but their ability to accommodate the intrusion of sorptive molecules will be restricted when the humic molecules are held more rigidly as the surface coatings of inorganic particles, or even in clay interlamellar spaces.

The initial part of many of the isotherms reported here showed regions of increasing slope, which can be described as S-type isotherms, which are characteristic of cooperative sorption. The interpretation of this behavior here is that initial penetration of sorptive, from the "surface" of the sediment organic matter into the humic structure, requires more substantial rearrangements of this structure than subsequent sorption. This change in the extent of rearrangement will occur if the uptake of sorbate results in sufficient "swelling" of the humic structure which progressively weakens the hydrogen-bond interactions which maintain its macrostructure. The S-type isotherms were more common for the fine fraction, which has a higher total amount of associated organic matter, than for the coarse fraction. While there is no clear-cut distinction between the organic matter associated with these two fractions, that associated with the fine particle size fraction has been found to have a higher organic carbon content, and a lower carbon/nitrogen ratio, than that associated with coarser particles (13). This generally more humified nature may correspond to a rather more condensed and rigid structure, which is less easily penetrated by sorptive than the coarse fraction organic matter. The shape of the coarse fraction isotherms were more generally L type, or Langmuirean, in which the sorption model proposes a constant energy of sorption and the noninteraction of sorbate molecules at different sorption sites.

The role of hydrogen bonding in the structure and conformation of sediment-associated organic matter will be greatly enhanced in any sediment that is subjected to drying, which has expelled loosely held water and allowed

shrinkage of the organic matter. Under such conditions hydrogen bonds may form between suitable sites (OH, COOH, SH, and NH<sub>2</sub>) on the organic macromolecules without the intermediary of water molecules. Strong intramolecular bonds may also be set up between hydrophobic portions of the macromolecules. The results presented here indicate that the sorptive behavior of dried sediments is restricted. This factor should be examined further to assess the sorption capacity of sediments liable to drying as a result of water level fluctuations, or as a result of dredging operations.

Desorption was a slower process than sorption, especially in the sediment fractions from which labile organic matter had not been removed. Similar kinetic effects have been observed in the sorption of nonpolar organic compounds (6). However, in the present study, a fraction of each sorbate was also irreversibly held by the sediment, in spite of the appreciable aqueous solubility of each phenol. The proportion of irreversible to reversible sorbate increased with the total sorption capacity and was higher in the fine fraction than in the coarse fraction.

Peroxide treatment of the sediment decreased the amount of irreversible sorbate, especially in the coarse fraction. The removal of labile organic matter by such a pretreatment probably will have had two main effects likely to be responsible for differences in sorption behavior. First, it will have made any residual organic matter much more accessible, by removing overlying material, even though the residual may have a more condensed structure than the whole. Second, it will have exposed inorganic surfaces, where the phenolic compounds may be able to sorb by interaction with metal cations through water of hydration, and at general hydrogen-bonding sites (27, 28). The inability of the treated fractions to sorb unsubstituted phenol shows that the modified sorbent surface was not able to compete with phenol-solvent interactions. Their sorption of the two less soluble chlorophenols was significant but was not proportional to sorptive hydrophobicity. The increased partition coefficient values compared with the untreated fraction (Table II) are calculated assuming that organic matter is the sole sorbent. The increase in the percentage of reversible sorbate presumably is due in part to sorbate held at inorganic surface sites, and hence, these partition coefficient values are overestimates. However, the amount of irreversible sorbate expressed on a per gram of organic carbon basis (Table I) is greatly increased in the treated sediments, and it is concluded that exposure of the small amount of residual organic matter results in more efficient sorption by that material. Oxidizing water treatments will degrade dissolved humic materials (29) and may reduce the organic matter content of suspended particles. The results presented here imply that such action may increase the sorption efficiency on a per carbon basis of the resulting materials, even if it reduces the total sorption capacity.

### Summary and Conclusions

A continuous flow stirred cell technique was used to measure the sorption and desorption of three phenolic compounds by sediment fractions. The results may be summarized as follows:

- (1) Desorption occurred (up to 0.3 mmol/g of sediment), which could not be described by simple linear isotherm models and which was limiting as sorptive concentration increased.
- (2) The sorption mechanism involved hydrogen-bond interactions between sorbate and sorbent in addition to purely hydrophobic interactions.

(3) The behavior of each sorptive was a complex function of its solubility and its hydrogen-bonding ability. In addition, it was influenced by the amount and nature of the organic matter associated with the sediment fractions.

(4) The penetrability of sediment-associated organic matter is proposed to exert a major influence on the progress of sorption of compounds which take part in hydrogen-bond interactions. This is due to interaction with inter- and intramolecular hydrogen bonds which contribute to the conformational structure of the organic macromolecules.

(5) Desorption was a slower process than sorption in all cases, and equilibrium was not established at mean equilibration periods of up to 3 times those required for sorption. A significant fraction of sorbate was irreversibly held by each sediment fraction.

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**Registry No.** 2-Chlorophenol, 95-57-8; 2,4-dichlorophenol, 120-83-2; phenol, 108-95-2.

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# Atmospheric Reactions of *N*-Nitrosodimethylamine and Dimethylnitramine

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■ The major atmospheric reactions of *N*-nitrosodimethylamine (NDMA) and dimethylnitramine (DMN) have been investigated in an ~3500-L environmental chamber utilizing in situ long-path Fourier transform infrared spectroscopy. Rate constants for the reactions of OH radicals with NDMA and DMN were measured relative to that for dimethyl ether at  $298 \pm 2$  K and resulted in values of  $k(\text{OH} + \text{NDMA}) = (3.0 \pm 0.4) \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> and  $k(\text{OH} + \text{DMN}) = (4.5 \pm 0.5) \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. Rate constants for the reactions of O<sub>3</sub> with NDMA and DMN were determined to be  $\leq 1 \times 10^{-20}$  and  $\leq 3 \times 10^{-21}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, respectively. The photolysis rate of NDMA measured in the presence of excess O<sub>3</sub> indicated the photodissociation quantum yield to be unity for  $\lambda \geq 290$  nm. The photolysis of NDMA in O<sub>3</sub> resulted in the formation of ~65% DMN together with lesser yields of HCHO, CH<sub>3</sub>NO<sub>2</sub>, and CO. A mechanism accounting for the observed products is presented. The rapid photolysis of NDMA leads to a tropospheric half-life of only ~5 min, while a half-life of ~2 days is predicted for DMN, with its major removal process being reaction with OH radicals.

## Introduction

*N*-Nitrosamines are distributed throughout a number of occupational environments (1-3) and are of concern because some of them are potent animal carcinogens (2, 4, 5). They have been detected in ambient air near a factory in West Germany producing secondary amines (6) and in areas in the U.S. (7, 8) adjoining industrial plants which used dimethylamine and *N*-nitrosodimethylamine in organic syntheses. Recently, they have been detected in ambient air in several urban regions of California (9).

The first definitive study of reactions in amine-NO<sub>x</sub>-air mixtures employed long-path Fourier transform infrared (FT-IR) spectroscopy and showed that parts per million (ppm) levels of dimethylamine and nitrous acid react in the dark to form *N*-nitrosodimethylamine [(CH<sub>3</sub>)<sub>2</sub>N-NO] (10). Subsequent experiments in a 50-m<sup>3</sup> outdoor smog chamber with sub ppm concentrations of precursors showed that diethylamine reacted in the dark with an NO-NO<sub>2</sub>-HONO mixture to form *N*-nitrosodiethylamine (11). Supplemental studies by long-path FT-IR spectroscopy verified that, in addition to the formation of the nitrosamines in the dark, the corresponding nitramines are major products formed during sunlight irradiation of dimethylamine-NO<sub>x</sub>-air and diethylamine-NO<sub>x</sub>-air mixtures (12), and mechanisms were advanced to explain these and other products (11, 13).

More recently, we have shown that *N*-nitrosodimethylamine is the major product of the dark reaction of 1,1-dimethylhydrazine [(CH<sub>3</sub>)<sub>2</sub>N-NH<sub>2</sub>] with ozone under simulated atmospheric conditions (14-17). Additionally, in accord with earlier results (11, 12), in sunlight the *N*-nitrosodimethylamine is rapidly converted into dimethylnitramine [(CH<sub>3</sub>)<sub>2</sub>N-NO<sub>2</sub>] (14-16). These observations are particularly relevant since 1,1-dimethylhydrazine has a variety of industrial/military uses, including being a fuel component of a major missile system.

In view of the demonstrated carcinogenic activity of nitrosamines (2, 4, 5) and nitramines (18, 19) in test animals and the apparent facile formation of these compounds from their gaseous precursors, it is clearly important to

study the loss processes which determine the lifetimes of these nitrogen-containing organics in the atmosphere. *N*-Nitrosodimethylamine (NDMA) and dimethylnitramine (DMN), the simplest pair of these related compounds, have been selected for this study.

Analogous to other organic compounds, *N*-nitrosamines and nitramines are expected to undergo degradation in the atmosphere primarily via reaction with the hydroxyl radical, reaction with ozone, and photolysis (20). As is generally true for *N*-nitroso compounds, NDMA photolyzes rapidly under atmospheric conditions (10, 12, 21). In contrast, DMN and other alkyl nitramines in general have a negligible absorption in the solar actinic region (22), and hence their photolytic decomposition in the atmosphere will be insignificant. The rates of the reactions of both NDMA and DMN with O<sub>3</sub> and OH radicals have not been previously established. Hence, in this work we have determined the rate constants, or upper limits thereof, for these reactions. In addition, we have investigated the rate and products of the photolysis of NDMA in the presence of O<sub>3</sub>.

## Experimental Procedures

The reaction vessel employed was an ~3500-L rectangular chamber constructed of 50 μm thick Du Pont FEP Teflon film, with approximate dimensions of 1.2 m × 1.2 m × 2.4 m. Irradiation of the chamber contents was provided by diametrically opposed banks of 20 Sylvania 40-W black lamps. The chamber was equipped with in situ, 2.13-m base path multiple-reflection optics for Fourier transform-infrared (FT-IR) spectroscopic measurements. Details of the chamber construction and of the interferometer and data system have been described elsewhere (17).

The light intensity was determined by NO<sub>2</sub> actinometry using the quartz flow tube technique described by Zafonte et al. (23), and the relative spectral distribution was monitored by using a calibrated photomultiplier-double monochromator combination (24). The volume of the chamber was determined by FT-IR and gas chromatographic (GC) analyses of injected known amounts of calibration compounds and was found to be reproducible to within ±2% at full inflation.

Injections of vapor samples into the chamber were carried out by flushing known pressures in calibrated Pyrex bulbs with a 20 L min<sup>-1</sup> flow of N<sub>2</sub> gas with simultaneous mixing by a fan rated at 300 L s<sup>-1</sup>. The partial pressures of the reactants were measured into calibrated 2- and 5-L Pyrex bulbs on a vacuum line equipped with an MKS Baratron capacitance manometer. Dimethylnitramine, which is a solid at room temperature, was introduced into the chamber by passing a stream of N<sub>2</sub> gas over a gently heated, weighed sample.

The time-concentration profiles of the reactants and products were monitored by FT-IR spectroscopy at 1-cm<sup>-1</sup> spectral resolution and optical path lengths of 68.3 or 102.4 m. Data were recorded with a time resolution as short as 1 min by first storing successive sets of 32 coadded interferograms and subsequently transforming them into spectra after completion of the experiment. Table I summarizes the infrared frequencies and absorption coefficients employed in this study. For kinetic measurements,

Table I. Infrared Measurement Frequencies and Absorption Coefficients

compound	frequency, cm <sup>-1</sup>	absorption coeff. <sup>a</sup> , cm <sup>-1</sup> atm <sup>-1</sup> , base e	ref
(CH <sub>3</sub> ) <sub>2</sub> NNO	1015.8	20.0	this work
(CH <sub>3</sub> ) <sub>2</sub> NNO <sub>2</sub>	1307.0	34	this work
(CH <sub>3</sub> ) <sub>2</sub> O	1178.8	15.5	this work
CH <sub>3</sub> NO <sub>2</sub>	1589.5	26.3	this work
HCHO	2766.9	10.5	this work
CO	2116.0	13	this work
HNO <sub>3</sub>	879.4	32	b
N <sub>2</sub> O <sub>5</sub>	1245.8	42	b
NO <sub>2</sub>	1631.0	41	this work

<sup>a</sup> At room temperature (296 K) and pressure (730 torr); 1-cm<sup>-1</sup> resolution (unapodized); peak-to-base line measurement. <sup>b</sup> Derived from the data of Graham (38) by comparing the broader features of the 1-cm<sup>-1</sup> resolution spectra with those of the published spectra at lower resolutions.

however, only the absorbance values vs. time were required. DMN was prepared by oxidation of NDMA with CF<sub>3</sub>CO<sub>3</sub>H and purified according to the procedure by Emmons (25). CH<sub>3</sub>ONO was generated by dropwise addition of 50% H<sub>2</sub>SO<sub>4</sub> to a saturated solution of NaNO<sub>2</sub> in CH<sub>3</sub>OH and purified according to published procedures (26). Ozone was produced in a Welsbach T-408 generator at a pre-calibrated voltage and input flow of high-purity O<sub>2</sub> (Liquid Carbonic, 99.995%) and collected in 5-L bulbs. NDMA (Aldrich, >99%), N<sub>2</sub>H<sub>4</sub> (Matheson Coleman & Bell, >97%), NO (Matheson, 99.0%), and CH<sub>3</sub>OCH<sub>3</sub> (Matheson, >99.87%) were used without further purification.

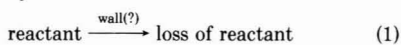
The specific experiments performed consisted of (1) measuring the dark decay rates of DMN and NDMA in dry air (<10% relative humidity at ~296 K) in the presence and absence of excess O<sub>3</sub>, (2) irradiating DMN-CH<sub>3</sub>OCH<sub>3</sub>-CH<sub>3</sub>ONO-NO mixtures in dry air and monitoring the relative decay rates of DMN and CH<sub>3</sub>OCH<sub>3</sub>, (3) flushing N<sub>2</sub>H<sub>4</sub> (in 2-L bulbs brought to 1-atm pressure with N<sub>2</sub>) with N<sub>2</sub> into the chamber containing DMN-CH<sub>3</sub>OCH<sub>3</sub>-O<sub>3</sub> or NDMA-CH<sub>3</sub>OCH<sub>3</sub>-O<sub>3</sub> mixtures in dry air and monitoring the relative changes in CH<sub>3</sub>OCH<sub>3</sub> and DMN or NDMA concentrations, and (4) measuring the decay rate of NDMA during its irradiation in the presence of excess O<sub>3</sub>. The reaction conditions, results, and data analyses for these experiments are described in the following section.

## Results

**Dark Decay and Reaction with O<sub>3</sub>.** The dark decay at 296 K of 4 ppm DMN was observed for 3 h, after which 12 ppm of O<sub>3</sub> was introduced into the chamber and the reaction monitored for an additional 3 h. The dark decay amounted to ~0.7% DMN loss over 3 h with no significant increase in the loss rate in the presence of excess O<sub>3</sub>. If it is assumed that secondary or chain reactions are negligible and thus that the DMN decay rate is given by

$$-d \ln [\text{reactant}]/dt = k_1 + k_2[\text{O}_3] \quad (1)$$

where  $k_1$  and  $k_2$  are the rate constants for reactions 1 and 2, respectively:

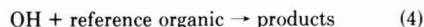
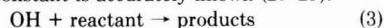


then this corresponds to an upper limit for the rate constant for the DMN + O<sub>3</sub> reaction of  $k_2 \leq 3 \times 10^{-21}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.

Similar experiments were conducted for NDMA. Approximately 0.5% of an initial 4 ppm of NDMA decayed in the dark after 3 h, while an additional ~2.5% loss was observed during the 3 h following the addition of 12 ppm of O<sub>3</sub>. After the dark decay rate was corrected for by using eq 1, an approximate rate constant of  $\sim 6 \times 10^{-21}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> was derived for the possible reaction of NDMA in the mixture in air containing excess O<sub>3</sub>. However, for reasons described under Discussion, this must rigorously be regarded as an upper limit, and we prefer to cite  $k_2 < 1 \times 10^{-20}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for NDMA.

**Hydroxyl Radical Relative Rate Constant Measurements.** Rate constants for the reactions of OH radicals with DMN and NDMA were determined by using two relative rate techniques. The first involved formation of OH radicals from the photolysis of CH<sub>3</sub>ONO in air (27, 28) and the second the generation of OH radicals from the rapid dark reaction of N<sub>2</sub>H<sub>4</sub> with O<sub>3</sub> (29). Both of these relative techniques have been shown to give results that are in good agreement with well-established absolute rate techniques for a variety of compounds (27-29).

Regardless of how they are generated, the OH radicals can, besides reacting with their precursors and other reaction products, react with the compounds of interest (DMN or NDMA) and a reference organic whose OH radical rate constant is accurately known (27-29):



If photolysis and reactions of the reactant and reference organic with O<sub>3</sub> and other species are negligible, then in the absence of dilution

$$-d \ln [\text{reactant}]/dt = k_3[\text{OH}] \quad (II)$$

and

$$-d \ln [\text{reference organic}]/dt = k_4[\text{OH}] \quad (III)$$

where  $k_3$  and  $k_4$  are the rate constants for reactions 3 and 4, respectively. Integration and elimination of the OH radical concentration from the expressions lead to

$$\ln \left( \frac{[\text{reactant}]_{t_0}}{[\text{reactant}]_t} \right) = \frac{k_3}{k_4} \ln \left( \frac{[\text{reference organic}]_{t_0}}{[\text{reference organic}]_t} \right) \quad (IV)$$

where  $[\text{reactant}]_{t_0}$  and  $[\text{reference organic}]_{t_0}$  are the concentrations of the reactant and reference organic, respectively, at time  $t_0$ , and  $[\text{reactant}]_t$  and  $[\text{reference organic}]_t$  are the corresponding concentrations at time  $t$ .

Equation IV is not strictly applicable to the technique where OH radicals are generated from the dark N<sub>2</sub>H<sub>4</sub> + O<sub>3</sub> reaction, since a small, known amount of dilution is caused by the injections of N<sub>2</sub>H<sub>4</sub> into the reactant-O<sub>3</sub>-air mixtures (29). As discussed previously (29), this dilution requires eq IV to be modified as in eq V:

$$\ln \left( \frac{[\text{reactant}]_{t_0}}{[\text{reactant}]_t} \right) - D_t = \frac{k_3}{k_4} \left[ \ln \left( \frac{[\text{reference organic}]_{t_0}}{[\text{reference organic}]_t} \right) - D_t \right] \quad (V)$$

where the dilution term  $D_t$  is given by

$$D_t = \frac{(\text{volume chamber})_t}{(\text{volume chamber})_{t_0}}$$

and  $(\text{volume chamber})_{t_0}$  and  $(\text{volume chamber})_t$  are the known volumes of the chamber at times  $t_0$  and  $t$ , respec-

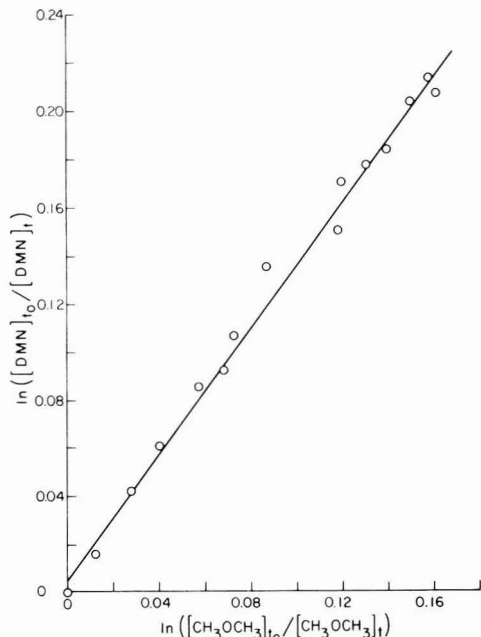


Figure 1. Plot of eq IV for the reaction of OH radicals with dimethylnitramine and dimethyl ether.

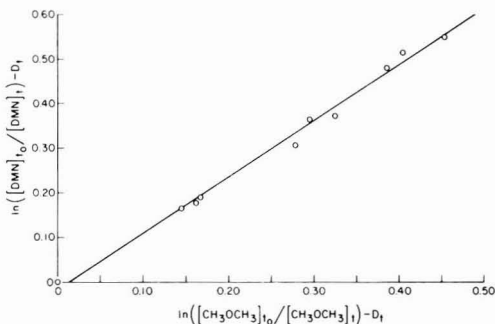


Figure 2. Plot of eq V for the reaction of OH radicals with dimethylnitramine and dimethyl ether.

tively.  $D_t$  was in all cases  $\sim 0.007$  (i.e., an  $\sim 0.7\%$  dilution) per  $N_2H_4$  addition.

For both techniques dimethyl ether ( $CH_3OCH_3$ ) was used as the reference organic since its OH radical rate constant has been determined using an accurate absolute technique (30) and it could be monitored in these mixtures, essentially free of interferences, by FT-IR spectroscopy.

The rate constant ratio  $k_3/k_4$  for the reaction of OH radicals with DMN, relative to that with  $CH_3OCH_3$ , was measured by using both the  $CH_3ONO$  photolysis and  $N_2H_4 + O_3$  dark reaction techniques to generate OH radicals. In the former case, a mixture of 4 ppm of DMN, 4 ppm of  $CH_3OCH_3$ , 10 ppm of  $CH_3ONO$ , and 20 ppm of NO in air at atmospheric pressure was irradiated for 110 min at a light intensity corresponding to an  $NO_2$  photolysis rate of  $\sim 2.5 \times 10^{-3} s^{-1}$ . The data obtained are plotted in accordance with eq IV in Figure 1, and least-squares analysis leads to a slope of  $k_3/k_4 = 1.32 \pm 0.07$ , where the indicated error limit is two least-squares standard deviations. In the latter case, three incremental additions of  $\sim 2$  ppm of  $N_2H_4$  were made into the chamber containing  $\sim 12$  ppm of  $O_3$

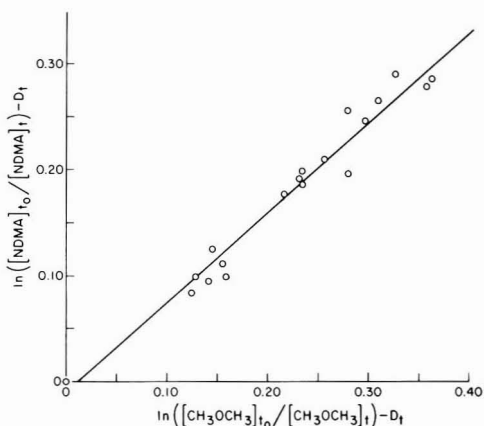


Figure 3. Plot of eq V for the reaction of OH radicals with *N*-nitrosodimethylamine and dimethyl ether.

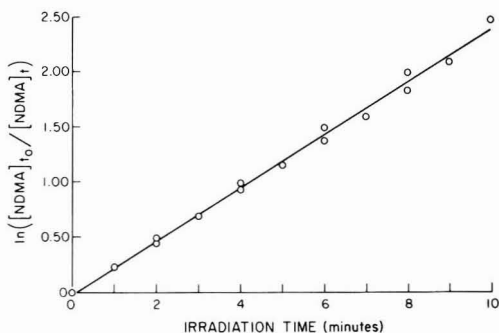


Figure 4. Semilogarithmic plot of *N*-nitrosodimethylamine decay vs. irradiation time during its photolysis in the presence of excess  $O_3$ .

and  $\sim 4$  ppm each of DMN and  $CH_3ONO$  in air, and the data are plotted in the form of eq V in Figure 2. Least-squares analysis of these data yields  $k_3/k_4 = 1.26 \pm 0.08$  (with the error limits again expressed as two least-squares standard deviations), in excellent agreement with the ratio obtained by using  $CH_3ONO$  photolysis as the source of OH radicals. For both of the plots in Figure 1 and 2, the least-squares intercept was within two standard deviations of zero.

Due to the appreciable photolysis rate of NDMA, its rate of reaction with OH radicals relative to that of  $CH_3OCH_3$  was determined by using only the  $N_2H_4-O_3$  nonphotolytic method. Each experiment consisted of the addition of three  $\sim 2$  ppm  $N_2H_4$  increments to a mixture with initial concentrations of 4 ppm of NDMA, 4 ppm of  $CH_3OCH_3$ , and 12 ppm of  $O_3$  in air. The data from two experiments are plotted in accordance with eq V in Figure 3, and least-squares analysis yields the rate constant ratio  $k_3/k_4 = 0.85 \pm 0.07$ , the indicated error limit being two standard deviations. Again, the least-squares intercept was within two standard deviations of zero.

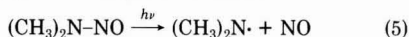
**Photolysis of *N*-Nitrosodimethylamine.** The photolysis rate of NDMA in air was measured in the presence of excess  $O_3$  in order to avoid the reformation of NDMA (see Discussion). Two photolysis experiments were carried out, each with initial concentrations of  $\sim 4$  ppm of NDMA and  $\sim 12$  ppm of  $O_3$  in air. The data obtained are plotted in semilogarithmic form of  $\ln([NDMA]_{t_0}/[NDMA]_t)$  against the irradiation time ( $t - t_0$ ) in Figure 4. The *N*-nitrosodimethylamine decays were obviously exponential, as expected for a first-order photolytic process. The



least-squares slope of this plot yields a photolysis rate constant of  $(4.0 \pm 0.2) \times 10^{-3} \text{ s}^{-1}$  (the indicated error being two standard deviations). The light intensity monitored before and after the experiments corresponded to an  $\text{NO}_2$  photolysis rate constant of  $7.5 \times 10^{-3} \text{ s}^{-1}$ , with an estimated overall uncertainty of  $\pm 15\%$ . The products detected and their approximate yields per NDMA consumed during the 10-min irradiation period were DMN (65%),  $\text{CH}_3\text{NO}_2$  (33%), HCHO (38%), CO (2%),  $\text{HNO}_3$  (13%),  $\text{N}_2\text{O}_5$  (3%), and  $\text{NO}_2$  (8%).

### Discussion

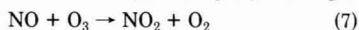
**Reaction of NDMA and DMN with  $\text{O}_3$ .** The present data indicate that the reaction of DMN with  $\text{O}_3$  is immeasurably slow under atmospheric conditions, with  $k_2 < 3 \times 10^{-21} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 296 K. On the other hand, our data suggest that NDMA may react with  $\text{O}_3$  with a low, but measurable, rate constant of  $\sim 10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . However, the more rapid decay of NDMA in the presence of  $\text{O}_3$  in our experiments was probably due to slow photolysis of NDMA caused by room light leaking into the chamber during the experiment. In the absence of  $\text{O}_3$ , the elementary photodecomposition reaction



would be reversed by the rapid recombination of the fragments to re-form NDMA

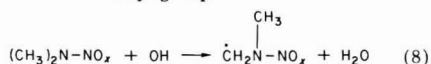


resulting in the net NDMA decay rate being far less than the rate of reaction 5. However, when excess  $\text{O}_3$  is present, the NO formed by the photolysis is rapidly scavenged



preventing recombination via reaction 6 and thus resulting in an overall NDMA decay rate which is that of reaction 5. While further experiments are required to establish more accurately the rate of the elementary NDMA +  $\text{O}_3$  reaction, the upper limit of  $\leq 10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  derived in this work indicates that this reaction is a negligible loss process for NDMA in the atmosphere (see below).

**Reaction of NDMA and DMN with OH Radicals.** From the average values of  $k(\text{OH} + \text{DMN})/k(\text{OH} + \text{CH}_3\text{OCH}_3) = 1.29 \pm 0.05$  and  $k(\text{OH} + \text{NDMA})/k(\text{OH} + \text{CH}_3\text{OCH}_3) = 0.85 \pm 0.07$  and the literature value of  $(3.50 \pm 0.35) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (30) for the OH radical rate constant of  $\text{CH}_3\text{OCH}_3$ , the rate constants  $k(\text{OH} + \text{DMN}) = (4.5 \pm 0.5) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $k(\text{OH} + \text{NDMA}) = (3.0 \pm 0.4) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  can be derived. These reactions of OH radicals with DMN and NDMA are expected to occur via H atom abstraction from a C-H bond on a methyl group



and can thus be compared with analogous abstractions from methyl groups on other classes of compounds. The rate constant per C-H bond (in units of  $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) of  $0.75 \pm 0.08$  for DMN and  $0.50 \pm 0.07$  for NDMA, can be compared with the rate constants (in the same units) of 0.07 for abstraction from primary C-H bonds in the simple alkanes (31) and with  $\sim 7$  for abstraction from the C-H bonds in the alkylamines (31). Thus, while the rate constants for the reactions of OH radicals with DMN and NDMA can be considered to be surprisingly slow when compared to the simple amines (presumably due to the electron withdrawing nature of the  $-\text{NO}$  and  $-\text{NO}_2$  groups), it is clear that H atom abstractions

Table II. Estimated Half-Lives ( $\tau_{1/2}$ ) of NDMA and DMN Relative to Various Atmospheric Removal Processes

	$\tau_{1/2}$	
	NDMA	DMN
photolysis	$\sim 5 \text{ min}^a$	(long) <sup>b</sup>
reaction with OH radicals <sup>c</sup>	3 days	2 days
reaction with $\text{O}_3$ <sup>d</sup>	$\geq 2 \text{ years}$	$\geq 7 \text{ years}$

<sup>a</sup> The minimum half-life (i.e., at a zenith angle of 0).

<sup>b</sup> Does not photolyze at a measurable rate. <sup>c</sup> For  $[\text{OH}] = 8 \times 10^5 \text{ cm}^{-3}$ , the estimated annual average value (35).

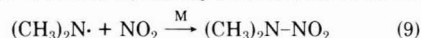
<sup>d</sup> For  $[\text{O}_3] = 1 \times 10^{12} \text{ cm}^{-3}$ , the background tropospheric concentration (36).

by OH radicals from these compounds are still much more rapid than those encountered in the simple alkanes.

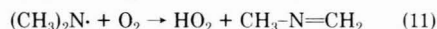
**NDMA Photodecomposition: Effective Quantum Yields and Products Formed.** As indicated above, when NDMA is photolyzed in the presence of excess  $\text{O}_3$ , the scavenging of the NO formed in the elementary photodecomposition reaction by  $\text{O}_3$  effectively inhibits the recombination reaction, and the observed NDMA decay rate should then be equal to the elementary photodecomposition rate. In this respect, our study complements the work of Lindley (32) who also studied NDMA photolysis rates by scavenging the dimethylamino radicals. Unfortunately, the light intensity employed in the experiments of Lindley (32) was not reported, so it is not possible to use these data to derive the overall photodecomposition quantum yield.

Figure 4 shows that the decays of NDMA in excess  $\text{O}_3$  were exponential over the duration of the irradiation experiments, with a decay rate of  $(4.0 \pm 0.2) \times 10^{-3} \text{ s}^{-1}$ . On the basis of (a) the absorption coefficients of NDMA given by Lindley (32), (b) our measured spectral distribution, (c) the  $\text{NO}_2$  photolysis rate in the chamber, which was measured to be  $(7.5 \pm 1.2) \times 10^{-3} \text{ s}^{-1}$ , and (d) the currently accepted  $\text{NO}_2$  absorption cross sections and photodecomposition quantum yields (33), we calculate that, assuming a photodecomposition quantum yield of unity for  $\lambda \geq 290 \text{ nm}$ , the elementary photodecomposition rate of NDMA in air would be  $3.3 \times 10^{-3} \text{ s}^{-1}$ . These data thus show that, taking into account the  $\sim 15$ – $20\%$  uncertainty in our light intensity measurements, the primary quantum yield for NDMA photodecomposition is essentially unity at wavelengths  $\geq 290 \text{ nm}$ , in agreement with the value of 1.03  $\pm$  0.10 determined by Geiger et al. (21) at 363.5 nm.

The observed products in the NDMA photolysis account for  $\sim 100\%$  of the carbon and  $\sim 95\%$  of the nitrogen in the NDMA consumed, with  $\sim 65\%$  of each being contained in the major product, DMN. Dimethylnitramine is expected (11, 13, 17) to be formed from the reaction of the dimethylamino radical with  $\text{NO}_2$ , the latter resulting from reaction 9. In addition, Lindley et al. (32, 34) observed



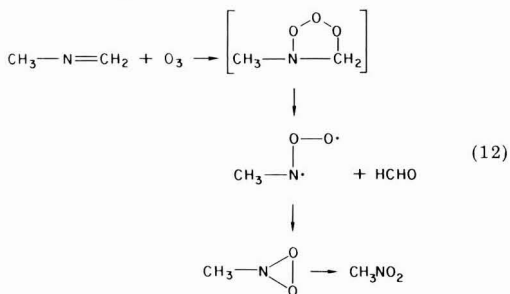
that when dimethylamino radicals are formed in air, methylmethyleamine formation also occurs via the following reactions:



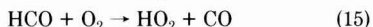
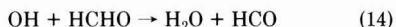
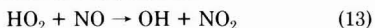
On the basis of rate constant ratios for  $k_{10}/k_9$  and  $k_{11}/k_9$  of  $(0.22 \pm 0.04) \times 10^{-7}$  and  $(3.9 \pm 0.3) \times 10^{-7}$ , respectively (34), and by use of the observed average  $\text{NO}_2$  concentrations for our irradiations, an  $\sim 65\%$  yield of DMN is predicted for our experiments, in excellent agreement with the observed yield. Thus, it appears that the dimethyl-

amino radical reacts only via reactions 9–11 in our system, and if the dimethylamino radical reacts with  $O_3$ , the rate constant must be  $\geq 100$  times slower than that for its reaction with  $NO_2$ .

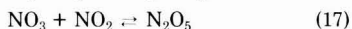
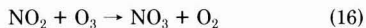
Although formation of methylmethyleamine from reactions 9 and 10 was expected, it was not observed in our experiments; instead, formation of  $CH_3NO_2$  and HCHO, each in  $\sim 35\%$  yield, and CO ( $\sim 2\%$  yield) was observed. The formation of these products can be attributed to a rapid reaction between methylmethyleamine and  $O_3$ :



The formation of small amounts of CO can be explained by the reaction of OH radicals with HCHO, since OH radicals are expected to be formed from the reaction of NO with the  $HO_2$  formed in reaction 11.



In addition to DMN and  $CH_3NO_2$ , the other major nitrogen-containing product observed was  $HNO_3$ , with smaller amounts of  $N_2O_5$  and  $NO_2$  also being present. The observed  $N_2O_5$  is presumably formed from the reaction of  $NO_2$  with  $O_3$



while  $HNO_3$  can be formed either from heterogeneous  $N_2O_5$  hydrolysis



or from the combination of OH radicals with  $NO_2$ :



Thus, all of the products observed in the present NDMA- $O_3$  photolysis experiments can be accounted for by the above mechanism.

**Atmospheric Lifetimes of NDMA and DMN.** The lifetimes of NDMA and DMN relative to the various possible atmospheric removal processes are summarized in Table II. These lifetimes are based on an estimated northern hemisphere, annual average OH radical concentrations of  $\sim 8 \times 10^5 \text{ cm}^{-3}$  (35), a background tropospheric  $O_3$  concentration of  $\sim 40 \text{ ppb}$  ( $\sim 1 \times 10^{12} \text{ cm}^{-3}$ ) (36), and calculated diurnal photolysis rates. The NDMA lifetime relative to photolysis was calculated for the equinox at a latitude of  $34^\circ$  (corresponding to Los Angeles, CA) by using the actinic irradiations and "best estimate" surface albedos given by Peterson (37), employing the NDMA absorption coefficients measured by Lindley (32), with an overall photodissociation quantum yield of unity, and neglecting re-formation of NDMA by reaction 6. The latter assumption is reasonable, since NO levels are very low in the unpolluted troposphere.

As expected, photolysis is by far the most important sink for NDMA, and its atmospheric lifetime is predicted to be very short during daylight hours. The major removal process for DMN is predicted to be reaction with hydroxyl radicals since reaction with  $O_3$  and photolysis is negligible. Hence, persistence of NDMA in the ambient atmosphere outside of the immediate area where it is formed will probably not be important unless the NDMA is formed or released at night. However, in terms of lifetimes, dimethylnitramine, the major oxidation product of NDMA, should be of greater concern since it may persist in the atmosphere for several days.

#### Acknowledgments

We wish to thank Richard V. Brown for assistance in conducting these experiments.

**Registry No.** OH, 3352-57-6;  $O_3$ , 10028-15-6; HCHO, 50-00-0;  $CH_3NO_2$ , 75-52-5; NDMA, 62-75-9; DMN, 4164-28-7.

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# Adsorptive Displacement from Activated Carbon: Recovery of 4,4'-Dichlorobiphenyl

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■ Adsorptive displacement, which has been proposed for determining multiple trace refractory adsorbates on activated carbon, was applied to 4,4'-dichlorobiphenyl (DCB) (a model compound for polychlorinated biphenyls). The adsorption of DCB was first determined in cyclohexane and in toluene (a weakly and a strongly displacing solvent) and then in each solvent with added (concentrated) naphthalene as a displacer; all loadings were in the milligram per gram range. Cyclohexane gave no detectable extraction, and toluene showed a significantly nonlinear isotherm. By contrast, linear isotherms were observed in both solvents with added naphthalene; this linearity makes it possible to analyze for trace DCB in these systems. The adsorptive displacement method was tested by shaking preloaded carbon samples (0.77-3.16 mg/g) with naphthalene-toluene (100 g/L), followed by determination of DCB in the equilibrium solutions. The average deviation between known and determined loadings was  $\pm 5\%$ .

## Introduction

The immediate objective of this study was to determine the applicability of the recently developed adsorptive displacement methods (1, 2) to the determination of small amounts of polychlorinated biphenyls (PCB's) on activated carbon. The model compound used for this study was 4,4'-dichlorobiphenyl, which is available as a relatively pure compound; the choice of this model eliminated the analytical problems associated with the study of complex commercial PCB mixtures.

Although adsorptive displacement for trace analysis has been described earlier, we here consider the principles in somewhat further detail. Earlier studies by Greenbank (4) and Greenbank and Manes (3, 5) had led to the expectation that the adsorption isotherms of multiple trace components should become linear and independent in the presence of a dominant component, provided only that the dominant component is not much more weakly displacing than any of the trace components (the criterion for displacement strength is the adsorption potential density, or adsorption energy per unit volume, a property that correlates strongly with refractive index). The Greenbank-Manes studies demonstrated linearity for single trace components over a wide concentration range but were largely limited to binary solutions in water. Gu and Manes (1, 2) observed the independence of multiple trace components, first in water solution and then in organic solvents. These articles contain the suggestion that the linearity and independence of trace adsorption isotherms under their stated conditions may well be a quite widespread phenomenon.

The importance of linear isotherms to the analysis of trace adsorbates is twofold: (a) in principle (although the process may be slow) one can achieve complete extraction of an adsorbate that exhibits a linear isotherm in the trace region, and (b) if the slope of the linear isotherm (under given conditions) is known, then one can, in principle, determine the amount of a trace component originally on the carbon by equilibrating it with a fixed concentration of some dominant component and determining the equilibrium concentration in the solution.

The calculations for adsorptive displacement are quite straightforward. First, we consider the determination of the isotherm slope, (or Henry coefficient),  $H$ . Assume, for example,  $m$  grams of carbon shaken with  $V$  liters of solution containing an initial adsorbate concentration of  $c_0$ , which goes to  $c$  at equilibrium. Then the mass adsorbed,  $x$  (in milligrams), is equal to  $V(c_0 - c)$ , where  $V$  is in liters and  $c_0$  and  $c$  are in milligrams per liter. For a linear isotherm

$$x/m = Hc \quad (1)$$

where  $H$  is the Henry coefficient, in liters per gram. Substituting  $x = V(c_0 - c)$ , we can write

$$(V/m)(c_0 - c) = Hc \quad (2)$$

or

$$H = (V/m)(c_0/c - 1) \quad (3)$$

If we denote the fraction of total adsorbate in the liquid phase ( $c/c_0$ ) as  $R$ , then

$$H = (V/m)(1/R - 1) = (V/m)(1 - R)/R \quad (4)$$

For  $R = 0.5$ ,  $H = V/m$ . The Henry coefficient as given here is therefore the number of liters required for 50% recovery of total original adsorbate into the solution. The adsorbate can obviously be assumed to originate either on the carbon or in the solution at the beginning of the experiment, i.e.,  $x_0 = Vc_0$ .

Once  $H$  is determined for a system, one can readily determine  $x_0/m$  as  $Vc_0/m$ , which is equal to  $(V/m)(c/R)$ . Solving for  $1/R$  from eq 4 gives

$$\frac{1}{R} = \frac{H}{V/m} + 1 \quad R = \frac{V/m}{V/m + H} \quad (5)$$

whence

$$(x_0/m) = c(H + V/m) \quad (6)$$

Let us consider an example. Suppose that a calibrating run shows the equilibrium concentration of trace component A to be 5.0 mg/L at a loading of 1.0 mg/g (i.e., that the Henry coefficient is 0.2 L/g), in the presence of 10.0 g/L of a dominant component or displacer (e.g., PNP in water). Assume now that a 0.5-g sample of a carbon is shaken with 50 cm<sup>3</sup> of 10 g/L PNP solution and that the concentration of A at equilibrium is 15 mg/L. Then the loading on the carbon is 15 mg/L  $\times$  0.2 L/g or 3 mg/g, or 1.5 mg on the sample, and the amount in solution is 15 mg/L  $\times$  0.05 L = 0.75 mg. The total original adsorbate on the carbon is 1.5 + 0.75 = 2.25 mg, and the original loading was 2.25 mg/0.5 g = 4.50 mg/g. The calculation is done a bit more rapidly by using eq 6. Here  $V/m = 0.1$  L/g,  $c = 15$  mg/L, and  $x_0/m = 15(0.2 + 0.10)$  or 4.5 mg/g. One can do the same calculation for multiple trace components, given the individual Henry coefficients and equilibrium concentrations, and one can determine all of these Henry coefficients in a single calibration run.

Although one can in principle determine multiple components at any equilibrium concentrations, the method loses sensitivity if the Henry coefficients are too large (i.e., at low fractional recoveries). The condition of substantial

recoveries requires at least significant solubility in the solvent, since no displacer can raise the equilibrium concentration of a trace component above its saturation concentration. However, very high solubility should not be necessary to achieve good recoveries, given a good displacer.

In this study we have determined the adsorption of 4,4'-dichlorobiphenyl (DCB), first in cyclohexane and in toluene without any displacer and then from these solvents with naphthalene as a displacer. The results illustrate the effect of the displacer in a strongly displacing solvent (toluene) and in a relatively weak displacing solvent (cyclohexane).

### Experimental Section

The carbon was a Filtrasorb-400 carbon (special CAL, 200–325 mesh) that was provided by the Calgon Corp.; it was dried overnight at 110 °C before use. The shaker bath was the same as in previous studies. The 4,4'-dichlorobiphenyl (DCB) came from the supplier at a specified 98% purity, and was used as received.

Equilibrium took place in 125-mL screw-capped Erlenmeyer flasks containing 1.0-g samples of carbon in 25 cm<sup>3</sup> of solution. Solutions were shaken for at least 36 h, following the procedure that was used earlier with water solutions. In all likelihood this longer shaking time was not necessary in the organic solvents.

Following equilibration the carbon was allowed to settle out and the supernatant solutions were centrifuged clear and analyzed by direct injection of 10-L samples on a Tenax column (1/4 in. × 6 ft) at 300 °C by using a flame ionization detector. Because of its higher volatility, the naphthalene came out sufficiently ahead of the DCP to give good separation; this was an important reason for the choice of naphthalene as the displacer.

The analytical determination of PCB on a contaminated carbon was simulated by first preloading carbon samples with measured amounts of DCB from cyclohexane solution, from which earlier experiments had shown it to be completely adsorbed. The cyclohexane was largely (but not completely) removed from the carbon by filtration and oven drying at 60 °C in a preheated oven (disconnected from the power source for safety) after which the carbon samples were equilibrated with naphthalene-toluene (100 g/L) and the original loading determined by using the previously described calculation method. (Small amounts of residual cyclohexane on the carbon were not considered significant.)

The solubility of DCB in cyclohexane and in toluene at 25 °C was determined by addition of solvent to a measured amount of solute in a shaker bath until solution was complete. The solubilities were 2.2% by weight in cyclohexane and 10.8% in toluene.

### Results and Discussion

The data for DCB from cyclohexane solution, with and without naphthalene displacer, are given in Table I. The data for naphthalene (40 g/L)-cyclohexane are plotted in Figure 1. Table II gives the data for DCB from toluene and from 40 and 100 g/L naphthalene in toluene; the data are plotted in Figure 2. Finally, Table III gives the results of the simulated analysis of the preloaded carbon samples.

We now consider the data in order of presentation. Table I illustrates the powerful effect of the naphthalene displacer in a relatively weakly displacing solvent such as cyclohexane. Whereas at these low loadings (of the order of mg/g) the DCB is all adsorbed by the carbon from pure cyclohexane, the fractional recovery with naphthalene displacer is approximately 20% (by eq 5, with  $V/m$  at

Table I. Adsorption of 4,4'-Dichlorobiphenyl (DCB) from Cyclohexane with or without Naphthalene as a Dominant Component onto Special CAL at 25 °C<sup>a</sup>

equilibrium concn, mg/L	$x/m$ , mg/g	Henry coefficient, $H$ , L/g
Without Naphthalene		
0	3.16	
0	2.33	
0	1.58	
0	0.79	
(Naphthalene) = 40 g/L		
3.74	0.54	0.144
7.79	1.07	0.137
12.1	1.60	0.132
17.3	2.10	0.121
20.4	2.65	0.130

<sup>a</sup> For these experiments ( $V/m = 0.025$  L/g), fractional recovery =  $0.025/(0.025 + H)$ .

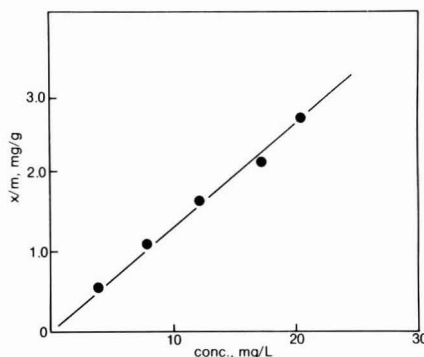


Figure 1. Adsorption of 4,4'-dichlorobiphenyl onto Special CAL from naphthalene (40 g/L)-cyclohexane solution at 25 °C.

0.025 L/g), which would suffice for a reasonably accurate estimate of the DCB. Figure 1 shows the linearity of the adsorption isotherm of DCB in the presence of naphthalene.

Table II shows, first of all, that the value of  $H$  and therefore the recovery of DCB with toluene alone are considerably better ( $R = 0.7$ ) than with cyclohexane-naphthalene, concomitant with a reduction of  $H$  by a factor of about 15. The improvement over cyclohexane-naphthalene may be at least in part ascribed to the higher solubility (about fivefold) in toluene. Whereas toluene is itself a rather powerful displacer, it is not quite powerful enough to impose linearity on DCB by itself; Figure 2 shows decided curvature in the isotherm, which is somewhat better seen from the tabulated data. By contrast, both naphthalene-toluene systems show good linearity. At 40 g/L the most striking effect of the naphthalene addition is in the linearity rather than in the recovery (0.78), and the increase in naphthalene concentration from 40 to 100 g/L lowers the value of  $H$  significantly. The effect is not large, however, and the somewhat improved recovery (0.78 to 0.85) is not critical. Note, however, that increasing recoveries are accompanied by decreased sensitivity of the accuracy of the method to the accuracy of  $H$ ; quite obviously, as the fraction adsorbed approaches zero (or as  $H \ll V/m$ ) it becomes less important to know its exact value.

Table III illustrates the simulated analytical determination of DCB at various loadings on activated carbon. Note the accuracy of the determination (average error at  $\pm 5\%$ ) and the lower limit of well below 1 mg/g. In all

Table II. Adsorption of DCB from Toluene with or without Naphthalene as a Dominant Component onto Special CAL at 25 °C<sup>a</sup>

equilibrium concn, mg/L	$x/m$ , mg/g	Henry coefficient, $H$ , L/g
Without Naphthalene		
16.2	0.18	0.0111
33.1	0.35	0.0106
53.5	0.53	0.0099
84.6	0.82	0.0097
110.6	0.98	0.0089
(Naphthalene) = 40 g/L		
12.1	0.073	0.0060
24.0	0.15	0.0063
35.0	0.25	0.0071
46.4	0.34	0.0073
58.3	0.42	0.0072
59.2	0.39	0.0066
72.8	0.54	0.0074
84.5	0.625	0.0074
(Naphthalene) = 100 g/L		
12.9	0.054	0.0042
32.3	0.130	0.0040
49.8	0.225	0.0045
60.6	0.285	0.0047
74.4	0.315	0.0042

<sup>a</sup> For these experiments, fractional recovery =  $0.025/(0.025 + H)$ .

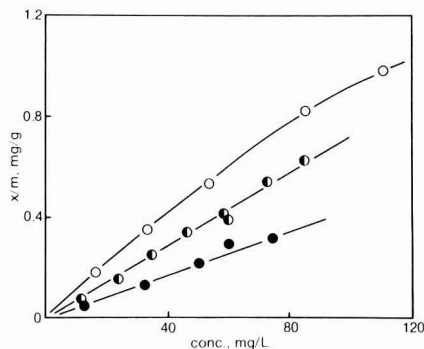


Figure 2. Adsorption of 4,4'-dichlorobiphenyl onto Special CAL from toluene with or without naphthalene at 25 °C. (O) Naphthalene = 0; (●) naphthalene = 40 g/L; (●) naphthalene = 100 g/L.

likelihood the sensitivity of the method could be increased by using an electron capture detector (evaporative concentration of the supernatant solution would be complicated by the dissolved naphthalene). Nevertheless, the low loadings that have been achieved thus far should, in water systems, correspond to equilibrium concentrations of PCB's that are well below the parts per trillion range and in all likelihood to concentrations below the detection limits of any available methods.

Table III. Analytical Results for DCB Preloaded on Special CAL<sup>a</sup>

preloading, mg/g	found, mg/g	preloading, mg/g	found, mg/g
0.77	0.70	1.30	1.18
0.79	0.79	2.23	2.24
0.79	0.73	3.16	3.16

<sup>a</sup> Preloading from cyclohexane and then extracted with naphthalene (100 g/L)-toluene solution.

Although the naphthalene-toluene system should be generally effective for PCB's (and in all likelihood for PBB's), it is by no means the only system that could work. However, hydrocarbon solvent-displacer systems do have the advantage of being particularly amenable to GLC with electron capture detectors, because of their low level of interference.

The adsorptive displacement method can in principle be used to examine a contaminated carbon (as, for example, from stream monitoring or from wastewater treatment) both qualitatively and quantitatively. In a qualitative examination a sample may be extracted by adsorptive displacement and individual components identified (for example, by GC-mass spectrometry methods). Once the identifications are made, the Henry coefficients for all of the identified components are made, the Henry coefficients for all of the identified components may be determined, again in an adsorptive displacement system, by a single calibration run, after which they may be quantitatively estimated by adsorptive displacement. Because of the expected independence of the Henry coefficients (1, 2), unidentified components should not ordinarily interfere with the analysis of the identified ones.

Finally, one may consider the possibility of using several solvent-displacer systems on different samples of the same loaded carbon. This might be necessary, for example, if the sample contains a diversity of components that are not all soluble in any single solvent or if a single displacer might interfere with the analysis of some component(s); in the latter case one could use several displacers, each on different samples.

Registry No. DCB, 2050-68-2; C, 7440-44-0; toluene, 108-88-3; naphthalene, 91-20-3.

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# NOTES

## X-ray Photoemission Spectroscopy of Environmental Particles

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■ Particulate samples from three different environments were analyzed by using X-ray photoemission spectroscopy and sputter-ion bombardment to determine elements and chemical species as a function of depth. Inorganic species of nitrogen and sulfur were observed to change with sputtering time. Elements were observed on the surfaces of one particulate sample in higher (As) and lower (K, Pb, and Mg) concentrations than those measured by bulk analyses. Arsenic was detected on the surfaces of one sample and lead on another, but their concentrations did not vary appreciably over depths up to 400 Å.

### Introduction

Fine particles play a complex role in the environment since they can catalyze transformations of pollutants as well as be pollutants themselves (1-3). Both roles are due largely to the surface, rather than the bulk, composition of the particles. Furthermore, high surface concentrations of certain elements, which may lead to increased chemical activity, might not be detected in analyses by bulk method.

We report here an investigation of the surface elemental compositions of three particulate samples of quite different origin, using the surface-sensitive technique of X-ray photoemission spectroscopy (XPS). The investigation was undertaken to determine the value of XPS in conjunction with sputter-ion bombardment as a means of obtaining "depth profiles" (composition variation vs. depth) of small pollutant particles. Samples were selected that had been analyzed by a separate bulk-composition technique in order to compare the results and demonstrate differing elemental sensitivities of the bulk technique and XPS. Each sample was analyzed after successive sputter-ion bombardments in order to obtain qualitative profiles of elemental concentrations with depth.

We were particularly interested in the effectiveness of XPS to answer the following questions: (1) Could XPS with ion bombardment be used to observe concentrated surface layers of low-bulk-concentration heavy metals which might not appear in volume analyses (4)?

(2) XPS has been used to observe and distinguish between different surface organic and inorganic species (1, 5). Does this method work in conjunction with sputter-ion bombardment to obtain depth profiles of these species? Are there any problems when sputter-ion bombardment is used on particulates?

We report here that elements present in the surface regions of the samples have been identified by using XPS. We are able in several cases to determine the chemical species of the elements (e.g., sulfate, sulfide) and observe changes of species with sputtering. We did not observe significant variations of concentration of several key elements (Pb, As) with depth over the depth range investigated (approximately 200-400 Å).

### Experimental Section

The three particulate samples differed considerably in origin. The first sample was ash taken from the precipitator of a coal-fired power plant located in Dickerson, MD. The second sample was obtained by air filtration in the urban environment of the Anacostia area of Washington, DC (6). The third particulate sample, Standard Reference Material SRM 1648, consisted of a mixture of urban particulates from the St. Louis, MO, area blended to give uniform concentrations of a wide variety of elements, as determined by bulk analysis (7). Bulk analysis data from neutron activation and other methods were available for these samples, making it possible to compare our surface results with data for the bulk.

The particles were distributed in size from approximately 0.1 to 100 µm. Samples were mounted by compressing a thin layer of the particles between two clean indium foils which were then separated. The majority of particles embedded in the indium was in the range 1-50 µm as determined by scanning electron microscopy (SEM).

The samples were analyzed under ultrahigh vacuum conditions (without baking of the sample chamber) in an ambient pressure of about  $1.3 \times 10^{-7}$  Pa ( $10^{-9}$  torr). The measurements were made with a magnesium anode X-ray tube and a double-pass cylindrical mirror analyzer (CMA). The spectra were taken with a resolution of 1.5 eV, and the data were accumulated in a multichannel analyzer.

Depth profiling was performed on the samples by sputtering with a 2 keV argon ion beam. Although sputtering rates are a widely varying function of surface morphology, atomic weight, and ion incidence angle (8), calibration with thin films supplied an average value of 10 Å/min for the thin-film sputtering rate. It should be emphasized that the intrinsic morphology of the particle samples together with preferential sputtering effects makes it impossible to remove material from the particle surfaces uniformly. Some back sputtering of indium onto the particles was also observed.

### Results

Figures 1-3 show XPS spectra for the Dickerson, Anacostia, and NBS 1648 (St. Louis area) samples, respectively. The spectra cover a range of binding energies of 0-1000 eV and were taken after extensive sputtering. Strong photoemission and Auger electron lines are visible from the indium substrate as well as the particles. In order to identify specific elements, the spectra were examined over narrower energy ranges.

Figure 4 shows XPS spectra of the Dickerson sample in the region 0-250 eV with no sputtering, light sputtering, and heavy sputtering. The elements were assigned only after correlating the energies and relative amplitudes of all peaks expected for a particular element. The energy resolution was adequate to allow specific identification of

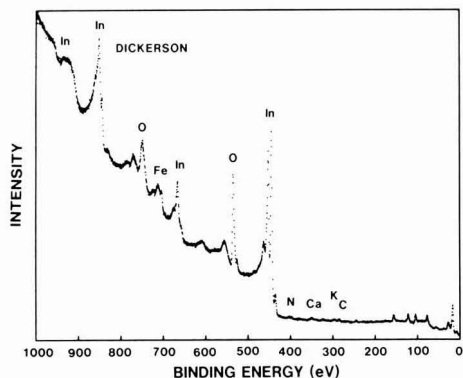


Figure 1. XPS spectrum of precipitator dust from the Dickerson coal-fired power plant after a 40-min sputter-ion bombardment.

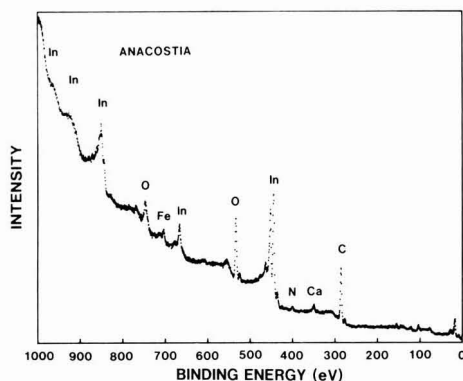


Figure 2. XPS spectrum of dust filtered from the air of the Anacostia area of Washington, DC, after an 18-min sputter-ion bombardment.

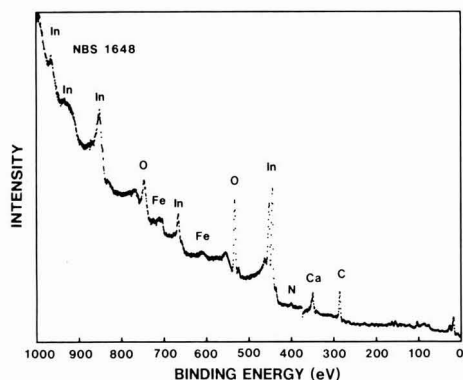


Figure 3. XPS spectrum of NBS Standard Reference Material 1648, a mixture of particulates from the St. Louis urban area, after a 40-min sputter-ion bombardment.

the sulfur as sulfate, silicon in the form  $\text{SiO}_2$ , and aluminum in the form  $\text{Al}_2\text{O}_3$ . Using the spectrum in Figure 4 and data of similar resolution out to 1000 eV, we have assigned to the surfaces of the Dickerson particles the elements summarized in Table I. Spectra in the region 250–500 eV binding energy indicated no nitrogen on the original surface but two weak peaks centered at 387 and 405 eV binding energy after heavy (40 min) sputtering. The elements in particles from the same source as deter-

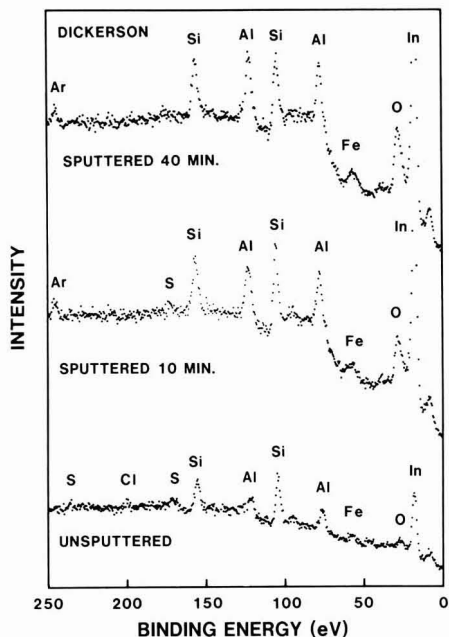


Figure 4. Expanded XPS spectrum of the Dickerson sample in the binding energy range 250–0 eV before and after sputtering.

Table I. Comparison of Elements Observed by Surface and Bulk Analysis

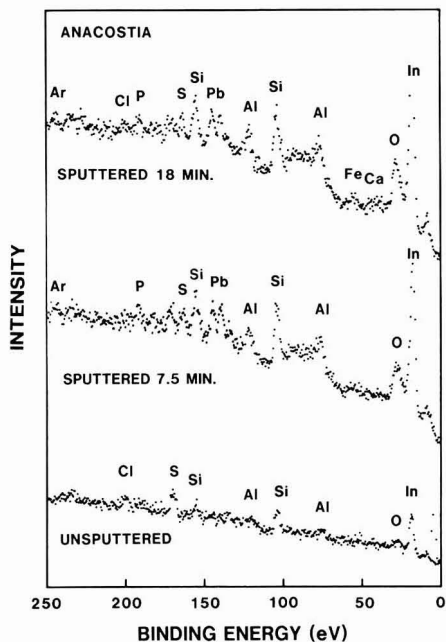
sample	elements observed (XPS) <sup>a</sup>	elements observed (bulk)
Dickerson	Al ( $\text{Al}_2\text{O}_3$ ), C (-), Ca, Cl, Fe, K (?) (+), Mo (-), N (+), Na (?) (-), O (-), S ( $\text{SO}_4$ ) (-), Si ( $\text{SiO}_2$ )	Al, Ba, Ca, Cl (50 $\mu\text{g/g}$ ), Fe, K, Na, S, Si, Sr
Anacostia	Al ( $\text{Al}_2\text{O}_3$ ), C (-), Ca (+), Fe, N (-), Na, Ni (?), O, P (?), Pb (+), S ( $\text{SO}_4$ ), Si ( $\text{SiO}_2$ )	Br, Cl, Fe, N, O, P, S, Zn
NBS 1648	Al ( $\text{Al}_2\text{O}_3$ ) (+), As, C (-), Ca (+), Cl (?), Fe (+), N (-), O, S ( $\text{SO}_4$ ) (-), Si ( $\text{SiO}_2$ ) (+), Br, Zn	Al, As (115 $\mu\text{g/g}$ ), Cl, Fe, K, Mg, N, Na, Pb, $\text{SiO}_2$ , $\text{SO}_4$ , Ti, Zn

<sup>a</sup> (+) = increased with sputtering; (-) = decreased with sputtering; (?) = most probable assignment based on one XPS line.

mined by neutron activation and electron microprobe analysis are also presented in Table I (9). Elements reported in these bulk analyses are included in the table if they occurred in concentrations of greater than 0.1 wt %, which is close to the threshold of detectability for a homogeneous distribution by XPS. Elements which were of lower bulk abundance but were observed by XPS are also included in Table I, along with their bulk concentration.

Figure 5 shows similar data for the Anacostia sample in the binding energy region of 0–250 eV. The elements identified on the surfaces of the particles have been summarized in Table I. From the position of the XPS peaks, we are able to determine that silicon was present as  $\text{SiO}_2$ , sulfur as sulfate, and aluminum as  $\text{Al}_2\text{O}_3$ . The sulfur peak at 170 eV (sulfate) is observed to decrease with sputtering while a peak at 162 eV (sulfide) appears with increased sputtering time. Spectra in the region 250–500 eV binding energy indicated a small nitrogen peak which shifted from





**Figure 5.** Expanded XPS spectrum of the Anacostia sample in the binding energy range 250–0 eV before and after sputtering.

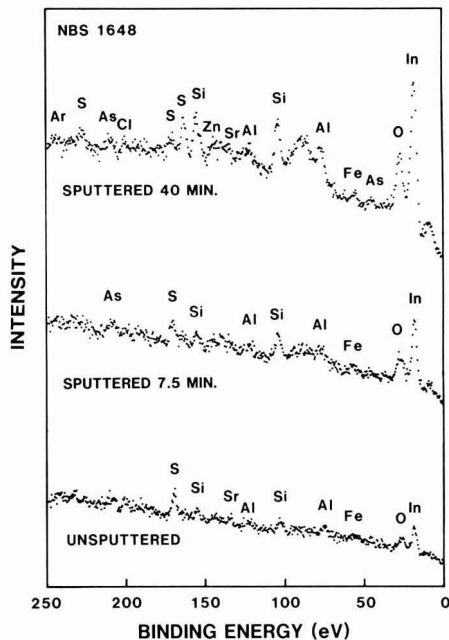
401 to 400 eV after moderate (17.5 min) sputtering. After sputtering the peak also showed some broadening. Bulk-analysis data, obtained by neutron activation analysis, are shown in Table I for this material (6).

Figure 6 shows XPS spectra for the NBS 1648 SRM (St. Louis area) particulate sample. From these spectra and similar data going out to 1000 eV binding energy, we have identified the surface elements listed in Table I. We again observe sulfur as a sulfate on the unspattered particle surfaces; after sputtering for approximately 40 min, a sulfide peak was observed as well. Spectra in the region 250–500 eV binding energy indicated a small nitrogen peak which shifted from 401 to 400 eV after heavy (37.5 min) sputtering. After sputtering the peak showed some broadening. Elements observed by several bulk analysis techniques (7) in this sample are included in Table I.

#### Discussion

The particle samples all show surface spectra consistent with large fractions of glassy aluminosilicates. SEM photos of individual particles supported this deduction. Coatings of carbon or carbon compounds were observed on the virgin surfaces of all the particle samples. The Anacostia and NBS 1648 (St. Louis) samples showed evidence of lead and arsenic, respectively, within 100 Å of the virgin surface; XPS thus has detected toxic elements close to the particle surface. The Dickerson particles did not show evidence of toxic heavy metals at the surface. After sputter removal of the outer contamination layers on the samples, no significant variation of concentration of the heavy elements (Pb, As) occurred over the depth range investigated (200–400 Å). Some changes of elemental concentration with the sputtering were observed, and these are indicated in Table I.

The changes observed in the sulfur XPS lines of the Anacostia and NBS 1648 samples could be due to any one of three possible effects. There may be sulfate compounds overlying sulfide layers on the particles. It is also possible



**Figure 6.** Expanded XPS spectrum of the NBS 1648 (St. Louis area) sample in the binding energy range 250–0 eV before and after sputtering.

that environmental sulfide layers have been oxidized at the surface as has been reported by Lichtman et al. (10). A third possibility is that the original sulfur compound is entirely in the sulfate form but that this has been partly reduced by the ion sputter bombardment.

The observation of nitrogen in these spectra was qualitatively similar in the Anacostia and NBS 1648 particulate samples and different in the Dickerson fly ash. To within the resolution of the measurements, the twin nitrogen peaks observed on the Dickerson sample are consistent with the uncovering of a nitride or nitrogen in a mixture of nitrate and nitride states (11). The small line shifts and the broadenings observed in the nitrogen for the Anacostia and NBS 1648 samples with sputtering are consistent with the reduction of surface nitrates to a mixture of nitrate and nitride states.

Comparison of the bulk analysis with the XPS results illustrates how the two techniques are complementary. For example, the level of arsenic after sputtering the particles of the NBS 1648 sample must be at least 0.1 atomic % to show up in the XPS spectra. Bulk analysis (6) shows the total arsenic level to be much smaller, about 0.01 wt %, suggesting that the arsenic may be concentrated in a layer of the surface of the particles.

By way of contrast, the bulk analysis of the NBS 1648 (St. Louis area) sample gave levels of potassium, lead, and magnesium which should have been visible by XPS but were not observed. This suggests that they may be concentrated in only the larger particles or deeper inside most of the particles of this sample.

In summary, we have used XPS to compare the surface and near-surface compositions of three environmental particulate samples with volume analyses. Our principal conclusions are as follows:

(1) XPS has been used here to observe both surface enhancements and depletions with respect to volume elemental analysis.

(2) We have observed variation of inorganic species with depth profiling; however, it may be difficult to separate actual variation of oxidation state with depth from changes induced by the ion-bombardment process itself.

(3) Two samples showed evidence of toxic elements on their surfaces. Arsenic was detected on the NBS 1648 sample at a concentration greater than the average volume level, and lead was detected on the surface of the Anacostia sample. There was no significant variation of the Pb and As signals with depth over a range of 200–400 Å. We did not, however, detect Pb on the surface of the NBS 1648 sample despite its identification in the bulk.

#### Acknowledgments

We thank J. Small and D. Newbury for providing some of the particulate samples and bulk analyses used here.

**Registry No.** Al, 7429-90-5; Ca, 7440-70-2; Cl<sub>2</sub>, 7782-50-5; Fe, 7439-89-6; K, 7440-09-7; Mo, 7439-98-7; N<sub>2</sub>, 7727-37-9; Na, 7440-23-5; O<sub>2</sub>, 7782-44-7; S, 7704-34-9; Si, 7440-21-3; P, 7723-14-0; Pb, 7439-92-1; Br<sub>2</sub>, 7726-95-6; Zn, 7440-66-6; Al<sub>2</sub>O<sub>3</sub>, 1344-28-1; SO<sub>4</sub><sup>2-</sup>, 14808-79-8; SiO<sub>2</sub>, 7631-86-9; C, 7440-44-0; sulfide, 18496-25-8.

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## CORRESPONDENCE

### Comment on "Acid Fog"

SIR: The March issue carried a feature article on "acid fog" (1). Concern is based on pH measurements made on samples obtained with a centrifugal collector. The low pH levels sound very damaging, but no damage to materials or health has been established. This lack of effect might be expected since damage depends on amount of acid-making contact as well as the degree of acidity as measured by pH. This follows because acid-damage actions consume acid and because buffers that neutralize acid are invariably present in some degree. Whether the buffer is sufficient to neutralize the acid depends on relative amount of buffer to acid. The amount of acid in acid fog is small relative to the buffering capacity of most biological systems. In the case of humans, the pulmonary system buffering capacity, partially ammonia, appears to exceed the acid content of inhaled air. The acidity per volume of air is the important factor to consider. Maximum acid content in Los Angeles basin air is about 30  $\mu\text{g}/\text{m}^3$  as nitric acid, and the amount of air inhaled per hour is about 0.4  $\text{m}^3$ . The ammonia content of expired air, expressed as nitric acid equivalent, was found to vary from 107 to 1927  $\mu\text{g}/\text{m}^3$  (oral) and from 48 to 170  $\mu\text{g}/\text{m}^3$  (nasal) (2).

I conclude that pH data on fog is meaningless in predicting harmful acid effects without information on acid concentration based on air volume as well as the degree of buffering. In the extreme case, nearly pure nitric acid

could theoretically be obtained by centrifugal collection methods.

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**W. B. Innes**

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Upland, California 91786

SIR: Mr. W. B. Innes has stated that "low pH levels sound very damaging, but no damage to materials or health has been established. This lack of effect might be expected...". I strongly disagree with Mr. Innes' suggestion that fogs with pH of 2 and lower will have no impact on plants, materials, or humans. With respect to potential effects, the aqueous concentrations of fog droplets, the acidity per volume of air, and the acid deposition rate are all important factors to consider. The pH of urban fogs does not tell the whole story; however, it is sufficient information to prompt us to examine the severity of the situation and review past findings on the subject.

Fog water collected by a rotating (impaction) collector in the Los Angeles basin (1) has been found to routinely have pH values between 1.7 and 3.0. These values can be compared to Los Angeles rainfall for 1978–1979 with a volume-weighted mean pH of 4.5 (2). On a volumetric basis, maximum fog water values observed were  $82 \mu\text{g}/\text{m}^3$  of  $\text{NO}_3^-$ ,  $27 \mu\text{g}/\text{m}^3$  of  $\text{SO}_4^{2-}$ , and  $1.7 \mu\text{g}/\text{m}^3$  of  $\text{H}^+$ . Mader et al. (3) measured total acidity in downtown Los Angeles fogs using a filtration technique; they reported a value of  $144 \mu\text{g}/\text{m}^3$  or 0.033 ppm as  $\text{H}_2\text{SO}_4$  on Nov 22, 1949. This concentration corresponds to a pH of approximately 1.8, assuming a liquid water content (LWC) of  $0.2 \text{ g}/\text{m}^3$ . Even greater values have been reported for London fogs, which are discussed later. Thomas et al. (4) reported that Swiss chard and table-beet leaves exposed to fog on the same day (Nov 22, 1949) were extensively pockmarked and developed spot lesions. Similar damage was reported for alfalfa and spinach. Scherbatskoy and Klein (5) have shown that seedlings of yellow birch misted with sulfuric acid at pH of 2.8 developed necrotic spots after one or more exposures. They also showed an increase in the leaching of  $\text{Ca}^{2+}$ ,  $\text{K}^+$ , and amino acids at pH 2.8 compared to pH 4.3 and 5.6. Taylor and co-workers (6) have presented evidence that a wide variety of plant species are injured significantly when misted with droplets in the pH range 1.7–2.5 (values commonly found in our field work).

The deposition of fog, mist, and cloud droplets by inertial impaction to vegetation can be a significant source of water and solute. In an extensive study in Japan, Yosida and Kuroiwa (7) reported an average fog water deposition rate of  $0.5 \text{ mm}/\text{h}$  in a coastal forest. Schlesinger and Reiners (8) found that artificial foliar collectors captured 4.5 times more water than open buckets, while Lovett et al. (9) have shown that direct cloud droplet deposition due to inertial impaction contributes about 46% of the total water in subalpine balsam fir forests. They also found chemical inputs via occult precipitation to range from 150–430% of bulk precipitation. In our own research, we (10) have found stratus clouds intercepting on the slope below Mount Wilson to have a median pH of 2.86 (38 samples in June 1982) with nitrate as the major anion (median  $[\text{NO}_3^-] = 1435 \mu\text{equiv}/\text{L}$ ). For a LWC =  $0.2 \text{ g}/\text{m}^3$ , this converts to approximately  $18 \mu\text{g}$  of  $\text{NO}_3^-/\text{m}^3$  of air. Assuming a water deposition rate of  $0.2 \text{ mm}/\text{h}$  and the median pH given above, the acid deposition could be greater than  $200 \mu\text{equiv}/(\text{m}^2\text{-h})$ . Thus, 8 h of fog precipitation at this rate can exceed the acid deposition accompanying 2 in. of average Los Angeles rainfall. Mr. Innes states that the buffering capacity of most biological systems is much greater than the amount of acid in "acid fog". The combination of occult precipitation with accumulated dry deposition may lead to a severe and damaging microenvironment for exposed plant tissue, beyond their buffering capacity. Fog water dripping from trees exposed to Los Angeles stratus (10) had a pH virtually the same as that in the fog, but with much higher solute concentrations—in one case  $[\text{NO}_3^-] = 19.9 \text{ mequiv}/\text{L}$ ,  $[\text{SO}_4^{2-}] = 5.9 \text{ mequiv}/\text{L}$ , and  $\text{pH} = 3.1$ . It appears that wetting by fog interception can dissolve accumulated solutes from dry deposition and fog water evaporate. The effect is more dramatic for fog than rain because rainfall can rinse off and dilute the accumulated material. At this sampling site severely damaged needles of the *Pinus radiata* × *P. attenuata* hybrid pine tree were found (11). Principal symptoms included necrosis and early abscission of second year and advanced yellow tip dieback of first year needle growth. Ozone damage cannot be excluded, but symptoms were evident following a particularly foggy spring, before summer ozone levels became significant. In

general, plant injury for sensitive tissues will be a function of aqueous concentration and exposure time. Acidity per volume of air will be less important, since plant surfaces often become fully coated by a fog water film. Los Angeles coastal fogs persist on the average for 4–12 h and occur on a significant number of days each spring and early winter. In the agriculturally rich San Joaquin Valley, "tule fogs" may persist 3–7 days on several occasions each winter. This year fog was observed in Bakersfield almost continually from Dec 28, 1982, to Jan 17, 1983.

In the case of material damage, Mr. Innes is again mistaken that exposure of material surfaces to low pH water derived from the atmosphere does not result in damage. Nriagu (12) has reviewed the literature on the subject of the deteriorative effects of sulfur pollution on materials. These effects have been well established. Sulfur dioxide and sulfuric acid at high relative humidities have been shown to damage extensively iron, steel, copper, zinc, aluminum, magnesium, limestone, building materials, paint, textiles, dyes, paper, wood, and leather. Fuzzi et al. (13) have reported pH values below 3 in Po Valley (northern Italy) fog. During the winter months fog frequently can be as high as 30%. Impaction of acid fog on the famous bronze Horses of San Marco in Venice has been thought to be the primary contribution to their visible degradation due to bronze disease [i.e., corrosion] (14, 15). The four horses stood for more than 700 years on the loggia high on the facade of the Basilica of San Marco with no visible sign of deterioration. However, since World War II extensive damage has occurred. In 1974, restoration was initiated in an attempt to preserve these famous statues that had survived in remarkable condition from antiquity. Locally, Mr. Eric Holtz, a California Science Fair winner, has established that metal plates painted with conventional car paints lose measureable spectral reflectivity after exposure to mists of the composition and pH reported by Waldman et al. (16) and Munger et al. (1). Significant losses of reflectivity were recorded for all paints except those with added hardeners. Painted plates covered with automobile wax were also found to susceptible to dulling.

Finally, Mr. Innes claimed that human health effects due to "acid fog" are not to be expected. Again, I believe that he is mistaken. On an historical basis (17) it is well-known that virtually all of the world's air pollution disasters occurred during fog events as indicated in Table I. To date the exact agent or combination of agents that caused death is unknown. Larsen (18) has speculated that the synergistic effect of  $\text{SO}_2$  and particulate matter was the primary factor in the recorded excess deaths. Others have speculated that sulfuric acid in the range of  $10^{-2} \text{ M}$  concentration was the principal agent (19). In addition to the human deaths, the fogs of the Meuse Valley (20) and London (21) resulted in numerous animal deaths. At the Smithfield cattle show held on Dec 5–12, 1952, a fog period during which 4000 excess human deaths were reported, 12 young cattle in prime condition died while 160 exhibited acute respiratory symptoms which required veterinary treatment (22). Goodeve (19) reported  $[\text{H}_2\text{SO}_4]$  ranging from 39 to  $149 \mu\text{g}/\text{m}^3$  in a 1934 London fog. These numbers can be compared directly to the range reported by Mader et al. (3) for L.A. fog in 1949 (25–157  $\mu\text{g}/\text{m}^3$ ). A maximum 24-h average concentration of  $\text{H}_2\text{SO}_4$  of 347  $\mu\text{g}/\text{m}^3$  was reported for the London fog of 1962 in which 700 excess deaths were recorded.

Mr. Innes points out  $\text{NH}_3$  in the human mouth may neutralize incoming sulfuric or nitric acid and that "acidity per volume of air is the important factor". I agree that this factor is important; however, the situation has been greatly oversimplified by Mr. Innes. With respect to human

Table I. Fog/Smog Episodes

meteorology	London	[SO <sub>2</sub> ], ppm	[H <sub>2</sub> SO <sub>4</sub> ] <sub>max</sub> , 24 h, μg/m <sup>3</sup>	excess deaths <sup>a</sup>	ref
fog	Dec 9-11, 1873			650	17
fog	Jan 26-29, 1880			1176	17
fog	Dec 28-30, 1892			779	17
fog	Nov 26-Dec 1, 1948	0.09-0.75		800	17
fog	Dec 5-9, 1952	0.09-1.34		4000	17
fog	Jan 3-6, 1956	0.19-0.55		1000	17
fog	Dec 2-5, 1957	0-0.4	144	250	27
fog	Dec 5-10, 1962	0-1.98	347	700	27
fog	Jan 7-22, 1963		88	700	27
	Meuse Valley, Belgium				
fog	Dec 1-5, 1930				20
	Dec 4-5, 1930			63	
	Donora, PA				
fog	Oct 27-31, 1948 (pop. 12 300)			20, 42.7% sick	28
	New York, NY				
haze	Jan 29-Feb 12, 1963	0.2-0.5 ppm		200-400	17

<sup>a</sup> Symptoms: bronchitis, emphysema, fever, wheezy chests, heart failure, cardiovascular problems, cough, sore throat, chest constriction, eye irritation, vomiting, nausea, vascular lesions, hypotension, asthma, and mucous membrane irritation.

health effects, other factors of importance will be the size of inhaled or respired droplet, the concentration of acid within the droplet, and the actual concentration of NH<sub>3</sub> in the oral cavity. Larson et al. (23) measured ammonia concentrations in expired human air in the range of 7-520 μg/m<sup>3</sup> and calculated that H<sub>2</sub>SO<sub>4</sub> droplets at a concentration of 20 μg/m<sup>3</sup> with a  $d_p = 0.3 \mu\text{m}$  at RH = 30% would be completely neutralized after 0.5 s in the nose ([NH<sub>3</sub>] = 28 μg/m<sup>3</sup>) and 0.1 s ([NH<sub>3</sub>] = 140 μg/m<sup>3</sup>) in the mouth. The residence time of air in the upper airway is about 0.1 s before reaching the trachea. Since the neutralization time per unit aerosol mass is proportional to  $r^2$ , larger fog water droplets would require much longer times for neutralization (23). Inhaled fog water droplets with  $d_p = 10 \mu\text{m}$  with an effective concentration of 20 μg/m<sup>3</sup> H<sub>2</sub>SO<sub>4</sub> would require approximately 20 s for complete neutralization in the nose and 4 s in the mouth. Clearly, with a residence time of 0.1 s very little of the acidity in fog water droplets would be neutralized before deposition in the trachea. This extrapolation assumes that no additional resistances to mass transfer are effective. Furthermore, the calculated neutralization times would be increased by depletion of gaseous NH<sub>3</sub>, by incomplete internal mixing in the droplet, and by increased ventilatory flow rates (e.g., during physical exercise). Recently, McMurry et al. (24) found slower reaction times for neutralization of submicron sulfuric acid aerosols than predicted above. For ammonia concentrations of 13-63 ppb (9-44 μg/m<sup>3</sup>) and particle size with  $d_p = 0.03-0.2 \mu\text{m}$ , the characteristic reaction time in a laminar flow reactor was determined to be  $5.0 \pm 0.5 \text{ s}$  at 24 °C and 6% RH. Extrapolation to fog water droplets of 10-μm diameter gives reaction times on the order of 3.5 h for complete neutralization. They also determined for particles of  $d_p = 0.1 \mu\text{m}$  that only 18% of the NH<sub>3</sub>-H<sub>2</sub>SO<sub>4</sub> collisions resulted in neutralization. This fraction was shown to decrease with an increase in particle size. Clearly, NH<sub>3</sub> in human lungs may not provide significant protection against highly acidic fog water droplets. In addition, NH<sub>3</sub> concentrations are a function of dental plaque levels in the human mouth. Consequently good oral hygiene will lower NH<sub>3</sub> production.

In this laboratory, we feel that health effects of acid fog may be related to the formation of sulfonic acids in the droplet phase. As described by Munger et al. (1), bisulfite addition complexes such as hydroxymethanesulfonate are found in high levels in L.A. and Bakersfield fog water.

Hydroxymethanesulfonic acid is a strong acid with a  $\text{p}K_a \sim -3.0$  (i.e., same  $\text{p}K_a$  as nitric acid). In many cases, as much as 20% of the acidity in the fog may be due to the in situ formation of sulfonic acids. Eatough and Hansen (25) have suggested that organic sulfur(IV) species found in aerosol may be both mutagenic and carcinogenic, while Amdur (26) reports that inorganic S(IV) salts are more irritating to animals than the corresponding S(VI) salts.

As illustrated in the above arguments, Mr. Innes' claim that "pH data on fog is meaningless" is unfounded. Given a knowledge of the liquid water content during a fog event, pH as a measured parameter is a direct indicator of the potential severity of a fog in terms of effects on materials plants, or health.

#### Appendix

J. Firket, Professor at the University of Liège, wrote the following (20):

"From the 1st to 5th of December, 1930, a thick fog covered a large part of Belgium along the Meuse Valley. A large number of people were injured, several hundred were severely attacked with respiratory troubles, and 63 died on the 4th and 5th of December. On the 6th of December, the fog disappeared; respiratory troubles improved. Wherever fogs of several days duration are frequent, public authorities were anxious to know the causes of this catastrophe. This apprehension was quite justified when, proportionally, the public services of London might be faced with the responsibility of 3,200 sudden deaths if such a phenomenon occurred there."

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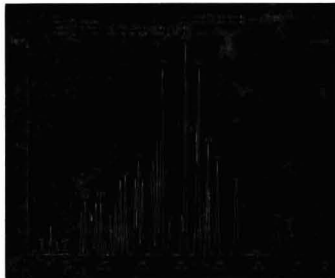
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