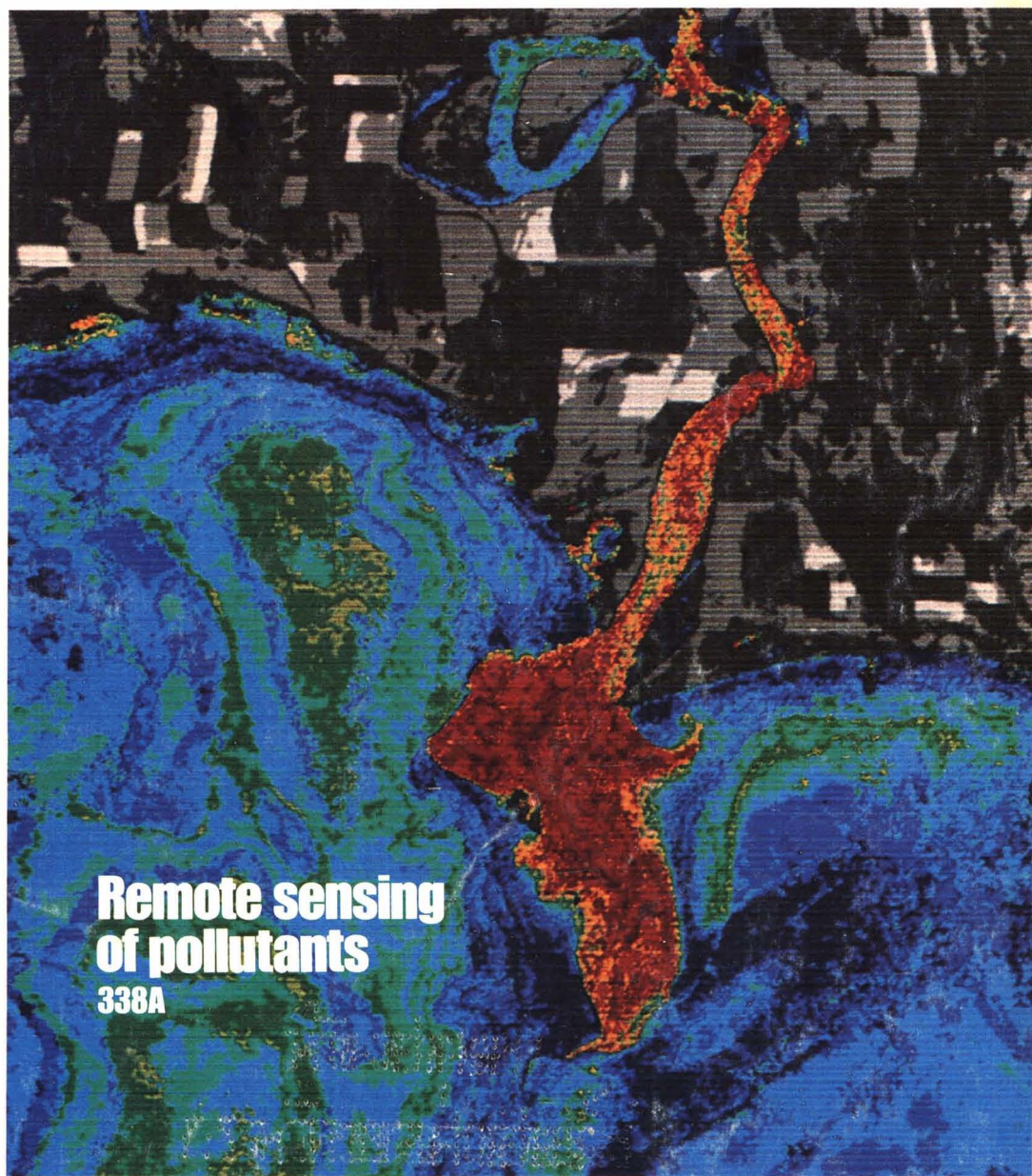


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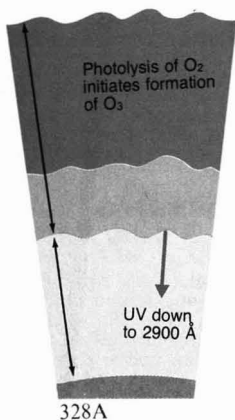
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## Design for sustainability and survivability

In the U.S. in 1972, we consumed roughly 115 pounds per person per day of virgin raw materials to sustain our life-styles. This figure is expected to grow substantially by the year 2000. Meanwhile developing countries that increasingly hold the "resource cards" upon which we grow more dependent with each passing year, consume but a tiny fraction of the earth's resource base.

Economic processes whereby we convert resources into a high material standard of living are basically entropic in the sense that we extract high quality (low entropy), nonrenewable resources from nature and diffuse them in extraction, production, consumption, and disposal into irretrievable waste products (high entropy) in the air, water, and land.

Developing countries seek to emulate our model—to aim toward our 115 pounds per capita per day as the model of the "good life." Or should we say "goods life"?

As we in the U.S. feel threatened by our growing import dependency, we prepare and arm ourselves to protect "our interests" with military muscle.

Gross disparities between "developed" and "developing" countries are the seeds of future holocausts unless we find ways to develop models less consumptive than contemporary ones—models with a dimension of justice and ethical stewardship for the resources and ecology of earth. We in the developed world have a moral responsibility to create new modes of sustaining ourselves and to be better models for developing countries to emulate.

Some models of sustainability and survivability in the technical-economic domain include technology and systems designed to be less energy consumptive; to use less material; to have greater durability, reduced wear, less corrosion etc.; to be more easily repairable; to be more easily adapted for alternative use after primary design use has been fulfilled; to be more easily remanufacturable; and to be more easily and efficiently recycled to basic materials.

Why is it so difficult for the above design criteria to become dominant ones in our contemporary period of great change? The answer lies in part in the inertias of our political-economic-ethical ideologies. Dominant philosophies associated with root values in our

society were taken from 17th-, 18th- and 19th-century thinkers and writers such as John Locke (1632-1704), who gave us a political philosophy of liberty; Adam Smith (1723-1790), a laissez faire economic philosophy; and Jeremy Bentham (1748-1832), a utilitarian ethical philosophy.

These men were excited and influenced by the emerging science and technology of their day. Their views were critical reactions against the entrenched institutions and vested interests of the old feudal society that was breaking up around them. Their world was one of small world populations. Enterprises were small and not deeply interconnected. Resources in the new world seemed limitless. Ecological consequences of technological applications could be ignored because the scale and magnitude of implementation was small, and nature's resiliency was not seriously disturbed.

None of their realities correspond with ours at the end of the 20th century. And yet the values we took from them still course strongly through our national veins.

John Locke, in his book "The Second Treatise of Government" (1690) in a discussion of property, said that a man's labor belongs to him, and that whatever a man took from nature and mixed with his labor became his property. However, he also said that this is fine and good "... at least where there is enough and as good left in common for others." We now live in a world where there is not enough and as good left in common for others. Thus we need to seek more sustainable and survivable modes of existence.



**Chuck Overby** is a professor in the Industrial and Systems Engineering Department at Ohio University, Athens, Ohio. A special interest of his lies in the area of "Engineering and Public Policy."

# ES&T LETTERS

## Trace analyses

Dear Sir: The article of John Glaser et al., "Trace Analyses for Wastewaters" (*ES&T*, Vol. 15, No. 12, 1981, pp. 1426-1435) details a procedure for estimation of the method detection limit (MDL). It appears that this procedure would yield low estimates of the MDL.

Formulation of a procedure for estimation of MDL is dependent upon interpretation of the definition of MDL. One interpretation leads to the following requirements of the statistical test of the null hypothesis (no analyte present) using the laboratory determination of concentration:

- If the analyte is not present, then the statistical test of the determination should yield the correct conclusion of absence 99% of the time.
- If the analyte is present at the MDL level, then the statistical test of the determination should yield the correct conclusion of presence 99% of the time.

This in effect defines the Type I and Type II errors of the statistical test (*t*) and requires consideration of two error distributions: distribution A—"the analyte absent" error distribution, and distribution B—"the analyte present at the MDL mean level" error distribution.

The critical value *C* of the statistical test would be the 99th percentile of distribution A and the first percentile of distribution B. The coincidence of these percentiles is obtained by appropriately locating MDL (i.e., distribution B). This procedure would yield an estimate of MDL that would be greater than that obtained from the authors' procedure in Equation 8, p. 1427.

## Reference

- (1) Ostle, B. "Statistics in Research"; The Iowa State University Press: Ames, Iowa, 1963; p. 109.

**Ronald L. Jacobson**  
Metropolitan Waste Control  
Commission  
350 Metro Square Building  
St. Paul, Minn. 55101

## Research support

Dear Sirs: In his letter (*ES&T*, Vol. 15, No. 11, 1981, p. 1250), Dr. Needleman questions Dr. Jerome Cole's views on the grounds that they were

based upon studies "... supported by lead industry funds." Since when in the U.S. is the accused denied the right to have his evidence presented and fairly evaluated rather than summarily dismissed as biased on the mere fact that the defendant presented them?

Since, however, Dr. Needleman raises this ethical question, it would seem only fair that his motives, too, be examined to determine whether, in fact, he himself is free of any bias. As a university professor, his record of research and publication is part and parcel of his claim to enhancement of his position, whether in status, research funds, salary, or whatever. I would venture that Dr. Needleman's studies had financial support for which he may have felt grateful to the extent that the results could easily have reflected that gratitude as well as an expectation of continued support.

While conscious or unconscious bias is a factor in all human views, scientists can reasonably be expected to overcome them at least to the extent that only supportable claims are put forth over which reasonable differences of opinion can be argued on scientific grounds. If that argument is reduced to charges equivalent to a personal lack of integrity, I can only conclude that the one raising that question might well be just as much suspect as the one he has charged.

**I. W. Tucker, Ph.D.**  
Professor of Environmental Engineering  
(Emeritus)  
University of Louisville  
1810 Crossgate Lane  
Louisville, Ky. 40222

## Airborne dusts

Dear Sir: I have become disabled by an occupational dust disease, industrial asthma, and cannot go back to my job. From August 1973 to September 1981, I worked for a tungsten carbide manufacturing plant, and was exposed to tungsten carbide, tantalum carbide, titanium carbide, niobium carbide, and cobalt—3% to 24% of matrix and graphite dusts. I hope my story saves some future workers from serious lung disease.

In September 1981 I became disabled by asthma. I had an initial physical and X-rays in August 1973, but no annual physical examination

was given or required by the company. To my knowledge, no air tests were ever conducted in the shop during my employment.

No prior asthmatic condition was present; I stopped smoking in 1977 (I was a moderate one-pack-per-day smoker prior to that time).

My symptoms started in January 1981. Exposure to fumes from carbide fires in January 1981 and April 1981 caused severe attacks, followed by illness. My condition has been termed permanent-partial disability. Exposure to these dusts is a health hazard; yet my employer told me it was a nuisance dust and could not hurt me or cause lung damage.

**Frank Johnson**  
Syracuse, N.Y. 13205

## Editorial excellence

Dear Sir: I take this opportunity to express my congratulations for the general high quality of the feature articles, news content, and research papers in *ES&T* over the past year. I am certain individuals have complaints about specific articles or news items. This is expected especially for science, which interacts substantially with management and policy in environmental quality issues. Overall, I think you and your staff are doing a fine job—so much so that I am going to alter a recent personal policy commitment not to subscribe to any more journals and place an order for a personal copy of *ES&T*.

**John W. Farrington**  
Associate Scientist, Department of  
Chemistry  
Director, Coastal Research Center  
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Woods Hole, Mass. 02543

## The global future

Dear Sir: Thank you for the copy of the article on "The Global 2000 Report," which appeared in *ES&T*, Vol. 16, No. 3, 1982. Bette Hileman presented the issues with balance, clarity, and thoughtfulness. I am glad to have it on hand to pass on to those wanting another overview of the report.

**Patricia Maimon**  
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## INTERNATIONAL

**A plan to preserve a portion of the world's rain forests** has been proposed by Dr. Ira Rubinoff, director of the Smithsonian Tropical Research Institute in Panama. He calls for setting aside 1000 reserves of 250 000 acres each in the 49 nations that have most of the rain forests. This would protect about one-tenth of the world's tropical moist forests. Such a system of reserves would be financed by about 40 developed nations in the temperate zone and administered by an international organization. Roughly half of the world's species are believed to live in the tropical forest. According to many scientists, an area of rain forest about half the size of California is lost each year, causing many species to become extinct.

## WASHINGTON

**Fourteen changes in the Clean Water Act are being proposed** by the Reagan administration. One such change is a deletion of the rule that mandatory national standards be established for treatment of industrial toxic wastes. The proposal would make some pretreatment standards effective by 1984, but leave others up to the agency's discretion. A four-year delay in the 1984 deadline for industry to install the "best available technology" for the treatment of toxic wastes is also proposed. A statement issued by seven major environmental groups called the EPA proposal a "cynical attempt to undermine one of the country's best environmental laws."

**A bill that would establish a national program** for storage of radioactive wastes has been passed by the Senate. The bill requires the secretary of energy to pick the first permanent burial site for high-level wastes by 1986, and a second site by 1992. As an interim solution,

the bill also requires the government to build temporary storage facilities where high-level wastes can be monitored and retrieved. The bill has not yet been passed by the House.



*Bazelon: invalidates NRC's standards*

**The Nuclear Regulatory Commission's (NRC's) environmental standards for nuclear power plants were invalidated** by the U.S. Court of Appeals in Washington. The rules fail to allow for "proper consideration of the uncertainties" surrounding the disposal of high-level nuclear waste, and for "proper consideration of the health, socioeconomic, and cumulative effects of fuel cycle activities," Judge David L. Bazelon wrote. The decision could affect five nuclear power plant licenses already granted. The NRC may ask the appeals court for a rehearing or appeal to the Supreme Court. This is the latest round in an administrative case that involves the relative powers of the courts and regulatory agencies.

**Controlled trading of emissions**, which allows the purchase, sale, and use of air pollution entitlements, "can yield equivalent air quality at a lower cost," according to a recent report prepared by the General Accounting Office (GAO). It recommends amending the Clean Air Act to allow emissions trading in place of new source performance standards, lowest achievable emission rate, and best available control technology requirements. The GAO report states that this approach makes it possible for firms "to find the most effi-

cient way to control pollution without jeopardizing the air quality standards of the Clean Air Act." On April 2, EPA announced an emissions trading policy that makes it possible for industry to use "bubbles" more widely.

**A new policy to encourage the development of minerals on public lands** for the purpose of building up a stockpile of strategic minerals has been announced by President Reagan. According to his report, 40-68% of public lands are closed to mineral exploration at present. Under this new policy, it would be easier to remove lands from the protection of the federal government. The premises of the report were challenged by environmentalists who said it would lead to a giveaway of public lands.

**No "insurmountable technical obstacles" stand in the way of constructing disposal sites** for high-level nuclear wastes in geological formations such as granite or basalt, according to the congressional Office of Technology Assessment report. It calls for the creation of an independent or semiprivate agency to manage the nuclear waste disposal program, and for a user's tax on utility customers to pay for building storage sites. The report concludes that the largest obstacle standing in the way of a successful nuclear waste management program is the "severe erosion of public confidence that the federal government . . . actually can and will do the job." David Berrick, nuclear waste expert at the Environmental Policy Center, disputed the report, saying it "did not adequately reflect the number of technological uncertainties still out there."

**At recent hearings, representatives of several large oil refineries urged** retention of EPA rules limiting gasoline lead content. The agency is considering relaxing or rescinding the lead standard of 0.5 g/gal for large refiners, and 2.65

g/gal for small refiners. The large refiners urged that a uniform lead standard be applied to all refiners including importers and small refiners. In a related development, according to sworn testimony in a report by EPA's inspector general, EPA administrator Anne M. Gorsuch privately promised a small oil refinery, Thriftway Company of New Mexico, that no penalties for violations of federal lead standards would be applied. Thriftway said that it faced financial ruin if it could not obtain quick relief from regulations. Rep. Toby Moffett (D-Conn.) said other small refiners were not told of this policy and sent a letter to President Reagan stating: "Mrs. Gorsuch's action is a clear incident of preferential treatment that destroys the credibility of the agency and corrupts its enforcement capabilities."



Florio: EPA is "delisting" wastes

Millions of tons of hazardous waste remain unregulated and are discharged into the environment each year, witnesses testified at a hearing conducted by Rep. James J. Florio's (D-N.J.) Subcommittee on Commerce, Transportation, and Tourism of the House Energy Committee. Twenty million tons of hazardous waste such as benzene, chloroform, and carbon tetrachloride, which are burned as fuels in industrial and home boilers, fall into this category. So do wastes from "small generators," those that dispose of less than 12 metric tons a year. Joel S. Hirschhorn, project director of the Office of Technology Assessment (OTA), said there was "no valid scientific basis" for applying any different standards to these wastes. In a recent report, OTA suggested that EPA eliminate the small quantity exemption altogether. Also exempt from regulation are wastes put into municipal sewers. EPA has been "delisting" specific wastes from those controlled, Rep. Florio said. An agency official testified that EPA has stopped regulating more than 200 such waste streams.

## STATES

**Residual levels of polybrominated biphenyls (PBBs) have been found in 97% of the residents of Michigan, according to a study by the Mount Sinai School of Medicine. In the summer of 1973, 1000-2000 lb of PBBs were inadvertently substituted as a feed additive for farm animals, and it took about nine months for the accident to be discovered. PBBs cause cancer in laboratory animals. The long-term health effects of the PBB contamination are still unclear, but reports have been made of damage to the nervous systems, livers, and immune systems of farm residents.**

**Two groups of state environmental officials have sharply criticized EPA proposals to streamline state grant programs and reduce federal grants funding by 19%. The Association of State and Territorial Solid Waste Management officials said that the savings would not be as great as those projected in the EPA analysis and "in some cases would have a definite adverse impact on the effectiveness of state programs." The State and Territorial Air Pollution Program administrators said that the reduced funding for special monitoring or air quality studies "may have major economic and environmental effects." EPA's acting policy head Joseph Cannon defended the cutbacks. He maintained that states can save money by not funding "low priorities" and by issuing "general" instead of "source-specific permits."**

## SCIENCE

**Chronic pollution, not a nuclear waste disaster, contaminated an area east of Kyshtym, U.S.S.R., said two scientists from the Los Alamos National Laboratory (LANL), taking issue with exiled Soviet scientist Zhorès Medvedev. Diane Soran and Danny Stillman believe that acid rain and radioactive emissions from a haphazardly operated nuclear weapons complex, plus perhaps "a series of relatively minor incidents," were responsible. Another culprit might have been chemical emissions from a 150-m smokestack at a spent-fuel reprocessing plant in the Kyshtym Complex. In general, Soran and Stillman believe that carelessness and disregard for the citizenry and en-**

vironment rather than a mini-explosion created this problem in the Soviet Ural Mountains.

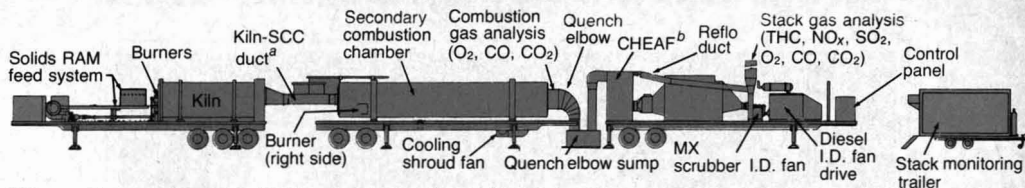
**A two-year program to study emissions—especially those from polynuclear aromatic hydrocarbons (PAHs)—is under way at the University of North Carolina. It is funded by EPA and the North Carolina Energy Institute. The aim is to determine whether sunlight, ozone, or other dilute smog products cause observable changes in PAHs on wood soot while these particles are aging in the captured air mass of an outdoor smog chamber. If chemical changes do occur, the associated biological implication from the standpoint of mutagenicity screening tests will then be studied and monitored. \$260 000 has been allocated to the project.**

## TECHNOLOGY

**The normally large size of Ocean Thermal Energy Conversion (OTEC) systems might be reduced with an innovative falling jet evaporator and condenser. This approach, being tested by the Solar Energy Research Institute (SERI, Golden, Colo.), would be applied to open-cycle OTEC. With the falling jet, apparently heat transfer characteristics are about an order of magnitude better than those of conventional surface contact evaporators and condensers. SERI researchers are also seeking improved ways to distribute water to the falling jets. Efficiency of water distribution and movement is important because, for example, a "typical" 500-MW open-cycle OTEC plant's combined flow rate for hot and cold water might have to equal approximately the Mississippi River's discharge.**

**How can gypsy moths be fought with cheap labor? Try the tiny parasitic wasp, *Apanteles flavicoxis*, recently discovered in the Kulu Valley of Northern India. The U.S. Department of Agriculture (USDA) estimates that with its way of mass-breeding this wasp using mass-bred gypsy moth larvae, the cost of the larvae has dropped from 10¢ to 1¢ each; and the cost per acre of distribution of the wasps could fall from \$25-\$50 (for other parasites) to \$2-\$5 for this wasp species. Other research efforts in gypsy moth control involve the Gypcheck virus, the use of ster-**

## Mobile incineration system



\*SCC = secondary combustion chamber. <sup>b</sup>CHEAF = cleanable high-efficiency air filter. Source: EPA.

ile males, and the use of pheromones.

**Pesticides, PCBs, and toxic organic substances can be destroyed** in a mobile hazardous waste incinerator recently unveiled by EPA and developed by joint EPA-industry effort. Substances are burned at 2200 °F, which is expected to achieve more than 99.9% destruction. Air pollution technology prevents the discharge of toxic gases. Residual ash is to be analyzed, and disposed of according to applicable laws and regulations. The incinerator can treat up to 100 tpd of dry hazardous waste, or 6 tpd of liquid hazardous wastes. A PCB trial burn is scheduled for this summer.

**Reduction of as much as 99.7% of SO<sub>2</sub> emissions may be possible** for the titanium dioxide (TiO<sub>2</sub>) manufacturing process with the liquid phase digestion (LPD) process developed by NL Industries (Sayreville, N.J.). Also, particle emissions could be reduced by more than 99.6%, and H<sub>2</sub>SO<sub>4</sub>/SO<sub>3</sub> by over 96.8%. Normally, the reaction of titanium ore with H<sub>2</sub>SO<sub>4</sub> to produce TiO<sub>2</sub>—for making pigments, for instance—is violent, and causes heavy emissions. The LPD process cuts out violent reactions and therefore most emissions, the company says. Other advantages of the new approach are energy savings (about 25%) and reductions in waste sulfuric acid, according to the company that won the Environmental Industry Council's highest award for this technology.

**One way to remove radionuclide ions selectively** could be with an electrolytic membrane separation (EMS) system developed by Innova, Inc. (Clearwater, Fla.). The system can be designed to remove only the radioactives, while leaving nonradioactive ions behind. According to Innova, this approach eliminates the need for ion exchange systems. A problem pre-

sented by an organic corrosion inhibitor was solved by the addition of an oxidation-reduction-coagulation cell developed by Innova scientists. A similar approach is used for concentrating and removing chromic acid and returning it to plating baths, thus mitigating a serious discharge problem. Innova tells *ES&T* that 36 chromic acid removal/recycling systems are in use in the U.S.

## INDUSTRY

**Better training for personnel who handle, treat, or dispose of hazardous and toxic chemicals** should be provided by their employers, Battelle's Columbus Laboratories urges. Results of a recent survey run by Battelle indicate that training programs are mostly limited at present, and that much of that instruction is "heavily supervised on-the-job training." The survey also found that companies often lack funds necessary for such programs, and that they do not believe that quality courses and training materials are available. Battelle is now proposing to develop training packages for this purpose, that companies can use as part of in-house educational programs.



Lynott: proven technology

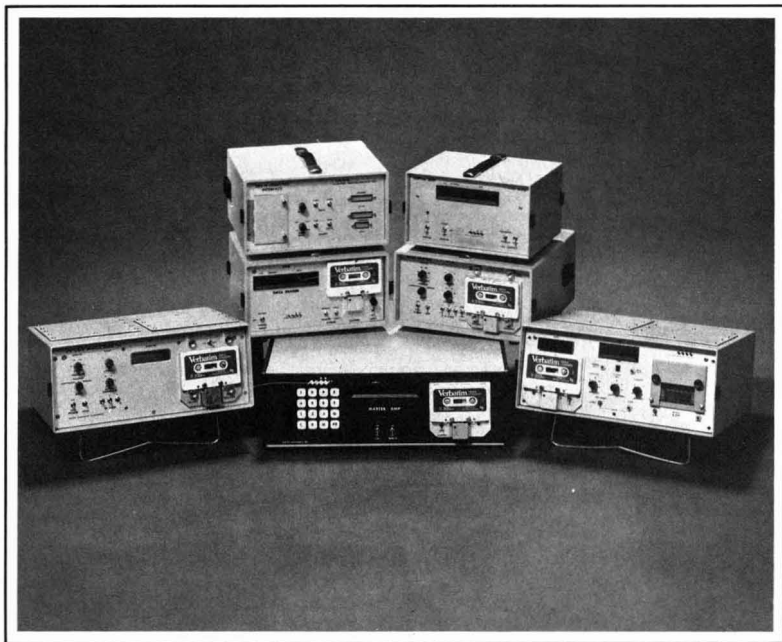
**An agreement to finance two vessels that would incinerate hazardous chemicals** at sea was signed by Tacoma Boatbuilding Co. (Tacoma, Wash.) and the U.S. Maritime Administration (MARAD). The con-

tract for building the vessels amounts to \$63 million to be provided through bonds sold under Title XI of the Merchant Marine Act of 1936. The vessels will ultimately be owned and operated by Apollo Co., and chartered to At-Sea Incineration, Inc., a wholly-owned subsidiary of Tacoma Boatbuilding. "This signals a new era in toxic waste treatment in the U.S. through its permanent elimination in an environmentally safe manner, using a proven technology," Tacoma Boatbuilding chairman Frank Lynott noted.

**To help to define acid rain problems, the Southern Co. (Atlanta, Ga.),** in conjunction with the Electric Power Research Institute (EPRI), is sponsoring an active program. Also, through a network of rain sampling stations, the company is gathering data across the Southeast in order to identify regional and seasonal variations in the acidity levels of rain. In 1980, Congress authorized a \$50 million study of acid rain to be conducted over a 10-year period. However, the Southern Co. has recommended that this program be accelerated to five years.

**A contract to develop a design of an acid gas removal unit** for a coal-to-gasoline system went to Lotepro Corp. (New York, N.Y.). The system itself will first convert syngas to methanol, and then to 50 000 bbl/day of gasoline made by the Mobil M process. The contract was let by Ralph M. Parsons Co., architect and engineer on the project. The design will call for a Rectisol unit to remove acid gases from a syngas stream from a Texaco coal gasifier. Clean syngas will contain less than 0.1 ppm hydrogen sulfide (H<sub>2</sub>S), and 0.1 ppm carbon sulfide (COS). The H<sub>2</sub>S- and COS-enriched stream will be sent to a Claus unit for sulfur recovery. Lotepro is a subsidiary of Linde AG of West Germany.

# Much more than measurement.



The full measure of Martek Instruments, Inc., is not only its complete line of water quality measurement systems, but also its expertise in the fields of environmental analysis and data acquisition. Since the late 1960's, the company has designed and manufactured its own sensors for use in one of the broadest lines of water quality systems available from a single source.

Martek-developed systems provide *in situ* measurement of conductivity, salinity, dissolved oxygen, pH, specific ions, turbidity, flow rate, depth/pressure, or temperature. Among the company's most advanced systems is the

Model DMP, a microprocessor-based data acquisition system designed specifically for continuous data collection and analysis. Separate modules are also available from Martek, such as the Model DLS Data Logger, which can log up to 99 analog or digital signals plus day and time of day. Another versatile product is the Mark VIII Water Quality Data Logger, a combination analyzer and data logger packaged in a single case, which can operate in manual, continuous, or program mode. These are but a few of the numerous instruments and systems available from Martek.

Martek systems run the gamut from hand-held portable systems to unattended buoy systems, from ultrapure water in nuclear power plants to brine solution in boreholes. They make measurement easier in such diverse fields as process control, ecology, agriculture, and oceanography, to name but a few.

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## Acid deposition

*Many new findings in this field were reported at the recent meeting of the American Chemical Society*

For the first time, the American Chemical Society in its semiannual meeting devoted an entire symposium to the subject of acid precipitation. The symposium took place in Las Vegas from March 29 to April 2. Eighty-three papers covering several fields that relate to acid deposition were presented. The pace of research in acid rain is rapid, generating so many new findings that only a fraction of the important papers can be mentioned in this article.

A number of researchers discussed the extent of areas receiving acid precipitation in the U.S., Canada, and Europe. Brand L. Niemann of the University of Illinois showed that the area of the U.S. and Canada enclosed by a pH isopleth of 4.5 is "generally symmetrical about and displaced slightly northeastward of the states with high SO<sub>2</sub> emissions." Furthermore, the area enclosed by a pH isopleth of 4.2 coincides almost exactly with the area with the highest SO<sub>2</sub> density—namely, the Ohio-Pennsylvania–West Virginia border area—and also includes a region extending into the Adirondacks and southwestern Ontario. A small separate area with pH 4.2 lies in the vicinity of the Sudbury smelter.

Leonard C. Duncan of Central Washington University reported that acid rain is falling on the mountains of central Washington. The high altitude lakes of this area are very sensitive to acidification, with 44% of them showing alkalinities less than 50  $\mu\text{eq/L}$ , but they do not appear to be acidified yet.

According to Ronald Becker of the Wisconsin Department of Natural Resources, the concentration gradient of acidity across the north central lake states is almost exactly the same as that which existed in Scandinavia when a great many of the lakes there became acidified. Furthermore, the



*Some lakes such as this one in Wisconsin are now threatened by acid deposition.*

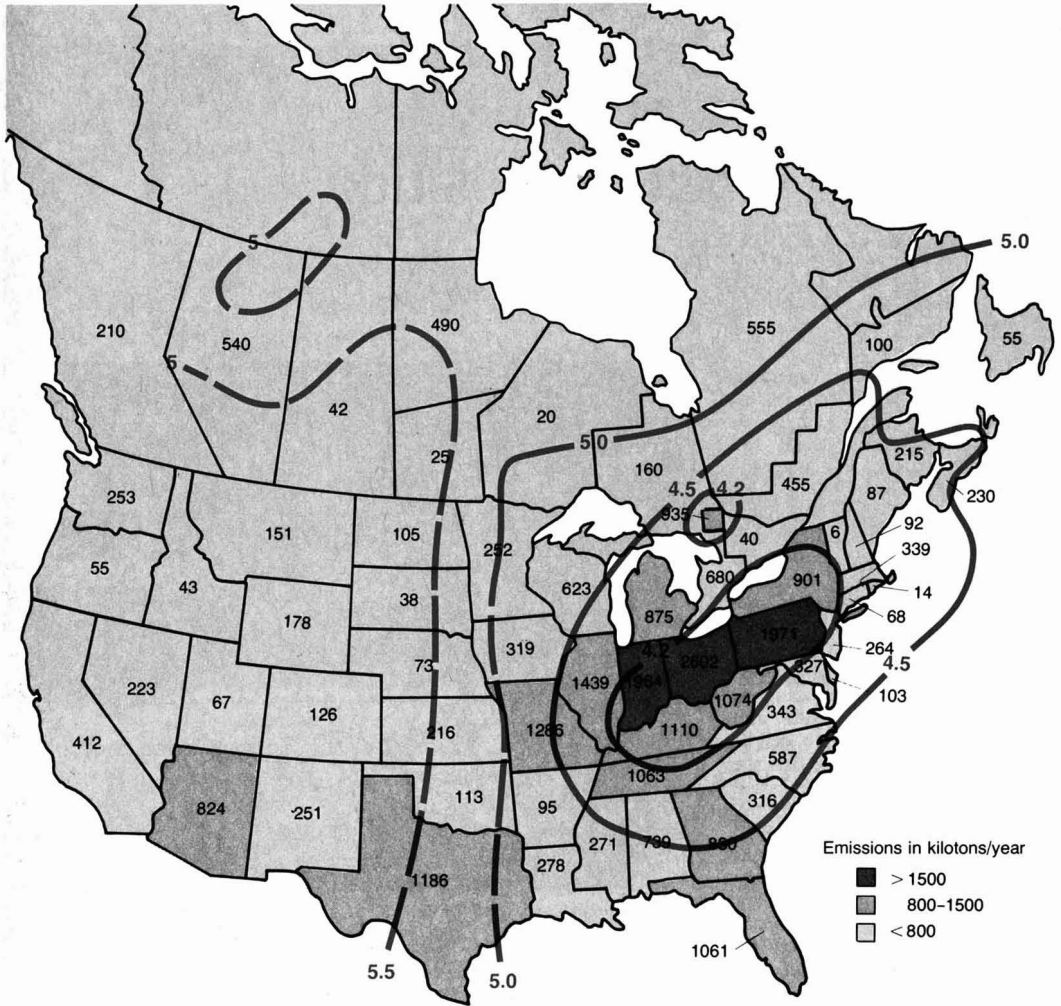
sulfate and nitrate being deposited by precipitation is exceeding the threshold amount for impact to aquatic systems that was determined in Scandinavia. As you move from west to east across this lake region, the sulfate wet loading triples from 14 to 45 kg/ha and the nitrate loading shows a similar gradient, 10–27 kg/ha. A large number of the lakes here are highly sensitive to acidification. The determination of how many have become acid lakes has not yet been made.

Len A. Barrie of the Atmospheric Environmental Service, Ontario, reported that for several stations in Canada, acid precipitation occurred only when the air flowed from certain directions. At Kejimikujik in southern Nova Scotia, for example, precipitation of low pH is restricted to times when the wind blows from the southwest or west. Likewise, a south or southwest wind is necessary for acid

rain at Chalk River, Ontario. He also found that airborne sulfate levels peak in summer and are at a minimum in winter and that the opposite is true for sulfur dioxide. The ratio of dry to wet deposition, on an annual basis, decreased from a value of approximately one near the center of major source regions to much less than one in remote areas.

A reason why the pH of rainfall might remain steady while SO<sub>2</sub> emissions rise or fall was suggested by Peter Winkler of Deutscher Wetterdienst, Meteorologisches Observatorium Hamburg. He said that although emissions of SO<sub>2</sub> in Central Europe have almost doubled in the past 50 years, the precipitation there has not become more acidic. The acidity of rain and snow in Scandinavia, however, has increased dramatically. Using these facts, he hypothesized that an increase in SO<sub>2</sub> emissions causes an

The region with rainfall of lowest pH includes nearly all states with the highest SO<sub>2</sub> emissions



Source: Article by Brand L. Niemann to be published by Ann Arbor Science in November 1982 in the *Proc. Symp. Acid Precipitation*. Spatial variation of precipitation-amount-weighted mean pH in North America in 1980 compiled from

Canadian (CANSAP, APN) and American (NADP, MAP3S) networks by the U.S.-Canada Work Group 2.

area of low pH to spread out, as it seemed to in Europe, but cannot depress the average pH of rainfall below a limit of about 4. A recent JASON Report, "The Physics and Chemistry of Acid Precipitation," published in November 1981 by SRI International, also expressed this theory. It does not take dry deposition into account, however. Dry deposition could cause the total sulfate and nitrate deposition to increase while the rainfall pH remains at about 4.

Winkler also suggested a reason for the precipitation of low pH that sometimes falls in remote areas of the world. He said that long-range trans-

port over distances of several thousand kilometers from both natural and man-made sources can occur. In areas such as Mauna Loa and the Arctic, a small amount of acid particles can produce rain of low pH because there are few cations from alkaline soil or other sources to neutralize a modest amount of sulfate or nitrate. The low pH level sometimes observed in these regions results from the ion balance, not from copious quantities of deposited acid.

#### Aquatic effects

A great many papers were presented on the effects of acid rain on surface

waters. These showed that the amount of injury to lakes is much greater than the destruction of fish life alone, and that harmful effects occur long before all the fish have disappeared from a lake. Much research centers on the search for a biological or chemical indicator that can be used as a general barometer to predict impending acidification.

Joseph M. Eilers of the Wisconsin Department of Natural Resources reported on a study in which approximately 2000 observations of the tolerance of aquatic organisms to low pH were compiled from the literature for major taxonomic groups. For each

group, the distributions of the minimum pH values were plotted. This revealed wide differences in tolerance between and within groups. He found that leeches and mollusks are the least tolerant, and fish and amphibians the most resistant. From this, he concluded that acidification causes dramatic changes in aquatic ecosystems before it wipes out economically important game fish.

The experimental acidification of a small precambrian shield lake (lake 223) in the Experimental Lakes area of Northwestern Ontario was described by Ken H. Mills of the Freshwater Institute, Winnipeg, Manitoba. Sulfuric acid was used to lower the pH from ~6.7 in 1975 to ~5.1 in 1981. Five fish species were living in the lake at the beginning of the study. At first, the populations of three species increased, while numbers of the other two declined drastically. The fathead minnows were the first to die out at about pH 5.5. The lake trout and white suckers showed no definite stress until 1981 (pH ~5.1) when reproductive failures occurred. Crayfish disappeared almost entirely and mats of filamentous algae developed along the shoreline. Most fish surveys carried out to find evidence of acid stress have focused on trout or white suckers. This study suggests that minnows would be

a better indicator.

A study of the species composition of 12 seepage lakes in Northern Wisconsin was described by James G. Wiener of the U.S. Fish and Wildlife Service (Lacrosse, Wis). Six of these lakes were acidic (pH 5.1-6.0), and six were nearly neutral. The species richness of the fish communities was substantially less in the six acidic lakes than in the six near neutral waters, and minnows were significantly less abundant in the acidic lakes.

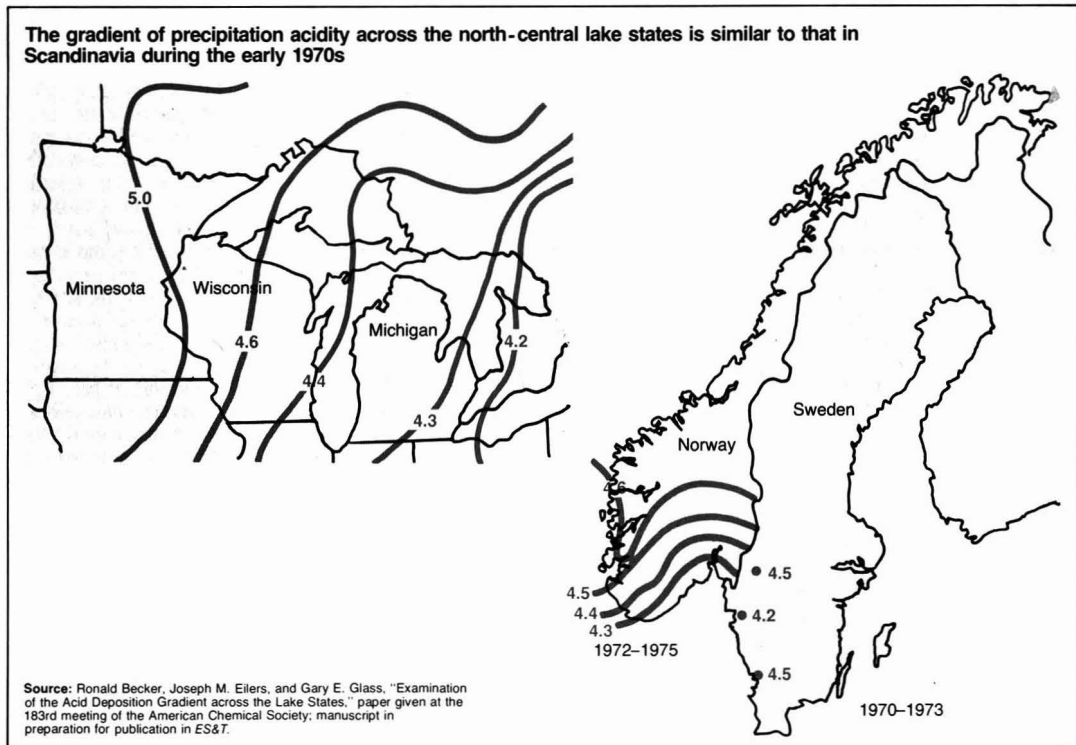
Harold H. Harvey of the University of Toronto reported on a study of surface waters that shows that abnormally high manganese concentrations accompany a reduction in pH and mark "the early stages of the release of other heavy metals into the aquatic environment." In acidified lakes, he also found that manganese was elevated fivefold in the vertebral bone of white suckers. From this he postulated that it may be possible to diagnose acidification from increased manganese concentrations in fish tissue. In addition, he noted very high concentrations of aluminum on the gills of fish killed from acidification. The gill aluminum ranged from 83-250 mg/g dry wt. "Aluminum is at least a good indicator of the death of these fish if it is not a primary cause. It probably is a primary cause," he said. It is well

known that acidity causes elevated concentrations of aluminum in surface waters.

A decrease in the decomposition of leaf litter in lakes results from an increase of acidity, A. J. Francis of Brookhaven National Laboratory reported. In addition, he found that fewer bacteria are present in water samples from acid lakes.

### Effects on forests

The evidence for the effects of acid rain on forests is far less conclusive than that for lakes. A substantial amount of progress, however, has been made in this research area over the past few years. David L. Correll of the Smithsonian Institution (Edgewater, Md.) explained why certain forest soils may be vulnerable to the increased leaching caused by acid rain. When soil is composed of noncalcareous acidic minerals, the amounts of calcium, magnesium, and potassium, all of which are required for growth, are severely limited. Native forest species are selected (by the process of evolution) for their ability to compete successfully for these ions and keep them tightly recycled. When the hydrogen ion concentration in rainfall increases by one or two orders of magnitude, as it has over many forest soils, it may cause increased leaching of these ions and, as



a consequence, inhibit the ability of plant species to successfully compete for them. Liming practices counteract these effects on managed agricultural lands, but natural forests and other ecosystems not receiving soil amendments are subject to ion depletion.

Approximately 900 cores from 10 tree species were collected and analyzed in a study reported by Arthur H. Johnson of the University of Pennsylvania. The geographic area extended from southern New Jersey to New Hampshire. Pitch pine and shortleaf pine in southern New Jersey (since 1957) and red spruce in the Green Mountains of Vermont (since 1965 or before) showed a "widespread, substantial, and sustained" reduction in growth rate. In addition, a sizeable dieback of red spruce has occurred throughout the Green Mountains. Precipitation having an annual average pH of about 4 with occasional events in the low 3s falls over both New Jersey and Vermont. A regression analysis of tree growth (for pitch and shortleaf pine) against 20 potential growth-controlling factors showed a significant correlation between growth rate and stream pH. Fire, pests, disease, and ozone did not correlate with reduced growth at a statistically significant level.

In related research, Richard M. Klein of the University of Vermont described a 17-year survey of trees in the Green Mountains of Vermont. He found a reduction in numbers of living red spruce, as well as alterations in the frequency of several other species. This study has not yet established a cause for the observed phenomena.

Acid precipitation can be expected to influence the microorganisms responsible for foliar or stem disease in trees, according to William H. Smith of Yale University. He hypothesized that "acid deposition can increase foliar and canker disease" by means of host predisposition or direct stimulation of the fungal disease agents and said more research is needed in this area.

Robert I. Bruck of North Carolina State University reported that the microbial populations of the poorly buffered soils in the Adirondack Mountains are shifting from a very diverse flora to one dominated by populations of bacteria and the species *pythium* and *phytophthora*.

#### Models for water chemistry

Several models have been developed for the purpose of predicting what acid inputs would cause a given change in

surface water chemistry. Carl W. Chen of the Electric Power Research Institute described a model that has been applied to two lakes in the Adirondacks and seems to describe the water chemistry of these lakes well. Eventually, it will be applied to 3000 lakes.

Models used in Norway to predict surface water chemistry were explained by Richard F. Wright of the Norwegian Institute for Water Research. He said the "models have succeeded well in describing the present-day situation," but that it remains to be seen whether they can accurately predict future acidification.

Thomas C. Winter of the U.S. Geological Survey (Denver) said that the interrelationship of groundwater and surface water in a lake can be extremely complex and this must be accounted for in any model that attempts to describe or predict surface water chemistry. Complicated interactions between surface and groundwater explain why two neighboring lakes that seem similar in every respect could have very different responses to acid inputs, he noted.

#### The process of acidification

The chemistry involved in the creation of acid precipitation was the subject of a number of papers at the Las Vegas meeting. Both heterogeneous oxidation of dissolved  $\text{SO}_2$  and  $\text{NO}_x$  in liquid aerosol droplets and homogeneous oxidation of these gases in the gas phase were described. Michael R. Hoffmann of the California Institute of Technology said it is clear today that both of these mechanisms are important processes for the conversion of  $\text{SO}_2$  and  $\text{NO}_x$  to sulfate and nitrate.

He pointed out that "numerous studies have provided conflicting experimental results on reaction rates, rate laws, and, in particular, pH dependencies" for the aqueous oxidation of  $\text{SO}_2$  and  $\text{NO}_x$  to strong acids. But the chemical mechanisms by which  $\text{SO}_2$  is converted to sulfuric acid are better known than those for  $\text{NO}_x$  conversion.

In cloud and rain droplets, the  $\text{H}_2\text{SO}_4$  pathway that is probably the most important is the oxidation of dissolved  $\text{SO}_2$  by dissolved  $\text{H}_2\text{O}_2$ . Under highly polluted conditions, however, a number of other reactions can also be significant, as noted by L. Robbin Martin of The Aerospace Corporation (Los Angeles). Jack L. Durham of the U.S. EPA at Research Triangle Park stated that  $\text{H}_2\text{O}_2$  "may be present in the northeastern U.S. atmosphere in concentrations as high

as 40 ppb." This concentration is not yet well established and is a subject deserving additional research.

Hoffmann suggested that the concentration of  $\text{H}_2\text{O}_2$  as well as HO and  $\text{HO}_2$  radicals (all involved in reactions with  $\text{SO}_2$ ) and the presence of certain trace metals in the atmospheric aerosol may be interrelated. This hypothesis is being tested at Caltech.

At this time, no experimental evidence exists to show the primary pathway for the formation of  $\text{NO}_3$  in raindrops. Alan W. Gertler of the Atmospheric Sciences Center (Reno, Nev.) noted that oxidation by  $\text{O}_3$ ,  $\text{H}_2\text{O}_2$ , and OH may prove to be important in the aqueous transformation of  $\text{NO}_2$ . He said it is unfortunate that few of these reactions have been investigated under simulated cloud conditions or in aqueous solution, and that cloud simulation experiments are needed.

Jack G. Calvert of the National Center for Atmospheric Research (Boulder, Colo.) presented a review of the gas-phase oxidations (homogeneous) of  $\text{SO}_2$  and  $\text{NO}_x$  in the atmosphere. He found that the OH-radical reaction with  $\text{SO}_2$  is the rate-determining step and the most important homogeneous mechanism for the oxidation of  $\text{SO}_2$ , and that the reactions subsequent to the OH-radical addition are not well defined. He also pointed out that homogeneous gas-phase reactions not only lead to  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$ , but create other reactants such as  $\text{O}_3$  and  $\text{H}_2\text{O}_2$ , which in turn produce acids as well. There is little doubt today that reactions of  $\text{SO}_2$  and  $\text{NO}_x$  in the atmosphere result in the formation of acids, he said. The fraction that reacts by homogeneous mechanisms is still unclear, however.

$\text{SO}_2$  is removed from the atmosphere by several different processes. In 1980, D. Möller calculated that homogeneous gas-phase oxidation accounts for 9%; liquid phase oxidation, 35%; dry deposition, 45%; and wet deposition of the absorbed gas, 11%. But even if he is correct, homogeneous reactions may account for more than 9% of the total conversion to sulfuric acid. After  $\text{SO}_2$  is dry deposited onto plant tissue or soil, much of it may react homogeneously with gases in the atmosphere, especially in arid climates. The remainder may react in surface water films with atmospheric gases to form additional acid.

John H. Seinfeld of the California Institute of Technology presented a mathematical model for aerosol growth and acidification that is "applicable virtually without modification to the entire spectrum of atmospheric



The average cyclonic storm tracks pass in an easterly or northeasterly direction and carry the precursors to acid rain



Source: Visher, S.S., "Climatic Atlas of the United States" (Harvard University Press: Cambridge, Mass., 1954).

particles and droplets." Therefore, the evolution of size and composition of submicron atmospheric aerosols as well as cloud droplets may be studied with this model.

A great many papers were presented on the atmospheric chemistry that leads to acid deposition. None of these mentioned what implications the results have for acid rain control strategies, nor did the papers say what effect the "needed" investigations might have on control policies. The general rates at which  $H_2SO_4$  and  $HNO_3$  are produced are a necessary part of long-range transport models, but no one discussed which reactions or which rate constants are important for these models or for their application to sensitive resources, nor did anyone mention how much more certain the models might be if the chemistry were more precisely specified.

#### Long-range transport

Computer models to simulate the long-range transport of air pollutants were discussed in several papers at the meeting. Perry J. Samson of the University of Michigan described a linear model used to diagnose the sources of acid precipitation for Whiteface Mountain in the Adirondack region, and to predict ambient sulfate and the sulfate deposited by precipitation at several locations.

"In general, the model does a very good job of predicting ambient sulfates," he said, but there were some differences between the observed and predicted values for sulfate deposited

by precipitation. In regions near emission sources, the sulfates were well estimated or overpredicted. At receptor locations further downwind, the sulfate wet deposition was underestimated, though it was of the same order of magnitude. From this, Samson concluded that "the basic model structure is inadequate for a full description of precipitation sulfates and the associated acid rain problem," and that "the next generation of regional transport models must include more complex chemical transformation processes."

Samson's model was also used to estimate what percentage of the sulfate deposited by precipitation in the Adirondacks was contributed by each state in the U.S. and regions of Canada. By modifying various parameters in his model, he concluded that the percentage contribution to sulfur wet deposition by each political subdivision is influenced much more by the general pattern of wind trajectories than by the parameters used to describe deposition and the chemical transformations leading to acidification. It would seem that Samson's model establishes percentage culpability consistently for various parametrizations but is less accurate for predicting deposited sulfate at regions far from emission sources.

#### Polarization

As speakers at other acid rain symposia have noted, controversy envelops almost all aspects of the acid rain issue. Informed individuals, including most

of the scientists who study the problem, have divided into two opposing groups. A reason for this polarity may be found in the composition of the two groups: those who live in regions that may be harmed by delaying acid rain controls, and those who enjoy the economic benefits of further delay. Thomas D. Crocker of the University of Wyoming expressed this idea when he said: "Opponents of control, those to whom the expected net benefits of control are negative, insist that more information is required before 'rational' control decisions can be made. . . . On the other hand, proponents, those to whom the expected net benefits of control are positive, fear the possible environmental effects of delay—they want control now." Currently, there are 10 bills before Congress that address the issue of acid rain. Polarization over this subject is so extreme that it is probable no action will be taken on the bills.

To those who say we have only circumstantial evidence to relate emissions to acid rain and that we must establish an indisputable cause and effect relationship before we can initiate controls, we might pose two arguments: All environmental action that has been taken in the past has been taken in the face of great uncertainty. When people were dying in the London Fog, controls were instituted when only the vaguest correlation had been established between the air pollution and the increased death rate. When we decided to limit disposal of phosphates in the Great Lakes, the situation was also ambivalent. We know unequivocally that some of the sulfur dioxide from the burning of fossil fuel is converted to sulfuric acid in the atmosphere. But the very nature of science itself dictates that we will never be able to establish an absolutely certain cause and effect relationship between anthropogenic emissions of  $SO_2$  and  $NO_x$  and acid precipitation, nor will science be able to say exactly how much the emissions should be reduced to stop acid rain damage. There will always be individuals who say that emissions and acid rain are not necessarily related, just as the American Tobacco Institute still insists that the etiology of cigarette smoking and lung cancer has not been "scientifically demonstrated." Inevitably, unanswered questions will remain. As Norman Cousins said, "Science at its best provides us with better questions, not absolute answers."

The papers given at the acid precipitation symposium will be published this year by Ann Arbor Science Publications. —Bette Hileman

# Stratospheric ozone: changing forecasts

*Will human activity cause losses, or might we expect no future change in total ozone?  
Could direct stratospheric sampling be a first step toward resolving this long-standing controversy?*

The ongoing controversy concerning the reduction of the stratospheric ozone ( $O_3$ ) layer was brought front and center once more by a report issued by the National Aeronautics and Space Administration (NASA) and the World Meteorological Organization (WMO) in January. This report did several things. First, it summarized all of the work done throughout the world in the physics and chemistry of stratospheric ozone. Second, and perhaps more significantly, it lowered an earlier prediction of ozone reduction.

In early April the National Research Council (NRC), a component of the National Academy of Sciences, published "Causes and Effects of Stratospheric Ozone Reduction: An Update." Myron Uman of the NRC Environmental Studies Board said that "the NRC report relies heavily on the NASA/WMO effort, and cites it extensively. One might well say that the NASA/WMO report is the definitive technical survey, while the NRC report is more of a summary." He added that the National Oceanic and Atmospheric Administration (NOAA) and the Federal Aviation Administration (FAA) contributed to the NASA/WMO report's preparation.

Back in 1979, the NRC had calculated an average decrease of 15-18% of the ozone after several centuries, given rates of introduction of chlorofluorocarbons (CFCs) into the atmosphere, and thence, into the stratosphere, as they were reckoned in 1977. This estimate has been reduced to a 5-9% steady-state ozone reduction on the basis of the same CFC introduction rate. Uman reminded *ES&T* that these calculations assumed constant CFC emissions at 1977 rates, and no other perturbations—a highly unlikely set of circumstances, he observed.

One explanation of the lower ozone reduction rate forecast arose from improved laboratory measurements of reaction rates involving the hydroxyl radical. Changes in these reaction rates diminish the importance of hydrogen gases in the lower atmosphere. This effect, in turn, seems to reduce the effect of chlorine on ozone. Actually, the hydroxyl radical is only one of several reactive species; it is important because it participates in several of the more critical reactions involving

stratospheric ozone. Uman pointed out that in a typical model there may be as many as 180 chemical reactions involving a number of interacting species.

The panel that prepared the NRC report considered effects of nitric oxide (NO) and other perturbations upon stratospheric ozone, and summarized all data acquired concerning effects of combinations of pollutants as of last December. It also noted that effects of CFCs and nitrous oxide ( $N_2O$ ) are not additive, because of nonlinear interactions between chlorine and nitrogen oxides. The panel consisted of two committees: a Committee on Biological Effects, chaired by Richard Setlow of the Brookhaven National Laboratory (Upton, N.Y.), and another on chemistry and physics of ozone depletion, headed by Charles Kruger, Jr., of Stanford University. Setlow told *ES&T* that the earlier ozone reduction projections were placed at 5-28% with a 95% confidence level, and that the 15-18% figures cited above represented an average.

Finally—and here is what might be considered the bottom line of this controversy—the NRC panel reaffirmed its full support of the findings that a decrease in stratospheric  $O_3$  will lead to increased ultraviolet radiation in the 2900-3200-Å range, also known as UV-B, reaching the earth's surface. Panel members estimated that for each 1% decrease in ozone, there could be a 2-5% increase in cases of basal-cell skin cancer, and a 4-10% increase in cases of squamous-cell (cells resembling scales) skin cancer, both non-melanoma types, ascribable to the added UV-B rays. Lighter skinned races would be especially at risk. As for light-induced melanoma, the NRC panel said that there are no reliable animal models for studying this dis-

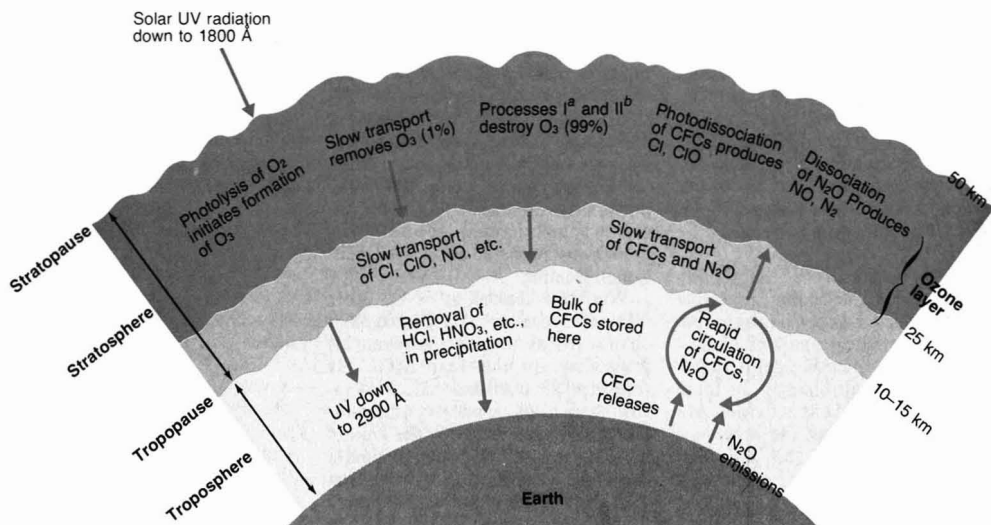
## UV-B and cancer—one clue

The only direct evidence that UV-B may cause cancer in humans comes from studies of people with an inherited disease known as xeroderma pigmentosum. This disease involves a known defect in the repair mechanism that would normally correct UV-B damage to DNA. Such people have a very high incidence of skin cancer, including melanoma. Also, sunburn and melanoma are often found in the same tissue, and sunburn is known to be caused by UV-B.

However, the association of sunlight with melanoma is not strong enough to make predictions of excess incidence of skin cancer ascribable to increased exposure to the UV-B portion of the light spectrum. There are not sufficient epidemiological data, and any corroborating data on xeroderma pigmentosa apply only to a small segment of the population. Although there is some evidence to suggest a connection, there are no unequivocal data from which to estimate dose-response relationships.

Source: Communication from NRC scientist Uman.

## How stratospheric ozone concentration is determined<sup>a</sup>



<sup>a</sup>Process I can involve these reactions, which are limited by the availability of oxygen atoms, for example:

|   |   |   |
|---|---|---|
| $\text{Cl} + \text{O}_3 \longrightarrow \text{ClO} + \text{O}_2$  | $\text{ClO} + \text{O}_3 \longrightarrow \text{Cl} + \text{O}_2$  | $\text{Cl} + \text{O}_3 \longrightarrow \text{Cl} + \text{O}_2$ |
| $\text{NO} + \text{O}_3 \longrightarrow \text{NO}_2 + \text{O}_2$ | $\text{NO}_2 + \text{O}_3 \longrightarrow \text{NO} + \text{O}_2$ | $\text{NO} + \text{O}_3 \longrightarrow \text{NO} + \text{O}_2$ |
| $\text{OH} + \text{O}_3 \longrightarrow \text{HO}_2 + \text{O}_2$ | $\text{HO}_2 + \text{O}_3 \longrightarrow \text{OH} + \text{O}_2$ | $\text{OH} + \text{O}_3 \longrightarrow \text{OH} + \text{O}_2$ |
| $\text{O} + \text{O}_3 \longrightarrow 2\text{O}_2$               |   |   |

<sup>b</sup>Process II involves reactions not limited by atomic oxygen, such as:

|   |  |
|---|--|
| $\text{OH} + \text{O}_3 \longrightarrow \text{HO}_2 + \text{O}_2$ | $\text{HO}_2 + \text{O}_3 \longrightarrow \text{OH} + 2\text{O}_2$ |
|---|--|

Source: NRC report.

ease. It noted that sunlight is a contributing factor, but that there are other as yet unknown factors as well.

### Ozone decrease or increase?

The CFCs at issue in the stratospheric ozone depletion debate are primarily CFC-11 ( $\text{CFCl}_3$ ), and CFC-12 ( $\text{CF}_2\text{Cl}_2$ ). Over a five-year period ending Dec. 31, 1981, measurements taken at NOAA's climate-monitoring stations located in clean-air areas suggested a global CFC-11 increase of 37%, to 187 parts per trillion (ppt). For CFC-12, the corresponding increase was estimated to be 31%, to 325 ppt. The clean-air areas included the South Pole, two Pacific islands, and the coast of the Arctic Ocean. These data were presented at the American Chemical Society's 183rd National Meeting, held at Las Vegas in March.

Atmospheric lifetimes for CFC-11 and CFC-12 are believed to be about 60 and 110 years, respectively, with measurements indicating a minimum lifetime for CFC-11 of 40 years. That of CFC-12 has not yet been estimated, Don Wuebbles of the University of California's Lawrence Livermore National Laboratories (LLNL) told *ES&T*; but Walter Komhyr, leader of

NOAA's ozone monitoring work at Boulder, Colo., mentioned an estimated 65-year minimum lifetime for CFC-12. Incidentally, NOAA did not have a direct input into the NRC report, although results of measurements taken by that agency "may have been considered," Komhyr told *ES&T*.

NOAA scientist Ellsworth Dutton, who reports on CFC trends, noted a "slight reduction" in the rates of increase of CFC-11 and CFC-12 in late 1979—perhaps because of a change in the pattern of the release of the source gases such as aerosol propellants.



Wuebbles: looked at combined effects

(More recent data have rendered conclusions concerning CFC-12 uncertain, Komhyr noted.) On the other hand, the NASA/WMO report forecasts that if current CFC use and rates of release continue, and present photochemical theory holds up, one should expect a 5-10% ozone reduction after several centuries. Nevertheless, several models show that stratospheric ozone should have decreased by around 0.5-1% in recent years (again, based on the assumption that CFCs were the only man-made substance reaching the ozone layer).

Even within NOAA, there seems to be disagreement on this point. For instance, Komhyr says that ozone decreased over North America during the 1970s. The decrease was of about the same size as that predicted for a "chemically eroded" ozone layer. But Komhyr added this qualification: "The cause of the indicated decrease is unknown. We cannot say whether it is caused by natural fluctuations or by depletion of ozone by CFCs. It may be that the effect of these compounds is masked by natural ozone fluctuations. However, if the observed trend persists for another 10-15 years, then we could be seeing the predicted chemical destruction of ozone in our measure-

ments."

Other researchers said that they could not detect an ozone decrease ascribable to chemical attack. For example, at NOAA's Air Resources Laboratories (ARL), James Angell's analyses of global total ozone data actually showed a worldwide increase in stratospheric O<sub>3</sub> of several percent during the 1960s, and "globally, a decrease of 1.5% between 1970 and 1980, and 0.5% between 1971 and 1980." As for the observed trends of ozone changes persisting over the next 10-15 years, "I bet they won't," Angell predicted.

Citing a portion of the NRC report, Joseph Steed, a senior research chemist at the Du Pont Company, also said that statistical analyses of historical ozone measurements have shown "no overall change" in total ozone, as a result of our activities. Although characterizing the report as generally "balanced," he said that "one major omission was its failure to discuss combined effects of a number of man's activities on stratospheric ozone."

Reiterating that the NRC report did, in fact, consider such combined effects, Uman agreed that no overall change in total ozone has been detected. However, he observed that any changes to be expected by this date are so small that they would be indistinguishable from the noise of the data. He added that no firm evidence of change should have appeared yet, given the natural variability of stratospheric ozone, but that this apparent lack of change in no way invalidates the basic chemical theory concerning

effects of certain substances on ozone.

### Computer model

Don Wuebbles of the LLNL looked into combined effects of certain chemicals, and developed a computer model aimed at predicting what those effects might be. One of the conclusions drawn from his model is that in contrast to other projections, his envisages essentially no reduction of the total ozone column, compared to the previous decade, when several chemicals act upon it simultaneously. His model was discussed at the ACS National Meeting.

Wuebbles looked at N<sub>2</sub>O, other NO<sub>x</sub>, carbon dioxide, CFCs, and other chlorocarbons together, and ran his projections to the year 2100. He tracked 133 chemical reactions involving up to 43 chemical constituents. His model extended from the ground to the top of the stratosphere. Wuebbles expressed the belief that while total O<sub>3</sub> may not change, there would be changes in ozone distribution as a function of altitude. (Uman noted that all models show similar shifts in the ozone profile with altitude.) Decreases would be expected in the upper stratosphere, while ozone increases would be seen in the lower stratosphere and troposphere. An outgrowth of any such ozone redistribution might be some atmospheric temperature pattern changes having "uncertain consequences," Wuebbles said.

### Nitrous oxide

Most scientists foresee at least some degree of ozone layer depletion. But

NOAA/ARL director Lester Machta notes the NRC revised its secular reduction projections downward from 18% to 6%, and said that these forecasts could be changed again. Indeed, the NRC report points out at least three discrepancies between observation and theory that are as yet unresolved, Uman reminded *ES&T*. "Either observations or theory will have to be improved, so there is a reasonable chance that the estimates will continue to change for some time," he added.



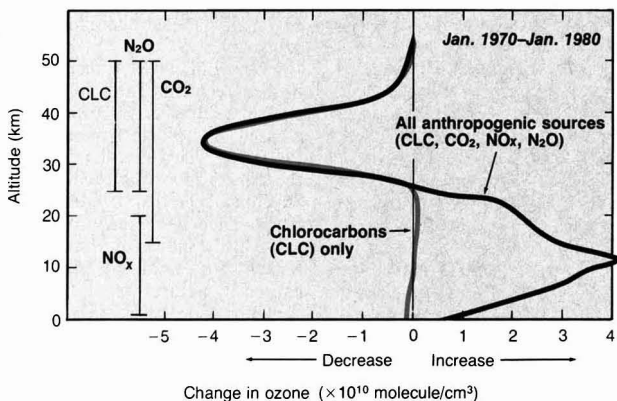
Machta: "forecasts can change again"

About five years ago, scientists developed an interest in the effects of N<sub>2</sub>O. Machta explained to a press conference that much like CFCs, N<sub>2</sub>O is essentially stable and unreactive in the lower atmosphere. Under stratospheric conditions, CFCs, made reactive by more intense UV radiation, lose chlorine atoms that catalytically break ozone down to oxygen; the chlorine atoms remain unchanged. In the case of N<sub>2</sub>O, however, UV radiation does not play a role; rather, a singlet oxygen atom attacks an N<sub>2</sub>O molecule to form nitric oxide (NO), which is an ozone destroyer.

Concern about NO has been called into question. For instance, the Civil Aeronautics Board spent many dollars to show that NO emissions from supersonic transport aircraft, for instance, do not affect the ozone layer.

On the basis of four years of measurements, the N<sub>2</sub>O concentration in the atmosphere is presently estimated to be increasing at about 0.2%/year, as reported last year by Ray Weiss in a paper in the *Journal of Geophysical Research* and confirmed by NOAA scientist Dutton. (The NRC report cites data indicating a 2.7% change over the past 16 years.) Dutton added that the globally averaged concentration of N<sub>2</sub>O is just under 300 parts per billion. That figure represents about 10<sup>-3</sup> times the abundance of CFCs, and approximately 10<sup>-3</sup> times that of CO<sub>2</sub>.

Changes in ozone at different altitudes, ascribed to pollutants



Source: Paper by Don Wuebbles at the ACS 183rd National Meeting.

Machta believes that most of the  $N_2O$  is evolved through denitrification of increasingly used nitrogen fertilizers in agriculture, although he also mentions the importance of combustion sources. He and Dutton are concerned about these and other types of contributions of  $N_2O$  from human activity that one day could alter the balance between production and destruction of stratospheric ozone. On the other hand, Weiss feels that combustion sources are more responsible for the recent increase in  $N_2O$ .

### A 60-story balloon

Perhaps one way to attempt to resolve some—though by no means all—of the uncertainties concerning what is occurring chemically in the stratospheric ozone layer is to take actual samples several times daily, if possible. To achieve this objective, James Anderson of the Center for Earth and Planetary Physics at Harvard University planned to suspend a balloon about 45 km above the surface of the earth (*ES&T*, Vol. 15, No. 4, p. 377). Instruments on a platform suspended below the 60-story balloon would be reeled down and up 20 km by means of a specially designed winch

and very light cable. These instruments would sample monatomic oxygen, ozone, chlorine oxide (ClO), and the  $HO_2$  radical (also a suspected threat to ozone), and would then be retracted into the platform. Reeling down and up could be done as often as 10 times a day. A large amount of data could be acquired with a single set of instruments, and telemetered to earth. Anderson's project was (and still is) funded by NASA.

Apparently, there has been some delay in getting this experiment off the ground. Last March, Anderson told *ES&T* that the first launch would be scheduled for this month. The object will be to determine whether an instrument cluster can indeed be lowered—in this case, to 50 000 ft below the balloon's platform—and then reeled up. The first flight will not carry a full array of instruments. "If we are successful this June, we will then move quickly on to the next step, which is to determine whether there is a chemical link between ozone and chlorine in the stratosphere," Anderson said.

If Anderson's experiment succeeds, perhaps scientists predicting ozone reduction (or no such reduction) may be able to acquire the refined data that

could improve their understanding of chemical processes in the stratospheric ozone layer. Others do not believe that the balloon experiment will yield enough data suitable for gaining such knowledge and eventually developing useful predictive models. Perhaps, given the conditions of temperature, pressure, and radiation one finds in the stratosphere, the data that Anderson might acquire will furnish a grab bag of surprises to keep the experts at the drawing board for a much longer time than they had hoped.

—Julian Josephson

### Additional reading

- National Research Council Report. "Causes and Effects of Stratospheric Ozone Reduction: An Update"; National Academy Press: Washington, 1982.
- Komhyr, W. D. et al. "F11 and F12 Abundances, Trends, and Residence Times Determined from 1977-1981 Measurements at NOAA/GMCC Baseline Stations," presented at the 183rd National Meeting, ACS, Las Vegas, 1982.
- Komhyr, W. D. et al. "1960s Ozone Increase Followed by a Decrease in Ozone over North America During the 1970s," presented at the 183rd National Meeting, ACS, Las Vegas, 1982.
- Wuebbles, D. et al. "Effect of Coupled Anthropogenic Perturbations on Stratospheric Ozone," UCRL No. 86870, presented at the 183rd National Meeting, ACS, Las Vegas, 1982.

# Groundwater Resource Recovery

Groundwater is a barrier that holds oils that leak into the ground. Most facilities that process, use or store oils, have accumulations of oils on the groundwater. Generally these oils are lost through slow leaks. A 1/8 inch (0.3 cm) stream of liquid is almost 100,000 gallons (378,530 litres) in a year. Some airports and refineries have lost several million gallons of oil that is now floating on the groundwater. These oils can be recovered by the SCAVENGER and reused.

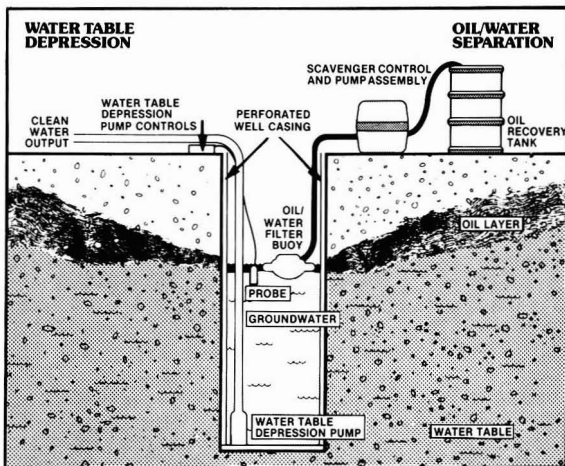
The SCAVENGER is a portable oil/water separator. It separates and retrieves light oil products such as gasoline, diesel oil, fuel oil and a wide range of other hydrocarbons from the water surface both above or below ground level. The SCAVENGER features a specially designed separator cartridge mounted in a floating collection unit. This unique cartridge

repels water, but allows oil to pass through to the collection bowl, where it is then pumped to a recovery tank. The recovered product is virtually 100% water-free.

The PROBE/PUMP is a submersible pump with a special probe attachment that permits automatic pumping of water from the recovery well. It is designed so that the pump will shut-down when the hazardous materials come near the pump's intake.

When this clean water is removed, a "Cone of Depression" is formed which causes a rapid flow of the hazardous materials from the surrounding area to the SCAVENGER in the recovery well.

Both units are intrinsically safe and operate unattended. This, plus the value of recovered material results in rapid return on investment.



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# Quality assurance, analytical methods, and hazardous wastes

*The name of the game is scientifically sound and legally defensible data*



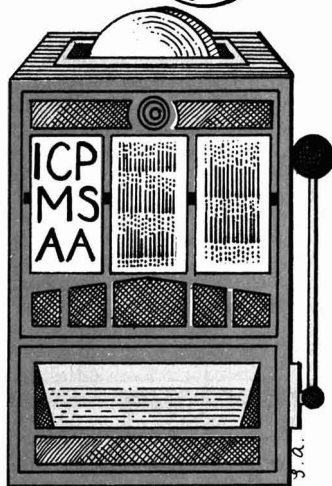
Quality assurance is the activity with which analytical chemists must be involved. The monitoring and measurement data that they gather must meet rigid standards. The goal of the quality assurance (QA) program that EPA enunciated in May 1979 was "to obtain scientifically valid, defensible data of known precision and accuracy to fulfill the agency's responsibility to protect and enhance the nation's environment." In his May 30, 1979, memorandum, then-EPA administrator Douglas Costle made participation in the agency's QA mandatory for all environmental measurements generated for or by EPA.

A year later final regulations were passed for hazardous waste management. The EMSL-Las Vegas lab is responsible for coordinating the sampling, analyses, and hazardous waste program. On the other hand, EMSL-Cincinnati has QA support for leachate, surface waters, groundwater, wastewaters, sludges, and sediments under RCRA. The EMSL-Research Triangle Park provides QA support for the ambient air data.

At the spring ACS meeting in Las Vegas there was a week-long symposium on quality assurance and analytical methods for monitoring hazardous wastes. Specific sessions were held on the monitoring aspects, assurance for analysis, sample preparation, analytical methodology, methods for analysis, and characterization of waste sites. Here are highlights of the papers presented.

## Monitoring hazardous wastes

David Friedman of the U.S. EPA said that a variety of tests must be conducted in gathering data for compliance with RCRA regulations. The use to which the data are to be put determines the design of the monitoring study. In much of this testing, exact numbers are not necessary; one need



only determine if a change is occurring in some property over time or whether a specific property of material exceeds a defined value. Such are the RCRA requirements, for example, for groundwater monitoring and monitoring the operation of a hazardous waste incineration. One of the major determinants of the cost of testing is the uniformity of the material being tested. Homogeneous materials are much less expensive than those that require representative sampling.

In some cases, uncontrolled hazardous waste sites are investigated by private, analytical-service organizations under contract to the EPA. Alfred F. Haeberer of the U.S. EPA said that the agency has established an analytical program under contract to identify and quantify the chemical compounds found at these sites. Concentrations may range from a low of 0.1  $\mu\text{g/L}$  for compounds such as chlorinated pesticides in well water to essentially 100% pure compounds in 55-gal steel drums. The samples are first shipped to EPA's National Enforcement Investigation Center

(NEIC-Denver) for extraction and preparation of samples.

In other cases, laboratory contracts call for the quantitative analysis of the 114 organic priority pollutants by GC/MS; additionally the laboratory is required to survey the 30 major components of highest apparent concentration not specified as priority pollutants. For inorganics, the lab contracts call for the analysis of 24 metals by inductively coupled argon plasma (ICAP) spectroscopy or a comparable alternative. The analytical program under such contracts receives quality assurance support from the QA division of the agency, specifically the Environmental Monitoring Support Laboratory (EMSL) in Las Vegas and from the NEIC in Denver. These contractor-operated labs are audited quarterly to ensure the terms of the contract with respect to chemical analyses, quality assurance, and deliverables. One of these labs is Mead-CompuChem at Research Triangle Park, N.C. Robert E. Meierer said its operation included 18 GC/MS systems for the analysis of samples from hazardous waste sites.

For the water category alone, studies were made involving 15 to 100 or more labs. John A. Winter of the EPA said that the agency has a repository for toxic and hazardous materials. At present, 51 repository standards are available; these are the quality control samples for the hazardous waste program.

M. H. Carter of the U.S. EPA effluents guideline division compared the effectiveness of selected automatic search programs to manual interpretation of the same GC/MS data. In general, the automated program identified 95% of those priority pollutant compounds that were manually identified from the same set of GC/MS data.

William L. Budde of the EMSL-

Cincinnati told how the agency manages its RCRA analytical quality control data. Typically, the GC/MS and the ICAP spectrometer are linked with dedicated microcomputers. These computers generate almost finished reports that require only reformatting and communication of reduced data to the laboratory data management system, which is stored in a PDP 11/70 of Digital Equipment Corp. Direct transmission to the laboratory data management system is feasible; however, at present the systems generating the partially finished or complete reports are interfaced to the laboratory data concentrator through a batch processing microprocessor buffer system. The prototype system has been operational with several instruments for some time. Budde discussed a series of measurements of toxic metals in soil and plant extracts.

Samuel R. Sax of EPA Region III said that during 1981 its Western Regional Laboratory and Environmental Center examined more than 400 hazardous waste samples. All quality control was performed by this center. Samples provided from elsewhere showed 90-110% reproducibility and recovery with duplicate and spiked samples. Twenty-two metals were examined by the atomic absorption (AA) technique.

#### Assurance for analysis

In brief, a laboratory QA/QC program incorporates a technique for defining a suitable quantitative measurement or linear dynamic "calibration range" for single point analysis. It also includes a series of complementary QA protocols that detail the preparation of synthetic samples for the purpose of method validation. The synthetic samples are used to evaluate the precision and accuracy of the analytical methodology to ensure the acquisition of timely verified data.

For example, macroreticular resin samples are widely used to collect ng/L quantities of trace organics from water. Few studies present quality assurance data to establish confidence in the experimental results. I. H. Suffet of Drexel University discussed QA of macroreticular resin samplers in trace organic analysis.

Robert G. Miller of the U.S. EPA Health Effects Laboratory in Cincinnati was concerned with lead analyses, specifically with the influence of the time of acidification after sample collection on the preservation of drinking water samples. The collection, storage, and preservation of these water samples for trace metal analysis are important factors in epidemiological,

toxicological, and hazardous waste monitoring studies. The control water was tap water in Cincinnati, while the water containing approximately 70 ppb lead was prepared in a vat by circulating tap water through a lead pipe. Lead data at the 70-ppb level indicate that up to 14 days after sample collection, samples can be acidified and analyzed 24 hours later, with no appreciable difference in lead concentrations from those analyses performed immediately after collection and acidification. For excellent lead analysis, the analyst should use the methods of addition techniques.

E. J. Subak, Jr., of PPG Industries, Inc. was concerned with the analysis of municipal sludges and its corresponding QA aspects. Complete QA data were obtained for overall recoveries and extraction efficiencies for so-called extraction liquids. The analyses found insignificant levels of all eight RCRA metals and lindane, endrin, and methoxychlor. These data suggest sensitivities of at least 10 ppb for lindane and methoxychlor in the extraction liquid. Similar data for endrin suggest sensitivity of approximately 0.1 ppb.

W. D. Pyle of Radian Corp. said there was a need to develop a procedure for the determination of the GC/FID relative response factor of deuterated vs. nondeuterated toxic pollutants reference standard used in the GC/MS protocol analysis for chemical waste samples. He reported that the analytical standards prepared from deuterated materials must undergo a rigorous quality control program following production.

Another goal is to develop a protocol for analytical methods for trace materials. It is necessary to have a fixed procedure that is expected to give satisfactory sensitivity, precision, and accuracy before a validation study is begun. This would avoid much wasted time and effort. But Douglas W. Bristol of the EPA Health Effects Laboratory indicated that validation of a method provides no guarantee that it will perform reliably when it is used to analyze field samples.

EPA has set up a repository for toxic and hazardous materials at Radian Corp. Alan W. Nichols of Radian Corp. said the quality control program of its repository provides a broad analytical data base in order to provide a high degree of confidence in the stated purity of each compound. Compounds in the repository are analyzed by at least two different methods. These methods include packed column and capillary gas chromatography, HPLC, differential scanning calorimetry, and

high performance thin layer chromatography (HPTLC). The repository quality control program provides a high degree of confidence in the stated purity of each compound. Compounds, commercially available as well as synthesized materials, that have undergone purity assay at Radian are submitted to two or more independent labs for referee analysis.

Viorica Lopez-Avila of Acurex Corp. described a QA protocol for the determination of priority pollutants (acids, base/neutrals, pesticides) using a fused silica capillary column. Five internal standards were recommended; prepared by Radian Corp., the standards for most of the priority pollutants had relative standard deviations of relative response factor less than 10%.

When environmental samples are extracted with organic solvents, there is the possibility of contamination. At other times, the reactions of the solvent can lead to artifacts that are difficult to deal with. Nicholas Pangaro of GCA/Technology Division looked at the types and quantities of artifacts produced when acetone was used as the extraction solvent in the Soxhlet apparatus. In all soil samples analyzed, simple dimeric products such as diacetone alcohol and mesityl oxide were found in varying amounts. Complex mixtures of dimers, trimers, and other complex derivatives were obtained from the acidic and basic soils. Of these, isophorone is the most important to cope with in environmental analyses because it is an EPA priority pollutant. All soil samples extracted with acetone contained significant amounts of artifacts.

The analysis of volatile organic compounds is also very important now for the analytical chemists. The analysis of volatile organic compounds using purge and trap instrumentation has become a widely accepted technique. But when standard compounds are spiked into natural water samples and the results compared to the distilled water analyses, it is not uncommon to obtain greater than 100% recovery of the spiked components. The ultimate goal of the research discussed by T. R. Smith of ERCO/Energy Resources Co., Inc., is to determine if there is an "ideal" salt type and concentration at which purge and trap extraction efficiency is optimally 100% relative to direct injection of the same component.

E. P. Brantly, Jr., of the Research Triangle Institute reported on the national QA program for asbestos analysis. EPA started a voluntary quality assurance program under the auspices

of the Asbestos-in-Schools Technical Assistance Program. Participation was open to commercial and noncommercial labs capable of analyzing bulk samples with polarized light microscopy. Mechanisms were developed for reporting program results to participating labs and for offering assistance to those labs having difficulty with the analyses.

Four rounds of the QA program have been conducted. About 150 labs are now participating. "Real-world" samples of asbestos materials removed from public buildings were distributed in rounds 3 and 4. The materials were defined as those containing more than 1% asbestos by weight. This was designed to exclude from consideration materials that inadvertently contain trace amounts of asbestos as a contaminant. It was important to point out that this percentage does not represent a finding by EPA that materials with less than 1% are not potentially hazardous. But in these rounds, positive results were those with more than 1% of asbestos by weight.

#### Sample preparation

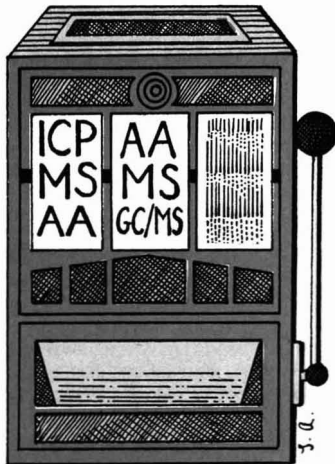
One of the weakest links in any analytical process is sampling. Shortcomings in sampling, including sample stability, can lead to erroneous data for analysis. Some measurements are no good because not enough attention has been paid to sampling and analysis problems.

Other analysts were concerned with extractable organics in sludge. One alternative to the EPA method consists of a base/neutral extraction followed by an acid extraction, both with methylene chloride solvent using the homogenization-centrifugation technique. Gel permeation chromatography (GPC) can be used to remove high-molecular weight interferences in the base/neutral and acid fractions of priority pollutants. GC/MS identification is used for the GPC fractions of the extractable organics. R. H. Wise of the EPA in Cincinnati took a look at the amount of organic interferences in municipal activated sludges.

Laurence W. Stratton of the National Enforcement Investigations Center in Denver told about procedures for sample preparation that were developed there. Waste samples with high concentrations of hazardous materials are prepared in the Regulated Substances Laboratory at the NEIC, which is operated under contract by Fred C. Hart Associates, Inc. Organic parameters consist of the organic priority pollutants and require the preparation of separate extracts for the pesticide analysis, volatile organic

analysis, and analysis of the base/neutral and acid fractions. The analyses were performed by GC with flame ionization detector (FID) or Hall electrolytic conductivity detector (HECD) at the NEIC. The other samples can be sent for GC/MS or electron capture (EC) detector analysis. Available QA data indicates spike recoveries in the range of 65-85% for most base/neutral and acid and pesticide compounds.

J. H. Lowry of the NEIC in Denver said that the NEIC has been preparing samples collected from hazardous waste disposal sites. Two general approaches have been taken in regard to sampling: One separates the sample into its physical phases; the other does not.



The analysis of PCBs has stirred much controversy. These chemicals are found in electrical capacitors and transformer oils. EPA sponsored a round robin for validation. Four combinations of GC were used for the study, including packed and capillary columns with either a Hall conductivity detector and an electron capture detector. All standards were obtained from the EMSL in Cincinnati.

B. N. Colby of Systems, Science, and Software was interested in the analysis of PCBs in solids, sediments, sludges, and oils. He described a simple, rapid method for PCB analysis; it involved an initial acid sample digestion followed by a single-step extraction and analysis by gas chromatography without further preparation. This method can be used for a variety of environments and requires about two hours for completion. It has a detection limit of 1 ppm but can be used on samples containing up to 100% PCBs by incorporating dilutions.

R. H. James of Southern Research Institute was concerned with analytical

methods for survey analysis of residual wastes. The scope of the analytical methods is intended not to be limited to priority pollutants but rather to be applicable to a broad range of organic compounds. Only limited consideration was given to sample preparation procedures but prime consideration was devoted to the evaluation of a fused silica capillary column for the specific analysis of organics.

Methods for the analysis of semi-volatile organic compounds in solid waste were evaluated and one method was selected for interlaboratory comparison by 10 labs. Calibration standards containing the 140 compounds were sent to the participating labs in the round robin. One of each pair of compounds was added at a high level and the other was added at a low level.

#### Methods of analysis

Much attention was focused on dioxin analyses and the technique of fused silica capillary columns. The state of the art in dioxin analyses suggests that acceptable protocols for screening and confirmation of the presence of the 2,3,7,8-TCDD and its isomers would include GC with electron capture detection, open column or HPLC, and GC/MS with low or high resolution. Complete agreement regarding an optimal separation and identification methodology has not been achieved, according to J. R. Donnelly of Lockheed Engineering and Management Service, Inc. But satisfactory results were obtained with methods comprising a two-stage HPLC separation using reverse phase (RP-HPLC) followed by normal phase HPLC procedures, using Zorbax-ODS (methanol eluent) and Zorbax-SIL (hexane eluent) columns, respectively. This procedure afforded separation of the 22 TCDD isomers into groups that were then separated by GC. The Lockheed scientists are looking further at confirmation methods, mass spectrometry involving methane and oxygen negative ion chemical ionization, and Fourier transform infrared spectroscopy.

T. O. Tiernan of Wright State University was concerned with the development and demonstration of analytical procedures for tetrachlorodibenzodioxins and tetrachlorodibenzofurans in fly ash and stack emissions. Samples that were analyzed in this study were collected by stack sampling trains or were residual materials such as fly ash from the electrostatic precipitator installed on a municipal incinerator. Both an SASS train and a modified Method 5 train were used to



collect stack emission samples. One sample of fly ash from a municipal refuse incinerator had at least 18 and probably all 22 TCDD isomers, including the highly toxic 2,3,7,8-TCDD. Tetrachlorodibenzofurans were also found; one sample suggested the presence of at least 16 TCDF isomers, including the 2,3,7,8-TCDF.

In most cases, fused silica capillary column (FSCC) chromatography offers better resolution than packed columns. Gary T. Hunt of GCA/Technology Division told how soils at two construction sites and emissions from an herbicide manufacturing process were found to have high levels of a variety of organics. Special attention was focused on nonpriority pollutant organic contaminants identified using FSCC GC/MS techniques. These include, for example, several chlorinated and nitrosubstituted anilines, chlorinated phenols, alkylated pyridines and quinolines.

B. N. Colby of Systems, Science, and Software reminded the audience that fused silica capillary column GC/MS data files are acquired at a faster rate than packed column files; more information is produced due to greater improved chromatographic resolution. Data were presented that could be used to optimize FSCC GC/MS analysis and data reduction strategies. It covered identification of "search windows" using absolute retention times, conventional relative retention times, and isotope dilution relative retention times. A summary of the "search window" widths was presented for 28 base/neutral and acid priority pollutants. These data files required approximately 27 minutes each to acquire, which allows about 50 s per compound for search and quantitation using external or internal standard approaches, and about 25 s per compound using isotope dilution.

R. G. Beimer of TRW, Inc., compared the use of FSCC with conventional packed columns. The use of FSCC reduces both time and cost of the analysis. In general, the capillary column provided results of at least equal precision to the packed column analyses. Additionally, the automated data routines used for data reduction tended to do a better job, with fewer false positive and false negative identifications, on the capillary column data than on the packed column data. This aspect of the capillary column resulted in less operator interaction with the individual data files and less time (and less cost) to produce the final value. The capillary column data also show better applicability to priority pollutant analysis.

A. D. Sauter of the EMSL at Las Vegas was concerned with predicting GC/MS response factors for organic compounds. He made estimates of concentration for organic compounds identified via manual interpretation in complex mixture analysis, those for which analytical standards are not readily available.

W. L. Fitch of Zoecon Corp. discussed theoretical approaches to the evaluation of GC/MS relative sensitivity ratios, while K. H. Shafer of the Battelle Columbus Laboratories compared GC/FTIR with GC/MS for the analysis of hazardous waste samples.

D. F. Hunt of the University of Virginia at Charlottesville said that the triple quadrupole mass spectrometer can be used for the direct analysis of organics in environmental matrices, be they gas, liquid, or solid. This instrument avoids large amounts of time required to perform a single analysis on a relatively expensive GC/MS data system. The organics are converted to derivatives before they are detected by the instrument. A scheme of analysis was presented for phthalates, polynuclear hydrocarbons, and phenols in industrial sludge. Phenols are converted to methyl carbamates on treatment with methyl isocyanate at room temperature and polynuclear aromatic hydrocarbons are converted to nitro compounds on exposure to a stream of dinitrogen tetroxide for 3-5 s. Procedures for the analysis of organics containing other functional groups are under development. These include amines as their methyl urea derivatives, and aldehydes and ketones as benzyloxylamine derivatives.

R. A. Yost of the University of Florida at Gainesville said that the tandem mass spectrometry is a promising new technique for the analysis of complex mixtures. First developed by this speaker and his colleague, the triple quadrupole instrument is commercially available from Finnigan Corp. and Sciex, Inc. The unique capability of this technique is to analyze rapidly complex mixtures with little or no prior separation or cleanup. A first quadrupole provides separation of the mixture components by selection of their molecular ion masses. The selected molecular ion is then fragmented by collision-induced dissociation, and the resulting mass spectrum obtained by scanning the third quadrupole.

The process is analogous to the traditional GC/MS technique, with the first quadrupole providing molecular weight separation of the components instead of chromatographic separa-

tion, and the mass spectral identification being provided by the final quadrupole. The separation is essentially instantaneous ( $10^{-5}$  s) so that analysis by MS/MS is much more rapid than analysis by GC/MS. Continuous real-time monitoring is possible and a definite advantage. In addition, samples not amenable to GC separation, for example those samples that are involatile or thermally liable, can be analyzed by MS/MS. There are operating modes that are particularly useful to screen rapidly whole classes of compounds in the mixture. For example, all phthalates in a mixture may be quickly identified. The technique is particularly advantageous for trace analysis of complex mixtures. It has been applied to a diverse range of problems, including the analysis of toxic substances in plant tissue, physiological fluids, water, air, and hazardous wastes. Moreover, it has great potential to help solve the problems of hazardous waste monitoring.

Karl Bratin of Pfizer said that most liquid chromatography/electrochemistry (LCEC) experiments are performed with single-electrode transducers, but that it is a simple matter to monitor the current at two different working electrodes. This is analogous to the so-called "dual wavelength UV absorption detector." He described methodology for the detection of explosive compounds in environmental samples at detection limits below 10 ppb. It can also be used to remove dissolved oxygen from samples with limited sample volume. In the past, the flow of nitrogen through such a small sample would lead to much frothing and loss of sample. One way to bypass this problem is to employ a dual-electrode, thin-layer transducer. Operating the reductive LCEC system with the dual-electrode transducer allows a direct injection of the sample without the need to remove dissolved oxygen.

Robert S. Houk told how the ICP-MS concept can be used for trace elemental and isotopic analysis during continuous introduction of solution aerosols. He and his colleagues are looking at a "cooled" inductively coupled argon plasma (ICP) for the direct identification and determination of organic and organometallic compounds in aqueous solutions.

Sidney A. Katz of Rutgers University was concerned with the determination of heavy metals in municipal sewage sludges. Several laboratories participated in a round robin; one conclusion was that the nitric acid-hydrogen peroxide digestion procedure is at least equivalent to the other wet ashing procedures, but that it is supe-

rior to dry ashing in terms of metal recovery. This procedure is used to prepare samples of sewage sludge for atomic absorption spectrometry. The precision and accuracy of the nitric acid-hydrogen peroxide procedure are acceptable from the results of the round robin.

Eugene A. Burns of Systems, Science, and Software said that there were few analytical chemistry techniques capable of characterizing toxic and speciating compounds present in hazardous inorganic wastes. Since wastes are generally amorphous, the common technique of X-ray methodology cannot be used. He said that infrared spectroscopy permits the opportunity to characterize noncrystalline inorganic compounds. The use of Fourier transform infrared (FTIR) spectroscopy extends this application to quantitate the presence of spectrally active compounds at low concentration. The method was applied to samples of particulate emissions from a copper smelter in which the arsenic (III) was determined in a mixture of arsenic (III) and (V) oxide emissions. The reputation of arsenic as a poison is due largely to the toxicity of the arsenic (III).

M. P. Miller of the Battelle Columbus Laboratories said that it is also important to be able to tell the arsenic species present in leachates from hazardous waste sites and groundwater samples. The method most commonly used for analysis of total arsenic incorporates the generation of arsine gas with subsequent detection by atomic absorption spectrometry. He described the use of the pH-dependent, hydride-formation, atomic absorption technique for the specific analysis of arsenic (III), total arsenic, and arsenic (V) in samples taken from a dump site known to contain high concentrations of organoarsenicals.

J. A. Oppenheimer of James M. Montgomery, Consulting Engineers, Inc. reported on a literature assessment for the analysis of the 14 priority pollutant metals. He presented the relative merits of the methods—INAA, XRF, and ICP—as routine multi-element methods for the analysis of hazardous wastes.

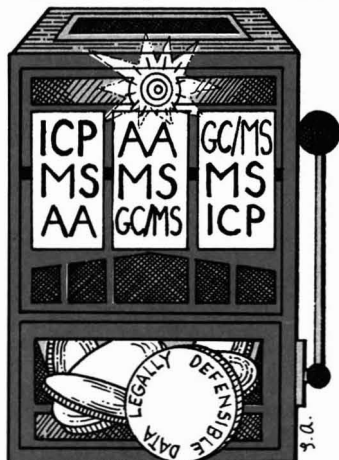
A. Eaton of the same organization said that the multi-element techniques have a significant cost advantage over slower single element methods like atomic absorption, but such techniques must first be verified as accurate and comparable techniques. For example, INAA and XRF require minimal sample preparation for solids whereas ICP requires sample digestion.

E. P. Brantly of Research Triangle

Institute told of the use of polarized light microscopy (PLM) and X-ray powder diffraction (XRD) for the analysis of bulk samples of asbestos. Because there was no existing standard procedure for the analysis of asbestos in bulk materials, EPA sponsored an effort to produce a practical and objective analytical protocol. The procedure that was developed includes procedures for qualitative and quantitative analysis of bulk samples by PLM and XRD.

#### Characterization of waste sites

B. E. Schulte of Atlantic Research Corp. told of field measurements for the 16 Class A poisons, gases and liquids, defined by the Department of



Transportation. By definition, a poisonous liquid or gas when mixed with air is dangerous to life. For hydrocyanic acid, 16 reagent detection systems are good for screening of this poison. Nine reagent detection systems are available for the detection of arsine. Detection systems were discussed for all such poisons.

Schulte also looked forward to the development and evaluation of analytical procedures for on-site use for toxic and hazardous waste materials. In particular, he was looking for ways to determine 11 inorganic metals. Major emphasis was placed on commercially available methods that might be adapted for field analysis of sludge and applied in kit form. Electroplating wastes were chosen as the sludge matrix for evaluation.

William R. Lower of the University of Missouri said that monitoring the mutagenic and biochemical effects of environmental pollution in situ in the complexity of real-world conditions is a new and developing aspect of environmental toxicology. The methods developed thus far are applicable to the

assessment of the toxicity of hazardous wastes. For example, if both soil and airborne pollutants are present, soil removed and tested in the laboratory will provide information on the soil component; plants placed on site in the contaminated soil will provide information on combined effects of soil and air; plants grown on site in pots of clean soil will provide information on the airborne components. The system was illustrated by selecting biochemical and physiological measurements from the lead smelter.

Gerald E. Walsh of the EPA lab at Gulf Breeze, Fla., described a method for analyzing complex industrial and municipal wastes. The method uses chemical fractionation and subfractionation combined with laboratory toxicity tests on marine and freshwater algae and crustaceans to determine bioactivity of toxic components. Algae were usually more sensitive to the liquid wastes than crustaceans. But it was suggested that the liquid effluents must be fractionated in order to determine the potential effects on organisms in receiving waters. Bioactive fractions can be analyzed chemically to determine the factors that are the most likely to have an effect. Baghouse dusts from electric arc furnaces are classified as a hazardous waste; these dusts can contain lead, cadmium, and chromium at levels above the maximum allowable concentration (MAC).

Leachability of metals from ash residues from incinerators is of prime concern. Bent E. Christensen of EAL Corp. set out to determine if such ash is nonhazardous, according to the California testing protocol for hazardous waste. The concentration of heavy metals in the ash from municipal solid waste reached levels of 300–1000 mg/kg each for chromium, lead, manganese, and zinc. The soluble threshold limit concentrations (STLCs) in the current California regulations were exceeded for chromium, lead, nickel, and zinc. The organic priority pollutants were not detected in the refuse sample.

Ihor Lysyj of Rockwell International talked about another approach for characterizing hazardous wastes. He suggested that the pyrographic method of analysis be used; this method was developed in the early 1970s under EPA sponsorship for the detection and source identification of various industrial wastes in natural waters. Lysyj said the method is a viable means for class characterization of chemical content of hazardous wastes under field conditions of operation.

—Stanton Miller

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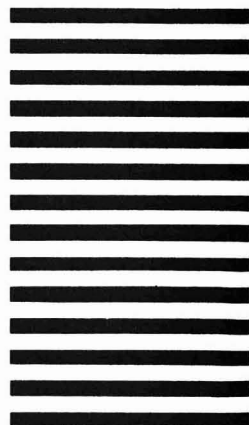
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# EPA's new bubble and banking policies



Michael R. Deland

More "bubbles" and increased "banking" are the foundations of a new emissions trading policy recently announced by EPA Administrator Anne Gorsuch. She predicts that "savings from bubble trades alone could top \$1 billion by the end of this year, with equal or better air quality results."

The bubble policy, developed in 1979 by the Carter administration, places an imaginary "bubble" over a plant and then applies a single emission limit to it in lieu of traditional stack-by-stack controls. It thus gives plant managers the flexibility to develop less costly ways to meet air quality requirements.

The "banking" policy, developed concurrently with the bubble, enables a company to get credit for emission reductions by storing them in a "bank" in a legally protected manner. Three air pollution control districts—Louisville, Ky., the San Francisco Bay area, and Puget Sound—opened banks in 1980. Thus far, their business hardly has been booming. Seventeen firms have made deposits in the Puget Sound bank, 10 in Louisville, and five in the Bay area bank. The only withdrawals have come from the Louisville bank.

Meanwhile, the bubble policy has been slowly gaining acceptance. EPA has approved 18 bubbles involving a variety of industries and several different pollutants. More than 90 addi-

tional bubbles are in various stages of review or are being actively developed by companies. The bubbles have resulted in substantial savings. For example, a bubble in New Jersey saved Du Pont more than \$12 million in capital expenditures and several million dollars in annual operating costs. In Louisville, General Electric paid \$60 000 to lease 445 tons of VOC (volatile organic carbon) credits banked by International Harvester. GE also retains an option to lease additional credits until its VOC emitting lines are phased out in two years. GE thereby avoided the need to spend \$1.5 million to construct an incinerator that it wouldn't have needed after 1983.

## New initiatives

EPA's recent initiatives are the first major proposals developed by its regulatory reform staff and are an attempt to stimulate further the slow but successful start to bubbling and banking. The new "policy statement" became effective as "interim guidance" upon publication in the *Federal Register* on April 7, 1982, and will be final following the close of the comment period July 6.

The policy provides industry and the states far greater flexibility in the use of the bubble. Among the more significant changes are to extend the use of bubbles to nonattainment areas and to allow firms that are pollution sources to use bubbles to come into compliance with regulations. The states are urged to adopt generic trading rules for all criteria of pollutants, thereby eliminating the need for a state implementation plan revision for each bubble.

The policy has built-in safeguards such as a requirement that each bubble must result in no greater ambient impact than the original emission limits. It also specifies that only reductions

that are "surplus, enforceable, permanent, and quantifiable" can qualify as emission reduction credits and thus be banked or used in an emissions trade.

## Reaction to the policy

Industry applauds the policy, characterizing it as "an excellent example of what regulatory reform is all about." The states also are generally enthusiastic. EPA had already approved a generic VOC rule for New Jersey and Massachusetts; rules for more than 20 other states, several involving multipollutants, are in the process of approval or development. However, some states are concerned that the proposal will increase their administrative costs at precisely the time EPA is substantially slashing their federal monies.

Environmental groups under the leadership of the Natural Resources Defense Council (NRDC) strongly object to the new policy. NRDC's main concern is that by extending the bubble policy to nonattainment areas, compliance will never be achieved. NRDC also fears that the dramatic reduction in federal oversight is an invitation for states to enact less stringent regulations and to ignore their enforcement in the hopes of luring industry to relocate.

EPA's proposal, which will be further debated in the coming weeks, is the first major test of environmental regulatory reform. The policy provides the states and industry the opportunity to reduce reliance on the traditional "command and control" approach to regulation and to explore creatively whether market-oriented techniques can control pollution more cost effectively.

Deland writes this monthly column and is employed by ERT, Concord, Mass.

*Here is a menu of new and expanded  
 environmental applications for the technology of*

## Airborne remote sensing

**Glenn E. Schweitzer**

*U.S. Environmental Protection  
 Agency  
 Environmental Monitoring Systems  
 Laboratory  
 Las Vegas, Nev. 89114*

During the past several years, a number of new environmental applications of active and passive airborne remote-sensing technologies have been successfully demonstrated. Engineering sophistication in designing remote-sensing programs, and analytical skills in interpreting acquired data have developed concurrently with improvements in hardware systems.

Federal agencies have a major role in further development of the remote-sensing state of the art, as well as in assurance of the quality of data acquired in this manner, that are used for environmental decision making. Also, on both the federal and state levels, consideration of the use of remote sensing has become an integral part of the process of planning environmental assessments. Moreover, commercial firms can now provide a wide range of services in both acquisition and interpretation of data.

Traditionally, pollution monitoring has been conducted by collecting samples for later analysis in a laboratory. In some cases, automated methods were developed to provide continuous measurements at specific monitoring sites, and to telemeter data to analytical facilities. Remote sensing supplements these "contact" monitoring techniques. It provides the speed, perspective, and mobility necessary for the collection of large amounts of environmental information

that would otherwise be prohibitively expensive or even impossible to obtain by contact monitoring alone.

EPA's Environmental Monitoring Systems Laboratory, headquartered in Las Vegas, which also has facilities in Warrenton, Va., has significantly expanded the use of remote sensing in the environmental field. Building on technologies developed by the Department of Defense, NASA, the U.S. Geological Survey, and other agencies, as well as commercial firms, the laboratory has applied multispectral scanning (MSS), laser technology, and aerial photography to a wide range of environmental problems throughout the country. Figure 1 identifies remote-sensing projects carried out during 1981.

### Multispectral data

Many applications of airborne multispectral scanning for environ-

mental monitoring and assessment have been demonstrated during the past decade. A number of federal and state agencies have used data acquired from satellite and aircraft platforms in order to address a variety of land-use and resource problems. However, only during the past several years has EPA begun to use MSS technology to address a significant number of important environmental problems. Table 1 identifies projects employing this technology, which were conducted last year.

The airborne multispectral scanner used by the laboratory, a Daedalus DS-1260, acquires data at altitudes ranging from 500-20 000 ft above ground level. The 11-band system records radiant energy data in the ultraviolet through thermal infrared portions of the electromagnetic spectrum. As shown in Figure 2, the scanner has a rotating mirror that scans across the ground scene, perpendicular to the line of flight. Radiant energy from the ground surface is reflected through focusing optics onto a beam splitter that diverts the visible radiation (0.38-1.10  $\mu\text{m}$ ) to a 10-channel spectrometer, and the thermal infrared radiation (8-14  $\mu\text{m}$ ) to a solid-state detector. Electronic signals from the 11 detectors are digitized and recorded on magnetic tape in a high-density format. The scanner is equipped with internal visible and thermal reference sources for data calibration.

With the aid of a digital analysis system, the data are calibrated, and geometric corrections are applied to rectify scan-line distortions. Primary data analysis and processing involves classifying pixels (individual picture elements) in categories of energy reflectivity. Single- or multichannel

### What is multispectral scanning?

Multispectral scanning (MSS) is a system that uses no cameras. Rather, it has radiation detectors that pick up visible and invisible light reflected from the earth.

One major application of MSS is found in the LANDSAT satellite. Equipment in that spacecraft converts light intensities to digital signals that are sent to earth at the rate of 15 million bits/s. At ground stations, a computerized signal-deciphering system translates the data into images on photographic film. The resulting images reveal details of earth not obtainable by conventional aerial photography.

images as well as enhanced and classified images can be studied on a video monitor. In addition, statistical parameters computed from the data can be extracted for detailed analysis. Hard copy records that can be generated at this stage in data processing include black and white and color film images, electrostatic paper plots from each channel, and statistical printouts.

Further processing is required before the final product can be made. Data are color-coded, and enlargement as well as reduction factors are computed. Optional programs in this phase include a geographic rectification routine to match the image to selected map projection scales, as well as input image annotations. Final products include hard copy color or black and white film images (positive or negative) and electrostatic paper plots.

### Applications

An early application of the MSS system was for inference of selected water quality parameters and trophic indices to indicate the trophic state of lakes. Demonstration projects in several states have shown that MSS data, when coupled with water quality measurements at the surface that could serve as "ground truth," can provide a good indication of relative lake conditions. One would compare spectral changes during and after restoration efforts, and compare restored lakes with those not being restored. Figure 3 presents maps developed for classifying spectral differences associated with water quality variations in a Montana lake. Colors show nitrate-nitrogen distribution and temperature patterns. Shades of white and gray represent different land classifications.

Another early MSS application using the thermal band involved the measurement of temperature gradients associated with industrial discharges into waterways. MSS technology can be very effective in delineating thermal plumes attributable to point sources, and in ascertaining surface temperature pattern characteristics of water bodies.

A recent use of MSS technology is in the evaluation of applications for permits to discharge sewage and associated wastes into coastal areas. MSS imagery can readily identify such discharge areas in relation to other point-source discharges. Also, this technique provides excellent perspectives of discharge areas in relation to shoreline residential areas, beaches, kelp beds, fishing grounds, and other

FIGURE 1  
More than 100 remote sensing projects nationwide<sup>a</sup>

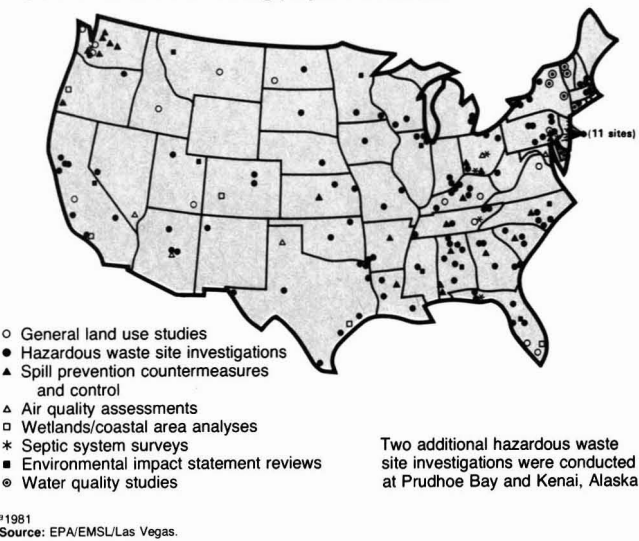


TABLE 1  
Projects employing MSS imagery<sup>a</sup>

|                               |   |
|-------------------------------|---|
| Flathead River Basin, Mont.   | Study water quality, including trophic conditions                               |
| Vermont                       | Study water quality of lakes  |
| Mono Lake, Calif.             | Locate warm and cold internal spring influences                                 |
| Moose Lake, Windemere, Minn.  | Inventory natural resources, analyze septic systems, and thematically map lakes |
| Flaming Gorge Reservoir, Wyo. | Survey water quality  |
| Monarch Mines, Wyo.           | Locate underground coal mine fires  |
| Big Bend National Park, Tex.  | Classify vegetation   |
| Wyoming (selected areas)      | Analyze land cover  |
| Rio Blanco Basin, Colo.       | Assess water quality  |

<sup>a</sup> Projects conducted in 1981.

areas of interest. MSS imagery might also be useful for plume tracking, and for identifying ecological impacts of outfalls; however, such applications have not yet been fully demonstrated.

Classification of vegetative cover has been of considerable value in assessing the impact of air pollutants, such as SO<sub>2</sub> and the use of pesticides, and in mapping vegetation types and vigor in a variety of settings. Also of major interest is the impact of land development on wetlands ecology, a problem well suited for MSS-supported investigations.

The list of actual and potential MSS applications is long. While additional demonstrations are needed, and refinements of both the data acquisition and processing systems are in order,

the technology has been used on many occasions. In numerous ways, this approach not only saves time and money, as compared to other data collection techniques, but it can also provide data not otherwise available.

### Airborne laser sensing

In the early 1970s, the feasibility of using laser-induced fluorescence to detect changes in concentrations of chlorophyll *a* in water bodies was demonstrated. Since that time, the Las Vegas laboratory has developed an airborne system capability to measure changes in chlorophyll *a* levels (*I*). Studies have also shown that this system probably has the potential for monitoring dissolved organic carbon (DOC).

Elevated chlorophyll *a* associated

FIGURE 2  
A multispectral scanner

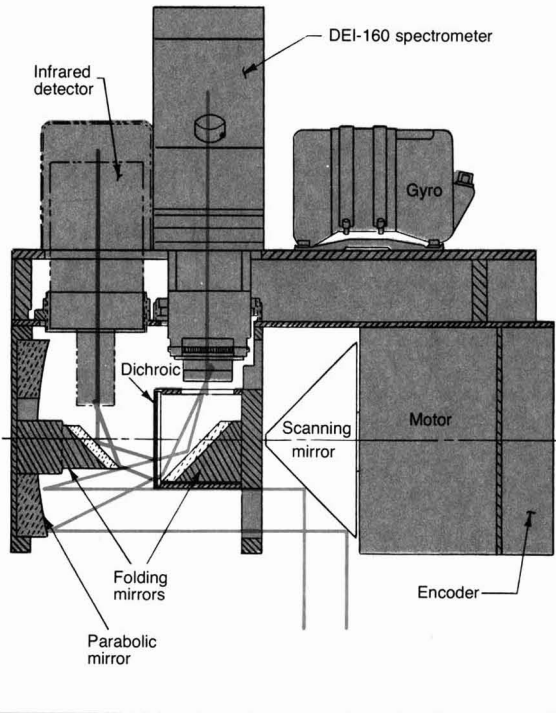


TABLE 2  
Air quality monitoring projects

|   |   |
|---|---|
| 1980  |   |
| Midwest and Northeast Corridor (PEPE/NEROS 1980)            | Regional studies of mixing, layer depth, polluted air mass structure, and urban and point-source plume structure and dispersion |
| San Jose and Santa Clara Valley                             | Urban plume structure and transport   |
| South Coast Basin (Los Angeles)                             | Urban and point-source plume structure and transport  |
| 1981  |   |
| Illinois and Missouri                                       | Power plant plume structure and dispersion in cold weather  |
| South Coast Basin and adjoining desert basins (Los Angeles) | Urban and point-source plume structure, transport, and diffusion  |

Source: EPA Environmental Monitoring Systems Laboratory (Las Vegas).

with algae most often results from high levels of waterborne nutrients. If present in sufficient quantity, algae "blooms" can generate foul-smelling water and even toxic water conditions. Conversely, abnormally low populations of algae, indicated by low chlorophyll *a* concentrations, may result from the presence of substances toxic

to algae, and possibly to higher life forms, including humans.

The concentration of DOC in surface waters may indicate the presence of either man-made or natural polluting substances. Although as a rule such substances may not be highly toxic in low concentrations, they might act as carriers for more toxic inorganic and

organic man-made pollutants. In addition, their presence in raw sources of drinking water causes concern, since during chlorination trace amounts might be converted into chemicals suspected of being carcinogenic.

Of particular interest is the use of an airborne laser fluorosensor to help locate both point and nonpoint sources of pollution, which are indicated by abnormal levels of chlorophyll *a* and DOC. Also, the airborne laser fluorosensor can be used to monitor phytoplankton populations in a number of ways; for example, by observing variations in distribution over different seasons. Moreover, it can be employed to provide baseline data on the quality of pristine lake water, and to help evaluate the results of lake cleanup and restoration efforts. Fluoresensing can assist in designing a water sampling network, modeling an ecosystem, and investigating seasonal changes.

The laser fluorosensor is based on the principle that the intensity of the fluorescence excited in chlorophyll *a* or DOC by a constant light source is in direct proportion to their concentration in the water sample. The operation of an airborne system is depicted in Figure 4. The use of a blue or ultraviolet (UV) pulsed laser excites fluorescence in both the chlorophyll *a* and DOC present in the surface layers. A small fraction of this multidirectional fluorescence is collected by a large-diameter telescope and focused onto a photodetector. This signal is then displayed in real time, and is also digitally recorded on magnetic tape for later analysis.

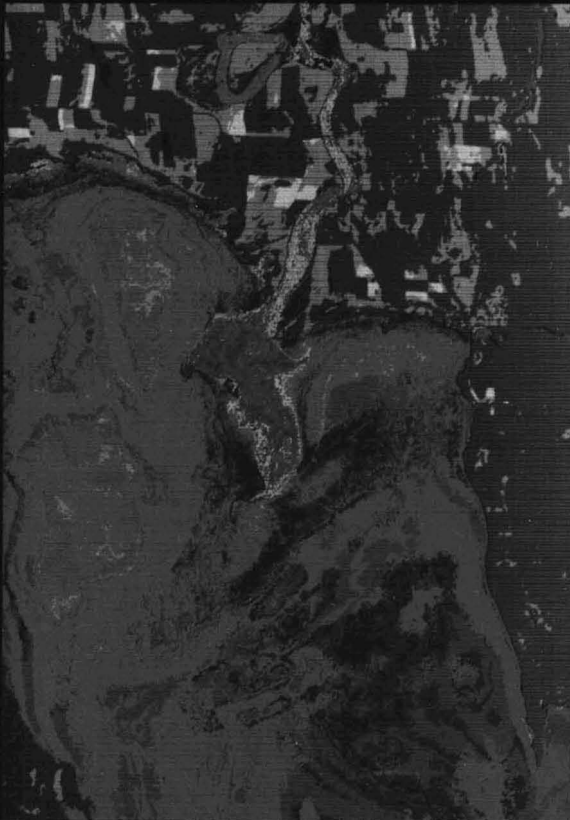
During its development, the airborne system was tested in a series of helicopter flights over Lake Mead, Nev., to measure changes in chlorophyll *a* concentrations. An aircraft altitude of 300 m above the water surface and a ground speed of about 30 m/s were maintained for the test. With a laser repetition rate of one pulse/s and a beam divergence of 10 mrad, the system sampled 3-m diameter volumes of surface water every 30 s.

Changes in the concentration of dissolved and particulate materials between sample locations a short distance apart can cause large variations in the vertical component of transmission of light through water. These variations affect the depth of penetration of the laser beam. The fluctuations in the fluorescence data that result from these variations often are not related to the chlorophyll *a* or DOC concentrations. This problem has been overcome by monitoring the simultaneous Raman emission of water, which is a property of water



FIGURE 3  
**MSS can show water quality variations<sup>a</sup>**

<sup>a</sup> Done with a Daedalus 1260 12-channel MSS, operating between channels 3-10, or 0.45-1.10  $\mu\text{m}$ . Ground data (simultaneous) were collected and analyzed by the University of Montana Biological Station (Big Fork).



Nitrate-nitrogen distribution in  $\mu\text{g/L}$

- 0-10
- 11-20
- 21-30
- 31-40
- 41-50
- 51-60
- 61-70
- 71-80
- 81-90
- 91-100
- >100
- Land 1
- Land 2
- Land 3
- Land 4
- Land 5
- Land 6



Approximate scale:  
 1:150 000

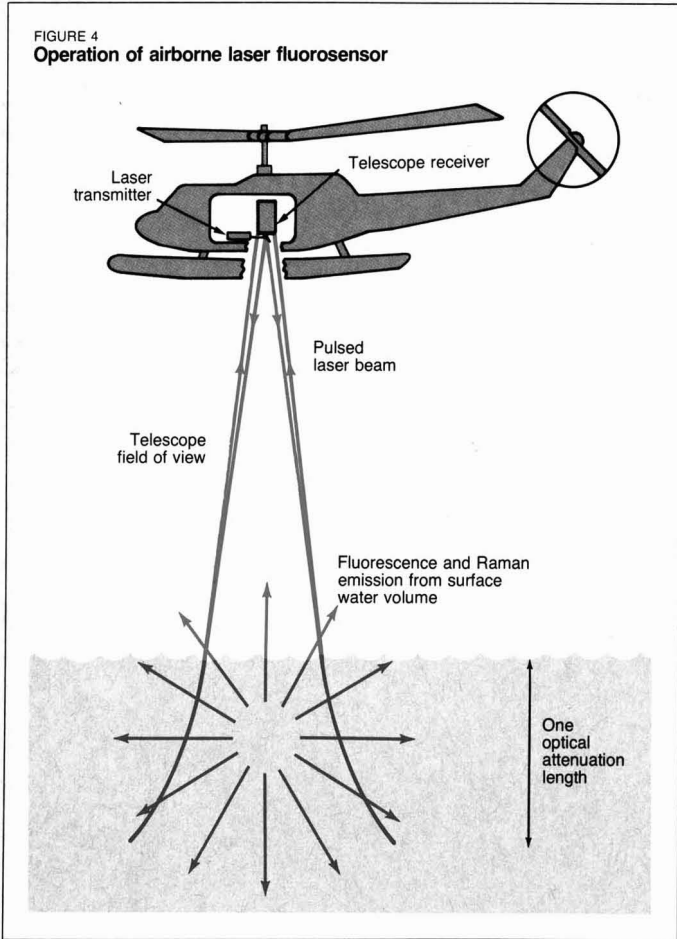
Surface temperature patterns in  $^{\circ}\text{C}$

- <9
- 9-10
- 10-11
- 11-12
- 12-13
- 13-14
- 14-15
- 15-16
- 16-17
- >17
- Land 1
- Land 2
- Land 3
- Land 4
- Land 5
- Land 6



Approximate scale:  
 1:50 000

FIGURE 4  
Operation of airborne laser fluorosensor



alone. Variations in emission intensity indicate a change in the transmission of light when it passes through the water. With the ratio of the chlorophyll *a* or DOC fluorescence signals to the Raman signal for water, one can obtain a new fluorescence indicator that is insensitive to changes in optical transmission.

Results of one flight over a 10-km section of Lake Mead are shown in Figure 5. The continuous profile produced by the laser system is compared to the concurrent chlorophyll *a* ground truth data obtained from 28 fixed sampling sites on the water surface under the flight path. A high degree of correlation between the ground truth and airborne data was achieved. With accurate navigation data, it should be possible to produce maps showing isopleths of chlorophyll *a* or DOC fluorescence for the surface layers of lakes, rivers, and coastal waters.

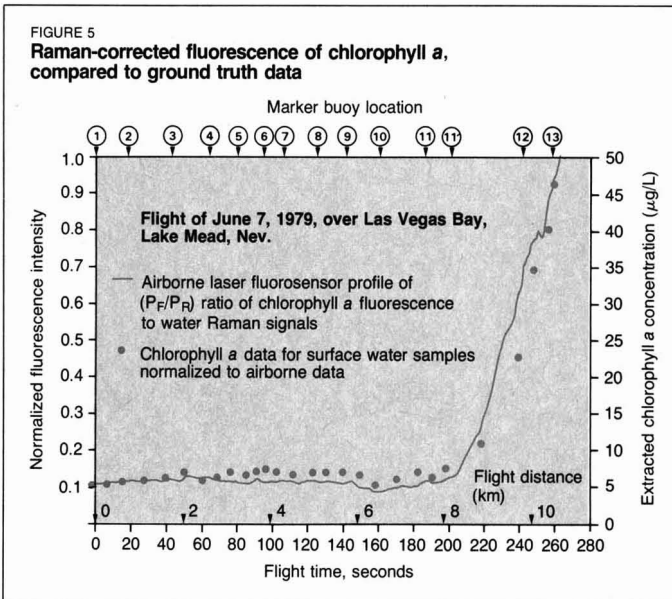
### Air quality monitoring

Current methods of monitoring air pollution with ground-based instruments are not able to provide rapid, area-wide measurements of atmospheric pollution effectively. Such area-wide measurements are necessary to understand the long-range transport of pollutants. They can provide input information to mathematical models. Also, they can reveal the structure of urban plumes, point-source plumes, and their interactions. Finally, they can provide quantifiable information on specific pollutants and their precursors.

Downward-looking laser systems called "lidars" have been built and tested, and their success has been demonstrated as a means of providing these difficult measurements and characterizations of atmospheric pollution. Researchers at the Las Vegas laboratory have developed devices that map the aerosol distribution in the atmosphere (2). Data obtained have been used to define mixing-layer depths; to describe point-source plume dimensions; and to characterize large polluted air masses. Airborne lidars have also been used to position other aircraft, equipped with in situ measuring and sampling equipment, in plumes and in air masses. Table 2 lists several recent air quality monitoring projects that the laboratory carried out.

Measurements are made by observing the relative back-scattering of the intense, extremely short pulse of laser light as it interacts with the suspended particles and droplets below the aircraft. Electronic analyzers on board monitor the elapsed time be-

FIGURE 5  
Raman-corrected fluorescence of chlorophyll *a*, compared to ground truth data



tween the firing of the laser and the scattering returns, and thereby "range" or measure the distances to the aerosol layers.

The laboratory's latest, and now operational, lidar is a two-frequency system consisting of a neodymium-YAG (yttrium-aluminum-garnet) laser transmitter, a Newtonian telescope receiver, and an electronics system that provides a real-time display of the aerosol cross-section data. The two wavelengths—one in the green portion of the spectrum ( $0.53 \mu\text{m}$ ), and the other in the near-infrared ( $1.06 \mu\text{m}$ )—provide a means to differentiate particle size ranges associated with the two major aerosol sources, natural and man-made. This latter feature was designed to permit the measurement of the relative contribution of individual aerosol plumes within an aged air mass.

Specialized high-speed digital electronics are needed to take the signals from the photomultiplier tubes, convert them to digital format, correct them for background and instantaneous laser peak-power values, display the sounding data on an oscilloscope, and store the data in a buffer memory. Timing restrictions are handled through a bit-sized microprocessor subsystem developed for signal conditioning, which uses an instruction set specific for this type of application. The real-time display subsystem is combined with the systems controller, and consists of a microprocessor with various peripheral devices.

#### Lidar applications

Two examples of lidar applications consist of delineation of a power plant plume, and characterization of a regional pollution problem. The lidar provides air quality scientists and modelers with fairly high-resolution maps of the mixing layer for the pollutants, and the aerosol distribution over the geographic area of interest. The system plays a key role in monitoring plume trajectories and dispersion characteristics, and provides data useful for model development and validation efforts. It does not, however, measure discrete particle size, or provide size distribution data beyond the two general ranges described earlier. Those measurements would require the interpretation of the differences in backscatter intensity from several lasers operating simultaneously at different wavelengths.

A pollutant-specific remote monitoring system based on laser technology, which is still under development and shows great promise, is the differential absorption lidar (DIAL).

FIGURE 6  
SO<sub>2</sub> and O<sub>3</sub> absorption coefficients for UV-DIAL system

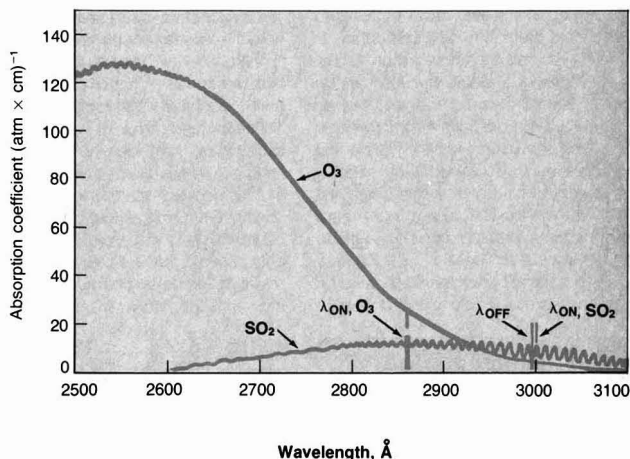
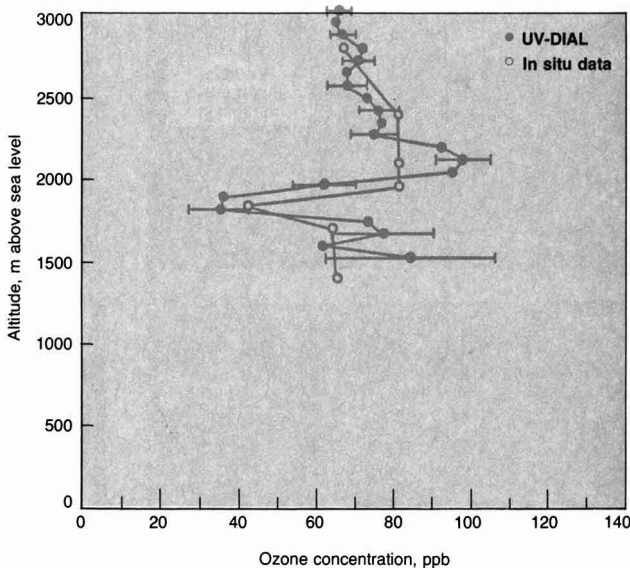


FIGURE 7  
Comparison of UV-DIAL and aircraft in situ measurements



This system also uses two lasers very close in frequency output. One is tuned to an absorption peak for a specific molecule, and the other is tuned off the absorption peak. The scattering cross-section is the same for the two laser pulses as they traverse the atmosphere, while the absorption cross-section of one is related to the specific molecule. The difference in the return

signal is a direct measure, therefore, of the concentration of the molecular pollutant. Figure 6 shows the differential absorption concept for two air quality criteria pollutants—ozone (O<sub>3</sub>) and sulfur dioxide (SO<sub>2</sub>).

A high spatial resolution airborne system designed to measure O<sub>3</sub> and aerosols has already been tested by Browell et al. of NASA, and has

## Aerial photography: new uses

**Investigating hazardous waste sites.** Hazardous wastes have been deposited in pits, ponds, lagoons, landfills, and fields throughout the nation, and particularly in and around industrialized urban areas. Many of these disposal sites are readily identifiable. Others have been covered and abandoned, or converted to other uses. As shown in Figure 8, historical photographs provide an authoritative record of the history of waste sites, and provide insights into current and future environmental problems that may help to guide remedial actions.

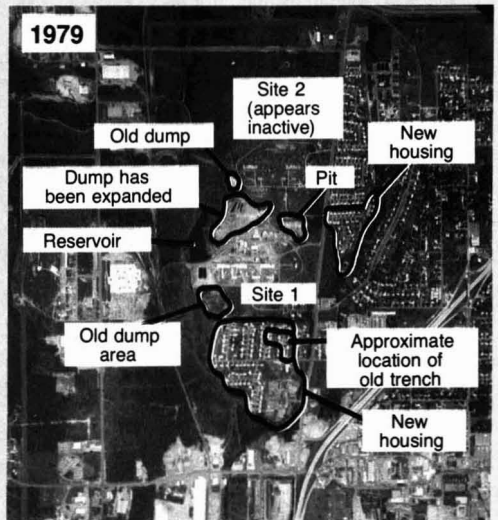
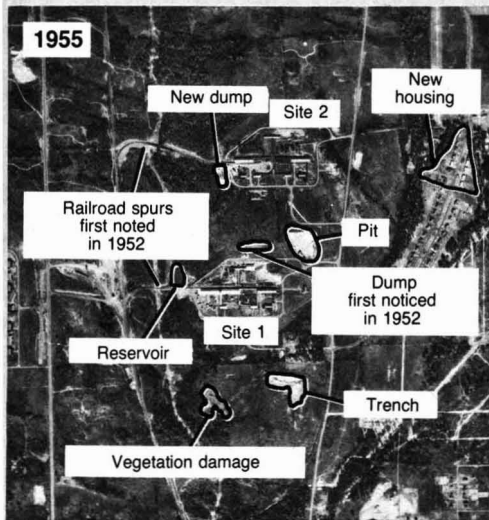
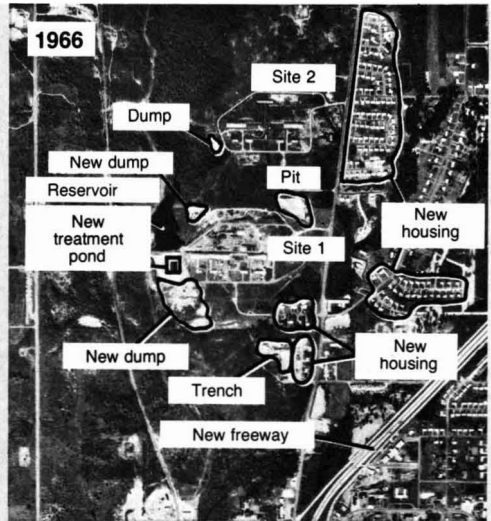
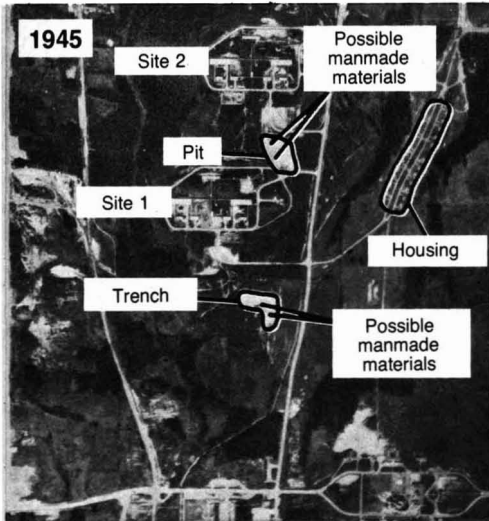
Historical photographs are available for many areas of the country. The bulk of

these photographs may be obtained through the National Archives, or at the U.S. Geological Survey's data center in Sioux Falls, S.D.

**Chemical exposure assessments.** Innovative uses of photo-interpretation techniques for supporting studies of human exposures to toxic chemicals are being explored. Earlier projects using aerial photography have been directed to such problems as identifying contaminant leakage into waterways or aquifers used as drinking water supplies, and determining the proximity of populations to chemical spills and explosions. However, only recently have serious efforts been made to link aerial photography capabilities with the design of exposure monitoring networks in a systematic manner.

Monitoring systems to support exposure assessments should be able to characterize the level and extent of chemical contamination in different environmental media. Also, the design of these systems should facilitate predicting how contaminants may be transported to people in an affected area. Aerial photography is a powerful tool for determining time-varying population densities in specific geographical locations, and thus can aid in the placement of monitoring sites.

For example, aerial photography provides a means for subdividing census information on population characteristics



into small geographical subunits useful for designing exposure monitoring networks. Housing counts (the number of houses in an area) can provide residential population estimates, while commercial building counts can be used to estimate labor force populations. These estimates help to determine population densities for specific areas and times of day.

Aerial photography can also be used to pinpoint populated areas of special concern, such as high-density apartment complexes in contrast to sprawling residential areas; business district shopping malls in contrast to office buildings; or industrial areas open to the environment in contrast to those that are relatively insulated. Moreover, schools, playgrounds, and hospitals can be located. Again, these distinctions help to determine the possible placement of monitoring sites.

Possible contamination of local food supplies is a major concern in exposure assessments. Aerial photography can be effective in locating agricultural plots in the geographical areas under study. For example, in connection with the nuclear power plant accident at Three Mile Island, Pa., all dairies in the area were rapidly catalogued with the aid of aerial photographs. Current emphasis is on techniques for locating and categorizing small garden plots—particularly plots located downwind from air emission sources, or along drainage paths from hazardous waste sites.

Because of the complexity of changing meteorological conditions, mathematical models of the air flow over an area are essential to determine the patterns of ambient pollution concentrations to which people are exposed. These models can provide the basis for determining the best locations for air monitoring stations.

An important input for such models is information that characterizes the roughness of the terrain over which air pollutants flow. This roughness consists not only of the natural contour of the earth, but must include man-made structures that extend upward from the surface of the earth into the normal air flow. Land use categories, determined from the interpretation of aerial photographs, can be related to roughness, given the characteristics of the specific geographical area (for example, topography, height of forests, and height and density of buildings). These relationships can then be fed into dispersion models.

**Assessing septic system performance.** Eligibility for federal construction grants for sewage collection systems has required documentation of septic system failures in an area in which such construction is planned, along with assessments of the public health impact of such failures. In 1978, the Las Vegas laboratory introduced the use of aerial photography for providing the necessary documentation and guidance for assessing such health impacts.

A map scale of 1:8000 provides the necessary resolution quality, and at the same time gives enough area coverage to make the method cost-effective. Color-infrared imagery is the primary vehicle for interpretation of septic field failure. True-color photography, done at the same time, is used primarily for purposes of comparison.

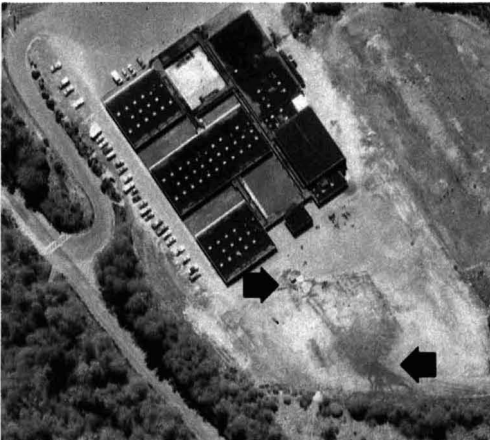
Each land parcel where there are no sewers is examined for signs of unusual vegetative growth, plant foliage distress, and excessive soil moisture levels. The growth-stress-death vegetative patterns associated with the upward and lateral movement of septic effluent appear dif-

ferent from those of surrounding vegetation in both color and color-infrared aerial photography. Any sign of the upward or lateral movement of septic effluent represents a potential for surface failure and water quality problems.

The identifiable signature of septic system failure on infrared aerial photographs is a deep red outline of the absorption field, often accompanied by deep red plumes flowing downhill. Dark gray or black spots depict the surfacing effluent. They may be surrounded by pale gray or tan spots showing stressed and dead vegetation. However, a situation of this type is characteristic only of overt failures occurring at the time of overflight.

Signatures of vegetative growth and stress, similar to standard septic signatures, may be caused by such unrelated items as manure piles, compost heaps, animal droppings, and feedlot runoff. Small springs or leaky hoses can produce a plume effect in vegetation patterns similar to some absorption field designs. Since false signatures are likely, a limited field check of each study area should always be conducted.

There may be secondary indications of septic system failure. Homeowners often remove the effluent from failing systems by channeling it in small ditches or trenches. Wash water may be rerouted through small hoses or pipes to relieve strain on the septic system. In both cases, the effluent is usually diverted into nearby drainage ditches or storm sewers. Another common practice is covering a failing absorption field with an impervious material, such as clay. All of these situations are readily identifiable on aerial images, and are classified as surface failures.



**Septic system failure.** This "textbook example" is characterized by dead vegetation and surface effluent, as indicated by arrows.



**Color infrared photo (left)** shows this failure more sharply than does true color photo (right)

yielded results of the type displayed in Figure 7 (3). The graph of altitude vs. concentration shows an excellent correlation between the profile, as measured with the DIAL system, and that measured with in situ instrumentation on board an aircraft flying a spiral pattern, both measurements being made at the same time. The lowest concentration measured, that is, approximately 35 ppb, does not indicate the detection limit for this system, but, rather, the lowest level encountered. In practice, the system would provide a three-dimensional map of a measurable pollutant over the study area from beneath the aircraft to the ground.

The Jet Propulsion Laboratory developed a laser absorption spectrometry system that has expanded the technology for using the infrared DIAL system for specific pollutants (4, 5). CO<sub>2</sub> waveguide lasers provide the impulse source, and heterodyne methods (use of more than one frequency at a time) are employed for increasing the detection sensitivity. Originally developed for space applications, this technique has been tested and used in aircraft.

EPA has conducted research on infrared DIAL systems with pulsed CO<sub>2</sub> lasers for column concentrations that use earth reflectance (6, 7). Information obtained from studies has indicated that a range-resolvable system could be constructed. Emphasis is being placed on the development of an ultraviolet DIAL system with this capability.

A feasibility review of developing airborne remote-sensing systems for the measurement and profiling of specific pollutants for which criteria have not yet been established, and for chemically more complicated pollutants, indicated several major factors constraining further efforts. First of all, ambient levels of those compounds would be expected to be extremely low, with the possible exception of elevated concentrations existing only at fairly localized sites. Since their cost-effectiveness stems from their large-area coverage capabilities, airborne remote-sensing techniques are not well suited to this application. Secondly, the specificity of the sensors for the many pollutants potentially of concern, coupled with high-sensitivity requirements, augur poor prospects for near-term success.

However, there are ground-based, pollutant-specific remote-sensing instruments that do not employ lasers. They are now in use or under development, and have the potential of measuring long-path absorption directly, or of making emission mea-

surements of gaseous pollutant concentrations.

#### Aerial photography

Aerial photography is used almost routinely in environmental assessments. Its value for locating, delineating, and documenting environmental problems for planners and for regulatory agencies has been clearly established. However, during the past several years, a number of additional applications of aerial photography have emerged.

The information resulting from this technique can be supplied not only as photographs themselves, but also as annotated overlays on map sheets. Sample infrared photographs from the study area, land use information, an explanation of the basic technique, and results of the preliminary environmental analysis may be included, as well. Photo enlargements and mosaics could be particularly useful for purposes of public participation at hearings.

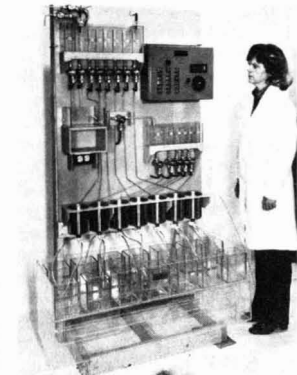
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- (2) McElroy, J. et al. Data Atlas for PEPE/NEROS, 1980, EPA Report TS-AMD-82026.
- (3) Browell, E. V. et al. "An Airborne Lidar System for Ozone and Aerosol Profiling in the Troposphere and Lower Atmosphere," presented at *IAMAP Symp., Boulder, Colo.*, August 1980.
- (4) Menzies, R. T.; Shumate, M. S. *Appl. Opt.* 1976, 15, 2025.
- (5) Shumate, M. S.; Menzies, R. T. "The Airborne Laser Absorption Spectrometer," *Proc. 4th Joint Conf. Sensing of Environ. Pollut., American Chemical Society, Washington*, 1977.
- (6) Guagliardo, J. L.; Bundy, D. H. *Proc. Int. Telecommunications Conf.* 1974, 10, 414.
- (7) Guagliardo, J. L.; Bundy, D. H. *Proc. 7th Int. Laser Radar Conf.* 1975.



**Glenn E. Schweitzer** directs one of EPA's 14 national laboratories. With the enactment of Superfund, the laboratory's remote sensing activities have expanded rapidly. In the early 1970s, Schweitzer served as director of AID's Office of Science and Technology, and was instrumental in introducing remote sensing resource surveys to a number of developing countries. This article includes contributions from many researchers at the Las Vegas laboratory.

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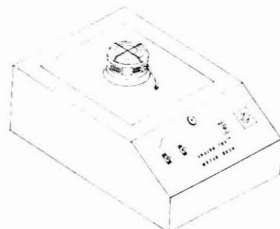
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# ES&T PRODUCTS

## Acid rain collector

This device has two buckets, one for wet deposition and one for dry deposition. Solid state circuitry enables the device to be powered by a solar panel, battery, or standard AC power. Climatronics 101

## Spectrometer

Fourier transform nuclear magnetic resonance spectrometer has improved sensitivity, a 300:1 signal-to-noise ratio using a 10-mm probe. According to the manufacturer, the instrument also has improved software capabilities such as pulse sequence generation. The device has a control system consisting of two independent processors with separate memories. Varian Associates 102



## Sulfur dioxide analyzer

This device has a detection limit of 0.5 ppb SO<sub>2</sub> with span ranges from 0-50 ppb to 0-1000 ppb and is EPA approved for all ranges. It uses the flame photometric method of detection and can be operated unattended for up to 28 days. Columbia Scientific Industries 103

## Analytical balance

Microprocessor-controlled balance has an airhood that eliminates posts and sliding glass doors and allows total access to the weighing pan. The balance has automatic push-button calibration and is equipped with zero and recall buttons to determine subtotal and total component weights of a mixture. Cahn Instruments 104

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



## Portable air sampler

High volume air sampler collects particulates as small as 0.01  $\mu\text{m}$ . Air flow up to 70 CFM is measured by means of an indirect, variable orifice meter. This device can perform spot or continuous sampling both indoors and outdoors and can use interchangeable filter holders. Staplex 105

## Pressure transducer

This is a submersible instrument for groundwater measurement. Available in ranges from 5-250 psig, it operates on 12 V DC at 8 mA and has an output of 0-5 V DC. The transducer is molded to a polyurethane cable with an internal breather tube that compensates for barometric pressure changes. Enviro-Labs 106

## Field averaging spectrograph

Designed to screw directly over the lens of most 35 mm SLR cameras, this device photographically records the integrated spectral distribution of remote objects. It averages image structure and motion and leaves only spectral information on the film. As a result, the instrument can be handheld for long exposure times. Total wavelength range is from 0.4-0.7  $\mu\text{m}$  with spectral resolution of 0.03  $\mu\text{m}$ . Trax Instrument 107

## Wastewater sampler

Designed to collect either a time-controlled composite or a flow-proportional composite, this sampler has a peristaltic pump that purges itself and the supply line after each sample is taken. Jensen Consultants 108

## Fluid monitor

Analyzes the quality of water and other fluids by measuring pH, specific ion, or conductivity. It can record the readings on paper tape and alarms can be set for preset limits. McNab 109

## Microfilter

Separates samples in the 20  $\mu\text{L}$ -2 mL range with sample recovery up to 95%. Filtration is accomplished by brief, low-speed centrifugation. The microfilter is chemically resistant to 115 commonly used solvents. Schleicher & Schuell 110

## HPLC controller

Microcomputer-based gradient controller for HPLC has a built-in 5/4-in. floppy disk drive for file storage, plus capabilities for use as a microcomputer. Software is available to allow programming in most popular computer languages. The system controls up to three pumps and can be used to upgrade HPLC systems from several manufacturers. Gradient profiles can be displayed on the 12-in. CRT screen, with a cursor to show current run status. Cole Scientific 111



## Microbial air sampler

Six-stage air sampler collects and divides all airborne microorganisms into six aerodynamic size fractions from 0.65  $\mu\text{m}$  to 7.0  $\mu\text{m}$  and above, and provides data about the number of viable particles per cubic meter of air sampled. It has a flow rate of 1 ft<sup>3</sup>/min and a constant pressure drop. Andersen Samplers 112

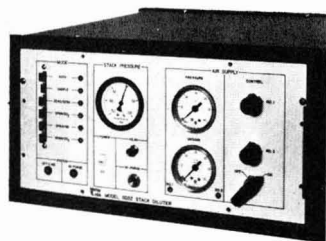
*Companies interested in a listing in this department should send their releases directly to Environmental Science & Technology, Attn: Products, 1155 16th St., N.W., Washington, D.C. 20036*

### Recorder system

Data acquisition, manipulation, and display instrument combines the functions of a chart recorder, integrator, and scientific calculator with a video presentation and an RS232C computer system interface. It connects to both laboratory instruments and computers and presents data by combining graphics with numerical values. Instrumentation Graphics 113

### Solvent cleaning system

Removes contaminants from solvents that have a boiling point less than 340 °F. It automatically distills 14 gallons of solvent in 8–10 h and in this way reclaims up to 95% of the contaminated solvent. Contaminants are collected as semisolid residue in disposable plastic bags. Zerpa Industries 114



### Stack analysis system

Sampling device prepares the sample entirely within the stack at temperatures up to 600 °C and transports the sample without condensation through an unheated sample line to the analyzer. Ambient air monitors analyze the sample. Wide ranges from 100–10 000 ppm full-scale are measured with simple field changes. SO<sub>2</sub>, H<sub>2</sub>S, total sulfur, NO, NO<sub>x</sub>, CO<sub>2</sub>, and hydrocarbons can be analyzed with this technique. Columbia Scientific Industries 115

### pH meters

Portable compact meters and testers provide millivolt and temperature measurement in addition to pH measurement. They are battery operated and include a visual battery test. Using an adapter, they can also be operated on AC current. Pope Scientific 116

### Macropipettes

Positive displacement pipettes have reusable pipette tips and are available in 1–5 mL and 2–10 mL sizes with readability to 0.01 mL. The volume is displayed digitally and the selected volume can be locked into place. Corrosive reagents may be used with these pipettes. Brinkmann Instruments 117

### Membrane filters

These can be used with all HPLC solvents from water to acetonitrile. Available in 0.2- $\mu$ m and 0.45- $\mu$ m pore sizes, they are hydrophilic, require no prewetting, and are resistant to high temperatures and physical stress. Millipore 118

### Universal dispenser

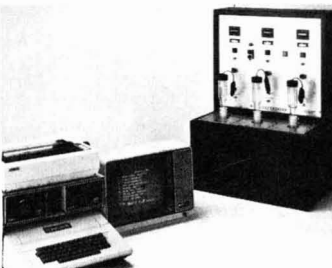
A system composed of a Teflon plunger and ruby valves can be used to dispense all corrosive media except hydrofluoric acid. Nine different models with dispensing volumes from 1–300 mL are available. All have a precision of  $\pm 0.1\%$  and an accuracy of  $\pm 0.5\%$ . EM Science 119

### Spectrophotometer

UV/visible spectrophotometer corrects for stray light and has spectral storage capabilities. This instrument is useful for quantitative analysis of minute amounts of materials. Some of the functions it performs are wavelength scanning, kinetics, gel scanning, slab gel scanning, and multicomponent analysis. Beckman Instruments 120

### Transmissometer

Measures the particle emission from baghouses, scrubbers, electrostatic precipitators, and smoke stacks. It is a single pass, dual beam system consisting of a light transmitter at one side and a receiver at the other. Datatest 121

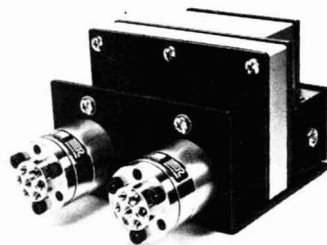


### BOD Respirometer

BOD system uses an Apple II computer. It graphically displays and prints out cumulative oxygen demand vs. time for 15 separate channels. On each channel, data sampling intervals can be selected from one-per-minute to one-per-day. OI Corporation 122

### Miniature Teflon tubing

Teflon tubing is available in dimensions down to 0.001 in. inside diameter with a wall thickness of only 0.007 in. It can be used for collecting, detecting, or infusing very small samples of liquids or solvents. Zeus Industrial Products 123



### LC column selector

As many as five LC columns can be connected and disconnected from a chromatograph with this device. It consists of two rotary valves geared together on a tandem pneumatic actuator. When a column is switched off-line, it is automatically sealed at both ends. Rheodyne 124

### Helium cadmium lasers

These lasers operate at either 442 nm or 325 nm. For operation at 442 nm, these models yield 10, 14, and 40 mW. At 325 nm, they yield 1.5, 2.5, and 10 mW. They all have closed-loop electronic circuitry and resonator kinematic mounts. Liconix 125

### Air mass flow calibrator

Measures air flow in four ranges and can be used for personal air samplers and laboratory flows. This portable instrument is sold with 15 ft of cable, a battery charger, and carrying case. Sierra Instruments 126

### Water level monitor

Shows water level accurate to 1-mm on a digital readout, or transmits it with phone lines or radio to a computer terminal. This microcomputer-based system stores up to 30 days of water level data in an electronic memory and can be adapted to existing mechanical gauges. Canadian Applied Technology 127

### Radiation alarm system

A gamma instrument with a range of 1 MR/h to 100 R/h has an alarm that can be preset over the entire range. External probes up to 300 ft are available for use in 100% humidity or under water. Dosimeter 128

### Graphic recorder

Single-channel instrument has a position feedback accuracy of almost 100% and can be operated with a battery or AC. The writing tip of the recording stylus contacts the chart paper vertically, and according to the manufacturer, eliminates trace variations. Astro-Med 129



# ES&T LITERATURE

**Conductivity meter.** Flyer describes Model 101 conductivity meter for 1  $\mu$ mho to 1 mho measurements over seven switch positions. 0.1-1% full-scale sensitivity. Orion Research **151**

**Residual gas analyzer.** Flyer sheet describes MiniQuad quadrupole mass analyzer for gas analysis in the 2-100-amu mass range. Digital readout, easy cleaning, alarm system. Pressure readout also available. CVC Products **152**

**UV detector.** Brochure describes the Spectroflow 769 Variable Wavelength Ultraviolet (UV) detector for use with high performance liquid chromatography (HPLC). Low noise, high sensitivity. Kratos **153**

**Drinking water analysis.** Paper tells how to test for cadmium, chromium, and lead in drinking water by means of atomic absorption (AA) spectrophotometers. Minimal operator skill needed. Varian Instruments **154**

**DO meters.** Catalog lists line of dissolved-oxygen (DO) meters with easy-to-read display, automatic temperature compensation, and salinity compensation. Field and laboratory use. Yellow Springs Instrument **155**

**Metering pumps.** Bulletin DP-1100-82 includes diaphragm chemical metering pumps. Accessories are also listed. Neptune Chemical Pump **156**

**Air emissions testing.** Service brochure lists and describes company's air emissions testing services, including in situ particle sizing and resistivity measurement, hot-wire anemometers, and others. Entropy Environmentalists **157**

**Disc control valve.** Bulletin 51.6:8555 lists features, operating principles, specifications of high performance, lugged-body, eccentrically mounted

disc control valve. For use where very low leakage rates are tolerable. Fisher Controls International **158**

**Air/fuel ratio adjustment.** Bulletin P-82 describes system that automatically adjusts air/fuel ratio to compensate for air, fuel, and boiler condition variations. Improves combustion efficiency. AMETEK **159**

**Chromatography.** 1982-1983 handbook and general catalog lists and describes products for gas, liquid, and thin-layer chromatography (GC, LC, TLC), along with methodologies, reagents, derivatizations, and references. A section is devoted to biosearch. Pierce Chemical **160**

**Particulate collection.** Bulletin 75-900004 offers information on a patented submicron particulate collection system used for pollution control, known as CHEAF. Andersen 2000 **161**

**Emissions control.** Brochure describes new TriMode scrubber for controlling emissions from furnaces, especially those used in the electronics industry. Ceilcote **162**

**Gas calibrator.** Brochure describes Model 1800 programmable gas calibrator. It can furnish calibrations for SO<sub>2</sub>, H<sub>2</sub>S, NO, NO<sub>2</sub>, CO, ozone, and methane. Permeation can also be calibrated. Columbia Scientific Industries **163**

**Separations.** 1982 catalog lists products for electrophoresis, chromatography, cell biology, and immunochemistry, and has been used as a separations technology textbook. BIO-RAD **164**

**Wastewater collection.** Brochure describes Vactor Jet-Rodder Model 800, which permits preventive maintenance programs for wastewater collection systems. Large reduction in cleaning costs and emergency calls claimed. Peabody Myers **165**

**SO<sub>2</sub> analyzer.** Brochure describes CSI/Meloy Model SA700 continuous fluorescence SO<sub>2</sub> analyzer with ranges

0-250, 0-500, and 0-1000 parts per billion (ppb). Columbia Scientific Industries **166**

**IR spectroscopy.** 1982 catalog lists a full line of accessories for infrared (IR) spectroscopy for many analytical applications. Foxboro Analytical **167**

**Safety equipment.** Catalog lists safety equipment, laboratory furniture, fume hoods, and many other laboratory items. Blair **168**

**Grease filter installing.** Form GF-1898 explains how to install grease filter-equipped kitchen exhaust systems. Research Products **169**

**Venturi scrubbers.** Bulletin 78-900075 provides technical and dimensional information for a complete line of venturi scrubbing systems, and tells how to calculate efficiency. Andersen 2000 **170**

**Dust collectors.** Bulletin APCP-011-116 describes Arrestall self-contained dust collectors with capacities of 200 and 400 cfm. American Air Filter **171**

**Composting.** Release announces composter that can break down sewage sludges, manures, leaves, urban refuse, and similar organic materials at lethal temperatures. It is a diesel-powered, 15-ton machine. Eagle/Cobey Composter **172**

**Balance.** Release announces new balance for micro and ultramicro weighing with the Cahn 29 UltraMicro Electrobalance, able to weigh down as far as 0.1  $\mu$ m/g. Cahn Instruments **173**

**Separation technology.** Bulletin No. 6, "S&S Filters for Soil Analysis," describes ways to measure chemical

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

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

components of soils down to ppb ranges. Schleicher & Schuell 174

**Identification products.** 1982-1983 catalog lists tags, decals, name plates, and other such products for safety, security, many other applications. Seton Name Plate 175

**Environmental services.** Brochure describes broad range of capabilities in environmental planning, waste treatment and disposal studies, water resources engineering, air quality, many other services. Tetra Tech 176

**Diffuser.** Brochure announces availability of Wyss Flex-A-Tube Diffuser, a fine bubble diffuser for water or wastewater technology. Has municipal and industrial applications. Water Cleaning 177

**VOC monitoring.** Technical Note describes volatile organic carbon (VOC) monitoring at gasoline bulk terminals. Harmon Engineering & Testing 178

**Energy R&D.** Literature describes energy R&D, including combustion study, water treatment, chemical analysis of fuels, deposits, and the like,

and many other types of work and services at Kreisinger Development Laboratory. C-E Power Systems 179

**Fluorescence spectroscopy.** House organ, SPEX SPEAKER, details widespread applications of fluorescence spectroscopy to many areas of chemistry and biochemistry. Sampling and fluorometry are discussed. SPEX Industries 180

**Dissolved oxygen.** Brochure describes Model 56 Dissolved Oxygen Monitor with automatic temperature compensation. Can measure 0-5, 0-10, or 0-20 ppm; or 0-100% saturation. Freshwater and saltwater applications. Yellow Springs Instrument 181

**Baghouse.** Bulletin DCB-325C describes newest in Fuller Jet-Pulse line of baghouse. Operations principles are set forth. Fuller 182

**Chromatography.** Catalog lists complete line of gas and liquid chromatography accessories/supplies, high-performance liquid chromatography (HPLC) pumps, other such items. P. J. Cobert Associates 183

**Biological waste treatment.** Brochure, "Improving Waste Removal Performance Reliability of a Waste Treatment System Through Bioaugmentation," by James Chambers, explains how microflora enhance waste treatment. Flow Laboratories 184

**Pressure instruments.** Catalog lists differential pressure instruments for monitoring pressure loss, flow rate, and liquid levels. Orange Research 185

**Blowdown control.** Solutrol B Bulletin tells how automatic boiler surface blowdown can be controlled with increasing heat transfer efficiency and fuel savings. Mogul 186

**Clean rooms.** Catalog lists clean rooms and associated equipment and accessories. Clean Air Technology 187

**Spectrofluorometer.** Brochure lists whole line of spectrofluorometers with accessories, such as an HPLC conversion kit, multichannel analyzer, many others. Farrand Optical 188

**Industrial hygiene tests.** Literature package describes industrial hygiene, other testing services offered by company. Includes wastewater, water, organics. Fee schedule is given. Princeton Testing Laboratory 189

**Trace element analysis.** Applications report outlines environmental uses for the CSI 740 portable X-ray fluorescence analyzer for analyzing particulates and wastewaters for specific trace elements in  $\mu\text{m/g/cm}^2$ ,  $\mu\text{m/g/m}^3$ , mg/L, other units. Columbia Scientific Industries 191

**HPLC column monitoring.** Press release announces new variable-wavelength monitor for column monitoring in high-performance liquid chromatography (HPLC), known as the LKB 2151. Response time  $<0.25$  s. LKB Instruments 193

**Electronic balances.** News release announces Sartorius Series 1400 balances (top-loading), only 2 1/2 in. high, with weighing capacities of 600-5500 g, and readability of 0.01-0.1 g. Sybron/Brinkman 194

**pH/ion meters.** Brochure describes the "1500" series of digital pH/ion meters that can read as low as 0.1 mV. Easy pH-to-ion changeover. Separate calibration controls remove the need to recalibrate after changeover. Pope Scientific 195

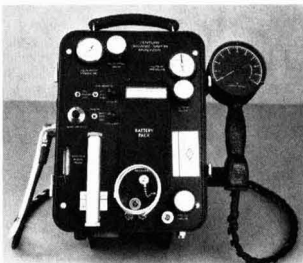
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**Oil spill control.** Brochure describes OILFENCE oil spill control booms. All-plastic construction makes them corrosion-proof, company says. They are rugged in other ways, as well. Albany International 190

**Sludge control.** Bulletin PB-5272F describes a fuel oil conditioner for the effective control of tankside sludges, and for water in boiler fuel systems. Mogul 192

**Groundwater heat pump use.** Technical Report No. 9 by Raphael Kazmann discusses use of twin wells and water-source heat pumps for energy conservation. Department of Civil Engineering, Louisiana State University, Baton Rouge, La. 70803 (write direct)

**Energy assistance.** "A Guide to State Energy Assistance Offices, 1981-1982" lists where low-income people can go for assistance in paying heating or cooling bills, and weatherizing their homes. Publications and Distribution Section, American Petroleum Institute, 2101 L St., N.W., Washington, D.C. 20037 (write direct)

**Photovoltaics.** Photocopies of "Will Solar Sell?" from *Science* 82 (April), discussing photovoltaics, are available in limited quantities for journalists. Jeffrey L. Teramani, American Association for the Advancement of Science, 1515 Massachusetts Ave., N.W., Washington, D.C. 20005 (write direct)

**Waste exchange.** Listings catalog for wastes with reuse value. Issue No. 3, February 1982. Northeast Industrial Waste Exchange, 700 East Water St., Room 711, Syracuse, N.Y. 13210 (write direct)

**PAH analysis.** Standard Reference Material 1647, Priority Pollutant Polynuclear Aromatic Hydrocarbons (PAH) (in acetonitrile) is announced on a technical sheet. For analytical work. Actual material will cost \$108/unit. Office of Standard Reference Materials, Room B311, Chemistry Building, National Bureau of Standards, Washington, D.C. 20234 (write direct)

**Regulatory information.** Periodical, "Environmental Update," will provide general information on environmental

and regulatory matters of interest to company's customers. Lancy Laboratories, 525 West New Castle St., Zelenople, Pa. 16063. (write direct)

**Groundwater monitoring data.** Cooperative Groundwater Report 7, "Procedures for the Collection of Representative Water Quality Data from Monitoring Wells," by James Gibb et al., Illinois State Water Survey, Illinois State Geological Survey, Champaign, Ill. 61820. (write direct)

**"Laboratory Digest."** Brochure describes "Laboratory Digest," a streamlined means by which to advertise chemical equipment and services to potential customers. Costs less than 2¢/name. CENTCOM, Ltd., Suite 425, 1 Belmont Ave., Bala Cynwyd, Pa. 19004. (write direct)

**Power system innovations.** Directory, "Public Power Innovation," lists 609 innovative projects in solar energy, synthetic fuels, energy storage, fuel cells, many other fields, being carried by locally owned utilities. American Public Power Association, 2301 M St., N.W., Washington, D.C. 20037. (write direct)

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## ES&T BOOKS

**Aquatic Chemistry.** Werner Stumm and James J. Morgan. 2nd ed. 780 pages. John Wiley & Sons, Inc., New York, N.Y. 1981.

*Reviewed by Meinrat O. Andreae  
Department of Oceanography  
Florida State University  
Tallahassee, Fla. 32306*

A rigorous understanding of the fundamental principles that govern the chemistry of natural waters is an obvious prerequisite for studying the composition of fresh and marine waters, and the processes that control this composition. This fact applies to the investigation of pristine as well as polluted waters, including wastewaters.

To provide this understanding, Stumm and Morgan's book has, since its first appearance in 1970, built the necessary bridge between "pure" thermodynamic theory and the "applied" disciplines of water chemistry. As is to be expected in a rapidly advancing field, the first edition of their book was becoming dated both in its understanding of the discipline and in its choice of examples. Thus, the second edition (1981) was eagerly awaited by those of us who use the book regularly for teaching and reference. This review, therefore, must address two questions:

- What is the role and importance of this book in its discipline?
- How much of an improvement is the second edition over the first?

The text begins with a short introduction on the scope of aquatic chemistry, followed by a chapter on chemical thermodynamics and kinetics. This section introduces fundamental concepts of thermodynamics and kinetics as a kind of refresher course for those who may have become rusty in this area. I find it a useful summary and reference for desk use.

When the book is used as a course text, this chapter gives students an opportunity to decide for themselves whether they should continue in the course, or if they should go back to take a semester of physical chemistry before venturing further into this course. It also reflects the profound change in our (and the authors') appreciation of the role of chemical kinetics for aquatic chemistry—while

the first edition treated this topic on only two-and-a-half pages, it occupies 30 pages in the second.

A chapter on acids and bases follows, presenting discussions on activity coefficients, pH scales, buffer intensity, and the like. The graphical treatment of acid-base problems is strongly emphasized, which provides the student with a powerful tool for treating these problems rapidly and efficiently.

The chapter dealing with the dissolved carbonate systems presents a lucid explanation of this topic, which is of great importance to biogeochemistry. This section has been updated significantly, and several short paragraphs have been included on the changing CO<sub>2</sub> content of the atmosphere, the air-sea exchange of CO<sub>2</sub>, carbon isotope chemistry, and related material. It exemplifies one of the major changes in the 1981 edition—the inclusion of significantly more applied examples, and information extracted from current discussions in the literature of chemical oceanography.

However, I am not sure about the benefit of this approach for the use of this book as a class text. The section on carbon isotopes, for example, is certainly not adequate for students of chemical oceanography; this material needs to be covered much more extensively. In fact, it should be taught in another course.

Students in other subdisciplines may welcome the short outline of carbon isotope chemistry in this text, as it may be peripheral to their discipline, and may not be addressed in a different class. Moreover, it could give the student a feeling of participating in the excitement of an evolving field; however, the inclusion of much material from current research brings with it the risk of the text's becoming outdated more rapidly. Probably we should thank the authors for offering us a wide selection of materials, and face up to making the choice of what to include from it in lectures and reading assignments.

Chapters on precipitation and dissolution and on coordination chemistry follow. Here emphasis is placed on the role of the oxo-, hydroxo-, and carbonato-compounds. The fundamental relationships between solids formation

and complex stability are brought out didactically, with great success. The influence of activity coefficients on the stability of complexes and of solid phases is discussed in detail. An appendix on the various activity and pH scales used in natural water systems is a useful clarification of what is largely a confusing field. The authors emphasize correctly the need for chemical speciation in natural water chemistry. However, this is a rapidly developing field, and the section will probably soon need revision.

The heightened appreciation of the importance of kinetically controlled processes and of biological catalysis is also felt in the revision of the chapter on oxidation and reduction. I would have liked to have seen a discussion of the role of biological reduction in photosynthetically active surface waters, with respect to the chemistry of the minor and trace elements. The synthesis of reduced forms of sulfur, selenium, arsenic, and the like takes place here, as does that of reduced carbon compounds.

This chapter concludes the more fundamental part of the book. The following chapters deal with aspects of organic carbon geochemistry, the regulation of the chemical composition of natural waters, the solid-solution interface, and concepts of water pollution and control. Of somewhat eclectic necessity, this portion is useful in relating the concepts acquired in the previous chapters to geochemical problems. The chapter on solid-solution interface has been thoroughly revised, and is now an excellent, up-to-date introduction to this important, albeit thorny, field.

In view of the importance of this book both as a class text and as a desk reference (as well as its not inconsequential price), it is disappointing to find it laden with editorial and typesetting errors. A number of figures are mislabeled; signs in equations are wrong; reference is made to page numbers in the old, rather than in the new edition; and a carbon atom with five bonds can be found on the cover. In the appendix, the table on thermodynamic properties is given in kilojoules; the text uses kilocalories. I hope that these errors and inconsistencies will be corrected in future printings.

Aside from these editorial problems, Stumm and Morgan's "Aquatic Chemistry" remains the foremost textbook in the field; it is an essential reference for scientists active in any aspect of water chemistry. The new edition is a significant improvement over the previous one. It is well worth replacing one's old copy.

**The Health Effects of "Agent Orange" and Polychlorinated Dioxin Contaminants.** Technical report. iv + 39 pages. Division of Scientific Activities, American Medical Association, 535 North Dearborn St., Chicago, Ill. 60610. 1981. \$5 (plus \$1 for shipping), paper.

This report examines "Agent Orange" and dioxins, and discusses animal and human toxicity; it also examines health surveys of exposed populations in different countries, environmental fates, and current and proposed studies. Prior studies, such as one in Oregon, are considered critically; 2,4-D, 2,4,5-T, and TCDD are examined.

**Aerosol Science and Technology.** (Quarterly.) B. Y. H. Liu, Editor-in-Chief. Elsevier North-Holland, Inc., 52 Vanderbilt Ave., New York, N.Y. 10017. \$90/year.

This journal will cover many aspects of aerosols, including filtration, health effects, radioactive aerosols, industrial emissions, laminar and turbulent flow, nucleation phenomena, pollution control, and many other pertinent topics.

**The Politics of Clean Air.** Eric Ashby, Mary Anderson. viii + 178 pages. Oxford University Press, 200 Madison Ave., New York, N.Y. 10016. 1981. \$34.50, hard cover.

This work is a historical and public affairs approach to the air pollution problem, especially in Britain. It looks at air pollution from the 17th century to the present, with the problems that came up; approaches by the authorities; and present-day difficulties with automobiles, acid rain, costs of clean-up, and the like.

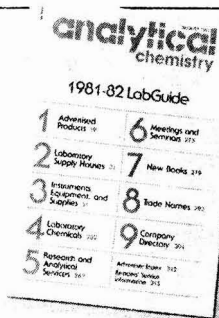
**Model for Simulating Runoff and Erosion in Ungaged Watersheds.** B. B. Ross, et al. vii + 72 pages. Virginia Water Resources Research Center, Virginia Polytechnic Institute and State University, Blacksburg, Va. 24060. 1983. \$6 (\$8 if order must be billed), paper.

Not all streams are gaged. This report, Bulletin 130, sets up a finite element storm hydrograph model to simulate erosion processes that can result from runoff along ungaged streams and watersheds, with application to nonpoint pollution control planning efforts.

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# ES&T MEETINGS

**June 20-25** New Orleans, La.  
**75th Air Pollution Annual Meeting and Exhibition.** Air Pollution Control Association

*Write:* Gus A. Von Bodungen, Air Quality Division, Department of Natural Resources, P.O. Box 60630, New Orleans, La. 70160; (504) 568-5121

**June 21-24** Gaithersburg, Md.  
**1st Conference on Radioprotectors and Anticarcinogens.** National Bureau of Standards and others

*Write:* Dr. Michael G. Simic, 216 Radiation Physics Building, National Bureau of Standards, Washington, D.C. 20234

**June 22-23** Arlington, Va.  
**Superfund: Outlook for the 80s.** Center for Energy and Environmental Management (CEEM)

*Write:* Center for Energy and Environmental Management, P.O. Box 536, Fairfax, Va. 22030; (703) 250-5900

**June 24-26** Bellingham, Wash.  
**Symposium on Acidic Precipitation and Atmospheric Deposition: A Western Perspective.** Center for Canadian-American Studies of Western Washington University

*Write:* Dr. David F. Brakke, Huxley College, Western Washington University, Bellingham, Wash. 98225; (206) 676-3520 or 3504

**June 27-29** College Park, Md.  
**14th Mid-Atlantic Industrial Waste Conference.** University of Maryland and others

*Write:* Dr. James E. Alleman, Department of Civil Engineering, University of Maryland, College Park, Md. 20742; (301) 454-3108

**June 28-July 1** Ithaca, N.Y.  
**Impact of Waste Storage and Disposal on Groundwater Resources.** U.S. Geological Survey, Cornell University, Center for Environmental Research and others

*Write:* Richard P. Novitzki, U.S. Geological Survey, 521 W. Seneca St., Ithaca, N.Y. 14850-4094.

**July 12-16** Johnson, Vt.  
**New Measurement Techniques for Ambient, Source, and Workplace Atmospheres.** ASTM Committee D-22 on Sampling and Analysis of Atmospheres and others

Fee \$150. *Write:* Alice Cavallaro, ASTM Standards Development Division, 1916 Race St., Philadelphia, Pa. 19103; (215) 299-5486

**July 14-16** Minneapolis, Minn.  
**1982 National Conference on Environmental Engineering.** American Society of Civil Engineers, Environmental Engineering Division and others

*Write:* Dr. Walter K. Johnson, Conference Chairman, Metropolitan Waste Control Commission, 350 Metro Square Building, St. Paul, Minn. 55101; (612) 222-8423

**July 20-23** Orlando, Fla.  
**Symposium on Groundwater in Southeastern Coastal States.** Groundwater Committee of the American Society of Civil Engineers' Irrigation and Drainage Division

*Write:* Clyde S. Conover, U.S. Geological Survey, 325 John Knox Rd., Suite F-240, Tallahassee, Fla. 32303; (904) 386-1118

**July 25-29** Honolulu, Hawaii  
**10th Annual WSIA Conference and International Trade Fair: Water Supply Improvement in the Next Decade.** Water Supply Improvement Association

*Write:* Patricia A. Burke, Executive Director, Water Supply Improvement Association, 26 Newbury Rd., Ipswich, Mass. 01938; (617) 356-7656

## Courses

**June 20** New Orleans, La.  
**RCRA—Past, Present, and Future.** Air Pollution Control Association

Fee: \$210 (APCA member); \$235 (nonmember). *Write:* Air Pollution Control Association, P.O. Box 2861, Pittsburgh, Pa. 15230-2861

**June 21-23** Madison, Wis.  
**Hazardous Waste Management Practices.** University of Wisconsin, Madison

Fee: \$360. *Write:* Philip R. O'Leary, Department of Engineering and Applied Science, University of Wisconsin, Extension, 432 North Lake St., Room 701, Madison, Wis. 53706; (608) 262-1299

**June 21-24** East Brunswick, N.J.  
**Industrial Hygiene Practice.** The Center for Professional Advancement

Fee: \$820. *Write:* Edith Webb, Registrar, P.O. Box 964, East Brunswick, N.J. 08816-0964; (201) 249-1400

**June 21-25** Cincinnati, Ohio  
**Basic Gas Chromatography.** Finnigan MAT Institute

Fee: \$850. *Write:* Nancy Kranpitz, Registrar, Finnigan MAT Institute, 11 Triangle Park Dr., Cincinnati, Ohio 45246; (513) 772-5500

**June 25** Irvine, Calif.  
**Conference on Hazardous Materials Management.** University of California, Irvine, Southern Occupational Health Center

Fee: \$60. *Write:* Joan Brown, University of California Southern Occupational Health Center, Irvine, Calif. 92717; (714) 752-2335

**June 28-July 2** Cincinnati, Ohio  
**Analysis of Priority Pollutants by Chromatographic Techniques.** Finnigan MAT Institute

Fee: \$850. *Write:* Nancy Kranpitz, Registrar, Finnigan MAT Institute, 11 Triangle Park Dr., Cincinnati, Ohio 45246; (513) 772-5500

**July 12-16** Cambridge, Mass.  
**Environmental and Safety Risk Management.** Massachusetts Institute of Technology

Fee: \$850. *Write:* Director of the Summer Session, Room E19-356, M.I.T., Cambridge, Mass. 02139; (617) 253-2101

**July 12-16** Princeton, N.J.  
**Groundwater Pollution and Hydrology.** Princeton Associates

Fee: \$675. *Write:* Iva Barros, Director, Princeton Associates, P.O. Box 2010, Princeton, N.J. 08540; (609) 924-4163

**July 12-16** Ann Arbor, Mich.  
**Combustion Engine Performance, Economy, and Emissions: The University of Michigan.** College of Engineering

Fee: \$675. *Write:* Viola E. Miller, The University of Michigan, College of Engineering, Engineering Summer Conferences, Chrysler Center, North Campus, Ann Arbor, Mich. 48109; (313) 764-8490

## International

**August 2-13** Halifax, Nova Scotia  
**Joint Oceanographic Assembly.** Scientific Committee on Oceanic Research and others

Fee: \$300 (regular); \$150 (student and retired). *Write:* Mr. H. B. Nicholls, JOA Registration Office, Bedford Institute of Oceanography, P.O. Box 1006, Dartmouth, Nova Scotia, Canada, B2Y 4A2; (902) 426-7879

## Call for Papers

**July 1 deadline**  
**6th Ozone World Congress.** International Ozone Association

The congress will be held in Washington, D.C., the latter part of May 1983. *Write:* International Ozone Association, Tower Suite 510, 301 Maple Ave. West, Vienna, Va. 22180; (703) 255-2210

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## Particle Dynamics in Seawater: Implications for Predicting the Fate of Discharged Particles

James R. Hunt<sup>1</sup>

W. M. Keck Laboratory of Environmental Engineering Science, California Institute of Technology, Pasadena, California 91125

■ Experimental data are presented that verify theoretical predictions for Brownian and shear coagulation in continuous particle-size distributions. Three clay minerals (kaolinite, illite, and montmorillonite) and a silica mineral (Min-U-Sil) were destabilized in artificial seawater and were subjected to uniform fluid shear over the range 0.5 to 32 s<sup>-1</sup>. Clay aggregate size distributions are described by the coagulation predictions at low shear rates, but aggregate breakup became dominant at higher shear rates. Considerable variability exists among the results for the three clays and is explained by the variation in clay aggregate porosity. These experimental and theoretical results are utilized to predict the removal of particles discharged into coastal waters, illustrating a procedure for quantitatively incorporating particle coagulation into models for assessing marine disposal of wastewaters.

The transport of particles in natural waters is influenced by various mechanisms of settling, turbulent resuspension, particle coagulation, and aggregate breakup. This paper examines particle coagulation and breakup in continuous particle-size distributions and discusses the importance of these mechanisms in controlling the fate of particles and associated pollutants discharged into coastal waters. Previous comparisons of coagulation theory with experimental results have been limited to the initial rate of coagulation for particles uniform in size (1, 2). The results for monodisperse suspensions cannot be applied quantitatively to coagulation in broad, continuous distributions of particle sizes as are commonly encountered in natural waters.

Recently Hunt (3, 4) presented predictions of continuous particle-size distributions for Brownian, shear, and differential sedimentation coagulation, following an approach used by Friedlander (5, 6). Experiments with clay particles in artificial seawater verified the Brownian and shear coagulation predictions. This paper reviews the assumptions in the derivation, summarizes the experimental techniques, and discusses the differences observed in the experimental results for three clay minerals and a silica mineral. This paper also utilizes the theoretical and experimental results to demonstrate a method for predicting the fate of particles following discharge into coastal waters, incorporating a

quantitative assessment of particle coagulation.

### Theory

No general solution exists for describing the particle-size distribution dynamics during coagulation and settling. The approach taken is to make certain assumptions that allow prediction of particle-size distributions by dimensional analysis. This section reviews the assumptions in the derivation, presents particle-volume distribution predictions, and summarizes techniques adopted in the experimental testing of the predictions.

Four basic assumptions were employed to arrive at particle-size distribution predictions. The first assumption was that only one coagulation mechanism is dominant at a given particle size. Brownian coagulation is expected to be dominant at the smallest sizes, shear coagulation for intermediate particles, and differential sedimentation coagulation for the largest particle sizes. Second, the particle-size distribution was assumed to be in a dynamic steady state maintained by a flux of particle volume through the size distribution. For a small particle-size interval, the particle volume coagulated into the interval is balanced by the volume coagulated out of the interval. Large particles are removed from the fluid volume by settling. The flux of particle volume is represented by  $E$ , with units of particle volume per fluid volume per time. The third assumption was that the particles are destabilized, such that particles stick when they collide. Finally, the coagulation mechanisms were assumed to be represented by parameters independent of particle size. The parameters are defined as follows: Brownian,  $K = kT/\mu$ ; shear,  $G$ ; differential sedimentation coagulation,  $S = g(\rho_p - \rho_f)/\mu$ , where  $k$  is the Boltzmann constant,  $T$  is the absolute temperature,  $\mu$  is the fluid viscosity,  $G$  is the fluid shear rate or mean velocity gradient,  $g$  is the gravitational acceleration, and  $\rho_p$  and  $\rho_f$  are the particle and fluid density, respectively.

Particle distributions are represented as volume distributions,  $dV/d(\log d_p)$ , the total suspended-particle volume in a logarithmic interval of particle diameter,  $d_p$ . The transformation of number distributions  $n(v)$  based on particle volume  $v$  to volume distributions (7) is given by

$$\frac{dV}{d(\log d_p)} = \frac{2.3\pi^2}{12} d_p^6 n(v) \quad (1)$$

With the above assumptions, the following volume distributions were obtained by dimensional analysis (4):

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Brownian:

$$\frac{dV}{d(\log d_p)} = 5.0A_b(E/K)^{1/2}d_p^{3/2} \quad (2)$$

shear:

$$\frac{dV}{d(\log d_p)} = 6.9A_{sh}(E/G)^{1/2} \quad (3)$$

differential sedimentation:

$$\frac{dV}{d(\log d_p)} = 7.7A_{ds}(E/S)^{1/2}d_p^{-1/2} \quad (4)$$

Friedlander (5, 6) obtained the Brownian coagulation prediction and a prediction for settling dominance. In eq 2-4  $A_b$ ,  $A_{sh}$ , and  $A_{ds}$  are dimensionless constants that must be determined experimentally. Note, the dimensionless constants follow the notation used in ref 4 rather than ref 3.

The predicted coagulating size distributions have been integrated (3) to obtain an expression for the rate of change in total suspended-particle volume,  $V(t)$ , during batch experiments, giving

$$dV(t)/dt = -bV^2(t) \quad (5)$$

for particle volume reported as parts per million by volume (1 ppm by volume =  $10^6 \mu\text{m}^3/\text{cm}^3$ ),  $b$  has units of  $\text{ppm}^{-1}/\text{s}$ . The second-order removal rate constant has the form

$$b = \frac{G}{A_{sh}^2}(\alpha + \beta \ln G)^{-2} \quad (6)$$

where  $\alpha$  and  $\beta$  are constants dependent on parameters for Brownian and differential sedimentation coagulation and on dimensionless constants. The solution to eq 5 is

$$V(t)/V_0 = 1/(1 + V_0bt) \quad (7)$$

where  $V_0$  is the total suspended particle volume at  $t = 0$ . In eq 7 the term  $V_0bt$  appears as a dimensionless parameter characterizing particle-volume removal. From eq 6  $V_0bt$  is nearly proportional to  $V_0Gt$ , an empirical parameter that correlates with coagulation performance in water and wastewater treatment (8).

In the experimental program designed to test the validity of the coagulation predictions, volume distributions were measured as a function of diameter for a range of volume fluxes and shear rates. Experimental volume distribution data possibly dominated by differential sedimentation coagulation were not obtained because larger aggregates were broken up during counting. For comparison of the observed to the predicted dependence of volume distributions on particle-volume flux and shear rate, particle diameters and volume distributions were normalized. Following normalization all experimental data should collapse onto a single curve if the predictions are valid. Particle diameters were normalized by a characteristic diameter separating Brownian and shear coagulation dominated domains. The separation between mechanisms occurs at a particle diameter of  $(2K/G)^{1/3}$ , and a characteristic particle diameter  $(K/G)^{1/3}$  was used to define  $\delta$  as a dimensionless particle diameter:

$$\delta = d_p(G/K)^{1/3} \quad (8)$$

With this diameter normalization, Brownian coagulation is expected to be dominant for  $\delta \ll 2^{1/3}$ , and shear coagulation is expected to be dominant for  $\delta \gg 2^{1/3}$ .

Table I. Clay Minerals

| clay            | API No. | location             |
|-----------------|---------|----------------------|
| kaolinite       | 4       | Oneal Pit, Macon, GA |
| illite          | 35      | Fithian, IL          |
| montmorillonite | 24      | Otay, CA             |

The normalized volume distribution,  $d\bar{V}/d(\log \delta)$ , was defined as

$$\frac{d\bar{V}}{d(\log \delta)} = \frac{dV}{d(\log d_p)}(G/E)^{1/2} \quad (9)$$

The normalized predictions for Brownian and shear coagulation are given in eq 10 and 11, respectively. With

$$d\bar{V}/d(\log \delta) = 5.0A_b\delta^{3/2} \quad (10)$$

$$d\bar{V}/d(\log \delta) = 6.9A_{sh} \quad (11)$$

this normalization scheme, experimental data in agreement with Brownian and shear coagulation predictions at different shear rates and volume fluxes should collapse onto a single curve described by eq 10 for  $\delta \ll 2^{1/3}$  and eq 11 for  $\delta \gg 2^{1/3}$ .

### Experimental Section

This section is a brief summary of the experimental procedures developed for testing the predictions; a more complete description is available elsewhere (3).

All experiments were conducted in artificial seawater following a recipe of Lyman and Fleming given in Riley and Skirrow (9). Suspended particles were removed by 0.22- $\mu\text{m}$  Millipore filtration.

Three common clay minerals and a silica mineral were selected for the experiments. The clay minerals were obtained from Ward's Natural Science Establishment, Inc., and representative of the clays analyzed by the American Petroleum Institute's (API) Clay Mineral Standards Project (10). Table I identifies the kaolinite, illite, and montmorillonite clays. Clay-particle surfaces were converted to their sodium form following cleaning procedures recommended by van Olphen (11). After being cleaned, clay particles greater than 2- $\mu\text{m}$  equivalent spherical diameter were removed by quiescent settling. The silica mineral (Min-U-Sil 5, Pennsylvania Glass Sand Corp.) was cleaned following Vuceta (12) and particles greater than 2  $\mu\text{m}$  were removed by quiescent settling.

Particle-size distributions were measured with a Model ZBI Coulter Counter interfaced with a Nuclear Data particle-sizing amplifier and multichannel analyzer. As particle aggregates pass through a small aperture, the electrical resistance across the aperture increases, and the resistance change is proportional to particle volume. Because of high fluid shear rates near the aperture, larger aggregates are broken up and cannot be sized as illustrated later.

Batch experiments were conducted in the gap between two concentric cylinders, where the fluid shear rate was controlled by the outer cylinder rotation rate. The cylinders were aligned vertically to allow settling to remove larger aggregates during the experiments. Shear rates of 0.5-32  $\text{s}^{-1}$  were possible, although experimental results indicated that a fluid instability developed at  $G = 32 \text{ s}^{-1}$ , probably caused by cylinder surface roughness.

An experiment was started by briefly mixing 2 mL of concentrated particle suspension with 200 mL of filtered artificial seawater. The suspension was then poured into the gap between the rotating cylinders. After 10-60 min of shearing, the first sample was removed for analysis. Analysis included measurement of particle-size distribution

and total suspended volume. Samples were withdrawn and delivered through a large-bore tube connected to a graduated pipet at a flow rate of less than 0.5 mL/s. The slow flow rate and 0.3-cm minimum bore diameter were adopted to minimize aggregate disruption during sampling. Because larger aggregates were not counted by the particle counter, total suspended particle volume could not be obtained by integrating over the size distribution. Total suspended volume was determined with a small sample volume by measurement of optical absorbance within a shaken suspension. Calibration curves were prepared with known solid concentrations in artificial seawater and shaken prior to absorbance measurement.

The volume flux through the size distribution was estimated from changes in total suspended volume, that is

$$E(t) = -dV(t)/dt \quad (12)$$

and from eq 5

$$E(t) = bV^2(t) \quad (13)$$

The second-order volume removal rate constant,  $b$ , was obtained from the slope of the inverse total suspended volume plotted over time, a linearization of eq 7.

Experiments were conducted at room temperature (22–24 °C) and total suspended-volume concentration less than 100 parts per million (ppm) by volume, which fixed the value of the Brownian coagulation parameter,  $K = kT/\mu$ .

### Results

The Brownian and shear coagulation particle-size distribution predictions were verified with the kaolinite and illite experimental results. The montmorillonite size distribution data were in partial agreement with the shear coagulation prediction, and the silica results were not described by predicted coagulating particle-size distributions. The experimental results for the four solids are presented as second-order volume-removal rate constants measured at various shear rates and as normalized volume distributions. The original data are available elsewhere (3).

The major limitation in the experimental program was the narrow range over which particle-size distributions could be measured because of aggregate breakup during counting. Typically, valid sizing data could be obtained only over the diameter range 0.6–2  $\mu\text{m}$ . This problem is illustrated in Figure 1 with two examples of volume distributions for montmorillonite aggregates in artificial seawater. In Figure 1a volume distributions were recorded for one sample of montmorillonite in seawater after 50 min of shearing at  $G = 0.5 \text{ s}^{-1}$ . Measurements taken with 30-, 70-, and 140- $\mu\text{m}$  diameter apertures are not in agreement in the regions of overlap because of aggregate breakup during counting. Figure 1b contains volume distributions measured with 30-, 70-, 140-, and 280- $\mu\text{m}$  apertures for a montmorillonite suspension in seawater sheared at  $16 \text{ s}^{-1}$  for 110 min. At this higher shear rate, partial agreement exists between apertures, although disruption still occurs, preventing measurement of the distribution beyond about 8  $\mu\text{m}$ . The partial alignment between apertures only at the higher shear rate indicates an increase in aggregate strength as discussed later.

Figure 2 is a summary of the second-order removal rate constants for the four solids in seawater over a range of shear rates. Removal rates initially increase with increasing shear rate up to some maximum and then decline. Data at  $G = 32 \text{ s}^{-1}$  are suspect because of a probable fluid instability which hindered kaolinite and silica removal and prevented illite and montmorillonite removal. With the

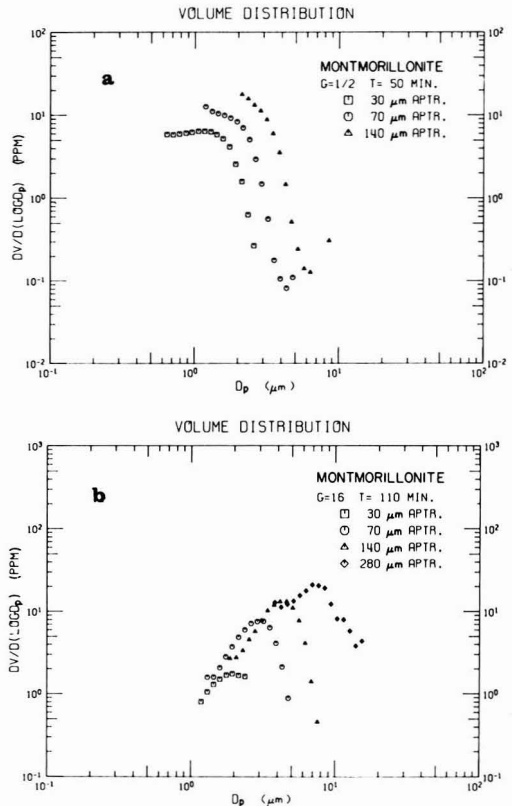


Figure 1. Multiple-aperture volume distributions for montmorillonite in seawater after (a) 50 min of shearing at  $G = 0.5 \text{ s}^{-1}$  and (b) 110 min of shearing at  $G = 16 \text{ s}^{-1}$ .

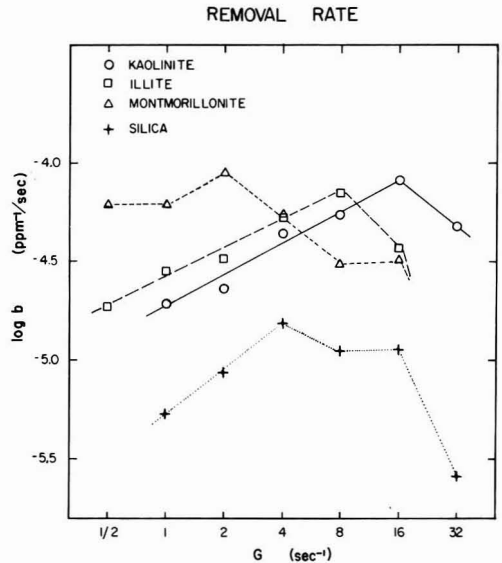


Figure 2. Volume-removal rate constants as a function of shear rate for kaolinite, illite, montmorillonite, and silica experiments in artificial seawater.

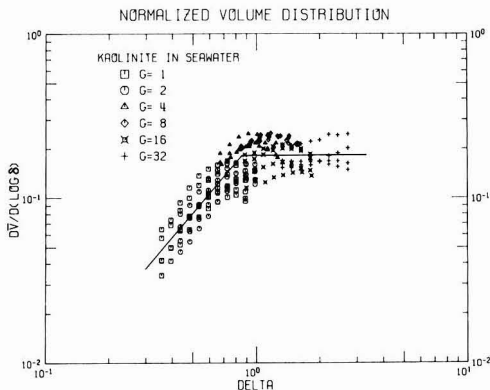


Figure 3. Normalized volume distributions for kaolinite at  $G = 1, 2, 4, 8, 16,$  and  $32 \text{ s}^{-1}$ .

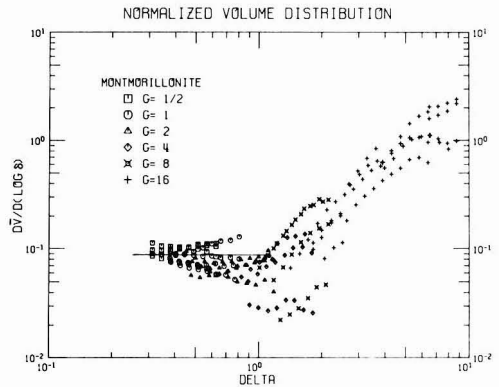


Figure 5. Normalized volume distributions for montmorillonite at  $G = 0.5, 1, 2, 4, 8,$  and  $16 \text{ s}^{-1}$ .

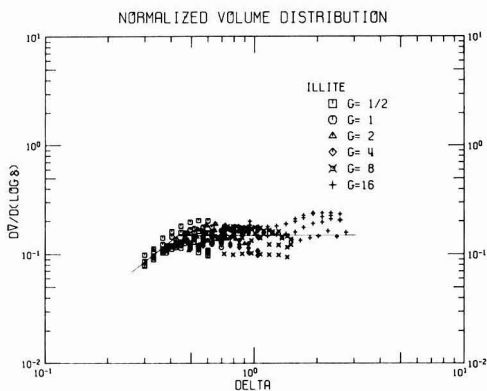


Figure 4. Normalized volume distributions for illite at  $G = 0.5, 1, 2, 4, 8,$  and  $16 \text{ s}^{-1}$ .

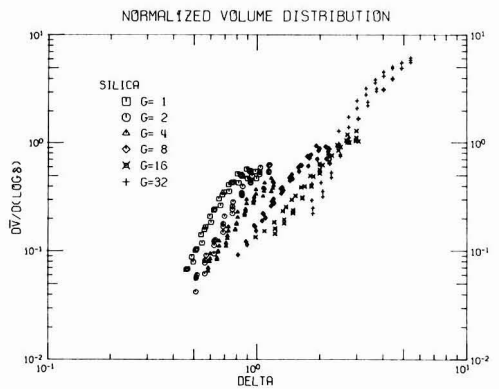


Figure 6. Normalized volume distributions for silica at  $G = 1, 2, 4, 8, 16,$  and  $32 \text{ s}^{-1}$ .

exception of the silica experiment at  $G = 32 \text{ s}^{-1}$ , all the other experiments were repeated at least once, and except for the specific cases mentioned below, removal rate constants were within 20% between replicates. Exceptions to the 20% variation occurred with montmorillonite at  $G = 16 \text{ s}^{-1}$ , where the repeated rate constant was 2.4 times the value plotted in Figure 2, and with silica at  $G = 4 \text{ s}^{-1}$ , where the difference between replicates was 34% (unpublished data).

Figure 3 is a plot of normalized kaolinite volume distributions measured at shear rates of 1, 2, 4, 8, 16, and  $32 \text{ s}^{-1}$ . A line of slope  $3/2$ , the Brownian prediction given in eq 10, fits the trend of the data for  $\delta < 0.9$ , and a level line, the shear prediction from eq 11, fits the data for  $\delta > 0.9$ . The vertical spread in the normalized data at each shear rate is because the volume flux is estimated from changes in total suspended volume with eq 13. Values of the dimensionless coagulation constants determined from Figure 3 are  $A_b = 0.05$  and  $A_{sh} = 0.03$ .

Normalized illite volume distributions are plotted in Figure 4 for experiments conducted at shear rates of 0.5, 1, 2, 4, 8, and  $16 \text{ s}^{-1}$ . The Brownian prediction fits the trend of the data for  $\delta < 0.44$ , and the shear prediction fits the data for  $\delta > 0.44$ . The normalized volume distributions at  $G = 16 \text{ s}^{-1}$  are not level and are above the trend of the other data. At this higher fluid shear rate, aggregates were being disrupted in the rotating cylinder apparatus as discussed later. For shear rates of  $8 \text{ s}^{-1}$  and less, the di-

dimensionless coagulation constants are  $A_b = 0.10$  and  $A_{sh} = 0.021$ .

Figure 5 is a summary of the montmorillonite data for shear rates of 0.5, 1, 2, 4, 8, and  $16 \text{ s}^{-1}$ . The normalized volume distributions for  $G = 0.5, 1,$  and  $2 \text{ s}^{-1}$  are in approximate agreement with a level shear coagulation prediction. At higher shear rates there is considerable vertical spread, and the trend of the data is not described by the coagulation predictions. The shape of the distributions and the decline in the removal rate constants at shear rates of  $4 \text{ s}^{-1}$  and greater indicate that aggregate breakup by fluid shear is occurring in the rotating cylinder apparatus. An estimate of the shear coagulation dimensionless constant from Figure 5 is  $A_{sh} = 0.013$  for the  $G = 0.5, 1,$  and  $2 \text{ s}^{-1}$  data.

Normalized volume distributions for the fourth solid, silica, are given in Figure 6, measured at shear rates of 1, 2, 4, 8, 16, and  $32 \text{ s}^{-1}$ . While the normalized volume distributions obtained at each shear rate have little vertical spread, there is no agreement among normalized volume distributions at different shear rates. Silica aggregate size distributions are not described by the coagulation predictions. The lack of agreement with the coagulation size-distribution predictions and the low volume-removal rate constants given in Figure 2 indicate that silica particles are not completely destabilized in artificial seawater. Particle destabilization was assumed in the derivation. Lawler (13) has observed similar aggregate size distribu-

Table II. Sediment Percent Solid Volume and Cation-Exchange Capacity for Kaolinite, Illite, and Montmorillonite

| clay            | sediment percent solid volume | cation-exchange capacity, <sup>a</sup> mequiv/100 g |
|-----------------|-------------------------------|---|
| kaolinite       | 1.4                           | 12.2  |
| illite          | 1.1                           | 25.0  |
| montmorillonite | 0.11                          | 153.0   |

<sup>a</sup> Reference 10.

tions for silica in a thickening column.

### Discussion

While experiments with clay particles in artificial seawater were able to verify the Brownian and shear coagulation predictions, considerable differences among the clays were observed and require discussion. The three clays differed in (1) normalized diameter separating Brownian and shear coagulation dominance, (2) volume-removal rate constants at low fluid shear rates, and (3) the fluid shear rate with maximum volume-removal rate. These differences can be explained by considering the porosity of the clay aggregates in seawater.

The three clays were observed, qualitatively, to have different aggregate porosities by letting 300 ppm by volume clay suspensions in artificial seawater settle quiescently for 24 h in 100-mL graduated cylinders. With the resulting volume of sediment and the initial particle volume concentration, the percent solid volume in the sediments was calculated and is given in Table II along with reported cation-exchange capacities. Sediment percent solid volume is an approximate inverse indicator of aggregated porosity; the lower the percent solids concentration in the sediment, the greater the individual aggregate porosity. Clay aggregate porosities are directly related to the cation-exchange capacities of the clays. Individual particles are in the shape of thin sheets with negative charges on the faces and positive charges on the edges. The dependence of aggregate structure on the cation-exchange capacity and the solution ionic composition has been discussed by van Olphen (11). With increasing ionic strength, there is a shift from porous edge-to-face aggregates to denser face-to-face aggregates; the ionic strength for this transition increases with increasing cation-exchange capacity. Thus in seawater, montmorillonite is expected and observed to have a more porous aggregate structure than illite, which would be more porous than kaolinite, corresponding to different degrees of edge-to-face clay particle association.

Among the three clays, the observed shift in normalized diameter separating regions of Brownian and shear coagulation dominance is probably an artifact of the sizing technique. The change in electrical resistance across the aperture as an aggregate is pulled through the aperture is proportional to the volume of the solids and not to the aggregate volume that contains conducting electrolyte. For a very porous montmorillonite aggregate, the reported diameter would be much smaller than the aggregate diameter. Experimentally, Brownian coagulation was not observed with porous montmorillonite aggregates at normalized diameters of  $\delta = 0.3$ , while less porous illite aggregates were dominated by Brownian coagulation for  $\delta < 0.44$ , and kaolinite aggregates, with the lowest porosity, had a Brownian dominated regime for  $\delta < 0.9$ .

At low fluid shear rates of  $2 \text{ s}^{-1}$  and less, the three clays have different suspended-particle volume-removal rates. The removal rate increases with increasing aggregate po-

rosity, because for a given solid volume in an aggregate, the aggregate size increases with porosity. The greater the aggregate volume, the greater the collision cross section which increases the collision frequency and thus the volume removal rate constant.

At high fluid shear rates the more porous clay aggregates are more easily broken, which affects the particle-size distribution and the volume-removal rate. At shear rates of  $4 \text{ s}^{-1}$  and greater the montmorillonite-size distributions were not explained by the coagulation predictions, and the volume removal rates declined with increasing shear rate. These results imply that aggregate breakup by fluid shear within the rotating cylinder apparatus was the dominant mechanism. For illite, breakup became dominant at shear rates of  $16 \text{ s}^{-1}$  and greater, and for kaolinite, breakup was dominant at shear rates greater than  $16 \text{ s}^{-1}$ . Thus, at low fluid shear rates porous aggregates have volume-removal rates greater than less porous aggregates, but the more porous aggregates are more susceptible to breakup at higher shear rates.

When aggregate breakup is dominant at high fluid shear rates, the size distribution is changed and the aggregates appear to be stronger. For illite at  $G = 16 \text{ s}^{-1}$  and montmorillonite at  $G = 4 \text{ s}^{-1}$  and greater, volume distributions increase with particle diameter, indicating an accumulation of particle aggregates at larger sizes compared with the level shear coagulation prediction. A change in aggregate strength is implied in Figure 1 for multiple-aperture sizing of montmorillonite aggregates. No region of overlap between apertures is observed at  $G = 0.5 \text{ s}^{-1}$ , but when aggregate breakup dominates the size distribution at  $G = 16 \text{ s}^{-1}$ , overlap between apertures is obtained. The combination of aggregate coagulation and aggregate breakup would tend to select stronger aggregates than coagulation alone.

### Comparison of Results with Previous Coagulation Studies

These results for clay and silica coagulation in continuous particle-size distributions cannot be directly compared to previous coagulation studies with nearly monodisperse suspensions. In an experiment with narrow initial particle-size distributions, a collision efficiency is obtained that is the ratio of the observed coagulation rate to the theoretical rate for Brownian or shear coagulation. At this time there is no quantitative relationship between collision efficiency and the dimensionless coagulation constants,  $A_b$  and  $A_{sh}$ , although qualitatively, collision efficiency and  $A_{sh}$  are inversely related. High collision efficiencies correspond to high coagulation and volume-removal rates. From eq 6, a higher volume-removal rate constant implies a lower value of the shear coagulation constant.

There are a number of studies of initial clay and silica coagulation kinetics for nearly monodisperse suspensions (Edzwald et al. (14), Eppler et al. (15), Hahn and Stumm (16), and Lawler (13)). In general, montmorillonite has the highest collision efficiency and silica has the lowest, as was observed in the volume-removal rates at low fluid shear given in Figure 2. Kaolinite coagulated faster than illite in the previous studies (14, 15), opposite of the present results. This difference in coagulation rate is reasonable considering that the clays were not from the same geographical location and only the clays used in this work were cleaned.

### Implications for Particle Disposal in Coastal Waters

Because suspended particles in sewage effluents contain the majority of the metal and organic pollutants, there is considerable interest in understanding the fate of these

particles after discharge into coastal waters. The accumulation of particles and associated pollutants in the sediments following discharge has the potential for negating the initial effluent dilution achieved by submerged ocean outfalls.

There are three general approaches to estimating the removal of suspended particles from the water column and accumulation in the sediments. Sediment accumulation rates have been calculated by analyzing sediments around a discharge site for chemical tracers present in the effluent (17, 18). Attempts have also been made to measure sedimentation rates with sediment traps (19, 20). These two approaches are suitable only for characterizing an existing discharge site and cannot be used to predict the particle-accumulation rate following a change in effluent quality or for the design of a new outfall. The third method of analyzing particle fate in coastal waters is the development of models for particle removal from the water column and accumulation in the sediments, utilizing laboratory measurements of particle-settling velocity and estimates of waste field dispersion (21, 22). One advantage of models for particle accumulation is that they can be applied in the design of an ocean disposal system, including degree of waste treatment and outfall configuration.

The purpose of this section is to discuss the limited applicability of particle removal models based solely on particle settling and then illustrate a procedure for incorporating particle coagulation into particle-removal models by using the experimental results for kaolinite. For particle-settling models, a settling-velocity distribution of the suspension is required and is usually measured in a quiescent tank containing the particle suspension diluted with aqueous media of interest. The assumption underlying this procedure is that particles settle individually without formation of aggregates. Faisst (23) has measured anaerobically digested sewage sludge settling velocity distributions in seawater under quiescent conditions. Higher settling velocities occurred at higher sludge concentrations, demonstrating the importance of particle coagulation. Morel and Schiff (24) have compared Faisst's settling velocity distributions at different sludge concentrations and sampling depths, and they have concluded that particle coagulation was controlling particle removal.

In measurements of settling velocity distributions under quiescent conditions, the lack of fluid shear does not adequately represent the fluid turbulence existing in natural waters. Turbulence has two effects on a coagulating suspension. First, turbulence generates small-scale fluid shear, which controls the importance of shear coagulation and the suspended-particle-volume removal rate. Second, turbulence disperses the discharged particle suspension, which decreases the particle concentration and lowers collision and removal rates. While these two effects of turbulence are compensating, neglecting turbulence in obtaining "settling-velocity distributions" under quiescent conditions is not justified for destabilized suspensions. As Camp (25) has written, "it is impossible to make a settling-velocity analysis of a suspension of flocculent particles because the number of particles and the settling velocity of each one are changing continuously as a result of flocculation."

For destabilized suspensions of small particles, the particle-volume removal rate by coagulation and settling is the important input to a model for predicting particle accumulation in sediments near a discharge site. With a given particle suspension, destabilizing aqueous media, and fluid shear rate, the total suspended-volume removal rate can be fit to a second-order expression, for both low shear

Table III. Particle Volume Removal by Coagulation and Settling from a Waste Field for  $V_0 = 3$  ppm,  $G = 0.1 \text{ s}^{-1}$  and  $1 \text{ s}^{-1}$ , and a Transport Time of 1 Day

| shear rate (G), $\text{s}^{-1}$ | removal rate constant (b), $10^{-5} \text{ ppm}^{-1} \text{ s}^{-1}$ | suspended volume remaining, ppm | removal, % |
|---------------------------------|--|---------------------------------|------------|
| 0.1                             | 0.6  | 1.2                             | 60         |
| 1.0                             | 1.9  | 0.5                             | 83         |

rates when coagulation dominates and higher shear rates when aggregate breakup hinders volume removal. Even for particle suspensions not completely destabilized, as was the case for silica in seawater, the removal rate was still second order in total suspended volume.

Calculation of particle removal from the water column incorporating particle coagulation is illustrated by utilizing the kaolinite experimental results. The example is representative of conditions encountered in the disposal of sewage effluent through submerged ocean outfalls, assuming only for the purpose of discussion that a kaolinite clay suspension is similar to sewage particles. The effluent, containing 200 ppm by volume suspended particles in freshwater, is discharged into a coastal water containing a background of 1 ppm. The submerged outfall at a depth of 60 m initially dilutes the effluent by a factor of 100 in the rising plume before becoming trapped in the thermocline, with a resulting total particle-volume concentration of 3 ppm. The effluent field is transported at a current speed of  $10 \text{ cm s}^{-1}$ . These are reasonable conditions for the Los Angeles County ocean outfall at Whites Point in Southern California (22, 26-28). Because of thermal stratification in the oceanic thermocline, the fluid turbulence is suppressed, resulting in a low shear rate. Although no measured values of shear rates in coastal thermoclines are available, a reasonable range of shear rates would be  $0.1-1.0 \text{ s}^{-1}$  based on energy-dissipation rates measured in oceanic waters (29). With the low level of turbulence, dispersion of the field would be small in a period of 1 day and is neglected for simplicity. So that the volume removal rate at  $G = 0.1 \text{ s}^{-1}$  could be obtained, the removal rate constant is extrapolated by an empirical expression fitting the kaolinite data given in Figure 2:

$$b = 1.9 \times 10^{-5} G^{1/2} \text{ (ppm}^{-1} \text{ s}^{-1}\text{)}$$

for  $G$  in  $\text{s}^{-1}$ . Extrapolation of volume-removal rate constants to lower shear rates is questionable because at some shear rate, shear coagulation will no longer have a region of dominance, and the volume-removal rate constant will be independent of shear rate.

With these assumptions, the total particle-volume concentration remaining in the waste field is calculated by eq 7. Table III gives the removal rate constants and calculated suspended-particle volumes remaining after 1 day, corresponding to a horizontal advection of 8.6 km. For  $G = 0.1 \text{ s}^{-1}$ , 60% of the suspension is removed by coagulation and settling, and for  $G = 1 \text{ s}^{-1}$ , 83% is removed. This is not to say that 60% and 83%, respectively, of the discharged particles reach the sediments within 1 day, because the particle aggregates would have to settle through approximately 40 m of water to reach the sediments. The calculated removal rates are far greater than the 1-5% frequently estimated for sewage particle accumulation by use of other procedures (17, 22).

The above example illustrates a procedure for incorporating coagulation into a model for predicting particle removal from a waste field in coastal waters. The analysis requires considerably more information than other ap-



proaches, but the experimental results presented in this paper and size distribution data reported for coastal waters (30) indicate that particle coagulation is an important mechanism in coastal waters and should not be neglected.

The hydraulic and oceanographic information required in the design of submerged ocean outfalls for sewage effluent disposal has been summarized by Fischer et al. (31). The inclusion of particle coagulation in the design process adds to its complexity. First, the rate of particle-volume removal as a function of shear rate is needed over the range of shear rates likely to be encountered at the discharge site. Second, within the rising plume, the effect of turbulent intensity on particle coagulation and aggregate breakup has not yet been considered. Third, information is required on the horizontal dispersion of the waste field following initial mixing, recognizing that mean particle-volume concentration may underestimate particle removal by coagulation if localized regions of higher concentration exist. Finally, an estimate of aggregate-settling velocities is needed to calculate the rate of sediment accumulation following aggregate removal from the waste field.

### Summary

Experimental data verifying predicted particle-size distributions for Brownian and shear coagulation were presented for three clay minerals in artificial seawater. The differences in the coagulation rate and in the susceptibility to aggregate breakup at higher fluid shear rates of the kaolinite, illite, and montmorillonite clay minerals were explained, qualitatively, by the variation in aggregate porosity caused by the different cation exchange capacities.

Silica aggregate size distributions measured in seawater did not agree with the predicted coagulating size distributions, although the total suspended volume-removal rate was second order in suspended-particle volume like the clay results. The clay and silica particle-volume-removal kinetics were in qualitative agreement with previous coagulation studies conducted with nearly monodisperse suspensions.

These theoretical and experimental results are applicable to understanding the fate of particles discharged into coastal waters. For small particles destabilized in seawater, particle coagulation by fluid shear controls the rate of particle removal from the water column. Previous efforts to measure particle-settling-velocity distributions for destabilized suspensions under quiescent conditions have not adequately represented the fluid turbulence existing in coastal waters receiving discharged effluents. A hypothetical example was constructed with the kaolinite coagulation results to illustrate a procedure for incorporating particle coagulation into models for predicting particle removal from coastal waters.

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## Toxaphene Residues in Fish: Identification, Quantification, and Confirmation at Part per Billion Levels

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■ We developed an integrated analytical procedure for organochlorine contaminants that enables quantitation of toxaphene residues as low as 0.1  $\mu\text{g/g}$  in fish tissue. Preparation of the sample requires extraction of ground tissue with dichloromethane, cleanup of the extract by gel permeation chromatography, and fractionation by Florisil and silica gel chromatography. Toxaphene residues are then characterized and quantified by capillary-column gas chromatography with electron capture. An automated data system is used to select and quantitate peaks and to eliminate interference from the high-resolution chromatograms. Selected components are then confirmed by gas chromatography-negative-ion mass spectrometry (NIMS). This procedure consistently yields results within 1% of spike concentrations. Substitution of conventional packed-column gas chromatography into the procedure reduces accuracy slightly; values average 7% below spiked concentrations. We also evaluated several confirmation techniques and other methods for eliminating analytical interferences. Nitration of the toxaphene-containing fraction before gas chromatography successfully eliminated interferences from the DDT complex but not from chlordane components. This procedure also altered the composition of the toxaphene mixture. Among the gas chromatography-mass spectrometry confirmation procedures evaluated, NIMS proved superior to the more conventional electron-impact mass spectrometry because toxaphene components were far more sensitive to NIMS.

### Introduction

Toxaphene, an inexpensive, broad-spectrum pesticide, is the most heavily used insecticide in the United States. As recently as 1976,  $1.8 \times 10^7$  kg was applied to major U.S. crops, with cotton pests the target of 85% of all agricultural applications (1). Thus, California, Texas, and the South-eastern-South Central states have accounted historically for most of the toxaphene used domestically. However, other uses are increasing; toxaphene is now registered for use against a variety of other arthropod pests including those associated with livestock, sunflowers, and ornamental plants (1). Worldwide, it is used to control grey flies [Romania (2)], alfalfa beetles [Hungary (3)], and insects that attack corn [Mexico (4)], cabbage [Federal Republic of Germany (5) and Poland (6)], and cotton [USSR (7)].

Much of the toxaphene applied annually to crops is probably lost to the atmosphere through volatilization and dust. Sieber et al. (8) found that 59% of the toxaphene applied to cotton plants as an aerially applied emulsion and 52% of that deposited on the soil vaporized in 58 days. It is therefore not surprising that residues have been detected at sites remote from applications—Bidleman and Olney (9) found an average of 0.6  $\text{ng/m}^3$  in air samples from the North Atlantic more than 1600 km from the nearest known use, Bidleman et al. (10) found up to 0.13  $\text{ng/m}^3$  in air samples from the Canadian Northwest Territories, and Munson (11) found up to 0.28  $\mu\text{g/L}$  in Maryland rainwater.

Because of its extreme toxicity to fish (12-15), chemists at the Great Lakes Fishery Laboratory of the U.S. Fish and Wildlife Service became concerned in 1973 when a complex unknown contaminant that chromatographed like toxaphene began to interfere with the analysis of organochlorine pesticides in lake trout (*Salvelinus namaycush*) from Lake Michigan (16). We identified the contaminant as toxaphene and concluded that its occurrence in Lake Michigan probably resulted from atmospheric transport because the compound has never been heavily used in the Great Lakes watershed (17, 18).

Other reports of toxaphene occurrence in fish from localities remote from application sites have appeared subsequently. Residues of 0.068  $\mu\text{g/g}$  were found in the lipid extracts of Antarctic cod (*Dissostichus eleginoides*) from the South Atlantic Ocean near the island of South Georgia, 0.125  $\mu\text{g/g}$  of lipid was found in Arctic char (*Salvelinus alpinus*) from an alpine lake in the Tyrolian Alps (7), and Jansson et al. (19) reported residues of 9  $\mu\text{g/g}$  in lipid in Arctic char from an oligotrophic lake in southern Sweden and 13  $\mu\text{g/g}$  of lipid in Atlantic herring (*Clupea harengus*) from the Baltic Sea. Based on these findings, Zell and Ballschmitter (7) concluded that toxaphene contamination of fish is a global problem and that the level of contamination in remote areas may even exceed that of PCB contamination.

Despite the apparent ubiquity of toxaphene, its persistence in the environment, and its toxicity toward some nontarget organisms, our participation in interlaboratory round-robin studies has shown that methods for identifying and quantifying toxaphene residues in environmental samples are poorly documented and vary greatly among laboratories. Toxaphene is a multicomponent residue which, when analyzed by conventional packed-column gas chromatography with electron-capture detection (GC/ECD), yields chromatograms containing peaks that overlap those of other ubiquitous organochlorine contaminants including DDT and its homologues, PCB's, and certain chlordane components. It is essential that these difficulties be overcome; an accurate and reproducible analytical method is needed to enable evaluation of the extent and magnitude of the potential environmental threat represented by toxaphene. A method for residue analysis in aquatic organisms is especially important because toxaphene tends to accumulate and persist in aquatic ecosystems, and aquatic animals are highly sensitive to contamination.

Of the methods used for the characterization and quantitation of toxaphene residues in fish tissues, we are most familiar with two: (a) a variation of the most commonly used multiresidue procedure for organochlorine contaminant analysis, which consists of a solvent extraction (petroleum ether/diethyl ether) of ground sample followed by gel permeation chromatography (GPC) cleanup, fractionation on Florisil (20) and silica gel chromatographic columns, and subsequent gas chromatography-mass spectrometry (GC/MS) residue determinations using packed columns (21, 22), and (b) the procedure we report in detail here, which consists of extracting ground tissues with dichloromethane, cleanup by GPC, fractionation on

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## GPC on SX-3 Bio-Beads

60 GRAMS 2.5X48 CM  
5 ML/MIN C6H12/CH2CL2 50/50

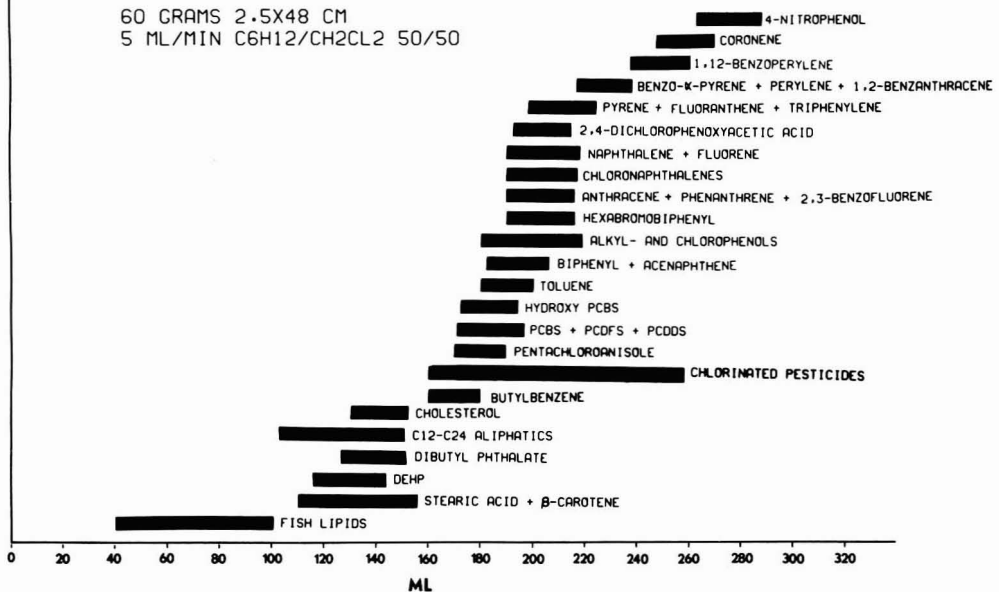


Figure 1. GPC elution profiles of selected biogenic compounds and environmental contaminants: 60 g SX-3 Bio Beads, 2.5 cm  $\times$  48 cm column, cyclohexane/dichloromethane 1:1, 5 mL/min.

Florisil and silica gel, characterization and quantitation of residues by GC/ECD using wall-coated open-tubular (WCOT) glass-capillary columns, and confirmation by GC/MS. Details of our procedures and our evaluation of alternative methods for characterization, quantitation, and confirmation of toxaphene follow.

### Experimental Section

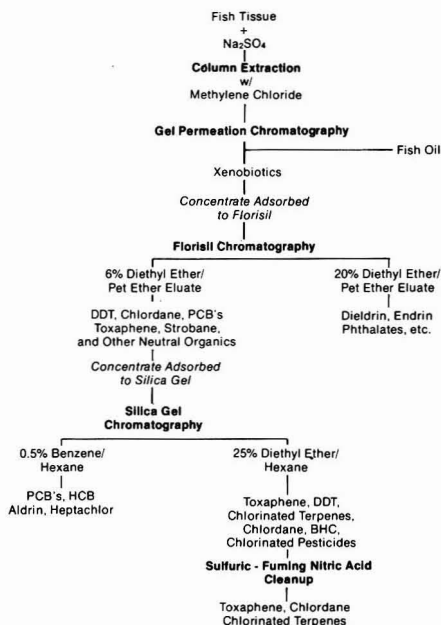
**Samples.** Ground fish tissue representing a tissue blank, tissue spiked with 4.0  $\mu\text{g/g}$  of technical toxaphene, and a sample of fish tissue from specimens collected from a field site known to be contaminated by toxaphene were prepared. The blank and spiked samples consisted of whole, adult brook trout (*Salvelinus fontinalis*) grown at our laboratory that had been prepared and ground in the manner described by Schmitt et al. (23). The tissue blanks were analyzed in triplicate and were found to contain no toxaphene or related components but did contain *p,p'*-DDE (0.01  $\mu\text{g/g}$ ), *cis*-chlordane (0.005  $\mu\text{g/g}$ ), and *trans*-nonachlor (0.005  $\mu\text{g/g}$ ). The field sample was a ground homogenate composed of five adult channel catfish (*Ictalurus punctatus*) from the Arroyo Colorado, a floodway in the lower Rio Grande valley near Harlingen, TX. This area is intensively farmed for vegetables and cotton, and fish from this region are known to contain substantial organochlorine insecticide residues (24). These fish were collected and stored according to the procedures outlined by Schmitt et al. (23) and then sent to a commercial laboratory where they were ground as described by Kaiser et al. (21) and Cromartie et al. (20). Frozen, blind-labeled homogenates were then returned to our laboratory for analysis.

At the laboratory, 10 g of fish tissue was mixed with 40 g of anhydrous  $\text{Na}_2\text{SO}_4$ . The dried mixture was ground to a fine powder and packed into a 30 cm  $\times$  2 cm i.d. chromatographic column (Ace Glass) fitted with a 200-mL reservoir and removable Teflon stopcock. The samples

were extracted with 200 mL of dichloromethane at an adjusted flow of 3–5 mL/min. The lipid extracts were collected in a 250-mL round-bottomed flask, and the solvent was reduced to approximately 5 mL by rotary evaporation. The concentrated extracts were then diluted to 10 mL with GPC solvent.

Automated GPC was used to separate the PCB's, toxaphene, and other chlorinated pesticides from the bulk of the lipid. A 60-g bed of SX-3 Bio Beads gel resin (Bio Rad) was used with a 1:1 mixture of cyclohexane in dichloromethane solvent system. The resin was packed in a 2.5 cm i.d.  $\times$  48 cm glass column fitted with two adjustable end plungers (Glenco Scientific). The column was placed on an automated low-pressure GPC Autoprep 1001 chromatograph (ABC Labs), and solvent was pumped through the column at 5 mL/min. Five milliliters (but not more than 1 g of lipid) of the sample extract was placed on the GPC column. The first 150 mL (dump cycle) was discarded and the next 110 mL (collect cycle) was collected in a 250-mL round-bottom flask (Figure 1). The GPC eluates were rotovaporated to approximately 1 mL and subsequently diluted to 5 mL with hexane before Florisil fractionation.

Florisil columns were prepared by placing 1 cm of anhydrous  $\text{Na}_2\text{SO}_4$  on a pledget of glass wool in a 1 cm i.d.  $\times$  30 cm chromatography column (Ace Glass) fitted with a 75-mL reservoir. Five grams of 60/80 mesh Florisil (Fisher Scientific), activated at 130  $^\circ\text{C}$  for 16 h, was then added and topped with another 1-cm layer of  $\text{Na}_2\text{SO}_4$ . Each column was then washed with 20 mL of hexane. When the hexane wash reached the top of the upper  $\text{Na}_2\text{SO}_4$  layer, the GPC concentrate was quantitatively transferred to the column and allowed to drain onto the bed of Florisil. The column walls were washed with 5 mL of the elution solvent (40 mL of 6% diethyl ether in petroleum ether). When the solvent reached the top of the Florisil, the remaining elution solvent (35 mL) was added,

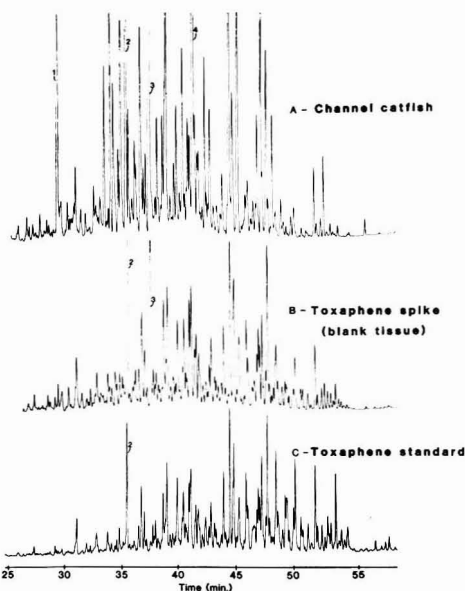


**Figure 2.** Flow scheme of the procedure used for sample preparation in multiresidue analysis.

and the eluate was collected for further separation.

PCB's were separated from the toxaphene by using 70/230 mesh Silica Gel 60 (E. Merck) activated at 130 °C for 16 h. The columns and extracts were prepared in the same manner as the Florisil columns. The first eluate, 0.5% benzene in hexane (PCB fraction), contained the PCB's, HCB, heptachlor, aldrin, mirex, and most of the *p,p'*-DDE. The second eluate, 25% diethyl ether in hexane (pesticide fraction), contained toxaphene, DDT and its homologues, technical chlordane, oxychlordane, heptachlor epoxide, methoxychlor, BHC, and other organochlorines. Total volume of the eluant depended on the activity of the silica gel and was calculated on a per-batch basis. In general, 35–45 mL of the PCB eluant and 25–35 mL of pesticide eluant were needed. The eluate volumes were reduced by rotoevaporation, and the resulting concentrates were diluted to 5 mL with isooctane prior to GC/ECD. We also treated a portion of the pesticide fraction from silica gel chromatography (Figure 2) with concentrated  $H_2SO_4$ -fuming  $HNO_3$  (nitration reagent), as described by Klein and Link (25), and evaluated the effectiveness of this technique in removing interfering aromatic compounds (i.e., DDT and PCB's) and its effects on the toxaphene mixture.

**Gas Chromatography.** All GC/ECD analyses were performed with a Varian 3700 gas chromatograph with a direct capillary injection system and a standard  $^{63}Ni$  electron-capture cell. For the chromatography we used both WCOT and packed columns. Our WCOT columns were 30 M  $\times$  0.22 mm i.d. methylsilicone fused silica (Hewlett-Packard), 55 M  $\times$  0.32 mm i.d. SE-54 (methyl-, 5% phenyl-, 1% vinylsilicone) fused silica (J & W Scientific), and 20 M  $\times$  0.25 mm i.d. OV-17 borosilicate (Chrompak U.S.A.). Hydrogen carrier gas with a linear velocity of 40 cm/s (pressure fixed) at maximum program temperature was used to chromatograph samples; an initial temperature of 140 °C was held for 10 min, programmed to 250 °C at 2 °C/min, and held at final temperature for



**Figure 3.** WCOT column chromatogram of toxaphene-containing fraction of two samples and technical toxaphene standard. Chromatogram A is from a channel catfish from the Arroyo Colorado; chromatogram B is a 4.0  $\mu g/g$  spike of brook trout; chromatogram C is a toxaphene standard. The numbered peaks are (1) dacthal, (2) *trans*-nonachlor, (3) *p,p'*-DDE, and (4) *p,p'*-DDD + *cis*-nonachlor. Conditions: 55 M  $\times$  0.32 mm i.d. fused-silica SE-54 column, temperature programmed with a 10-min hold at 140 °C to 250 °C at 2 °C/min;  $H_2$  carrier gas; 10% argon in methane makeup gas for ECD.

12.5 min. The injector temperature was 180 °C, the detector temperature was 320 °C, and a flow of 3 mL/min was used to sweep the septum. The detector makeup gas was argon/methane (9:1) at a flow rate (when added to the carrier gas) of 40 mL/min. To reduce the detector dead volume, we inserted the column up to the detector source with the makeup gas introduced before the end of the column and introduced the samples with a Varian 8000 autosampler, using a syringe purge and rinse cycle between injections to eliminate cross contamination.

For packed-column GC analysis we used a 1.83 M  $\times$  2 mm i.d. glass column packed with 1.5% SP-2250/1.95% SP-2401 on 100/120 mesh Supelcoport (Supelco). The carrier gas was argon/methane (9:1) at a flow of 20 mL/min; no makeup gas was used. The samples were chromatographed at 180 °C (isothermally). All other conditions were the same as those used in WCOT analyses.

**GC Quantitation and Data Collection.** The WCOT chromatograms were quantified by summing selected peak areas assignable to the toxaphene mixture that did not coelute with peaks representing known interferences (Figure 3). No peaks appearing earlier than *trans*-nonachlor were considered in the quantitation; this excluded some toxaphene components and metabolites that coelute with chlordane, another ubiquitous, multicomponent insecticide (19). The peaks representing toxaphene components were identified by using a method of relative retention index (RRI) matching. We used *trans*-nonachlor, with absolute retention time in the range of 35.50  $\pm$  0.10 min and an assigned RRI of 1.000, as the reference peak (Table I) and computed RRI values for toxaphene peaks as the ratio of the individual peak retention times to that of *trans*-nonachlor. Retention times for the *trans*-no-

Table I. Identification of Toxaphene Components in Catfish by Matching Relative Retention Indices<sup>a</sup>

| peak no. | toxaphene standard | catfish sample | peak no. | toxaphene standard | catfish sample |
|----------|--------------------|----------------|----------|--------------------|----------------|
| 1        | 1.036              | 1.036          | 16       | 1.275              | 1.274          |
| 2        | 1.043              | 1.042          | 17       | 1.293              | 1.294          |
| 3        | 1.089              | 1.089          | 18       | 1.297              |                |
| 4        | 1.099              | 1.099          | 19       | 1.322              | 1.323          |
| 5        | 1.125              | 1.124          | 20       | 1.331              | 1.332          |
| 6        | 1.140              | 1.140          | 21       | 1.345              | 1.345          |
| 7        | 1.154              | 1.152          | 22       | 1.365              |                |
| 8        | 1.158              | 1.156          | 23       | 1.387              | 1.387          |
| 9        | 1.170              | 1.170          | 24       | 1.390              |                |
| 10       | 1.176              | 1.176          | 25       | 1.412              | 1.412          |
| 11       | 1.194              | 1.194          | 26       | 1.461              | 1.461          |
| 12       | 1.207              | 1.207          | 27       | 1.476              | 1.477          |
| 13       | 1.237              | 1.236          | 28       | 1.483              | 1.481          |
| 14       | 1.253              | 1.253          | 29       | 1.510              | 1.509          |
| 15       | 1.263              | 1.262          |          |                    |                |

<sup>a</sup> Retention indices based on *trans-nonachlor* = 1,000. The retention time of *trans-nonachlor* = 35.56 min in toxaphene standard and 35.48 min in catfish sample. The identity range has been chosen as  $\pm 0.002$  relative index units.

nachlor were very reproducible ( $\pm 0.28\%$ ), which permitted us to use a peak-matching identity range of  $\pm 0.002$  RRI units for peaks in reference standards and in samples.

Peaks 1-29 (Table I) were considered for quantitation. These peaks are representative of those in technical toxaphene and in environmental samples and were shown to be identical by GC/MS. The chromatographic data were also analyzed in terms of similarity and analogy by a multivariate statistical procedure (26). The similarity analysis showed that the 29 toxaphene peaks in Table I out of the ~75 peaks present in a typical WCOT chromatogram contained the most useful information for describing similarity and/or dissimilarity among toxaphene and toxaphene-like residues. In our analyses, the quality-control spiked tissue had all 29 peaks and the catfish contained 26 of the 29 peaks (Table I).

Toxaphene was quantified by summing the areas of the peaks that correspond to peaks with identical RRI values in toxaphene standards (external-standard method). The use of as many as 29 peaks tends to reduce the systematic error inherent in the quantitation due to varying degrees of biological and chemical transformation of toxaphene in the environment, the varying ECD responses of toxaphene component peaks, and missing components in a sample. The samples were either diluted or concentrated to within a factor of 10 of the standard concentrations; our system is nonlinear for quantitating toxaphene when the sample concentrations are less than 1/10 or more than 10 times the standard concentration. Recoveries of technical toxaphene carried through the entire procedure were always  $100 \pm 2\%$ .

We collected capillary data with a Sigma 10 Laboratory Data Station (Perkin-Elmer), using programs supplied by the vendor for peak detection and integration and the parameters necessary to optimize the capillary gas chromatography. We wrote programs to quantitate the chromatograms, store the results, and eliminate the interferences resolved by the WCOT columns.

Quantitation of the packed-column chromatograms was more difficult because the separation was much less efficient and interfering compounds cochromatographed with major toxaphene components (Figure 4). In addition, characteristics of the chromatogram required that an arbitrary baseline be drawn (see Figure 4). The points used

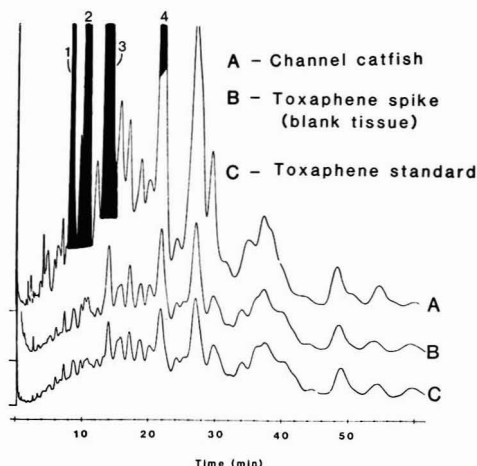


Figure 4. Packed-column chromatograms of the same samples as in Figure 3. Conditions: 1.8 M  $\times$  2 mm i.d. glass column packed with 1.5% SP-2250/1.95% SP-2401 on 100/120 mesh Supelcoport; isothermal at 180 °C with 20 mL/min flow of 10% argon in methane.

to draw the baseline are difficult to choose, and the choice significantly affects quantitation. Furthermore, the sample concentrations must be adjusted to the same approximate concentration as the standard due to nonlinearity in the response.

**GC/MS Confirmation.** All mass spectrometry was done with a Finnigan 4023 GC/MS and Inco 2300 Data System in either electron-impact (EI) or chemical-ionization (CI) mode with a methane plasma for ionization. Samples were analyzed by GC/MS with a WCOT column (approximately 20 M  $\times$  0.25 mm i.d.) coated with either SP-2100 (J & W Scientific, supplied by Supelco) or OV-17 (Chrompak U.S.A.) with helium carrier gas having a linear velocity of 35 cm/s. For all gas chromatography, we used an initial temperature of 100 °C held for 3 min, programmed to 240 °C at 3 °C/min, and then held at 240 °C for 8 min. Injection temperature was 250 °C, and the splitless injections were made through a standard Finnigan injection port. When EI spectra were acquired, the manifold pressure was about  $4 \times 10^{-7}$  torr; during negative ionization (NI), the manifold pressure was about 0.3 torr (all values read from standard Finnigan gauges). Other variables, which remained constant for both EI and NI, were temperatures (source, 250 °C; manifold, 120 °C; transfer oven, 240 °C), emission current (0.25 mA), and electron energy (70 eV). Spectra were acquired with the Inco data system scanning from 50 to 550 AMU every 2 s for EI and from 200 to 500 AMU every 2 s for NI. A methane plasma (99.99% methane, supplied by Matheson), maximized with perfluorotributylamine (FC43), was used for NIMS.

#### Results and Discussion

**Gas Chromatographic Characterization of Toxaphene Residues.** Visual examination of typical packed-column chromatograms (Figure 4) reveals little perceptible difference between technical toxaphene (chromatogram C) and that of the spiked tissue extract (chromatogram B). As Figure 4 illustrates, the peaks eluting after peak 3 in the fish tissue extracts from the Arroyo Colorado (chromatogram A) also resemble closely those of technical toxaphene. However, unresolved interferences in the early portion of chromatogram A make analysis of the toxaphene components eluting in this region

more difficult. The interference peaks in Figure 4A are (1) dacthal, (2) *trans*-nonachlor + *cis*-chlordane, (3) *p,p'*-DDE, and (4) *p,p'*-DDD. On this column *cis*-nonachlor immediately precedes DDD. Because packed columns do not have sufficient resolution to allow elimination of these interferences, only the later portion of the chromatogram is usually used for quantitation and characterization. As Figure 4 illustrates, the packed-column chromatograms of the three samples are similar; despite environmental degradation and interferences, packed-column comparisons, as in Figure 4, are widely used for confirmation.

Toxaphene chromatographed on packed columns typically yields 15–20 rounded peaks. Capillary columns, however, can resolve toxaphene into about 75 major, distinct, sharp peaks. As Figure 3 shows, the catfish sample, the spiked fish sample, and technical toxaphene contain many of the same components. However, the similarity in peaks from the spiked fish (Figure 3B) and the technical toxaphene (Figure 3C) is greatest because no environmental degradation has taken place, although there was a loss in the relative intensity of several later eluting peaks.

Retention time of toxaphene components increases with degree of chlorination and molecular weight; chromatograms from the WCOT procedure exhibited a definite reduction in the recovery of the higher molecular weight toxaphene components from the spiked fish tissues. Capillary GC/ECD analysis also showed a greater reduction in the later eluting components in the catfish sample extract than in the spiked-tissue extract (Figure 3). These differences were not apparent in the packed-column chromatograms (Figure 4). Analysis of a number of environmental samples indicated that the higher molecular weight components are not as persistent as earlier eluting, lower molecular weight components. Consequently, only small amounts of some of the later eluting components were found.

Interferences from the DDT group and PCB's can be removed by treating the sample with nitration reagent, which reacts with aromatic and unsaturated compounds. Furthermore, nitration removes some compounds present in tissue extracts that are not detected by GC/ECD and that can strongly interfere with GC/MS in the EI mode. Our experience has shown that nitration reduces toxaphene concentration by about 5%, as determined by both packed-column GC/ECD and by capillary GC/ECD.

The major shortcoming of nitration is that it affects the ratio of the toxaphene components. A visual comparison of the packed-column chromatograms for treated and untreated toxaphene shows little difference between the two (Figure 5A); the packed-column chromatograms of the toxaphene standard with and without acid treatment are similar. However, capillary-column analysis of the samples revealed differences in the individual components present (Figure 5B), indicating that toxaphene is not as resistant to nitration as it had appeared to be from packed-column analysis. In Figure 5B, we have identified the five areas of the two capillary chromatograms where nitration produced the most pronounced alterations. In each of these marked areas, two or more peaks were present; and within each group, the relative intensity of the peaks changed after acid treatment. These alterations would represent a problem in attempting to determine which components of the mixture are environmentally persistent.

A variety of WCOT columns are available for separation of the toxaphene mixture. Of those we tested—SE-54, OV-17, and methylsilicone—OV-17 yielded the most useful data from environmental samples. It also resolved *p,p'*-DDD and *cis*-nonachlor under the conditions found best

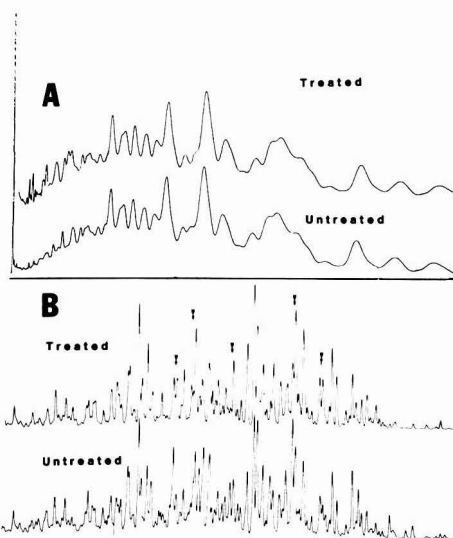


Figure 5. Chromatogram of technical toxaphene before and after treatment with  $\text{HNO}_3\text{-H}_2\text{SO}_4$ . WCOT column (B) and packed-column (A) conditions are the same as those in Figures 3 and 4. Arrows indicate peaks altered by nitration.

for resolution of toxaphene components. Although fused silica capillary columns are much easier to handle, OV-17 was not available on fused silica columns at the time we conducted our study. Alternatively, technical toxaphene is chromatographed adequately by SE-54, which is readily available on fused silica columns.

Degradation of toxaphene in the injection port can cause significant problems in identification and quantitation. We found two acceptable ways to minimize this degradation: an all-quartz injector is sufficiently inert that it can be used with little maintenance; or an all-glass injection system can be used if it is kept well cleaned and deactivated with silylation reagents.

The characterization of trace levels of a complex contaminant like toxaphene must ultimately show whether or not the most toxic components of the mixture persist in the environment. Although there are apparent visual differences between the capillary chromatograms of technical toxaphene and environmentally degraded samples, our analysis of these samples established that almost all peaks present in technical toxaphene were also present at some level in environmental samples. Detailed examination of the WCOT column data revealed that 95% of the peaks present in technical toxaphene were present in the spiked-tissue samples and 85% of the peaks were present in the catfish extract.

**Quantitation of Toxaphene Residues.** Toxaphene residues have been quantified in a variety of ways. In general, analysts prefer methods that they have performed consistently or methods certified by collaborative studies. However, there are little data with which to compare results from various laboratories analyzing comparable samples from biological matrices. Data from our studies provide a preliminary comparison of the accuracy of different methodologies. The results of our quantitation of the samples by both capillary and packed-column GC/ECD are presented in Table II. No toxaphene was found in the blank by either method, and results were within 1% of the spiked value by capillary column and 7% below it by packed column.

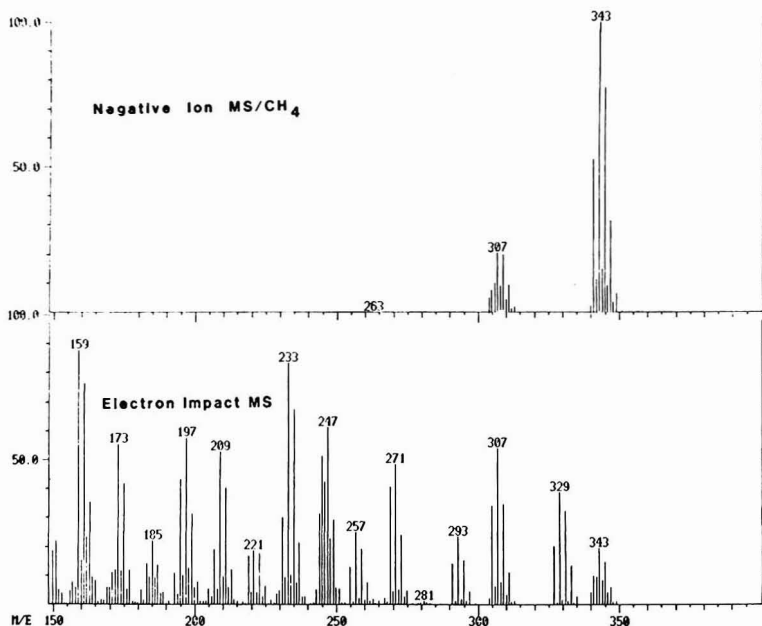


Figure 6. Mass spectra of toxicant B: top, negative chemical ionization; bottom, electron impact. A methane reagent gas plasma was used in negative chemical ionization mode.

Table II. Toxaphene Quantitations (Concentrations,  $\mu\text{g/g}$  Wet Weight) by Capillary-Column and Packed-Column GC/ECD. Means of Three Samples and Coefficient of Variation<sup>a</sup>

| method           | sample      |                    |
|------------------|-------------|--------------------|
|                  | catfish     | spike <sup>b</sup> |
| capillary column | 25.6 (2.8%) | 3.99 (2.2%)        |
| packed column    | 22.6 (3.5%) | 3.75 (2.7%)        |

<sup>a</sup> Both methods showed no toxaphene in a blank tissue sample. <sup>b</sup> Spike contained 4.0  $\mu\text{g/g}$  of toxaphene.

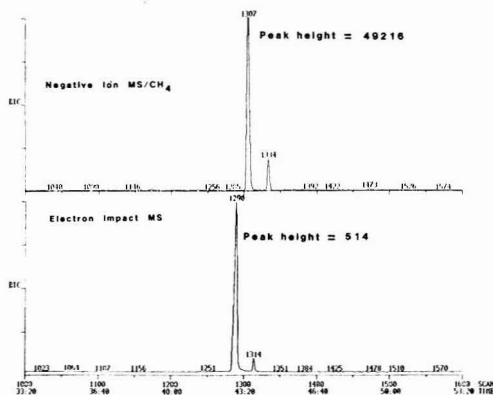
Analyses of the samples by our capillary-column GC/ECD procedure yielded accurate and precise values for the spiked sample primarily because of the high resolution afforded by the capillary columns (Table II). The results obtained by packed-column GC, although precise, were not as accurate as those obtained by capillary column. Packed-column GC/MS analysis (22) is comparable to analysis by capillary-column GC because mass spectrometry is used to differentiate toxaphene components from those interferences that the packed column cannot resolve. Without mass spectrometry, quantitations for spiked fish based on packed-column GC techniques will usually be below the level at which the fish were spiked because packed columns do not provide adequate resolution to separate toxaphene components from interferences in early portions of the chromatogram. Fewer early peaks can therefore be used in the quantitations, and a larger proportion of the peaks used for quantitation must come from later fractions of the chromatogram. Capillary-column analysis (Figure 3) showed that the most abundant peaks that persisted were those representing early eluting toxaphene components of lower molecular weight.

**Confirmation of Toxaphene Residues.** Toxaphene residues have been confirmed several ways, but the most widely accepted method is GC/MS. A confirmation technique involving dehydrohalogenation was suggested

by Gomes (27) [a variation of a procedure published by Crosby and Archer (28)], but no studies of the effect of this method on toxaphene in biological matrices have been published. However, Crist et al. (29) showed that the reaction of degraded toxaphene in sediments differed from that of a toxaphene standard when dehydrohalogenation was used. Jansson et al. (19) used capillary columns to confirm polychlorinated terpene residues in biota from Sweden. Other than GC/MS, the capillary-column method appears to offer the greatest potential for reducing interferences and providing reproducible results. The method we propose, that of characterizing and quantifying residues by using GC analysis followed by GC/MS confirmation, is also consistent with the proposed EPA protocol (22). Methods relying on packed column GC without MS may yield inaccurate results, as we showed (Table II).

Most confirmation is done by GC/MS analysis using EI, although other ionization techniques are available (30). One major limitation of GC/EIMS is a lack of sensitivity for toxaphene components. Biological samples contaminated with toxaphene at 1.0  $\mu\text{g/g}$  contain only about 0.05  $\mu\text{g/g}$  of the most prominent toxaphene component. This level is insufficient to permit analysis by full-scan EIMS because the response is too low. Budde and Eichelberger (31) developed a selected-ion monitoring method that increases the sensitivity of EIMS. However, the mass fragments used in this method are present in environmentally altered toxaphene residues and in all toxaphene components; consequently, they are not useful in determining the molecular weight of particular components. The poor sensitivity of EIMS for toxaphene is probably caused by extensive fragmentation of molecules that do not form stable molecular ions (formation of positive ions in EIMS is a very energetic process), and fragment ions must therefore be used to characterize compounds.

Figure 6 illustrates the EI mass spectrum of toxicant B [a ( $\text{C}_{10}\text{H}_{11}\text{Cl}_7$ ) toxaphene component with a molecular weight of 376] and shows how EIMS is of limited utility



**Figure 7.** WCOF chromatographs of equal amounts of toxicant B and an octachloro impurity detected in the NIMS (top) and EIMS (bottom) modes. Conditions: 25 M X 0.25 mm i.d. OV-17 borosilicate column, held 3 min at 100 °C, temperature programmed to 240 °C at 3 °C/min, He gas carrier flowing 24 cm/min. Retention-time differences are a result of stronger vacuum pull in the EI mode.

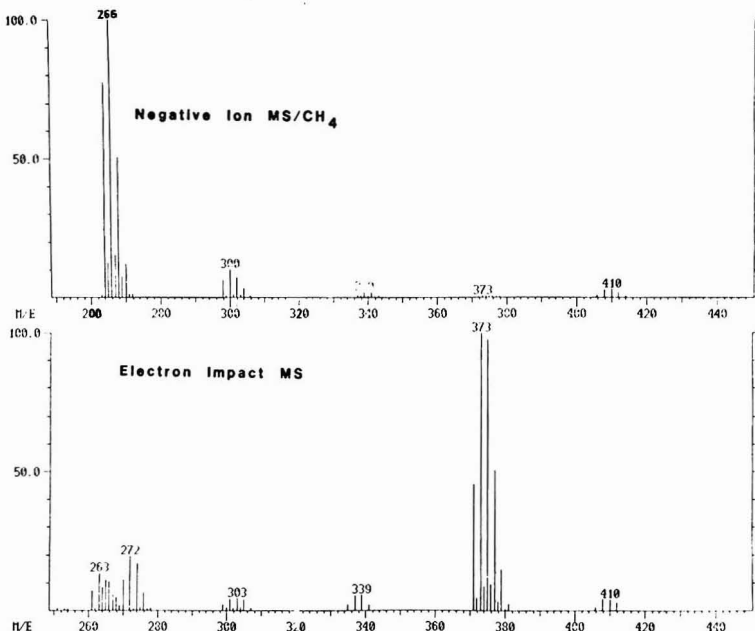
for trace-level toxaphene confirmation because many components have low responses and fragment extensively. Ion clusters due to fragmentation, with losses of chlorine or methyl groups or both, are present at masses 159, 231, 245, 291 ( $M - HCl - CH_2Cl$ ), 305 ( $M - HCl_2$ ), 327 ( $M - CH_2Cl$ ), and 341 ( $M - Cl$ ), yet there is no molecular cluster at mass 376. Interferences are present in the cluster at mass 231 from *p,p'*-DDD and *p,p'*-DDT, at 245 from *p,p'*-DDE, and at 341 from chlordane. Packed-column chromatography does not allow total elimination of these interferences, which distort the spectra of individual toxaphene components. In particular, chlordane components fragment in EIMS to give the ( $M - Cl$ )<sup>+</sup> ion cluster, which is the cluster containing the base peak in the mass spec-

trum. This peak overlaps with the ( $M - Cl$ )<sup>+</sup> ion cluster from toxaphene components with the same number of chlorines and can result in a major interference. Some of these problems can be reduced by selecting mass fragmentograms that do not include major interferences; however, when this is done, some peaks cannot be used in the quantitation because not all interferences can be eliminated.

One alternative to EIMS is chemical-ionization mass spectrometry (CIMS). In this process, which is less energetic than EIMS, either molecular ions or fewer fragment ions may be formed when a reagent gas (e.g., methane) plasma is used. The positive or negative ions formed from toxaphene in the methane plasma can then be analyzed. Positive CIMS has been tested previously for analysis of toxaphene and other compounds that are not amenable to EIMS analysis at trace levels and was also found to have a low response for most nonaromatic organochlorines (32).

As another alternative, some contaminants are known to be more responsive and to produce the molecular ion by negative-ionization mass spectrometry (NIMS), but responses vary significantly depending on the stability of the negative ions formed. [No single confirmation method permits the analysis of all trace-level components (33).] Dougherty et al. (33, 34) showed that NIMS was more selective and sensitive than EIMS to toxaphene, DDT, and some other pesticides. As illustrated by our comparison of the response of toxicant B by both methods (Figure 7), the response of toxicant B by NIMS was about 100 times that by EIMS. Increased selectivity results because toxicant B and other toxaphene components fragment to give the ( $M - Cl$ )<sup>-</sup> ion cluster containing the base peak, with all other ion clusters in the spectra giving a lower response.

Although the response for toxaphene components was greater in NIMS than in EIMS, the differences were not uniform for all components. The toxicant B standard we analyzed contained both heptachloro and octachloro components. The ratio of the heptachloro component to the



**Figure 8.** Mass spectra of an octachlorochlordane component: top, negative chemical ionization; bottom, electron impact.



octachloro component was nearly 3 times higher in EIMS than in NIMS; when we used EIMS for the analysis, the ratio for two peaks was 20:1, whereas NIMS yielded a ratio of 7:1.

Differences in the degree of chlorination or in positional isomerization may significantly influence NIMS response. This effect has already been established for the NIMS response of aromatic organochlorines, which are very sensitive to changes in substitution (35). A similar effect may occur for NIMS responses resulting from structural differences in saturated organochlorine compounds.

Chlordane components, which are major interferences, yield a small molecular ion cluster and almost no (M - Cl)<sup>-</sup> ion cluster in NIMS (Figure 8). As a result, the ions that chlordane does produce are different from the ions arising from toxaphene, and there are no mutual interferences. Chlordane components show only about a 10-fold increase in response compared with the 100-fold increase in toxaphene response, which further diminishes any interferences. Other potential interferences, including *p,p'*-DDT, *p,p'*-DDD, and *p,p'*-DDE have low NIMS responses, and the ions that result are different from the NIMS ions of toxaphene. Consequently, these compounds do not hinder toxaphene analysis. Indeed, we found the response for all the components of DDT to be less in NIMS than in EIMS, except for *p,p'*-DDT, which showed a slight increase. However, this enhancement was small relative to that of toxaphene.

Some of the environmental samples we analyzed were also contaminated with silicone-based compounds; however, the NIMS responses to these compounds were below detection limits, and no additional fractionation was required. Thus, as Dougherty et al. (33) pointed out, compounds that have high NIMS responses are less susceptible to interference because many potentially interfering compounds such as hydrocarbons have low responses.

In confirming toxaphene by GC/MS, the choice of the GC column depends upon the purpose of the analysis. Packed-column GC/MS confirmation of toxaphene yields a positive confirmation, but does not provide adequate resolution for confirmation of specific components. Only high-resolution capillary-column GC/MS can be used for compound identification and confirmation.

### Summary and Conclusions

Characterization of biological samples for toxaphene, as well as for PCB's and other anthropogenic pollutants, is complicated by several generic problems. First, the pollutants of concern must be separated from the biological matrix, possibly the most difficult part of the analysis; second, other xenobiotics (interferences) must be separated from toxaphene to allow accurate and reproducible identification and quantitation; third, all separations must be done reproducibly and with contaminant recoveries that are as high as possible. Our multiresidue procedure will accomplish these tasks for a variety of contaminants (35). Sample preparation effectively removes most interferences, including all PCB's, and the toxaphene is concentrated into a single fraction, which simplifies residue identifications and makes quantitations more accurate. High-resolution GC/ECD resolves toxaphene and other compounds, including chlordane, which minimizes the level of interference and further aids quantitation and identification. Resolution is sufficient to determine the relative abundance of some toxaphene components, and multivariate statistical procedures (e.g., ref 26) can then be used to analyze the results. NIMS is used for confirmation of residues because it is much more sensitive and selective than EIMS. Collectively, these improvements make the

method applicable for examining the transformation of toxaphene residues in the environment.

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## Trace Element Emissions on Aerosols from Motor Vehicles

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■ Concentrations and size distributions of 27 elements in aerosols collected near a highway and in a highway tunnel were measured on filter and cascade-impactor samples. Concentrations of many elements rise strongly near highways due to entrainment of road dirt. These elements are predominantly associated with large particles that settle out near the highway. Concentrations of elements relative to Pb on motor-vehicle aerosols of appreciable atmospheric residence time are as follows: Br,  $0.39 \pm 0.05$ ; Cl,  $0.22 \pm 0.04$ ; Ca,  $0.11 \pm 0.045$ ; Fe,  $0.08 \pm 0.04$ ; Mg,  $0.075 \pm 0.030$ ; Al,  $0.07 \pm 0.02$ ; Zn,  $0.017 \pm 0.004$ ; Ba,  $0.015 \pm 0.004$ ; Cu,  $0.007 \pm 0.003$ ; Mn,  $0.003 \pm 0.001$ ; Cd,  $0.0024 \pm 0.0006$ ; Sb,  $0.0014 \pm 0.0003$ ; Ni,  $0.0008 \pm 0.0006$ ; Co  $0.00011 \pm 0.00004$ ; Se  $0.000081 \pm 0.000034$ . The Ba/Pb ratio of aerosols from motor vehicles suggests that they are a major source of Ba in many U.S. cities. Except for Pb, Br, Cl, and Ba, motor-vehicle contributions for most elements measured account for <25% of observed atmospheric concentrations in most cities.

### Introduction

In recent years there has been much concern about the origins of elements, especially toxic elements, on urban aerosols. Automobiles burning leaded gasoline contribute large amounts of Pb, Br, and Cl to the atmosphere, but little is known about magnitudes of motor-vehicle contributions of other elements. Composition patterns of particles from motor vehicles are needed in receptor models (1), which are coming into use for determining contributions of various sources to urban suspended particulate matter. Extensive studies have been made on exhaust from automobile gasoline engines (2-5), but there are many other potential vehicular sources of particles: brake linings, tires, fuel additives other than lead compounds, and diesel exhaust. These sources could be studied individually, but it is more efficient to measure the integrated contribution of those sources for a mix of vehicles under urban traffic conditions.

Roadside-soil studies have shown strong concentration gradients of Ni, Cu, Zn, Cd, and Pb vs. distance from heavily traveled highways (6-9). These observations, however, do not demonstrate that these elements are present on particles small enough to remain suspended in air at long distances from highways. Feeney et al. (10) analyzed airborne particles collected near Los Angeles

freeways; however, due to interferences from entrained road dust, measurements of only a few elements clearly associated with vehicular emissions were possible. Dzubay et al. (11) collected particles over Los Angeles freeways with dichotomous samplers and analyzed the fine and coarse fractions. Pierson et al. (12-17) made several studies of particles in traffic tunnels and in the Los Angeles atmosphere. Recently, Rheingrover and Gordon (18) developed a wind-trajectory method by which they determined compositions of particles from motor vehicles by using the large data set taken in St. Louis in connection with the Regional Air Pollution Study (RAPS) (19). Alpert and Hopke used target-transformation factor analysis (TTFA) to extract a motor-vehicle component from the RAPS data (20). Despite numerous studies, it is difficult to define accurately the composition of particles that remain airborne for significant periods and to distinguish primary-vehicle emissions from entrained roadside dust.

In this work, two sites were chosen for the observation of particulate emissions from motor vehicles: a heavily traveled highway in Beltsville, MD, and the Baltimore Harbor Tunnel.

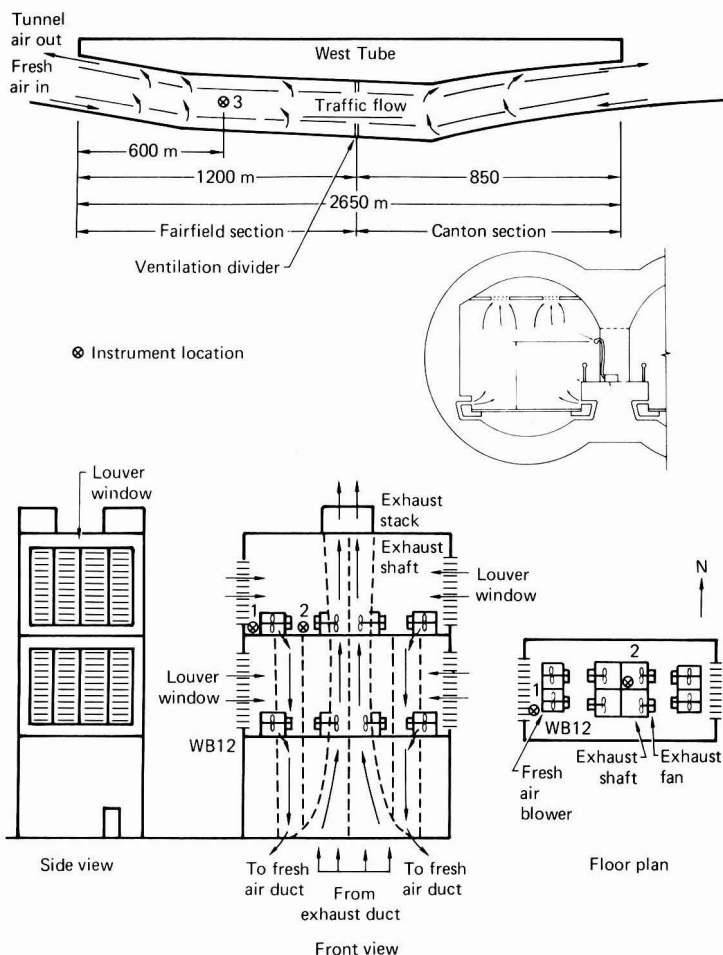
### Experimental Methods

**Sampling Sites.** The Baltimore Harbor Tunnel, running northeast-southwest beneath the Patapsco River, is a dual-tube tunnel, 2042 m in length. Each tube normally carries two lanes of traffic moving in the same direction, but when one tunnel is closed for maintenance, two-way traffic occurs in the other.

Transverse ventilation is maintained through each tube by blowers and exhaust fans located in ventilation buildings at both portals (see Figure 1). Each tube is divided into two sections, the Canton section (north) and the Fairfield section (south). Each section has its own ventilation system with four blowers pumping air into the tunnel and four exhaust fans withdrawing air for release through exhaust stacks atop the vent buildings. Longitudinal air flow is also induced by vehicles in the tunnel (the "piston effect"), accounting for up to 20% of the ventilating air flow. The residence time of air in the tunnel is about 5 min (21). Carbon monoxide is monitored by tunnel personnel, who set fan speeds to maintain CO below prescribed limits.

The other sampling site was on the grounds of the U.S. Department of Agriculture laboratory adjacent to U.S. Route 1 in Beltsville, MD. Large, open, grass-covered areas border Route 1, which runs SSW-NNE at this location. Prevailing winds from the northwest intersect the highway

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**Figure 1.** Diagrams of the Baltimore Harbor Tunnel showing ventilation system and sampling sites. Upper portion is side view of tunnel, with "3" indicating the tunnel sampling site. The middle diagram shows a cross section of a portion of the tunnel with a sampler near the crosswalk between the two sides of the tunnel. The lower part shows three views of one ventilation building with sampling sites for intake air (1) and exhaust (2).

in a perpendicular direction.

**Tunnel Experiments.** Sampling equipment was installed at three locations in the tunnel to monitor intake air (site 1), exhaust air (site 2) and tunnel air (site 3) (see Figure 1). The tunnel site was located 610 m from the south end of the tunnel at the crossover between the two tubes of the tunnel. During the first experiment (April 17-23, 1973), filter samplers were attached to the wall of the west tube (southbound traffic), about 1 m from the crossover and about 2.4 m above the road. An impactor was positioned on the catwalk below the filter holder. Eight sets of Nuclepore 47-mm filters of 0.4- $\mu$ m pore diameter were taken, as were eight impactor samples with use of a Scientific Advances CS-6 cascade impactor. Hourly traffic counts, fan speeds, and weather conditions were obtained from tunnel personnel. On the average, trucks, including both diesel- and gasoline-powered trucks, made up about 19% of the traffic.

Additional experiments were performed at the tunnel from December 1973 to March 1974, including simultaneous collections with cascade impactors at sites 1-3 and

a study in which Nuclepore filter samples were taken hourly at each location over 24 h ("24-h study"). The tunnel samples were taken in the east tube (northbound traffic). Data and conditions for the 24-h filter study of January 3, 1974, are shown in Figure 2. Light traffic conditions prevailed. Rain of variable intensity fell during most of the day, and predominantly easterly winds from 8 to 16 km/h were recorded. Ambient temperature was between 1 and 3 °C during the sampling period.

**Highway Experiments.** During August 1973, particulate samples were collected simultaneously at 4.5, 45, and 90 m downwind (east of Route 1) and at 45 m upwind with 47-mm diameter, 0.4- $\mu$ m pore Nuclepore filters and with cascade impactors. Samplers were mounted 1.5 m above the ground. Impactors were run at the upwind site and two downwind sites. Sample collection was controlled by a selected-sector activator that switched samplers on only when wind came from across the highway at a velocity >3 km/h.

**Analytical Techniques.** Samples were analyzed for up to 28 elements by instrumental neutron-activation

Table I. Median Concentrations and Concentration Ratios of Elements on Particles in Baltimore Harbor Tunnel (April 1973)

| element        | concentration, <sup>a</sup> ng/m <sup>3</sup> |               |              | concentration ratios <sup>b</sup> |                |
|----------------|---|---------------|--------------|-----------------------------------|----------------|
|                | intake  | tunnel        | exhaust      | tunnel/intake                     | exhaust/intake |
| <b>group 1</b> |   |               |              |                                   |                |
| Pb             | 3200 ± 1500                                   | 26000 ± 4900  | 27000 ± 5600 | 27 ± 6                            | 33 ± 11        |
| Br             | 320 ± 30                                      | 8600 ± 1000   | 8800 ± 1000  | 26 ± 10                           | 27 ± 11        |
| Ba             | 33 ± 10                                       | 265 ± 40      | 250 ± 60     | 7.8 ± 3.5                         | 8.0 ± 4.5      |
| Cl             | 3300 ± 400                                    | 6200 ± 800    | 6000 ± 700   | 6.1 ± 5.0                         | 6.3 ± 5.5      |
| Zn             | 74 ± 48                                       | 340 ± 50      | 465 ± 50     | 4 ± 2                             | 4.1 ± 2.4      |
| <b>group 2</b> |   |               |              |                                   |                |
| Sb             | 9.0 ± 1.0                                     | 33 ± 5        | 33 ± 4       | 3.1 ± 1                           | 2.5 ± 0.9      |
| Co             | 1.9 ± 0.2                                     | 5.3 ± 0.8     | 8.1 ± 1.0    | 2.9 ± 1                           | 2.7 ± 1        |
| Cr             | 26 ± 3  | 82 ± 11       | 33 ± 4       | 3 ± 2                             | 2.0 ± 1.4      |
| <b>group 3</b> |   |               |              |                                   |                |
| Mn             | 84 ± 8  | 180 ± 20      | 170 ± 20     | 2.3 ± 0.7                         | 1.8 ± 0.5      |
| Ca             | 3000 ± 220                                    | 5500 ± 620    | 4300 ± 600   | 2.3 ± 1.3                         | 1.6 ± 0.6      |
| Sc             | 0.30 ± 0.03                                   | 0.82 ± 0.08   | 0.45 ± 0.04  | 2.2 ± 1.4                         | 1.4 ± 0.5      |
| La             | 3.8 ± 0.4                                     | 7.5 ± 0.9     | 5.4 ± 0.6    | 1.8 ± 0.4                         | 1.4 ± 0.5      |
| Al             | 1650 ± 150                                    | 2650 ± 300    | 1900 ± 240   | 1.7 ± 0.8                         | 1.0 ± 0.3      |
| Ce             | 4.3 ± 0.5                                     | 7.0 ± 1.0     | 6.7 ± 0.7    | 1.5 ± 0.5                         | 1.4 ± 0.5      |
| Lu             | 0.15 ± 0.04                                   | 0.21 ± 0.09   | 0.13 ± 0.03  | 1.4 ± 0.2                         | 1.3 ± 0.4      |
| Fe             | 3600 ± 300                                    | 5400 ± 680    | 3700 ± 500   | 1.4 ± 0.3                         | 1.1 ± 0.3      |
| Mg             | 1500 ± 200                                    | 1900 ± 250    | 1100 ± 300   | 1.5 ± 0.9                         | 0.8 ± 0.2      |
| Eu             | 0.034 ± 0.006                                 | 0.029 ± 0.006 | 0.037 ± 0.02 | 1.2 ± 0.2                         | 1.1 ± 0.2      |
| Th             | 0.24 ± 0.03                                   | 0.35 ± 0.05   | 0.36 ± 0.05  | 1.2 ± 0.4                         | 1.0 ± 0.5      |
| <b>group 4</b> |   |               |              |                                   |                |
| Se             | 2.3 ± 0.3                                     | 3.2 ± 0.5     | 3.5 ± 0.6    | 1.0 ± 0.2                         | 1.0 ± 0.2      |
| Sm             | 0.39 ± 0.10                                   | 0.35 ± 0.09   | 0.24 ± 0.05  | 1.0 ± 0.4                         | 0.7 ± 0.5      |
| Na             | 1800 ± 180                                    | 1800 ± 200    | 1250 ± 150   | 0.83 ± 0.13                       | 0.77 ± 0.15    |
| V              | 200 ± 20                                      | 79 ± 9        | 95 ± 10      | 0.5 ± 0.2                         | 0.5 ± 0.1      |

<sup>a</sup> Median concentrations and analytical uncertainty (of a single observation) of up to eight separate experiments.

<sup>b</sup> Average and standard deviation of individual ratios.

analysis (INAA). Ca, Ni, Br and Pb were determined in samples from the 24-h study by using instrumental photon-activation analysis (IPAA). Atomic absorption spectrometry (AAS) was used to determine Cd and Pb on samples from the tunnel obtained from December 1973 to March 1974 and Pb on Route 1 samples. Lead was determined by IPAA on one set of three simultaneously run impactors and on filter samples obtained in the April 1973 tunnel experiments.

Nuclear analyses employed methods previously published (22, 23). Neutron irradiations were performed at the National Bureau of Standards (NBS) reactor and photon irradiations at the NBS electron linac. An Instrumentation Laboratory (IL) Model 353 unit was used for AAS measurements. Samples were prepared by extraction with a 1:1 mixture of redistilled concentrated HNO<sub>3</sub> and distilled water. Extractions were performed with use of a 15-min ultrasonic treatment. Wavelengths used were 217 nm for Pb and 228.8 nm for Cd. Analyses for Pb by AAS were in good agreement with those obtained by IPAA.

### Results and Discussion

**Tunnel Experiments.** Results of analyses of eight sets of filter samples collected in April 1973 are given in Table I. As expected, in the tunnel and exhaust, there are enormous increases of Pb, Br, and Cl relative to intake. Whereas Pb concentrations are typically 1 µg/m<sup>3</sup> in cities, the median value in the tunnel is 26 µg/m<sup>3</sup> and values up to 40 µg/m<sup>3</sup> over 4-h averaging times were observed.

Concentrations of most elements increased in tunnel air relative to intake air. Concentrations of elements attached to large particles (see below), including crustal elements such as Al, Sc, and rare earths, however, generally increased 2-fold or less in the tunnel and fell to nearly the

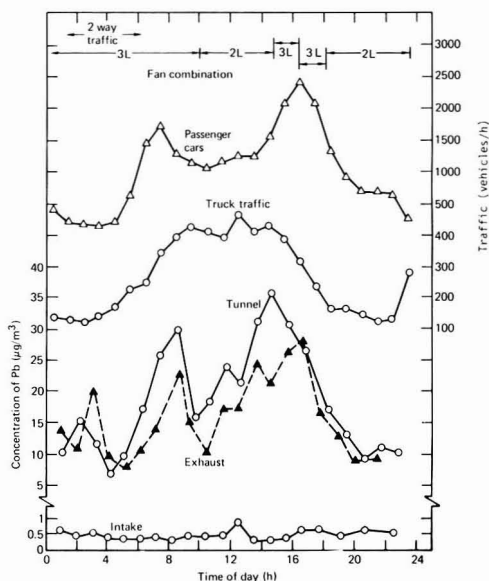


Figure 2. Passenger car and truck traffic, ventilation fan combination, and Pb concentrations during a 24-h period at the Baltimore Harbor Tunnel. Two or three fans were run at low speed (L) during the intervals indicated. Two-way traffic conditions prevailed from 0000 to 0415.

intake values in the exhaust room. Concentrations of Pb and Br, which are associated with motor vehicles, increased by a factor of 20 or more over the intake values and remained elevated at the exhaust room. In fact, concen-

trations of Pb, Cl, and Br in suspended particles often increased slightly between the tunnel and exhaust sites. These increases could result from deposition of gaseous elements on particles during the approximately 5-min period needed to reach the exhaust. However, measurements of condensation nuclei, light scattering, total particulate mass, and NO by Israel (24) all show increases along the length of the tunnel in the direction of the traffic flow. Concentrations at the tunnel sampling site were slightly lower than the average concentrations in the Fairfield tunnel section. Unless there is deposition of particles in the duct work, concentrations observed at the exhaust should reflect the averages for that section of the tunnel and, in this case, be higher than those measured at the tunnel sampling site. Thus, we cannot determine whether or not deposition of additional Pb and Br on particles from the gas phase occurs. There can be little deposition of gas-phase alkyllead compounds, as their concentrations are <5% of particulate Pb concentrations (25).

Increases of particulate Zn and Ba concentrations in the tunnel, which are maintained to the exhaust vent, indicate their association with motor vehicles. Sb, Co, and Cr (group 2 in Table I) were elevated by factors of 2-4 in both tunnel and exhaust air. Small amounts of these elements are apparently present on particles released by motor vehicles.

Concentrations of group 3 elements are elevated by factors from 1 to 2.3 in the tunnel and <2 in the exhaust. These elements are mostly present on large particles and have concentrations relative to Al similar to those of soil. Exhaust/intake ratios for most elements in group III are less than tunnel/intake ratios, suggesting that many are on large particles of dust raised by turbulence along the roadway, which partly settle out or become attached to duct walls before reaching the exhaust room. Other possible sources for large-particle elements are brake linings and tires.

Elements of group 4 (Se, Sm, Na, V) show no enrichment in tunnel air. The V concentration is reduced upon passage through the tunnel, as shown by ratios of 0.5 between the tunnel (or exhaust) and the intake. This suggests that V-bearing particles are deposited on duct and tunnel walls or scavenged by large particles that settle out quickly in the tunnel. Vanadium in eastern U.S. cities is mostly associated with fine particles from combustion of residual oil (26, 27). Electron-microscope pictures of particles collected in the tunnel reveal many dendritic particles with high surface areas per unit mass (28). These particles might provide excellent surfaces for removal of combustion aerosols such as V.

Concentrations of Pb determined in the 24-h experiment at each sampling site are plotted in Figure 2, and median concentrations of several other elements are listed in Table II. Combinations of two and three sets of ventilation fans were operated as indicated in the figure. There was two-way traffic in the east tube from midnight to 0415 while the west tube was closed for service. Lead enrichments in air relative to intake air ranged from 20 to 70 in the tunnel, depending on the time of day and traffic, and 20 to 50 in the exhaust room. Two peaks, at about 0800 and 1500, are observed in the Pb plots. These correspond roughly to maxima in traffic flow, but the Pb concentration does not correlate linearly with traffic because of changes in fan settings and variations in the piston effect. A third Pb peak occurred at about 0300, during the two-way traffic period, even though the traffic did not increase. Concentrations of Pb observed in tunnel air during this period,

Table II. Median Concentrations of Elements on Particles in the Baltimore Harbor Tunnel (24-h Experiment, January 1974)

| element | concentrations, <sup>a</sup> ng/m <sup>3</sup> |              |              |
|---------|--|--------------|--------------|
|         | intake   | tunnel       | exhaust      |
| Pb      | 340 ± 30                                       | 18000 ± 1700 | 15500 ± 1500 |
| Br      | 83 ± 8   | 8000 ± 800   | 6600 ± 700   |
| Cl      | 760 ± 230                                      | 17000 ± 2000 | 11000 ± 1400 |
| Ca      | 690 ± 100                                      | 5400 ± 800   | 3300 ± 500   |
| Fe      | 630 ± 80                                       | 5300 ± 700   | 3000 ± 400   |
| Mg      | 300 ± 100                                      | 2300 ± 800   | 3300 ± 500   |
| Al      | 400 ± 100                                      | 3800 ± 500   | 2000 ± 300   |
| Ba      | 16 ± 6   | 380 ± 60     | 325 ± 50     |
| Zn      | 170 ± 20                                       | 520 ± 80     | 420 ± 60     |
| Cu      | 20 ± 10  | 110 ± 30     | 115 ± 40     |
| Mn      | 37 ± 5   | 150 ± 20     | 67 ± 9       |
| Cd      | 11 ± 2   | 77 ± 12      | 37 ± 6       |
| Sb      | 9.0 ± 1.0                                      | 33 ± 5       | 33 ± 4       |
| Ni      | 25 ± 6   | 41 ± 16      | 25.5 ± 5.0   |
| Co      | 0.78 ± 0.30                                    | 2.2 ± 0.6    | 2.2 ± 0.4    |
| Se      | 2.0 ± 0.3                                      | 2.4 ± 0.4    | 2.2 ± 0.2    |
| Cr      | 25 ± 5   | 66 ± 10      | 45 ± 7       |

<sup>a</sup> One-way traffic data only. Uncertainties (1  $\sigma$ ) reflect analytical errors only.

however, are completely accounted for by tunnel dust (see below).

Under normal operation, traffic in the east tube is northbound. In this case, the piston effect increases concentrations of pollutants at the tunnel site relative to the average tunnel section, observed at the exhaust room. Thus, during one-way periods, concentrations of Pb in the exhaust are lower than in the tunnel. Lead levels in the intake air remained essentially constant throughout the sampling period.

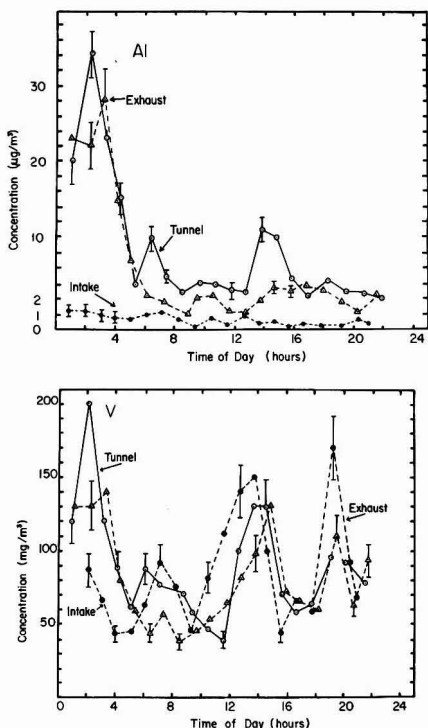
Concentrations of Al and V at the three sampling locations are plotted in Figure 3. Three Al peaks are observed for tunnel samples, the largest during the two-way traffic period. During this period, the piston effect is nullified, but the turbulence created as vehicles pass each other (in opposite directions) is dramatically increased and a large amount of road dust is suspended in the air. By contrast, peaks at about 0700 and 1400, corresponding to increased traffic flow, are only one-third as large. Enrichments of Al in tunnel air relative to intake air during the one-way traffic period range from about 25 to 40. For exhaust air, however, concentration enrichments range from about 1 to 10.

Concentrations of V in intake air varied considerably during the sampling period. Except during two-way traffic, V concentrations in intake air were generally higher than in tunnel and exhaust air, indicating deposition of V in the tunnel and/or duct work. Concentrations of V in the exhaust are often greater than in the tunnel. Thus, not all of the air brought in either by vehicles (the piston effect) or by the intake fans is mixed well enough to be measured at the tunnel sampling site, as some is probably drawn off by exhaust fans before mixing.

Large amounts of tunnel dust were suspended in tunnel air by turbulence, particularly two-way traffic. Assuming that tunnel dust is the major source of Sc in tunnel air, a soil component of the observed tunnel-air concentrations can be estimated as the product of the concentration of tunnel-air Sc and the ratios of elements to Sc in tunnel soil; i.e., the tunnel-dust contributions for each element on sample *i* are assumed to be given by

$$[X]_{i,dust} = [Sc]_i [X/Sc]_{dust}$$

where  $[Sc]_i$  is the Sc concentration observed on the *i*th

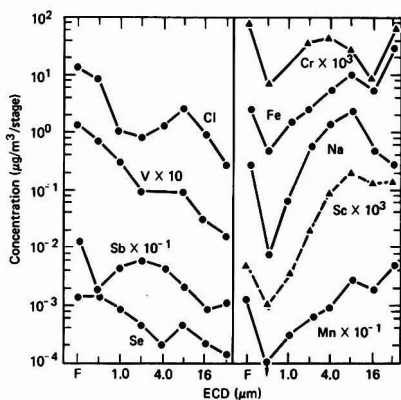


**Figure 3.** Concentrations of Al and V in aerosols at the intake, tunnel, and exhaust sampling locations at the Baltimore Harbor Tunnel during 24-h experiments. Note that for Al the scale from 0 to 2 is expanded to show low values more clearly.

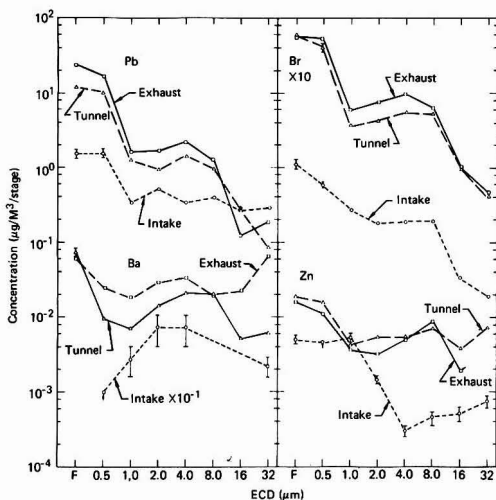
sample and  $[X/Sc]_{\text{dust}}$  is the ratio of concentrations of element X to Sc in the tunnel during two-way traffic. Road dust from the gutters was analyzed, but we felt the particles might be so large that those samples would not represent the composition of suspended dust as well as samples collected during two-way traffic. The net motor-vehicle component was then calculated by subtracting both the soil component based on Sc concentrations and a "background" based on concentrations in the intake air. As noted above, only a fraction of the material observed at the intake reaches the tunnel and exhaust sampling sites. From V concentrations during one-way traffic, we estimate the fraction to be about 60%. The resulting average ratios of net concentrations of elements normalized to Pb are listed in column 3 of Table III. No Cl value is given for this experiment, as both Cl and Na concentrations were very high in both the tunnel and the exhaust, probably indicating large contributions from road salt on this day.

Size distributions of particles bearing several elements at the tunnel and exhaust sites are shown in Figures 4 and 5. Most of the mass of Al, Sc, Hf, Th, Na, Ca, Mn, Co, Cr, Fe, and the rare earths is contained in large particles such as those derived from crustal weathering. Large quantities of these elements were often detected on the back-up filters; we attribute this to particle bounce-off (29) that was visually evident, despite an adhesive coating on collection substrates.

Concentrations of several elements, including Cl, V, Se, Br, and Pb, showed increases by up to 2 orders of magnitude with decreasing particle size over the range of di-



**Figure 4.** Typical concentration vs. particle-size distributions of elements on particles at the tunnel sampling location at the Baltimore Harbor Tunnel.



**Figure 5.** Concentration vs. particle-size distributions of Pb, Ba, Br, and Zn in aerosols at the intake, roadway, and exhaust sampling locations at the Baltimore Harbor Tunnel.

ameters 32–0.2  $\mu\text{m}$ . Distributions for Pb, Br, and Cl showed two maxima, one for particles with diameter  $\leq 0.5 \mu\text{m}$  and the other for particles with diameter in the 2–16- $\mu\text{m}$  range. Bimodal distributions are characteristic of exhausted emissions (5), the  $\leq 0.5\text{-}\mu\text{m}$  peak resulting from fresh combustion aerosols and the larger particles probably from expulsion of aggregates formed in the exhaust system or from the attachment of small particles by coagulation. Concentrations of Pb, Cl, Br, and Zn in the tunnel were generally well above their concentrations in intake air throughout the size spectrum. Concentrations of Ba on particles with diameter  $\geq 2 \mu\text{m}$  are accounted for by background aerosol. The Ba attached to particles of diameter  $\leq 2 \mu\text{m}$ , however, is clearly due to a tunnel source.

Abrasion of motor-vehicle surfaces, such as tires and brake linings, could also contribute to the large-particle components, but resuspended roadside tunnel dust or background aerosols are probably dominant. The concentration of Sc on each impactor stage was used to determine and subtract the tunnel-dust contribution from the stage as indicated in Table IV. This implies that

Table III. Ratios of Elements in Motor-Vehicle Particulate Emissions to Lead tunnel experiments

| element                | April 1973 <sup>f</sup> | January 1974 <sup>g</sup><br>(24-h expt) | highway expt,<br>Rte 1 (August 1973 <sup>h</sup> ) | adopted value,<br>this work <sup>i</sup> | Pierson<br>and Brachaczek, <sup>a</sup><br>tunnels<br>(1975-79) | Dzubay<br>et al., <sup>b</sup><br>freeway<br>(1976) | Feeny<br>et al., <sup>c</sup><br>freeway<br>(1972) | Rheingrover<br>and Gordon, <sup>d</sup><br>ambient<br>(1975-77) | Alpert<br>and Hopke, <sup>e</sup><br>ambient<br>(1976) |
|------------------------|-------------------------|--|--|--|---|---|--|---|--|
| Pb                     | ≅1.00                   | ≅1.00                                    | ≅1.00  | ≅1.00                                    | ≅1.00   | ≅1.00   | ≅1.00  | ≅1.00   | ≅1.00  |
| Br                     | 0.36 ± 0.05             | 0.42 ± 0.06                              | 0.35 ± 0.58  | 0.39 ± 0.05                              | 0.3   | 0.47  | 0.30   | 0.39 ± 0.02   | 0.28   |
| Cl                     | 0.22 ± 0.04             |  | 0.14 ± 0.12  | 0.22 ± 0.04                              | 0.06  | 0.24  | 0.30   | 0.14 ± 0.03   | 0.022  |
| Ca                     | 0.20 ± 0.04             |  |  | 0.11 ± 0.04 <sup>f</sup>                 | 0.2   | ~0.08   | 0.12   | 0.11 ± 0.01   | 0.10   |
| Fe                     | 0.17 ± 0.04             |  |  | 0.084 ± 0.037                            | 0.09  | ~0.1  | 0.19   | 0.085 ± 0.010   |  |
| Mg                     | 0.075 ± 0.029           |  |  | 0.075 ± 0.034                            | 0.2   | ~0.1  |  |   |  |
| Al                     | 0.073 ± 0.015           |  |  | 0.067 ± 0.034                            | 0.2   | ~0  |  |   |  |
| Ba                     | 0.012 ± 0.003           |  | <0.07  | 0.071 ± 0.020                            | 0.2   |   |  | 0.21 ± 0.01   | 0.05   |
| Zn                     | 0.017 ± 0.003           |  | <0.2   | 0.015 ± 0.004                            | 0.018   |   |  | 0.06 ± 0.02   | 0.0065   |
| Ba                     | 0.017 ± 0.005           |  |  | 0.017 ± 0.004                            | 0.02  |   |  |   | 0.007  |
| Cu (x10 <sup>3</sup> ) | 6.1 ± 1.1               |  |  | 7.2 ± 2.6                                | 10  |   | 5  |   | 5.6  |
| Mn (x10 <sup>3</sup> ) | 3.0 ± 1.0               |  |  | 3.0 ± 1.0 <sup>j</sup>                   | 12 <sup>k</sup>   |   |  |   |  |
| Cd (x10 <sup>3</sup> ) | 2.4 ± 0.6               |  |  | 2.4 ± 0.6                                | <0.3  |   |  |   |  |
| Sb (x10 <sup>3</sup> ) | 1.7 ± 0.5               |  |  | 1.4 ± 0.3                                | 0.05  |   |  |   |  |
| Ni (x10 <sup>3</sup> ) | 0.94 ± 0.6              |  |  | 0.8 ± 0.6                                | <0.8  |   |  | 5.1 ± 0.5   | 0.75   |
| Se (x10 <sup>3</sup> ) | 2.9 ± 0.5               |  |  | 1.1 ± 0.4 <sup>l</sup>                   | <0.8  |   |  |   |  |
| Co (x10 <sup>3</sup> ) | 9 ± 4                   |  |  | 8.1 ± 3.4                                | ≤0  |   |  |   |  |
| Sr (x10 <sup>3</sup> ) | 2.4 ± 0.5               |  |  | <1.5                                     | <0.4  |   |  |   |  |
| Cr (x10 <sup>3</sup> ) |                         |  |  |  |   |   |  |   |  |

<sup>a</sup> Reference 17. <sup>b</sup> Reference 11. <sup>c</sup> Reference 10. <sup>d</sup> Reference 18. Includes only fine fraction. <sup>e</sup> Reference 20. Includes only fine fraction. <sup>f</sup> Weighted average of up to 14 exhaust-room and tunnel samples not corrected for entrained soil. <sup>g</sup> Weighted average of up to eight exhaust room samples corrected for soil component and intake concentrations. <sup>h</sup> Based on eight experiments for most elements. <sup>i</sup> Ratio listed is the weighted average of the January and April 1974 values if the two agreed within uncertainties. The April value was excluded if significantly greater than the January value. <sup>j</sup> April, 1973 value excluded. <sup>k</sup> Higher than other Mn values because of Mn-containing additive MMT during many of the experiments.

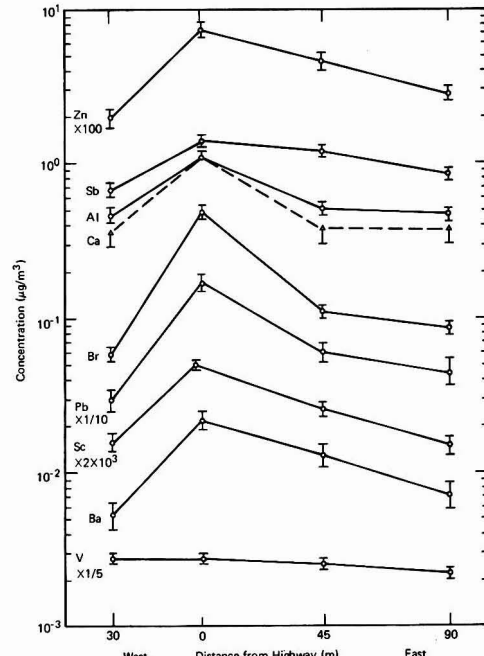


Figure 6. Concentrations of several elements in aerosols collected near U.S. Route 1 in Beltsville, MD. Wind was blowing from the west during sample collections.

tunnel dust has the same composition for particles of all sizes, which may not be strictly correct. We also subtracted a background for each element based on its concentration on the corresponding stage of the intake-vent impactor. As above, the amount subtracted (about half of the intake value) was determined by the ratio of the concentrations of V on the given stage of the tunnel and exhaust impactors to that of the corresponding intake impactor stage, assuming that the remainder was lost in the duct-work. Net concentrations for each impactor stage for typical data sets are listed in Table IV.

For Pb, Cl, Br, and Zn, contributions of intake air are negligible on all but the first and/or second stages (where the first stage collects the largest particles). Therefore, both peaks observed represent particles of motor-vehicle origin, and the data agree with exhaust-emission studies noted above (2, 3, 5). Except for Mn, a net motor-vehicle component for the remaining elements could not be distinguished from the tunnel-dust and intake components. Both Cr and Sb tended to have somewhat larger portions of their masses on smaller particles (Figure 4), but their concentrations were accounted for by background and resuspended tunnel-dust particles. Both Se and V are accounted for by nonvehicle sources outside the tunnel.

**Highway Experiments.** Typical concentrations of elements vs. distance from the highway are shown in Figure 6. The wind was blowing from west to east (left to right in the figure). Concentrations of most elements increased strongly immediately downwind from the highway; however, most dropped nearly to their upwind values before reaching the site at 45-m downwind. Concentrations of elements such as Br, which are known to be emitted from vehicles, remained elevated to at least 90 m downwind.

Table IV. Net Vehicle-Related Components of Pb, Br, Zn, Mn, and Cl as a Function of Particle Size (ng/m<sup>3</sup>)

| stage<br>ECD, μm | Pb                 |                                  |                                |       | Br                 |                                  |                                |      |
|------------------|--------------------|----------------------------------|--------------------------------|-------|--------------------|----------------------------------|--------------------------------|------|
|                  | gross <sup>a</sup> | intake<br>component <sup>b</sup> | dust<br>component <sup>c</sup> | net   | gross <sup>a</sup> | intake<br>component <sup>b</sup> | dust<br>component <sup>c</sup> | net  |
| 32               | 190                | 145                              | 180                            | 0     | 22                 | 3.0                              | 10                             | 9    |
| 16               | 120                | 135                              | 258                            | 0     | 140                | 3.0                              | 6                              | 131  |
| 8                | 1250               | 195                              | 414                            | 640   | 540                | 8.0                              | 7                              | 525  |
| 4                | 2200               | 170                              | 180                            | 1850  | 960                | 19                               | 4                              | 940  |
| 2                | 1750               | 255                              | 102                            | 1390  | 680                | 12                               | 1.9                            | 670  |
| 1                | 1600               | 170                              | 78                             | 1350  | 700                | 7.5                              | 1.4                            | 690  |
| 0.5              | 17000              | 785                              | 72                             | 16100 | 680                | 190                              | 1.4                            | 490  |
| filter           | 24000              | 750                              | 600                            | 22600 | 9500               | 210                              | 1.6                            | 9300 |

| stage<br>ECD, μm | Cl                 |                                  |                                |       | Mn <sup>d</sup>    |                                  |                                |      |
|------------------|--------------------|----------------------------------|--------------------------------|-------|--------------------|----------------------------------|--------------------------------|------|
|                  | gross <sup>a</sup> | intake<br>component <sup>b</sup> | dust<br>component <sup>c</sup> | net   | gross <sup>a</sup> | intake<br>component <sup>b</sup> | dust<br>component <sup>c</sup> | net  |
| 32               | 330                | 12                               | 165                            | 150   | 53                 | 31                               | 18                             | -26  |
| 16               | 970                | 30                               | 180                            | 760   | 18                 | 7.3                              | 11                             | -0.8 |
| 8                | 3000               | 85                               | 330                            | 2600  | 44                 | 10                               | 18                             | 16   |
| 4                | 1600               | 65                               | 110                            | 1400  | 42                 | 8.6                              | 9.5                            | 24   |
| 2                | 830                | 30                               | 25                             | 780   | 21                 | 6.9                              | 4.2                            | 9.9  |
| 1                | 1100               | 10                               | <4                             | 1100  | 14                 | 2.0                              | 2.0                            | 7.7  |
| 0.5              | 8100               | <400                             |                                | ~8000 | 5.2                | 3.2                              | 1.5                            | 1.3  |
| filter           | 14000              | 325                              | 520                            | 13000 | 93                 | 54                               | 43                             | 29   |

| stage<br>ECD, μm | Zn                 |                                  |                                |      |
|------------------|--------------------|----------------------------------|--------------------------------|------|
|                  | gross <sup>a</sup> | intake<br>component <sup>b</sup> | dust<br>component <sup>c</sup> | net  |
| 32               | 16                 | 3.8                              | 22                             | 0    |
| 16               | 23                 | 2.6                              | 25                             | 0    |
| 8                | 64                 | 2.3                              | 47                             | 15   |
| 4                | 39                 | 1.6                              | 13                             | 24   |
| 2                | 46                 | 7.5                              | 1.3                            | 37   |
| 1                | 58                 | 27                               | <0.2                           | 31   |
| 0.5              | 140                | <23                              |                                | ~120 |
| filter           | 290                | 25                               | 63                             | 200  |

<sup>a</sup> Exhaust site sample. Note that data for the various elements were not all obtained in the same experiment, so one cannot in general obtain emission ratios from the total net concentrations of one element relative to another. <sup>b</sup> Due to losses in the duct-work as predicted by V concentrations (typically ~60%), less than all of the intake concentration is subtracted. <sup>c</sup> Tunnel-dust component calculated for each impactor stage by using Sc concentrations on each stage, and ratios of elements to Sc on filters collected during two-way traffic in tunnel (see text): (Pb/Sc) = 2150 ± 180; (Br/Sc) = 700 ± 240; (Cl/Sc) = 1180 ± 100; (Zn/Sc) = 180 ± 230; (Mn/Sc) = 90 ± 10. <sup>d</sup> The Mn data were smoothed by averaging the net values for each stage *i* of the six individual tunnel and exhaust impactor sets. The average values for the gross, intake, and resuspended dust components are given; therefore, the net values listed are not those obtained by subtracting the various columns as is the case for the other elements.

Cascade-impactor studies showed that major additions at the highway for most elements were borne almost entirely by particles of diameter ≥ 8 μm and that added large-particle components had mostly disappeared at the 90-m downwind site. By contrast, about 90% of the Br added at the highway was in the diameter <0.5-μm fraction, with about 10% added in the larger particle range. It appears that concentrations of most elements increase strongly immediately downwind from the highway because of entrainment of large particles of roadside dirt. Most of this material travels only a few dekameters before settling. Most airborne Pb, Br, and Cl is on fine particles from the exhaust, which are strongly diluted but remain above background to the 90-m site.

Although in Figure 6, Zn and some other elements appear to remain slightly elevated at 90 m relative to the upwind site, when data from all Route 1 experiments are combined, we observe excesses outside of experimental error at the 90-m site for only Pb, Br, and Cl. As shown in Table III, we can only set upper limits on the motor-vehicle contributions of Zn and Ba relative to Pb. For remaining elements, there are no significant increases at 90 m downwind. The behavior of V is similar to that in the tunnel: its concentration is reduced downwind of the highway, suggesting that V-bearing particles are scavenged by large particles. If so, V is probably not unique in this behavior. However, one can observe the effect with V because its atmospheric concentration is so dominated by oil combustion that the amount entrained as roadside dust is small by comparison. By contrast, it would be difficult

to observe the effect for most other elements because of the sharp increase of concentration at the highway.

Results from the highway experiment generally agree with those from the tunnel, but the former are much less definitive. Three major problems with the highway experiment are (1) concentrations of resuspended road dust are greater than in the tunnel, yielding a higher background, (2) the motor-vehicle component is diluted quite strongly even at 30 m downwind, whereas there is little dilution between the tunnel roadside and the exhaust room, and (3) traffic densities were higher in the tunnel, yielding a larger source term.

**Motor-Vehicle Emission Ratios.** Emission ratios of various elements relative to Pb are listed in Table III. In the first tunnel experiment (April 1973), motor-vehicle components were calculated by subtracting concentrations observed in intake air from those in the exhaust air, as analyses of tunnel dust were not available. In the (January 1974) 24-h experiment, observed concentrations were corrected for both intake air and tunnel soil. Components based on highway data were estimated by subtraction of upwind values from concentrations of elements at the 90-m downwind site. Uncertainties quoted are the standard deviations of replicate measurements.

The Br/Pb ratios computed from the 24-h experiment are generally higher than the Br/Pb ratio in ethyl fluid [0.386 (11)]. Linear regression of Br and Pb concentrations in tunnel samples indicates a Br/Pb ratio of 0.38 as compared with the value of 0.42 reported in Table III. Br/Pb ratios for very fresh emissions are usually found to range



from 0.39 to 0.47, dropping as low as 0.10 for very aged particles that have lost Br to the gas phase (11, 12, 17). The Cl/Pb ratio of  $0.22 \pm 0.04$  compared well with the value of  $0.24 \pm 0.04$  for fresh emissions reported by Dzuby et al. (11).

Emission ratios of elements predominantly associated with large particles (i.e., Ca, Fe, Al, Mn, Co, and Cr) were generally higher in the April experiment than in the January experiment, probably because contributions of suspended tunnel soil were not removed from the April data. For elements with small-particle association, e.g., Br, Zn, and Ba, values obtained in the two experiments are in good agreement. An accurate emission ratio for Cl was not determined in the January tunnel experiment due to interference by road salt. Emission ratios for some elements based on the highway experiments are listed for comparison. Even Br could not be adequately detected above background at the 90-m site in most cases. Upper limits reported for Zn and Ba agree with the tunnel values.

Adopted values of elemental concentrations relative to Pb based on this work are listed in column 5 of Table III. Because of their greater accuracy, only tunnel data were used. If the January 1974 and April 1973 data were in agreement, a weighted average was used. If the April value was significantly larger than the January value, the former was rejected, as the April values may include tunnel-dust contributions.

Emission ratios determined by other workers are also listed in Table III. Pierson and Brachaczek's component (17), based on studies in the Allegheny and Tuscarora tunnels, should be the most comparable with this work. The Dzuby (11) and Feeney (10) components were obtained near freeways. Rheingrover and Gordon's (18) component was obtained from wind trajectories from ambient sampling stations to areas of high motor-vehicular activity at unknown distances from stations, but the high Br/Pb ratio suggests fresh emissions from nearby locations. Their component represents only the fine fraction ( $<2.5\text{-}\mu\text{m}$  diameter), in which the Pb concentration is  $14 \pm 4\%$  by weight.

Alpert and Hopke's component (20) was obtained from fluctuations of ambient concentrations (treated by target-transformation factor analysis) and may represent particles that have been present in the atmosphere for longer times than particles sampled in the other studies. Thus, all components except Alpert and Hopke's should represent fairly fresh motor-vehicle particles. The Br/Pb ratios of 0.3 or greater for those components agree with that conclusion, and the lower value obtained by Alpert and Hopke suggests loss of some Br during the longer residence time. The enormous variation of the Cl/Pb ratio is surely due to rapid losses of Cl under some conditions. From judgment of the highest values in Table III, the Cl/Pb ratio of fresh particles from engines burning leaded gasoline is about 0.24. Our value of 0.22 indicates that little loss occurred. Pierson and Brachaczek (17), who performed very similar experiments, suggest that the smaller Cl/Pb ratio observed in their tunnel studies resulted from losses of HCl caused by chemical reactions with  $\text{H}_2\text{SO}_4$ , present because of release from diesel engines. There was similar traffic in the Baltimore Harbor Tunnel, but perhaps the lower ambient temperatures existing during our experiments (in winter and spring) suppressed release of Cl. Pierson (private communication, 1981) has suggested that more  $\text{NH}_3$  may have been available for titration of  $\text{H}_2\text{SO}_4$  in the urban Baltimore air than in the rural areas of Pennsylvania, where their studies were performed. The component observed by Alpert and Hopke (20), which

should be the most aged, has the lowest Cl concentration and that of Rheingrover and Gordon is intermediate.

Many differences between our work and that of Pierson and Brachaczek (17) for remaining elements result from our attempt to remove soil from the motor-vehicle component, which they did not do. We have tried to provide a component appropriate for receptor-model use, with the idea that soil should be included as a separate component in those models. In part because of this difference, their component has higher concentrations of several crustal elements: Al, Ca, and Mg. Note that the high Al value obtained by Rheingrover and Gordon is for fine particles, whereas any soil associated with motor vehicles would be expected to be of large particle size. However, Rheingrover and Gordon suggest that Al in the fine-particle fraction may be an artifact of the X-ray fluorescence analyses of the samples (18).

Ba and Mn are of special interest. Pierson and Brachaczek (17) took accurate data on passenger car, light truck, and diesel traffic and had sufficient variation in the ratio of diesels to other traffic to resolve the concentration data into contributions from diesel- and gasoline-powered vehicles. They find that most of the Ba originates from diesels. Their Ba value is in good agreement with ours in accord with comparable fractions of diesel-powered trucks: 10–15% for Pierson and Brachaczek and about 19% "trucks" observed during our 24-h experiment, the latter from toll-booth data, which included some light gasoline powered trucks. The exact origin of the Ba from trucks is not known. The Ba-bearing particles were observed to be small, in agreement with our results, in Pierson and Brachaczek's experiments during the early 1970s. The small size is consistent with a combustion source, which would include Ba-containing smoke suppressant, occasionally used as a diesel-fuel additive, and Ba in motor oil. During the late 1970s, Pierson and Brachaczek found about the same Ba concentration but a shift of its size distribution to larger particles. The motor-vehicle components derived from ambient sampling in St. Louis are based on concentrations measured by X-ray fluorescence, which does not yield accurate Ba values at typical urban levels (19). Rheingrover and Gordon (18) did not obtain a strong correlation of Ba with Pb; however, the value obtained by Alpert and Hopke (20) is not unreasonable, as diesel trucks make up only 5% of the traffic on a national basis (vs. 10–15% in the tunnels) (17).

The Mn value of Pierson and Brachaczek (17) is considerably greater than ours, but they explain that the Mn-containing additive MMT (an octane booster that replaces Pb) was being used during many of their measurements but not during our studies. It was in use during some of the St. Louis RAPS, consistent with the somewhat elevated value obtained by Rheingrover and Gordon (18). The use of MMT has declined or been eliminated entirely, so a value closer to ours is probably more appropriate for use in receptor models for data taken outside of the 1976–1979 period. (However, see discussion below about changes in Pb consumption.)

There is rather good agreement on a value of Zn/Pb of about 0.02. This low value rules out the earlier suggestion (30) that a major fraction of ambient Zn originates from tire dust (see urban contributions below). Also, a value of Cu/Pb of about 0.007 is generally found. Contributions of Se and Co are so low and uncertain that disagreements are not unexpected. The low Cr values from tunnel studies are probably more reliable than the higher value from ambient studies (18). The most serious discrepancies are for Cd and Sb. Contributions of these elements are so

Table V. Concentrations of Elements Observed in Atmospheres of Several North American Cities (ng/m<sup>3</sup>)

| element | Baltimore, <sup>a</sup> | Washington,<br>D.C., <sup>b</sup> | Toronto, <sup>c</sup> | New York, <sup>d</sup> | Charleston,<br>WV, <sup>e</sup> | St. Louis, <sup>f</sup> | Tucson, <sup>g</sup> | Portland,<br>OR, <sup>h</sup> |
|---------|-------------------------|-----------------------------------|-----------------------|------------------------|---------------------------------|-------------------------|----------------------|-------------------------------|
|         | 1974                    | 1976                              | 1973-1974             | 1976                   | 1978                            | 1976                    | 1974                 | 1978                          |
| Pb      | 340                     | 440                               | 970                   | 1230                   | 780                             | 880                     | 690                  | 1810                          |
| Br      | 83                      | 135                               | 290                   | 260                    | 190                             | 180                     |                      | 620                           |
| Cl      | 76                      | 530                               | 1200                  | 835                    | 120                             | 340                     |                      | 4100                          |
| Ca      | 670                     | 860                               | 5300                  | 1510                   |                                 | 2950                    | 5300                 | 2300                          |
| Fe      | 600                     | 1000                              | 2200                  | 960                    | 740                             | 1490                    | 2900                 | 3500                          |
| Mg      | 500                     | 440                               | 1400                  |                        |                                 |                         | 1100                 | 670                           |
| Al      | 405                     | 1350                              | 2100                  | 970                    | 1180                            | 1410                    | 5700                 | 3600                          |
| Ba      | 16                      | 19                                |                       |                        |                                 |                         |                      |                               |
| Zn      | 170                     | 86                                | 320                   | 460                    | 42                              | 175                     | 170                  | 220                           |
| Cu      | 50                      | 17                                | <330                  | 105                    | 24                              | 43                      | 190                  | 150                           |
| Mn      | 39                      | 26                                | 74                    | 100                    | 17                              | 71                      | 55                   | 170                           |
| Cd      | 11                      | 2.5                               |                       |                        |                                 | 5                       | 2.4                  |                               |
| Sb      | 9                       | 2.1                               | 6.9                   |                        |                                 | 7                       |                      |                               |
| Ni      | 25                      | 17                                | 21                    | 75                     |                                 | 9                       | 6.0                  | 60                            |
| Co      | 1.0                     | 0.83                              | 1.0                   |                        |                                 |                         | 1.9                  |                               |
| Se      | 2.1                     | 2.4                               |                       | 6.5                    | >7                              | 5                       |                      |                               |
| Cr      | 25                      | 15                                | 26                    | <50                    |                                 | 15                      | 4.0                  | 50                            |

<sup>a</sup> This work, median values of tunnel intake. <sup>b</sup> Kowalczyk et al. (31); Cl value based on cascade impactors. <sup>c</sup> Paciga and Jervis (32). <sup>d</sup> Stevens et al. (33). <sup>e</sup> Lewis and Macias (34). <sup>f</sup> Dzubay (35). <sup>g</sup> Moyers et al. (36). <sup>h</sup> Cooper et al. (37).

Table VI. Motor Vehicle Contribution (%) to Observed Elemental Concentrations in Atmospheres of Several Cities<sup>a</sup>

| element | Baltimore, | Washington,<br>D.C.,  | Toronto,  | New York,             | Charleston,<br>WV, | St. Louis,            | Tucson, | Portland,<br>OR, |
|---------|------------|-----------------------|-----------|-----------------------|--------------------|-----------------------|---------|------------------|
|         | 1974       | 1976                  | 1973-1974 | 1976                  | 1978               | 1976                  | 1974    | 1978             |
| Pb      | 100        | 100                   | 100       | 100                   | 100                | 100                   | 100     | 100              |
| Br      | 160        | 130                   | 130       | 190                   | 160                | 190                   |         | 110              |
| Cl      | 80         | 12                    | 14        | 25                    | 140                | 57                    |         | 10               |
| Ca      | 5.5        | 5.6                   | 2.0       | 8.9                   |                    | 6.6                   | 1.4     | 8.7              |
| Fe      | 4.4        | 3.5                   | 3.5       | 10                    | 8.4                | 4.7                   | 1.9     | 4.1              |
| Mg      | 5.0        | 7.5                   | 5.2       |                       |                    |                       | 4.7     | 20               |
| Al      | 5.9        | 2.3                   | 3.2       | 9                     | 4.7                | 4.4                   | 0.9     | 3.6              |
| Ba      | 32         | 35                    |           |                       |                    |                       |         |                  |
| Zn      | 3.4        | 8.7                   | 5.1       | 4.5                   | 31                 | 8.5                   | 6.9     | 14               |
| Cu      | 4.8        | 19                    | >2        | 8.5                   | 23                 | 15                    | 2.6     | 8.7              |
| Mn      | 2.7        | 5.1 (20) <sup>b</sup> | 3.9       | 3.7 (15) <sup>b</sup> | 14                 | 3.7 (15) <sup>b</sup> | 3.8     | 3.2              |
| Cd      | 7.5        | 42                    |           |                       |                    | 42                    | 69      |                  |
| Sb      | 5.4        | 29                    | 20        |                       |                    | 18                    |         |                  |
| Ni      | 1.1        | 2.1                   | 3.6       | 1.3                   |                    | 7.8                   | 9.2     | 2.4              |
| Co      | 3.8        | 5.8                   | 11        |                       |                    |                       | 4.0     |                  |
| Se      | 1.3        | 1.5                   |           | 1.5                   | <1.0               | 1.4                   |         |                  |
| Cr      | <2         | <4.4                  | <5.6      | <3.7                  |                    | <8.8                  | <26     | <5.4             |

<sup>a</sup> Calculated from observed concentrations in Table V with the assumption that all of the observed Pb is from motor vehicles and that concentrations of other motor-vehicle-generated elements relative to Pb are the "adopted values" from this work in Table III. <sup>b</sup> Includes possible MMT contribution (see text).

small that they would not be observed in the studies that employed XRF, so the only values listed in Table III are those from Pierson and Brachaczek (17) and this work. Although contributions of these elements are quite low, our values are great enough that, if correct, motor-vehicle emissions would account for substantial fractions of urban ambient Cd (see below and ref 31). Much Cd in the environment results from its association with Zn, but the Cd/Zn ratio for our motor-vehicle component, about 0.1, is so high that the Cd probably cannot be explained as an impurity of Zn. Other than analytical error in one of the data sets, we have no explanation for either the Cd or the Sb disagreements.

To calculate motor-vehicle contributions to TSP levels based on observations of Pb or other elements in ambient air, one must know absolute concentrations of one or more elements in the particles from vehicles. As the masses collected in this work were so small that they could not be weighed accurately, we have not determined mass concentrations or absolute concentrations of elements in the particles. Thus, to use our motor-vehicle component

in receptor-model calculations, one needs an independent value of one absolute concentration, e.g., for Pb. This value depends on the mix of vehicles in traffic and the fraction of leaded gasoline in use. For vehicles burning only leaded gasoline, Pb constitutes about 40% of the particulate mass (30). The Pb concentration is much lower for a mix of traffic that includes diesel engines and vehicles burning unleaded gasoline. Values based on the St. Louis studies during the mid-1970s are 14 ± 4% (18) and 11% over 2 months at one urban station (20). In highway tunnels with 16% diesel-truck traffic, Pierson and Brachaczek obtained a value of 7%, but this would rise to about 13.5% for 5% diesel trucks, which is more typical of urban traffic (17).

**Motor-Vehicle Contributions of Elements on Urban Particles.** Concentrations of several particle-borne elements in atmospheres of representative North American cities are listed in Table V. Assuming that all observed Pb is from motor vehicles, we estimate the fractions of other elements contributed by motor vehicles by multiplying the Pb concentration by the "adopted values" of the emission ratio for the element (Table III) and dividing by

the observed concentration in the particular city to yield the values listed in Table VI. For data taken during 1976, we also list a 4-fold greater contribution based on the Mn/Pb ratio during periods of MMT use (17).

This approach overpredicts Br, apparently because there are no other large sources of Br and up to half of the Br on motor-vehicle particles is lost to the gas phase. A potential problem for this approach is that some of the Pb may originate from other sources. From chemical element balances of Washington, D.C., particles, Kowalczyk et al. (31) found that about 7% of the Pb is from refuse incineration. Unless a city has a strong source of nonautomotive Pb (e.g., a smelter), 7% is probably a typical figure for Pb contributed by other sources. Note that St. Louis, which has two Pb smelters and other chalcophile-element plants (18), has the highest overprediction of Br in Table VI. Thus, the motor-vehicle contributions calculated for the other elements in St. Louis are probably 30% too high.

Contributions of vehicles to urban Cl are highly variable. In Charleston, WV, Cl is overpredicted, presumably because Cl is partially lost to the vapor phase. In other cities, the Cl contribution ranges from 10% to 80%, depending on the strengths of other Cl sources, especially road salting and, in coastal cities, marine aerosols.

Motor-vehicle contributions of most other elements are less than 10%, the major exceptions being Ba, Zn (in Portland and Charleston), Cu, Cd, Mg (in Portland), Sb, and Mn, the latter especially during MMT use. Few data sets contain both Ba and Pb, so we cannot be sure that a large fraction of urban Ba is from motor vehicles, but it appears to be. The Zn on particles that remain airborne for an appreciable time accounts for only about 10% or less of typical urban concentrations.

Chemical element balances (employing our motor-vehicle component) indicate that refuse and vehicles account for comparable amounts of Cd and Sb in Washington, D.C. (31). There has been much concern about emissions of toxic elements on small, respirable particles from coal-fired plants (e.g., ref 38), but if our Cd and Sb values are correct, the major sources of these elements are motor vehicles and refuse incineration, not coal-fired plants.

Up to 19% and perhaps more of urban Cu may be explained by motor-vehicle emissions. Most older measurements of atmospheric Cu suffered from contamination by pump motors. Measurements given in Table V were done more carefully, so Cu contamination should be much less but cannot be ruled out. If some Cu data listed in Table V include contamination, the fraction of Cu accounted for by motor vehicles would be larger than the value shown in Table VI. The very small contribution in Tucson may reflect enhanced atmospheric Cu because of the many Cu smelters in that area (37, 39).

### Discussion

The aim of this study was development of a motor-vehicle component for use in receptor models. We measured many elements, in part to identify any that are contributed in large part by motor vehicles and that could, thus, be used as "markers" of motor-vehicle contributions. In this, we were only partially successful: among the elements measured, Pb, Br, Cl, Ba, possibly Cd and Sb, and, at times, Mn are contributed in substantial amounts. Cl and Br are not reliable markers, as substantial fractions are lost to the gas phase. However, these measurements are important for receptor-model use even for elements that are not contributed mainly by motor vehicles. As motor vehicles account for substantial amounts of TSP in urban areas, it is important to know concentrations of all elements on the particles reliably to determine residual

amounts that must be accounted for by other sources.

The composition of the motor-vehicle component is not static because of the phase-out of leaded gasoline, the sometimes use of MMT or Ba-containing additives, the changing ratios of diesel- to gasoline-powered vehicles, etc., so it will be necessary to continue to monitor it. Pierson and Brachczek (17), for example, find that the emission of Pb per gasoline-powered vehicle has dropped from about 17 mg/km in 1971 to 6 mg/km in 1979. Despite the changes, however, the data presented above are of considerable value, as several reliable, extensive data sets on urban particles taken during the mid-1970s are available. Receptor-model interpretations of these data sets have been only partially successful because of poor knowledge of the compositions of particles released from many important sources. As better information is becoming available on other components (e.g., ref 18), it is important that a reliable motor-vehicle component appropriate to that time be available.

Results of all studies of elements per se are not sufficient. Lead is the only strong marker element for the motor-vehicle component, and it is becoming less useful as leaded gasoline is phased out. Also, separate markers should be available for different types of vehicles, especially diesel- and gasoline-powered vehicles. Pierson and Brachczek (17) resolved these components, but only Ba emerges as a marker for diesels among the elements listed in Table III. It is an unsatisfactory marker as we do not know its origin on diesel-powered trucks, and size distributions indicate that the origin changed during the 1970s. Pierson and Brachczek (17) found that diesels contribute the major fractions of many elements of the motor-vehicle component, especially C, but for most of these, the total contributions of motor vehicles to urban atmospheres are so small that those elements could not serve as effective markers for diesels.

In conclusion, the search for elemental markers for motor-vehicle components has been done about as extensively as possible. In the absence of really satisfactory markers, a more fruitful approach for future studies would be detailed analysis of carbonaceous materials released, among which composition patterns may be found that can be unambiguously associated with diesels and with gasoline-powered vehicles, both leaded- and unleaded-gasoline burning.

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## Statistical Analysis of the Effect of Car Inspection and Maintenance Programs on the Ambient CO Concentrations in Oregon

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■ As mandated by the Clean Air Act Amendments several states have implemented car inspection and maintenance programs to reduce automobile emissions. This paper investigates the benefit of such a program on the ambient CO concentrations in Oregon.

### Introduction and Summary

A statistical analysis of carbon monoxide concentrations at five air-monitoring stations in the state of Oregon, covering the time span 1970-1979, is given. Four of the stations are located in Portland, where a car inspection and

maintenance (I/M) program has been in effect since July 1975. The remaining site is located in Eugene, which is not subject to this program.

A preliminary trend analysis of the ambient CO concentrations indicates reductions at all five locations. The average annual trend reductions at the Portland sites range from 3.4% to 7.3% and exceed the corresponding reduction at Eugene (1.9%).

Statistical models are constructed to determine how much of the reduction can be attributed to the progressively more stringent federal new-car-emissions standards and how much to the I/M program. Exogenous changes

Cars inspected (in thousands)

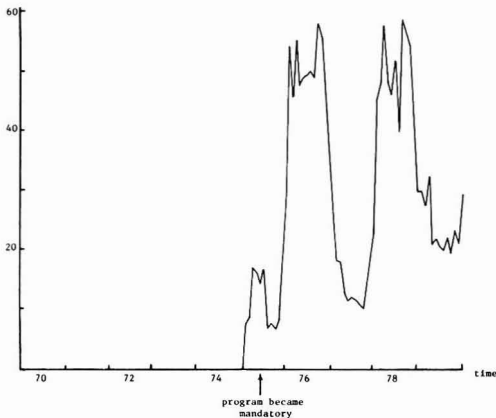


Figure 1. Monthly car inspections, Portland I/M program.

in traffic, meteorological conditions, and probe locations are factored into the analysis. A study of the diurnal patterns of CO, traffic, and various meteorological variables leads to the consideration of appropriate functional forms. The resulting models are then fitted to monthly CO averages from a Portland (CAMS) and the Eugene station. We find that the annual reduction attributable to the progressively more stringent federal emissions standards is approximately 5%. In addition we find evidence to indicate that the I/M program has had an additional beneficial effect in reducing the CO concentrations. The reduction ranges from 6% to 12% of what the CO levels would have been without the I/M program. Due to the biennial nature of the inspection program the benefits are highest in 1976 and 1978, years in which most of the cars are inspected.

A general discussion of I/M programs and a review of their effectiveness has recently been given by Elston (1). Additional empirical studies that discuss the impact of the New Jersey car-inspection program on ambient CO concentrations can be found in ref 2 and 3.

#### The Portland Car Inspection and Maintenance Program

The United States Clean Air Act Amendments require that states implement car inspection and maintenance (I/M) programs in certain of their major cities to reduce hydrocarbon (HC) and carbon monoxide (CO) emissions. In 1974 the state of Oregon initiated such a car inspection program within the boundaries of the Metropolitan District of Portland. This program became mandatory in July 1975. By state law, vehicles registered within this area must comply with the state HC and CO emissions standards and must obtain a certificate of compliance prior to registration renewal. Since, starting with 1974, car registrations in Oregon are valid for a 2-year period, the car inspection is required every other year. The monthly numbers of car inspections are shown in Figure 1. Due to the switch to a biennial registration system, more cars are inspected in even- than in odd-numbered years. Testing volume, however, will gradually stabilize, as the cars in the initial testing become a smaller part of the fleet. This is expected by the end of 1983. The failure rates among all inspections (initial and reinspection tests) have been roughly constant, ranging between 21% and 23%.

#### Carbon Monoxide Concentrations

The data consist of hourly CO concentrations recorded at four Portland sites and one Eugene site. The Portland measurement locations are at CAMS (at 718 West Burnside in downtown Portland), Alder (at the intersection of 4th and Alder), Hollywood (at the intersection of 41st and Sandy Blvd), and Lloyd Center (at 1420 NE Halsey). The Eugene station is at 11th and Willamette in downtown Eugene. It has been chosen as the control site, since cars in Eugene are not subject to the I/M program. Data on CO concentrations vary in length: CAMS (January 1970 to December 1979), Hollywood (January 1973 to December 1979), Alder (September 1975 to December 1979), Lloyd (November 1975 to December 1979), and Eugene (May 1971 to December 1979). Missing observations occur at all sites; this is worst at Eugene where several months of data are completely missing.

There were several changes in the location of the CO receptors during the time period under study. In particular, in August 1975 the CO probe at Eugene was lowered and moved closer toward the road; at CAMS the location of the receptor was changed in March 1978. In addition road construction at Burnside disrupted traffic throughout 1976.

#### Traffic

Previous studies (4-6) have shown that traffic is the primary source of CO emissions. Ideally our trend analysis should incorporate traffic data recorded in the immediate vicinity of the CO receptor. However, apart from a 14-month period (February 1978 to April 1979), for which hourly traffic counts at 11th and Willamette in Eugene are available, no such data could be obtained. Thus traffic data from other representative locations in the Portland and Eugene area had to be employed.

As traffic indicator for the Eugene location we use monthly averages of daily traffic counts recorded at the state-operated Franklin station at U.S. 99 Pacific Highway West, approximately 0.02 miles northwest of 11th Avenue. A previous analysis of overlapping traffic counts at the 11th and Willamette and the Franklin station has shown high correlation. As traffic indicator for the Portland carbon monoxide stations we use monthly averages of daily traffic counts on I-80N, Columbia River Highway at NE 21st Avenue. This highway is a major tributary to downtown Portland and should be representative of the downtown traffic.

#### Meteorological Variables

Apart from traffic, ambient CO concentrations are affected by meteorological conditions. Meteorological data from the Portland and Eugene airport on wind speed, wind direction, relative humidity, precipitation frequency, and temperature were obtained from the National Climatic Center (NCC) for the period 1970-1979. In addition to the NCC data, which are recorded every 3 h (starting at midnight), we also use in some of our analyses hourly windspeed and wind-direction data from a weather station in downtown Portland.

Previous studies on air-pollutant dispersion have shown that the vertical diffusion of CO depends on the inversion (or mixing) height (see ref 4, for example). Unfortunately mixing-height data are only available for Salem, OR, which is approximately 45 miles from Portland and 60 miles from Eugene. Daily morning and afternoon mixing heights for the 1970-1978 period have been obtained, even though it is questionable whether mixing heights at Salem are representative of mixing heights at Portland or Eugene.

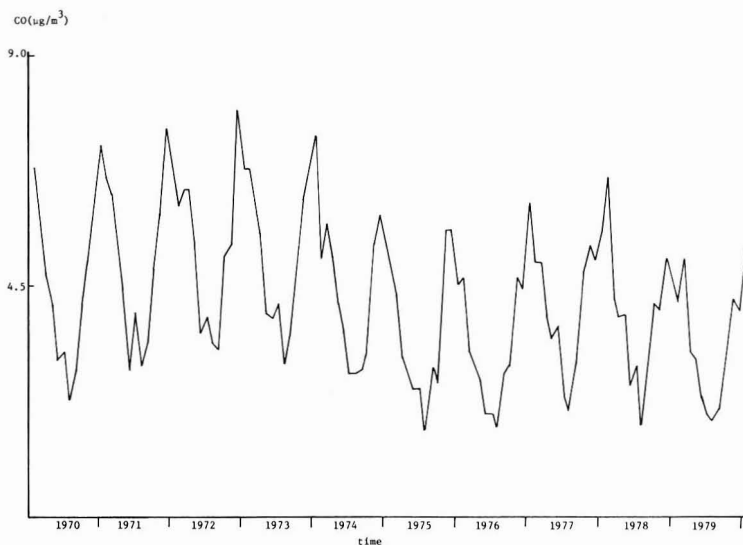


Figure 2. Plot of monthly [CO] averages (CAMS).

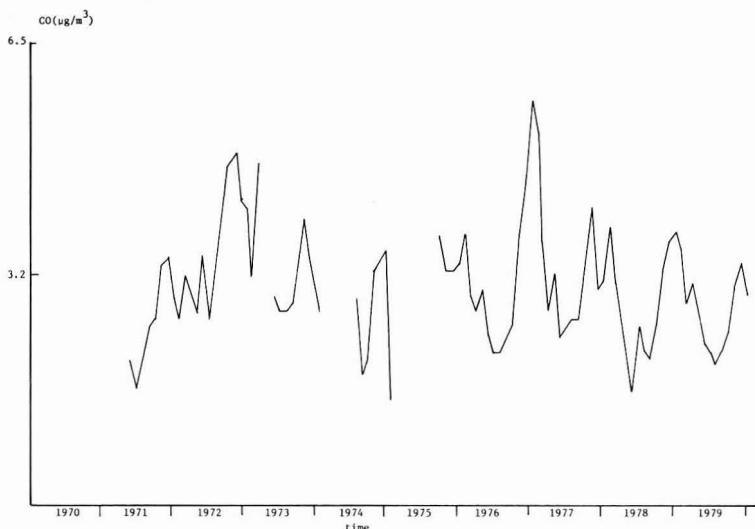


Figure 3. Plot of monthly [CO] averages (Eugene).

*Preliminary CO Trend Analysis*

A preliminary trend analysis of the CO data alone indicates that the concentration levels decreased at all five stations. During the period under study (1970–1979) the annual reductions of average CO are 3.4% at CAMS, 5.6% at Lloyd, 7.2% at Alder, 7.3% at Hollywood, and 1.9% at Eugene. The reduction at Eugene, the only station that is not in the I/M area, is much smaller than the corresponding reductions at Portland. However, one has to be cautious in attributing the full difference to the I/M program, since the probe change that occurred in Eugene in August 1975 and which moved the receptor closer toward the road could have also increased the Eugene CO concentrations.

In what follows, our analysis concentrates on CAMS and Eugene since these two sites have the longest data records.

Plots of monthly CO averages are given in Figures 2 (CAMS) and 3 (Eugene). A detailed description of the data at all five locations including tables and plots of monthly means and percentiles, diurnal diagrams of hourly averages separated according to day of week and season, and two-way tables of monthly averages of hourly CO concentrations are given in ref 7.

*Diurnal CO Models*

The diurnal models that are now developed serve to identify the main factors affecting CO concentrations and thus motivate the trend models considered in the next section of this paper.

We focus our attention on the Eugene station at 11th and Willamette and use data from the period March 1978 through January 1979, since hourly traffic counts are only

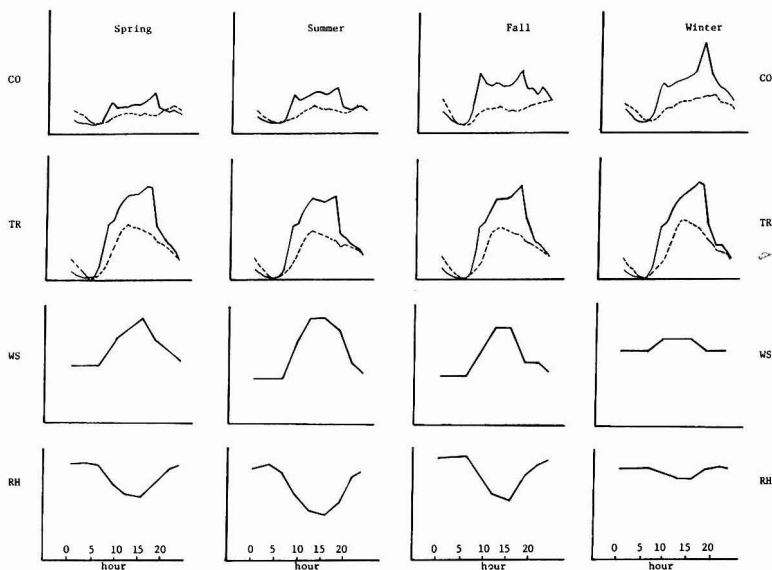


Figure 4. Diurnal diagrams of [CO], traffic TR, windspeed WS, and relative humidity RH for four seasons at Eugene: (—) weekday; (---) weekend.

available for this one station in this particular period. The data are first divided into four seasons: spring (March–May 1978), summer (June–August 1978), fall (September–November 1978) and winter (December 1978–January 1979). Plots of diurnal diagrams of the averages of CO, traffic counts (TR), windspeed (WS), and relative humidity (RH) for each of these seasons are given in Figure 4. Since there are differences between weekday (Monday–Friday) and weekend (Saturday, Sunday) traffic patterns, we have calculated weekday/weekend traffic and CO concentrations separately. The diurnal diagrams of the meteorological variables are obtained by linear interpolation of the averages which are calculated for every third hour.

Figure 4 shows that CO concentrations are approximately proportional to TR, implying a model of the form  $[CO]_t = \alpha + k(TR)_t + \epsilon_t$ , where  $t$  stands for the hour of the day,  $\epsilon_t$  is the error term, and  $\alpha$  and  $k$  are two parameters measuring, respectively, the background CO and the CO emissions. The scatter plots in Figure 5a–c illustrate the relationships between CO concentrations and the meteorological variables. Specifically, CO is plotted against WS in Figure 5a, mixing height MH in Figure 5b, and RH in Figure 5c. To keep traffic and seasonal effects constant, we consider only the afternoon (3–6 p.m.) weekdays of summer 1978. Large variability in the data would make it difficult to discern the relationships from scatterplots of the raw data. Thus the plots in these figures are constructed by first grouping the dependent variable [CO] according to nonoverlapping classes of the independent variable and then plotting the averages against each other. The class sizes are chosen such that each group has the same number of points. These plots show that [CO] decreases with increasing wind speed, increasing mixing height, and decreasing relative humidity. The inverse relationships between wind speed and CO concentration and between mixing height and CO concentration were expected, since these meteorological variables affect the vertical and horizontal diffusion of the pollutant. The positive association between relative humidity and [CO] can be explained by the fact that relative humidity acts as a proxy variable for air stability. Periods of low relative

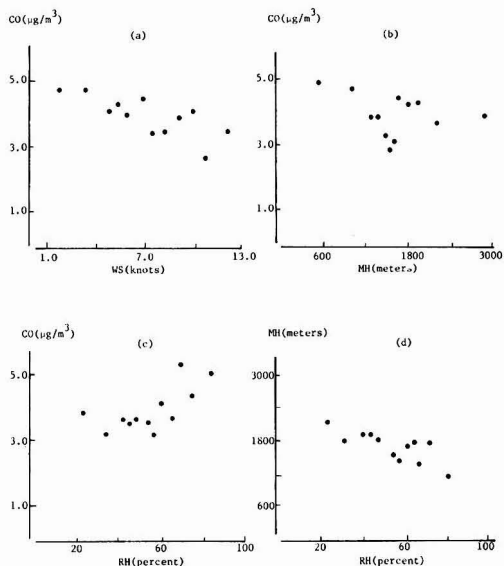


Figure 5. Plots of (a) [CO] vs. WS, (b) [CO] vs. MH, (c) [CO] vs. RH, (d) MH vs. RH; Eugene, summer 1978, weekday afternoon (3–6 p.m.).

humidity are usually associated with sunny periods and thus less stable air conditions. This in turn enhances the diffusion of CO and leads to lower CO concentrations. On the other hand, periods of high relative humidity are frequently associated with cloudy or foggy conditions; under stable air conditions the CO concentrations tend to be higher.

The scatter plot in Figure 5d also shows that relative humidity and mixing height are closely related. This indicates that relative humidity and mixing height act as proxy variables. Mixing-height data, however, could not be used in the diurnal models since only two measurements

**Table I. Root Mean Square Errors ( $\sigma$ ) for the Diurnal Models in Eq 1 Fitted to Eugene Carbon Monoxide Averages**

|        | M1       | M2    | M3    | M4    | M5    | M6    |
|--------|----------|-------|-------|-------|-------|-------|
| spring | WD 0.770 | 0.287 | 0.208 | 0.199 | 0.211 | 0.185 |
|        | WE 0.401 | 0.360 | 0.182 | 0.185 | 0.324 | 0.268 |
| summer | WD 1.019 | 0.219 | 0.164 | 0.148 | 0.230 | 0.257 |
|        | WE 0.433 | 0.204 | 0.095 | 0.088 | 0.115 | 0.154 |
| fall   | WD 1.430 | 0.663 | 0.485 | 0.514 | 0.454 | 0.420 |
|        | WE 0.617 | 0.519 | 0.300 | 0.331 | 0.418 | 0.350 |
| winter | WD 1.730 | 0.697 | 0.211 | 0.234 | 0.606 | 0.574 |
|        | WE 0.682 | 0.400 | 0.197 | 0.218 | 0.366 | 0.366 |
| av     | 0.885    | 0.419 | 0.230 | 0.240 | 0.340 | 0.322 |

were made each day. Thus our modeling concentrates on the relationships between CO and wind speed and relative humidity.

Figure 5 suggests several such models for relating the CO concentrations to traffic and the meteorological variables (eq 1, where  $\alpha$ ,  $k$ , and  $\delta$  are constants).

- M1:  $[CO]_t = \alpha + \epsilon_t$
- M2:  $[CO]_t = \alpha + k(TR)_t + \epsilon_t$
- M3:  $[CO]_t = \alpha + k(TR)_t / (WS)_t^\delta + \epsilon_t$
- M4:  $[CO]_t = (\alpha + k(TR)_t) / (WS)_t^\delta + \epsilon_t$
- M5:  $[CO]_t = \alpha + k(TR)_t(RH)_t + \epsilon_t$
- M6:  $[CO]_t = (\alpha + k(TR)_t)(RH)_t + \epsilon_t$  (1)

Model M1 is given mainly for comparison to evaluate the model improvements that are achieved by including traffic (model M2), and traffic and meteorological variables (models M3-M6). Model M2 relates CO to TR only; in models M3 and M4 the diffusion effect of WS is taken into account; models M5 and M6 express the effect of RH on CO. In models M4 and M6 the background  $\alpha$  is also diffused by the meteorological variables.

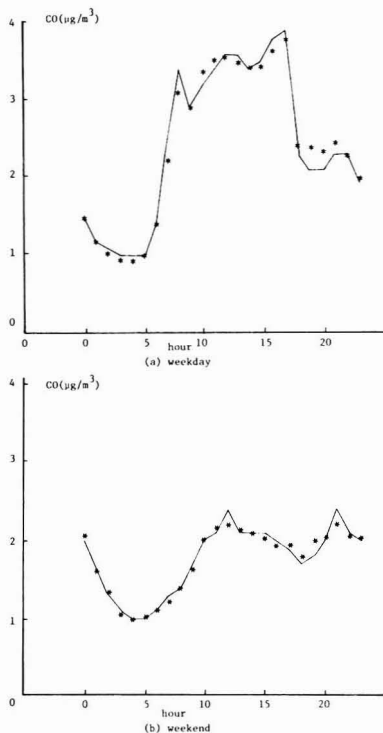
These models are fitted to hourly averages, separately for weekdays and weekends in each season. Least-squares estimates of the parameters and the mean square errors

$$\langle \sigma \rangle^2 = \frac{1}{24 - p} \sum_{t=1}^{24} ([CO]_t - \langle [CO]_t \rangle)^2$$

where  $p$  stands for the number of estimated parameters and  $\langle [CO]_t \rangle$  for the fitted value at hour  $t$ , are calculated. The root mean square errors ( $\sigma$ ) for these models are given in Table I. The results indicate that as expected traffic is the most important variable in explaining the variability in the CO concentrations. The inclusion of traffic reduces the average root mean square error by 52.7% (this corresponds to a coefficient of determination  $R^2 = 0.78$ ). In addition, the inclusion of windspeed and relative humidity leads to an appreciable further reduction in the root mean square error. On the average this additional reduction amounts to 44% for models M3 and M4 and 21% for models M5 and M6.

For the summer 1978 period, model M4 leads to the best fit. A plot of the observed  $[CO]_t$  values and fitted values  $\langle [CO]_t \rangle$  in Figure 6 illustrates the close agreement between them. The model is capable of tracking both weekday and weekend CO patterns; also the CO peak hours are modeled extremely well.

Various other models have been tried, including ones that use discounted traffic (see ref 4) and both windspeed and relative humidity. These models, however, did not lead to better fits.



**Figure 6. Observed (—) vs. predicted (\*) hourly [CO] averages. Model M4:  $[CO]_t = (\alpha + k(TR)_t) / (WS)_t^\delta + \epsilon_t$ ; Eugene, summer 1978.**

Apart from learning which variables affect the CO concentrations, one can use these models for a trend analysis provided detailed information on traffic is available. If hourly traffic counts for the period prior to March 1978 were available, one could calculate hourly weekday/weekend traffic averages for previous years, separated by season to adjust for seasonal differences. Then models of the form

$$[CO]_t^{i,s} = (\alpha + k_{i,s}(TR)_t^{i,s}) / ((WS)_t^{i,s})^\delta + \epsilon_t^{i,s} \quad (2)$$

could be fitted to averages of CO, traffic, and windspeed for season  $s$  of year  $i$ . The parameter  $k_{i,s}$  expresses the CO emission factor of season  $s$  in year  $i$ , after having accounted for possible changes in traffic and meteorological variables. Instead of using model M3, which incorporates windspeed, one could just as well have chosen models that include relative humidity (M5, M6) for such a trend analysis. We have used trend models similar to the one in eq 2 previously, when we analyzed the data from the Los Angeles catalyst study (3, 5, 6). In the present study, however, such an approach could not be used, since the traffic data for Portland and for Eugene prior to 1978 were available only as monthly averages of daily traffic counts and not at an hourly level.

#### A Trend Model for Monthly CO Averages

The reductions in the CO concentrations quoted earlier can be attributed to several factors.

(i) **Federal New-Car CO Emissions Standards.** During the last 10 years the federal CO emissions standards for new automobiles have become increasingly more stringent. For example, CO emissions are limited to 34



g/traveled mile for 1970-1971, to 28 g/mile for 1972-1974, and to 15 g/mile for 1975-1977 model-year cars. The effect of these changes on CO emissions  $k_t$  can be modeled as

$$k_t = ke^{\beta t} \quad (3)$$

where  $t$  stands for time (in months) and  $\beta < 0$  is a parameter controlling the reduction in the CO emissions. For example, a value of  $\beta = -0.005$  would translate into a monthly CO trend reduction of  $100(1 - e^\beta) = 0.5\%$ .

(ii) **Portland I/M Program.** This program is expected to lead to an additional reduction in the CO emissions. Previous studies by Becker and Rutherford (8) and Rutherford and Waring (9) have shown that the effect of car maintenance lasts approximately 9-12 months. Thus we use the discounted total number of car inspections

$$(I/M)_t^d = \sum_{j \geq 0} d^j (I/M)_{t-j} = (I/M)_t + d(I/M)_{t-1} + d^2(I/M)_{t-2} + \dots \quad (4)$$

where  $(I/M)_t$  stands for the number of inspections in month  $t$  (in thousands) and  $d$  is a constant between 0 and 1, and model the combined effect of the federal standards and the I/M program on the CO emissions as

$$k_t = ke^{\beta t}(1 + \theta(I/M)_t^d) \quad (5)$$

The parameter  $\theta$  measures the reduction that can be attributed to the I/M program. The discount coefficient  $d$  describes the immediate impact and the deterioration after car maintenance. A value  $d = 0$  means that the effect of the I/M program is immediate and loses its force after the first month. A value  $d = 1$  indicates that the effect of car maintenance is permanent. The value  $d = 0.7$  is chosen in our analysis. For this value the residual influence of inspections after 9 months becomes negligible.

The CO concentrations depend on the CO emissions, the traffic, and the meteorological conditions. The information gained from the diurnal models discussed in the preceding section leads us to consider models proportional to

$$[CO]_t \propto ke^{\beta t}(1 + \theta(I/M)_t^d)(TR)_t(RH)_t \quad (6)$$

Other models, including ones that incorporate windspeed (as in the diurnal models M3 and M4 in eq 1) and mixing heights, have also been considered and have led to similar conclusions (see ref 7).

In addition, probe changes and other exogenous interventions such as road construction near the receptor affect the CO concentrations. Time series intervention procedures (see ref 10) have proved useful in the context of assessing exogenous effects. To adjust for such effects, we use  $p$  indicator variables  $(IND)_{it}$  in

$$[CO]_t \propto ke^{\beta t}(1 + \theta(I/M)_t^d)(1 + \sum_{i=1}^p \alpha_i(IND)_{it})(TR)_t(RH)_t \quad (7)$$

These indicator variables take on the values 0 or 1 to signify the absence or presence of such interventions.

As illustrated in Figures 2 and 3, CO concentrations exhibit a strong seasonal pattern with high concentrations in the winter and low ones in the summer. This seasonal variation can be partially explained by changes in the meteorological variables. However, to adjust for any residual seasonal pattern that is not explained by relative humidity, we can make the emission constant  $k$  depend on the month and thus introduce 12 monthly seasonal coefficients  $k_s$  ( $s = 1, 2, \dots, 12$ ).

Furthermore, since the data on CO, traffic, and relative humidity are observed in the form of time series, the error or noise component (i.e., the CO component that is not

Table II. Parameter Estimates for CAMS Trend Model in Eq 8 (without Probe/Traffic Adjustments)<sup>a</sup>

| $10^{-4}k_s$ | $\beta$    | $\theta$   | $\phi$      |
|--------------|------------|------------|-------------|
| 1.06 (0.07)  | -0.004 09  | -0.001 06  | 0.19 (0.10) |
| 0.96 (0.07)  | (0.001 05) | (0.000 46) | 0.25 (0.10) |
| 0.84 (0.06)  |            |            | 0.29 (0.10) |
| 0.74 (0.06)  | -4.8%      | -12%       |             |
| 0.62 (0.06)  | (±1.2)     | (±5.2)     |             |
| 0.62 (0.06)  |            |            |             |
| 0.52 (0.06)  |            |            |             |
| 0.60 (0.06)  |            |            |             |
| 0.81 (0.06)  |            |            |             |
| 0.93 (0.06)  |            |            |             |
| 1.04 (0.07)  |            |            |             |
| 1.04 (0.07)  |            |            |             |

<sup>a</sup> Standard errors in parentheses.

explained by the model) is expected to be serially correlated. We characterize this serial correlation with a third-order autoregressive model. For a detailed discussion of such models, see ref 11.

The above considerations lead to the trend model

$$[CO]_t = k_s e^{\beta t}(1 + \theta(I/M)_t^d)(1 + \sum_{i=1}^p \alpha_i(IND)_{it})(TR)_t(RH)_t + n_t \quad (8)$$

where

$$n_t = \phi_1 n_{t-1} + \phi_2 n_{t-2} + \phi_3 n_{t-3} + \epsilon_t$$

and  $\epsilon_t$  are uncorrelated errors.

The parameters in eq 8 are estimated from monthly averages of CO, TR, and RH. A nonlinear least-squares routine (ZXSSQ of the IMSL library) is used in the estimation. The fitting results for CAMS and Eugene, the stations with the longest data records, are discussed below.

**Trend Analysis Results for CAMS.** At CAMS the location of the probe was moved in March 1978; furthermore during 1976 street construction disrupted traffic. To model these two interventions, we have specified two indicator variables: (i)  $(IND)_{i1} = 1$  for  $t \geq$  March 1978 and 0 otherwise; (ii)  $(IND)_{i2} = 1$  for January 1976  $\leq t \leq$  December 1976 and 0 otherwise. Since these interventions occur in even-numbered years, when most of the cars are inspected (1976, 1978), we expect a partial confounding of the effects of the I/M program and the two interventions. Therefore, the adjustment  $(1 + \alpha_1(IND)_{i1} + \alpha_2(IND)_{i2})$  will tend to reduce the significance of the I/M program.

The model in eq 8 is fitted with and without this adjustment; the estimates and their standard errors are given in Table II (without probe change adjustment) and Table III (with probe change adjustment). From Table II we find the trend estimate  $(\beta) = -0.00409$ . This implies an estimated annual reduction attributable to the progressively more stringent federal standards of  $100(1 - e^{12\beta}) = 4.8\%$ . Note that this percentage figure expresses the reduction in CO concentrations when traffic and meteorological conditions are kept constant. Since during the 1970-1979 period Portland traffic has increased at an annual rate of 1.4%, this reduction is larger than the one reported in our preliminary trend analysis of CO concentrations.

The estimate  $(\theta) = -0.00106$  indicates that the I/M program has led to an additional reduction of approximately 12% of what the CO levels would have been without this program (i.e.,  $100(\theta)I/M^d = 100(-0.00106)113 = -12$ , where  $I/M^d = 113$  is the average of the discounted inspection numbers). The estimated standard error

**Table III. Parameter Estimates for CAMS Trend Model in Eq 8 (with Probe/Traffic Adjustments)<sup>a</sup>**

| $10^{-4}k_s$ | $\beta$    | $\theta$    | $\alpha_1$ | $\alpha_2$ | $\phi$      |
|--------------|------------|-------------|------------|------------|-------------|
| 1.07 (0.07)  | -0.004 25  | -0.000 540  | -0.060     | -0.084     | 0.15 (0.10) |
| 0.96 (0.07)  | (0.001 15) | (0.000 677) | (0.079)    | (0.069)    | 0.26 (0.10) |
| 0.84 (0.06)  |            |             |            |            | 0.31 (0.10) |
| 0.74 (0.06)  | -5.0%      | -6.1%       |            |            |             |
| 0.62 (0.06)  | (±1.4)     | (±7.7)      |            |            |             |
| 0.62 (0.06)  |            |             |            |            |             |
| 0.52 (0.06)  |            |             |            |            |             |
| 0.61 (0.06)  |            |             |            |            |             |
| 0.81 (0.06)  |            |             |            |            |             |
| 0.93 (0.06)  |            |             |            |            |             |
| 1.05 (0.07)  |            |             |            |            |             |
| 1.05 (0.07)  |            |             |            |            |             |

<sup>a</sup> Standard errors in parentheses.

**Table IV. Additional Percentage Benefit for Fleet due to the I/M Program (Portland)**

| year           | $\overline{I/M}^d$ | additional % benefit due to I/M   |                                |
|----------------|--------------------|-----------------------------------|--------------------------------|
|                |                    | without probe/traffic adjustments | with probe/traffic adjustments |
| 1975           | 32.5               | 3.5                               | 1.8                            |
| 1976           | 145.8              | 15.5                              | 7.9                            |
| 1977           | 68.8               | 7.3                               | 3.7                            |
| 1978           | 143.7              | 15.2                              | 7.8                            |
| 1979           | 91.9               | 9.7                               | 5.0                            |
| av (1976-1979) |                    | 11.9                              | 6.1                            |

**Table V. Parameter Estimates for Eugene Trend Model in Eq 8**

| model | $\beta$                 | $\theta$                 | $\alpha$         | $\sigma$ |
|-------|-------------------------|--------------------------|------------------|----------|
| E1    | -0.002 01<br>(0.001 60) |                          |                  | 0.631    |
| E2    | -0.003 20<br>(0.002 55) | 0.000 843<br>(0.001 327) |                  | 0.633    |
| E3    | -0.004 65<br>(0.002 90) |                          | 0.206<br>(0.198) | 0.629    |
| E4    | -0.004 87<br>(0.003 34) | 0.000 330<br>(0.001 385) | 0.194<br>(0.220) | 0.634    |

interventions has reduced the estimated effect of the I/M program. Yearly percentage benefits are given in Table IV, showing that the I/M benefit is cut in half; the average benefit is estimated at 6.1%.

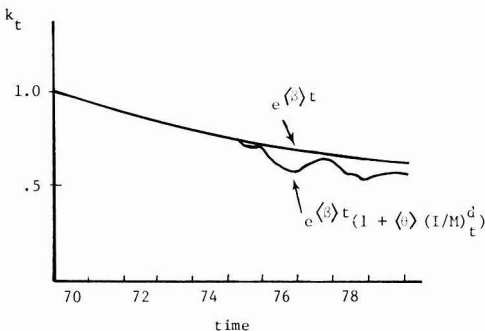
Since probe and traffic changes occurred during periods of high inspection volume, it is somewhat difficult to separate the effects of the car inspection program from those of probe changes. For this reason we have stated our conclusions in terms of two different I/M benefit estimates. These numbers, which were derived from models with and without probe/traffic adjustments, can be interpreted as the lower and the upper bound of the percentage effect of the Portland car inspection and maintenance program.

**Trend Analysis Results for Eugene.** Since at Eugene several months of data are completely missing, we have adopted a two-stage estimation approach. Initially the model in eq 8 is fitted by assuming independent errors ( $n_t = \epsilon_t$ ). The missing observations are then replaced by the fitted values and the complete model is reestimated.

We introduce an indicator (IND)<sub>t</sub> ((IND)<sub>t</sub> = 1 for  $t >$  August 1975 and 0 otherwise) to account for the probe change in August 1975. The monthly [CO] averages in Figure 3 show that the [CO] reduction is rather small if the probe change is ignored (1.9% as reported earlier). Taking the probe change into account, however, one can expect a larger trend reduction.

In the estimation of the model in eq 8 the Portland car inspection volume is used. Since the I/M program is restricted to the Portland area, we expect that only a small fraction of the inspected cars will ever come to Eugene. Therefore the I/M impact should be negligible, and the coefficient  $\theta$  should be 0.

The estimation results are given in Table V; only estimates pertinent to the trend analysis are reported. We find that, as expected, the parameter estimate of  $\theta$  for the I/M program is insignificant. If the probe change is ignored (model E1) the trend parameter is estimated as  $\langle \beta \rangle = -0.00201$ , which implies an annual reduction of 2.4%. Model E3 indicates that the probe change has led to in-



**Figure 7.** Plot of the estimated emissions constant  $e^{(\beta)t}(1 + \langle \theta \rangle (I/M)_t^d$  using parameter estimates given in Table II.

0.00046 in parentheses indicates that the I/M effect is statistically significant at the 5% level. A plot of the trend predicted by the model in Table II is given in Figure 7. The area between the curves  $e^{(\beta)t}$  and  $e^{(\beta)t}(1 + \langle \theta \rangle (I/M)_t^d$  represents the additional benefit that can be attributed to the inspection program. The annual percentage benefits are also calculated and are given in Table IV. Over the period 1976-1979, the average additional benefit is 11.9%. Different discount coefficients have also been tried and have led to the same overall I/M benefit. For example, the model with  $d = 0.9$  results in estimated annual percentage benefits of 2.0% in 1975, 10.2% in 1976, 9.7% in 1977, 12.3% in 1978, and 11.7% in 1979. While the pattern of the yearly benefits becomes smoother, the conclusions about the average I/M benefit are about the same.

The estimation results for the model in eq 8, when adjusting for the probe change and traffic disruption, are given in Table III. As expected, the inclusion of these two

increases in the CO concentrations. Adjusting for the probe change leads to a trend estimate ( $\beta$ ) = -0.00465. This implies an annual trend reduction of 5.4% attributable to federal standards and is in close agreement with the estimated trend reduction of 4.8% at CAMS.

*Concluding Remarks*

The empirical analysis of monthly CO averages at CAMS and at the control site in Eugene shows a reduction in CO concentrations that can be associated with the I/M program. The estimated benefit ranges between 6% and 12%.

In a more detailed report (7) results are obtained for an analysis of CO concentrations during peak periods (6-9 a.m. and 3-6 p.m.). A linear regression analysis of daily peak hour CO concentrations with traffic and meteorological conditions as exogeneous variables has lead to an estimated I/M benefit ranging between 8% and 15%. This is in good agreement with the findings based on the models for the monthly means.

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## Rapid Determination of Algal Chlorophyll by Gas-Liquid Chromatography

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■ A gas-liquid chromatography (GLC) procedure for algal chlorophyll quantitation has been described and evaluated. Following concentration of algae by filtration, cells were washed with a small amount of hexane (saturated with acetonitrile) and saponified in methanolic sodium hydroxide to release the phytol moiety, which was recovered by hexane extraction. GLC analysis was performed by flame ionization at 185 °C using a glass column containing 3% OV-225 coated Chromosorb Q (AW/DMCS, 60-80 mesh). Solutions of commercially available chlorophyll *a* and *b*, a unialgal culture of *Chlorella vulgaris*, and field samples were analyzed by the GLC method, and the results closely approximate those obtained by spectrophotometric analysis. The presence of chlorophyll degradation products, carotenoid pigments, and a number of terpene alcohols in the water samples did not interfere with the GLC analysis. With this procedure, the analytical time can be reduced to less than 1 h from the 18-20 h usually required.

*Introduction*

The rapid increase of algal populations in response to nutrient enrichment suggests that these microorganisms can be used as indicators of water pollution by sewage and/or agricultural runoff. The living phytoplankton biomass and productivity of aquatic environment are generally determined by spectrophotometric (1, 2) or fluorometric (3-5) measurement of algal chlorophyll *a* (*Ca*) content. It has been demonstrated that certain chlorophyll degradation products (chlorophyllides and pheophorbides) and carotenoid pigments (anthraxanthin, diadinoxanthin, violaxanthin, and fucoxanthin) may cause significant errors in the spectrophotometric estimation of *Ca* (6-11). The accuracy of the fluorescence method, on the other hand,

depends on the absence of chlorophyll *b* (*Cb*) (12, 13). Assessment of algal pigments with this technique is based on the assumptions that green algae that contain *Cb* (chlorophytes, prasinophytes, and englenophytes) are absent in the oceanic environment (13) or that they only cause a negligible interference in a taxonomically diverse population due to their low numbers (1). Using thin-layer chromatography (TLC), Jeffrey (12) was able to demonstrate that significant proportions of *Cb* are present in pigment extracts obtained from the Central North Pacific Ocean. Furthermore, this chlorophyll has been shown to occur through most of the euphotic zone down to 200 m. Such findings would cast serious doubts on the precision of the fluorometric technique for algal *Ca* determination.

This report details a gas-liquid chromatographic (GLC) analysis of phytol for the accurate measurement of algal photosynthetic pigments (*Ca* + *Cb*). With this procedure a more rapid and precise assessment of algal chlorophyll can be achieved.

*Materials and Methods*

**Reference Chemicals.** *Ca* (99% pure), *Cb*,  $\alpha$ - and  $\beta$ -carotene, xanthophylls, chlorophyllin, phytol and a number of terpene alcohols (Sigma Chemical Co., St. Louis, MO), pheophytin *a* and *b* (*Pa* and *Pb*; prepared from *Ca* and *Cb*, respectively, by acidification), unialgal cultures of *Chlorella vulgaris* (Carolina Biological Supply Co., Burlington, NC), and algae isolated from freshwater samples were used to evaluate the efficacy of the proposed procedure.

**Cleanup of Chemical Impurities in Solvents and Glassware.** Hexane and methanol were redistilled prior to use. All glassware was rinsed with redistilled hexane.

These cleanup steps were necessary because it was determined that solvents and glassware obtained from certain suppliers contained chemical residues that interfered with the GLC analysis.

**Spectrophotometric Measurement of Algal Chlorophyll.** A double-beam spectrophotometer (Model 200, Perkin-Elmer, Norwalk, CN) was used. Pigments were analyzed both with the acidification technique (1) and the trichromatic method (2).

**GLC Analysis of Phytol.** A Perkin-Elmer 900 gas chromatograph equipped with flame ionization detectors and a 1.43 m  $\times$  0.2 cm i.d. glass column packed with 3% OV-225 coated Chromosorb Q (AW/DMCS, 60–80 mesh, Applied Laboratory, Inc., State College, PA) was used for phytol analysis. The column temperature was 185 °C, the injection port and detector temperature were maintained at 250 °C, and flow rates of nitrogen carrier gas, hydrogen gas to the detector, and the air were kept at 35–40 mL/min.

Phytol was identified and quantified by comparing the retention time and peak area with those of the reference standard.

### Experimental Section

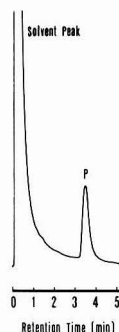
So that the feasibility of quantitating Ca and Cb by GLC analysis of their phytol fraction could be determined, benzene solutions of Ca, Cb, and various mixtures of Ca and Cb were each distributed equally to two series of vials. One series was analyzed spectrophotometrically, the other by GLC assessment.

GLC analysis for pigment determination was also evaluated by using a unialgal culture of *Chlorella vulgaris* and freshwater samples containing mixed populations of algae. Again, each sample was divided into two equal aliquots. Pigments of one aliquot were extracted by the 90% aqueous acetone procedure (14) or the XAD-1 column method (15) and analyzed spectrophotometrically. Chlorophyll (Ca + Cb) contents of the other aliquot were determined by GLC quantitation of phytol.

Concentration of phytoplankton was accomplished by filtering the samples (5–500 mL) through Whatman (G.F.) glass-fiber filters (2.4 and 4.5 cm diameter, depending on the volume of sample) under negative pressure. Cells collected on the filter were washed with 3–4 mL of hexane (saturated with acetonitrile) to remove possible nonpolar contaminants. To release phytol from its parent molecules, samples were saponified in 2–3 mL of 3% NaOH in 90% aqueous methanol at 80 °C for 10–15 min in a screw-capped vial. A Teflon liner was inserted to the cap to reduce solvent evaporation. Following addition of approximately 0.5 mL of water, the phytol moiety was recovered by extracting the saponified solution with 1 mL of hexane (two times). The hexane layer was transferred to another small screw-capped vial by careful aspiration. The combined hexane solution was then brought to dryness under a stream of nitrogen. Residues were redissolved in 50–100  $\mu$ L of hexane and used for GLC analysis.

### Results

**Alkaline Hydrolysis of Various Plant Pigments.** It has been reported that phytol, a diterpene alcohol, can be easily removed from its parent compound by mild alkaline hydrolysis (16, 17). Experiments, carried out to determine the optimal conditions for such a hydrolysis, demonstrated that maximum amounts of phytol were obtained by saponification in 3% NaOH in 90% aqueous methanol at 80 °C for 10 min. Increasing the NaOH concentration or the saponification time up to 10% and 30 min, respectively,



**Figure 1.** Gas chromatogram of phytol obtained from methanolic sodium hydrolysis of chlorophyll a. A glass column (1.43 m  $\times$  0.2 cm i.d.) containing 3% OV-225 coated Chromosorb Q (AW/DMCS, 60–80 mesh) was used. The column temperature and the temperature of injection port and detector were maintained at 185 and 250 °C, respectively. Gas flow rates were kept at 35–40 mL/min. A flame ionization detector was used.

**Table I.** Comparison of Quantities of Chlorophyll a as Measured by Spectrophotometric (Acidification Method) Analysis and by Gas-Liquid Chromatographic (GLC) Analysis of Phytol

| pigment soln, $\mu$ L | chlorophyll a, $\mu$ g |       |
|-----------------------|------------------------|-------|
|                       | spectrophotometric     | GLC   |
| 20                    | 1.68                   | 1.81  |
| 40                    | 3.45                   | 3.63  |
| 60                    | 5.29                   | 5.45  |
| 80                    | 6.98                   | 6.52  |
| 100                   | 8.66                   | 9.09  |
| 150                   | 13.15                  | 12.71 |
| 200                   | 17.64                  | 17.12 |
| 250                   | 21.89                  | 22.72 |

did not significantly affect the quantity of phytol recovered.

When phytol, Ca, Cb, Pa, Pb, chlorophyllin,  $\alpha$ - and  $\beta$ -carotene, xanthophylls, farnesol, geraniol, nerolidol, squalene, and nonadecanol were subjected to alkaline hydrolysis, GLC analysis indicated that phytol (and/or compounds having the same retention time) was detected only in the first five compounds.

**Gas-Liquid Chromatographic Analysis of Phytol.** Phytol can be satisfactorily chromatographed at 185–190 °C on the previously described column. Lowering temperatures and/or increasing the liquid phase loading or the column length resulted in a longer retention time and widening of the phytol peak.

When a series of phytol references ranging from 0.01 to 1.0  $\mu$ g was chromatographed at different attenuation ranges, linear relationships between the gas chromatographic peak areas and the quantities of phytol were observed.

A more accurate quantitation was achieved upon adjustment of the chromatograph attenuation range so that the phytol peak areas were within 1–3 cm<sup>2</sup>.

A typical gas chromatogram of phytol recovered from the methanolic sodium hydrolysis of Ca (Figure 1) indicates that the phytol peak (P) is not accompanied by detectable decomposition products. Similar chromatograms were obtained when commercial phytol and hexane extracts of saponified unialgal culture and freshwater samples containing mixed algal populations were analyzed.

Data presented in Table I indicate that the concentrations of Ca as measured by GLC analysis of phytol closely

Table II. *Chlorella vulgaris* Pigment Analysis

| vol of sample, mL | spectrophotometric analysis, <sup>a</sup> $\mu\text{g}$ |      |         | GLC, <sup>b</sup> $\mu\text{g}$ |
|-------------------|---|------|---------|---------------------------------|
|                   | Ca  | Cb   | Ca + Cb |                                 |
| 0.3               | 2.77  | 1.27 | 4.04    | 3.18                            |
| 0.5               | 3.89  | 1.79 | 5.68    | 5.08                            |
| 1.0               | 7.55  | 3.03 | 10.58   | 9.09                            |
| 1.5               | 10.49   | 4.82 | 15.31   | 15.15                           |
| 2.0               | 14.15   | 5.18 | 19.33   | 20.83                           |
| 2.5               | 17.16   | 5.86 | 23.02   | 24.85                           |

<sup>a</sup> Trichromatic method. <sup>b</sup> Phytol-containing pigments including chlorophyll *a* and *b*.

Table III. Comparison of Spectrophotometric and GLC Analyses of Chlorophyll Pigments from Fresh Water Samples

| water sample <sup>a</sup> | spectrophotometric ( $\mu\text{g}$ ) |      |         | GLC, <sup>b</sup> $\mu\text{g}$ |
|---------------------------|--------------------------------------|------|---------|---------------------------------|
|                           | Ca                                   | Cb   | Ca + Cb |                                 |
| 1                         | 8.42                                 | 1.85 | 10.26   | 10.08                           |
| 2                         | 3.80                                 | 4.21 | 8.01    | 7.98                            |
| 3                         | 0.94 (0.72)                          | 0.38 | 1.32    | 1.62                            |
| 4                         | 1.97 (1.76)                          | 0.77 | 2.74    | 2.58                            |
| 5                         | 2.90 (2.73)                          | 1.13 | 4.03    | 3.79                            |
| 6                         | 4.95 (4.57)                          | 1.32 | 6.27    | 7.12                            |

<sup>a</sup> Water samples 1, 2, and 3-6 were obtained from eutrophic and mesotrophic water bodies and fish tanks in our laboratory, respectively. Major species of algae in sample 1 were *chlamydomonas* spp., *Ankistrodesmus* spp.; those in sample 2 were not determined. The fish-tank samples contain mainly *Chlorella* spp. Volumes of sample used ranged from 5 to 500 mL. Both the trichromatic method and the acidification technique (values shown in parentheses) were employed. <sup>b</sup> Phytol-containing pigments.

approximate those from spectrophotometric estimation. Comparable results were also observed when Cb was used. From employment of mixtures of predetermined amounts of commercially available Ca and Cb, it was found that the values of photosynthetic pigment calculated from the GLC quantitation of phytol are closely equivalent to the sum totals of Ca and Cb. Similar results were obtained with unialgal culture of *Chlorella vulgaris* (Table II).

So that the feasibility of this GLC procedure for algal chlorophyll quantitation could be further ascertained, algae isolated from eutrophic and mesotrophic water bodies and samples from fish tanks in our laboratory were analyzed. It was found that chlorophyll contents as determined by the GLC method correspond to those of Ca + Cb as measured by spectrophotometric estimation (Table III).

It is conceivable that pheophytin and phytol, when present in substantial quantities, may interfere with the GLC assessment of chlorophyll. Overestimation of the chlorophyll contents was indeed observed when the hexane-washing step was omitted in experiments where 1-5  $\mu\text{g}$  of these degradation compounds was mixed into the testing samples. Such interferences, however, disappeared when the hexane cleanup process was reinserted into the GLC procedure. Whether a similar removal of these chlorophyll-degradation products in deep-water and estuary samples can be achieved has not been determined. Judging from the results of freshwater samples analyzed in this study, it appears that either significant amounts of these compounds were removed by the hexane-washing step, or conversely, most of the pheopigments in phytoplankton samples are non-phytol-containing double-degradation products that do not interfere with the GLC

estimation (12, 18). Nevertheless, this hexane-washing step is necessary to remove certain unidentified nonpolar compounds that have been shown to interfere with the subsequent GLC analysis.

### Discussion

Phytol (3,7,11,15-tetramethyl-2-hexadecen-1-ol) was first described by Willstatter and Hocheder (19) as the alcoholic moiety of the chlorophyll molecule. This long-chain alcohol comprises approximately one-third of the molecular weight of chlorophyll *a* and *b* and pheophytin *a* and *b*. Interest in the formation of this diterpene alcohol and its role in the biosynthesis of chlorophyll has led to a number of studies in the identification and quantitative determination of this compound (17, 20-24).

Of the various analytical methods, GLC appears to be most sensitive for the measurement of this long-chain alcohol. The existing GLC analyses, however, are considered unsatisfactory due to the possible pyrolysis of this monounsaturated alcohol, the transientness of the column, and/or the lengthy analysis time required (20-25 min). In this study, it was determined that columns employing a moderately polar compound, OV-225 (25% cyanopropyl, 25% phenyl, and 50% methyl silicone) as the stationary phase was suitable for the identification and quantitation of phytol. The retention time of phytol is approximately 3-4 min. The stability of the column is evident by the unaltered resolution after using the column daily for several months. Results of this study have indicated that phytol can be gas chromatographed under the experimental conditions without thermal decomposition. Furthermore, the sensitivity of this GLC analysis has been shown to be comparable to or better than those reported thus far.

Although actively growing phytoplankton populations generally contain no demonstrable pheopigments, significant amounts of these compounds have been detected in natural algal samples (1, 8, 9, 12, 18). It is suggested that decaying algal cells in mud particles adhering to the living organisms are responsible for the presence of these degradation products (8). It has been determined that the main components of these pheopigments consist of chlorophyllides and pheophorbides which are devoid of the phytol moiety (18). Thus, their presence would not interfere with the GLC quantitation of the algal photosynthetic pigments. Pa, a phytol-containing compound that has been regarded as one of the major chlorophyll degradation products (14), was found only in trace quantities (12, 18). Phytol, when present, may constitute a major source of interference in the GLC analysis. Although high concentrations of free phytol have been detected in the lake-sediment samples, no appreciable amounts of this long-chain alcohol were found in phytoplankton pigment extracts (25). Furthermore, among other nonpolar compounds, this diterpene alcohol, together with pheophytins, may be removed from samples by hexane washing. Saturating the hexane with acetonitrile facilitates the cleanup process. Though the actual mechanism has not been determined, it is possible that acetonitrile may render the chlorophyll degradation products, trapped in the interior of the cell mass and/or shielded inside the aqueous envelopment of the cells, more accessible to the action of hexane due to its miscibility with both water and hexane.

With this new GLC procedure, the extraction of algal pigments is not necessary, and the intact cells are subjected to saponification. Since phytol obtained from Ca is identical with that from Cb, values of chlorophyll computed from the phytol analyses represent the sum of Ca

+ *Cb*. If the chlorophyll content measured by this method is used as "*Ca*" for algal biomass assessment, the presence of *Cb* would undoubtedly result in an overestimation. Certain adjustment in the equation for biomass calculation is thus necessary. This may be expedited by a simple microscopic examination to determine the percentage of *Cb*-containing algal species in the total population. Since the ratio of *Ca* to *Cb* in these algae is usually a constant (6), this percentage can be applied to the computation of the actual biomass. If the occurrence of *Cb* is indeed widespread in the marine environment, it might be more desirable to include this pigment in the algal chlorophyll assessment than falsely measuring it as a pheopigment, resulting in "grossly exaggerating the pheopigment value" (18) and an underestimation of the *Ca* (4, 13, 18).

The most outstanding feature of this new procedure is its rapidity in the analysis. By omission of the maceration and replacing the time-consuming solvent extraction processes with simple alkaline methanolic saponification and hexane liquid-liquid partitioning to obtain the released phytol, the analytical time is reduced from its usual 18–20 h to within 1 h. Omission of the cell maceration, required in the routine procedure for complete pigment extraction, avoids the possible breakdown of the light-sensitive, heat-labile *Ca* molecules. It is also less tedious, especially in situations where a large number of samples have to be processed. Furthermore, it has been found that following filtration and hexane cleanup, algal samples can be stored at –4 °C for 2 weeks prior to the GLC quantitation without affecting the analyses. The value of this procedure is evident in field studies where immediate analysis is often not feasible. Finally, this procedure can be employed for a more precise determination of *Ca* in research studies in which unialgal cultures and/or mixtures of known algae are tested.

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## Comparison of the Reaction of Aqueous Free Chlorine with Phenolic Acids in Solution and Adsorbed on Granular Activated Carbon

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■ The reaction of aqueous free chlorine with three phenolic acids was examined before and after adsorption on granular activated carbon. Organic products were extracted from aqueous solution and off the carbon surface and analyzed by using gas chromatography/mass spectrometry. Complex reaction products and incomplete separations warranted the selection of a single compound, vanillic acid, for further study. Many products were formed on the carbon that were not present in the influent to the column. These products included several polyphenols and hydroxylated quinones that were tentatively identified from their methylated and silylated derivatives. The environmental significance of these reactions is discussed.

### Introduction

Activated carbon, both powdered and granular, is frequently contacted by both organic compounds and residual chlorine when it is used in water treatment. Carbon is an effective adsorbent of trace organic substances and is also a very effective reductant of free and combined chlorine. Although much work has been devoted to these separate roles of carbon, little attention has been given to studying the combined effects of chlorination and adsorption. For example, chlorine may react with organic compounds adsorbed on carbon to produce compounds not normally found in aqueous chlorination reactions. It has been shown that activated carbon can promote many kinds of reactions including redox processes (1-3), peroxide decomposition (4), substitution (5), racemization (6), and cis-trans isomerization (7). The possibility that carbon may also participate in the reactions of organic compounds with chlorine formed the basis of this study.

It has been shown in previously reported work that the reaction of chlorine with activated carbon produced a mixture of polymeric, brown-black colored products and volatile organic compounds at very high chlorine concentrations [in excess of 2 g of free chlorine reacted as  $Cl_2/g$  of carbon (8)]. The harsh conditions required to produce these compounds led to the conclusion that such reactions would not occur to a significant extent in drinking-water treatment facilities. This work was followed by an analysis of the reaction of chlorine with humic substances adsorbed on the activated carbon surface (9). A total organic halogen (TOX) mass balance was used to demonstrate that the reaction of chlorine with adsorbed humic material did not produce large quantities of halogenated compounds. However, extraction and analysis using GC/MS of the influent to the column and the activated carbon showed several dihydroxy and chlorinated dihydroxybenzenes on the carbon that were not present in the influent.

A major disadvantage of humic acid as a model compound was the fact that very few reaction products could be characterized. The TOX that could be accounted for in identified products in these experiments was less than

8%; most of the chlorine was bound to large humic molecules that were not sufficiently volatile to be analyzed by gas chromatography.

This paper reports the results of a similar series of reactions in which phenolic acids were used in place of the humic acid. Three compounds, *p*-hydroxybenzoic acid, vanillic acid, and syringic acid were applied to activated carbon together with chlorine. These compounds were selected because they are constituents of natural waters (10-12), are structural breakdown products of humic acid (13), and were shown to be chlorinated in aqueous solution to products readily analyzed with gas chromatography (14, 15).

### Materials and Methods

The carbon used in all experiments was a bituminous base granular activated carbon (GAC) (F-400, Calgon Corp., Pittsburgh, PA). The carbon was prepared by sieving, washing, and drying at 175 °C for 1 week to eliminate volatile compounds as previously described (8).

The phenolic acids *p*-hydroxybenzoic acid (Aldrich Chemical Co., Milwaukee, WI), vanillic acid (3-methoxy-4-hydroxybenzoic acid) (Sigma Chemical Co., St. Louis, MO), and syringic acid (4-hydroxy-3,5-dimethoxybenzoic acid) (Aldrich Chemical Co., Milwaukee, WI) were used without further purification. Solutions were prepared by dissolving carefully weighed quantities of each acid into 500 mL of distilled water made alkaline with several pellets of NaOH. This solution was then added to a carboy containing 45 L of distilled, deionized water buffered with 0.001 M phosphate to pH 6.0. The carboy was capped with aluminum foil and covered with dark plastic.

Chlorine stock solution was prepared by bubbling high-purity chlorine gas (Linde Specialty Gas, Union Carbide, New York) into distilled, deionized water made alkaline with several grams of NaOH/L. The concentration was determined with the DPD procedure (16). Chlorine solution for the column runs was prepared by diluting the stock solution in distilled, deionized water buffered to pH 6 with 0.001 M phosphate. The solution bottle was covered with dark plastic and capped with aluminum over a Teflon seal.

Total organic halogen (TOX) was determined by combusting carbon that had been washed with nitrate solution. The halides liberated during the combustion were measured with a digital microcoulometer (Model C-300, Dohrmann Envirotech, Santa Clara, CA).

**Column and Reactor Configurations.** The carbon bed (Figure 1) was identical with that described in previous works (9). The upflow column was constructed of glass, Teflon, and stainless steel parts. The flow rate for each column was 76.3 L/(m<sup>2</sup> h) (1.87 gpm/ft<sup>2</sup>), and the empty bed contact time was 5.0 min. There was a short time ( $t_1$ ) during which the chlorine and organic compounds reacted before coming into contact with the carbon. In addition to the carbon column, a reactor column containing only glass wool was used which had a contact time of  $t_1$ ; therefore, effluent from this column had a composition identical with that of the solution applied to the carbon.

**Extraction Procedures and GC/MS Analysis.** Ten-liter samples of effluent were acidified to pH 1 with

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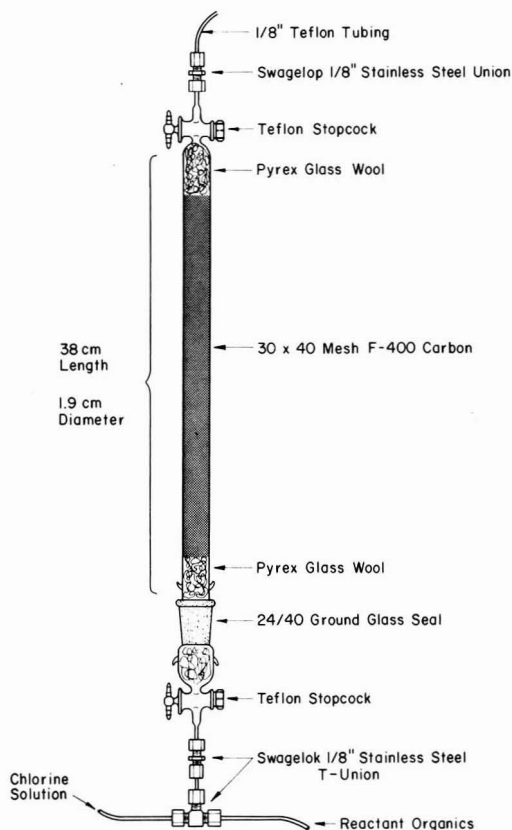


Figure 1. Carbon column configuration.

nitric acid and pumped through XAD-2 macroreticular resin (Rohm and Haas, Philadelphia, PA). The resin was then eluted with 2 mL of methanol followed by 75 mL of methylene chloride (Burdick and Jackson, distilled in glass, Muskegon, MI). Samples (1–2 g) of carbon were removed from the GAC columns, centrifuged, and Soxhlet extracted with methanol–methylene chloride for 24 h.

The concentrated extracts were either methylated with diazomethane generated from Diazald (Aldrich Chemical Co., Milwaukee, WI) or silylated with bis(trimethylsilyl)-trifluoroacetamide (BSTFA, Supelco, Bellefonte, PA). The extracts were then injected into a GC/MS (Hewlett-Packard 5985A, Avondale, PA). Further details of the extraction and identification procedures are given in a previous paper (9).

### Results and Discussion

Initially, the organic compounds (22 L, 10 mg/L of each of the three acids) were first applied to the GAC column followed by the chlorine solution (32 L, 15.6 mg/L). After the chlorine had passed, sections of the carbon were removed for TOX determination and for Soxhlet extraction. The TOX was 440  $\mu\text{g/g}$  at the inlet to the column and dropped to the value of the virgin carbon approximately 15 cm into the bed. A total amount of 3.2 mg of TOX (0.09 mmol Cl) was recovered from the column. Since 3.9 mmol of organic compounds were applied to the column, approximately 2.3% of the compounds were substituted with chlorine (assuming monosubstitution) at the conclusion

Table I. Compounds Identified in an XAD-2 Extract of Phenolic Acids Chlorinated in Aqueous Solution

| compound                                     | mol wt |
|--|--------|
| 1. monochlorophenol <sup>a</sup>             | 142    |
| 2. dichlorophenol                            | 176    |
| 3. trichlorophenol                           | 210    |
| 4. monochloromethoxyphenol                   | 172    |
| 5. monochlorophenol (not deriv)              | 128    |
| 6. <i>p</i> -hydroxybenzoic acid             | 166    |
| 7. dichloromethoxyphenol                     | 206    |
| 8. monochlorotrimethoxybenzene               | 202    |
| 9. monochloro- <i>p</i> -hydroxybenzoic acid | 200    |
| 10. vanillic acid                            | 196    |
| 11. dichloro- <i>p</i> -hydroxybenzoic acid  | 234    |
| 12. monochlorovanillic acid (one deriv)      | 216    |
| 13. monochlorovanillic acid                  | 230    |
| 14. syringic acid                            | 226    |
| 15. monochlorosyringic acid                  | 260    |

<sup>a</sup> Molecular weights are presented for the fully or partially methylated compounds.

of the column run. A total of 7 mmol of chlorine was applied to the carbon bed, of which only 1.2% was incorporated into TOX and the remainder was reduced at the carbon surface. These results are similar to our previous work; humic acid adsorbed on carbon reacted with chlorine to a similar extent (9). The yields of products from either adsorbed humic acid or phenolic acids are low because most of the chlorine is chemically reduced by the GAC before reaction can occur.

The carbon at the inlet to the column was Soxhlet extracted for 24 h, yielding a dark red solution. The extract was methylated and analyzed for chlorinated compounds by using GC/MS. A small peak for a monochlorosyringic acid (methylated derivative, mol wt 260) and another chlorinated compound (mol wt 334) that could not be identified were found in the extract. The chromatogram was searched for known chlorination products by using mass-reconstructed chromatograms, but none were found.

The remainder of the GAC columns received a mixture of organic compounds and free chlorine which reacted for approximately 2 min before reaching the carbon. Somewhat higher yields of surface reaction products could be obtained, possibly, because the surface reaction could take place before the organic molecules migrated far into the carbon particles. The composition of the solution (i.e., pH, chlorine concentration, organic products, and reacted phenolic acid) that reached the activated carbon surface was determined by using the reactor column. In all cases, free residual chlorine and unreacted compounds were present in the solution that reached the carbon bed. The organic compounds in the influent to each bed were compared to those recovered from a Soxhlet extract of carbon at the column inlet to determine those compounds produced by surface reactions.

A solution of 1.3 mg/L of each of the three phenolic acids and 15.1 mg/L of free chlorine was allowed to partially react and was passed through the GAC column. The compounds in the influent included unreacted starting material as well as some aqueous chlorination products of each phenolic acid (Figure 2 (top), Table I). For example, before reaching the GAC, *p*-hydroxybenzoic acid produced a mono- and dichloro acid as well as mono-, di-, and trichlorophenols formed by decarboxylation reactions, in accordance with the work of Larson and Rockwell (15). Vanillic acid (I) produced a monochlorovanillic acid (II) as well as the mono- (III) and dichloro (IV) phenolic decarboxylation products (Table I, Figure 3). Syringic acid produced only a monosubstituted chlorine product; de-



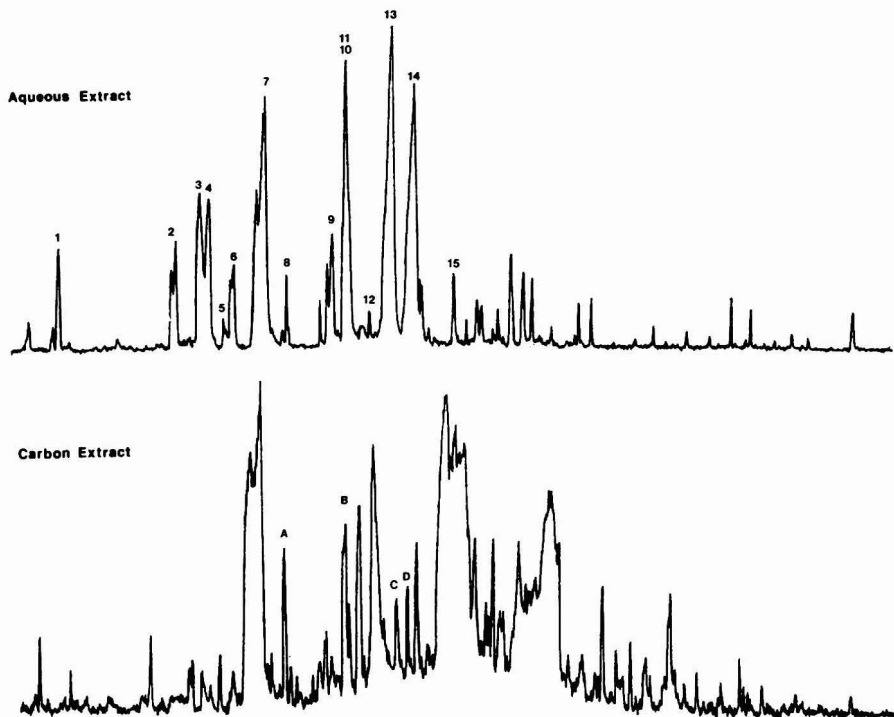


Figure 2. Total ion current (TIC) chromatogram of phenolic acids chlorinated in aqueous solution. The numbered peaks correspond to the identified compounds in Table I (top). TIC chromatogram of carbon that received phenolic acids and chlorine influent (bottom).

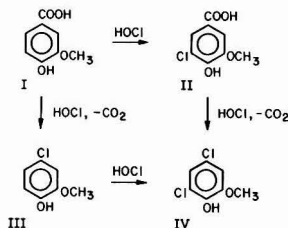


Figure 3. Reaction scheme for the chlorination of vanillic acid in aqueous solution.

carboxylation products were not observed, consistent with previous results (15). The chromatogram of the methylated extract of the GAC showed peaks for the unreacted phenolic acids and the chlorinated compounds in the influent, as well as several more peaks, indicating that additional compounds had formed on the carbon (Figure 2, bottom). One compound (A) had a molecular ion at 198 with fragment ions of 167, 137, and 109. These corresponded to the successive loss of a methoxy group, two methyl groups, and CO. A tetramethoxybenzene or a trimethoxyquinone is consistent with this spectrum. A second compound (B) also had a molecular ion at 198, with fragment ions of 183, 155, 140, and 125. These corresponded to the successive loss of one methyl group, CO, and two more methyl groups. Either a tetramethoxybenzene or a trimethoxyquinone is also consistent with this spectrum.

Bowie et al. (17) have reported that the mass spectra of methoxybenzoquinones are somewhat more complicated

than the spectra of methyl- and hydroxy-substituted benzoquinones. For a variety of methoxy- and methyl-methoxybenzoquinones the researchers saw a pronounced (M - 71) ion corresponding to the formal loss of two molecules of carbon monoxide and a methyl group from the molecular ion. The (M - 71) ion then decomposed by loss of CO to give an (M - 99) ion. Since a pronounced (M - 71) or (M - 99) ion was not observed for compounds A and B, the assignment of a tetramethoxybenzene is more consistent with the spectra. The retention time and spectra of known standards are necessary before positive identification can be made.

Two additional compounds (C, D) were found which were the monochloro derivatives of parent molecules having molecular weight 198. The fragmentation pattern of both derivatives closely resembled that of compound B. A single trimethoxyquinone or tetramethoxybenzene would not produce two monochloro isomers, so the compounds probably arose through chlorination of compounds A and B. These compounds were not found in the influent solution to the column and have presumably been formed from the reaction of chlorine with the organic compounds at the carbon surface. Several additional compounds were found that could not be identified.

The chromatogram of the carbon extract of the mixture of all three phenolic acids was difficult to interpret; products could not always be assigned to the acid from which they were derived, and severe overloading of the capillary column led to poorly resolved peaks. For these reasons a single compound, vanillic acid, was used for the remainder of the experiments.

A vanillic acid and chlorine solution (2.6 mg/L of vanillic acid, 10.0 mg/L of chlorine, 124 L total) was reacted for

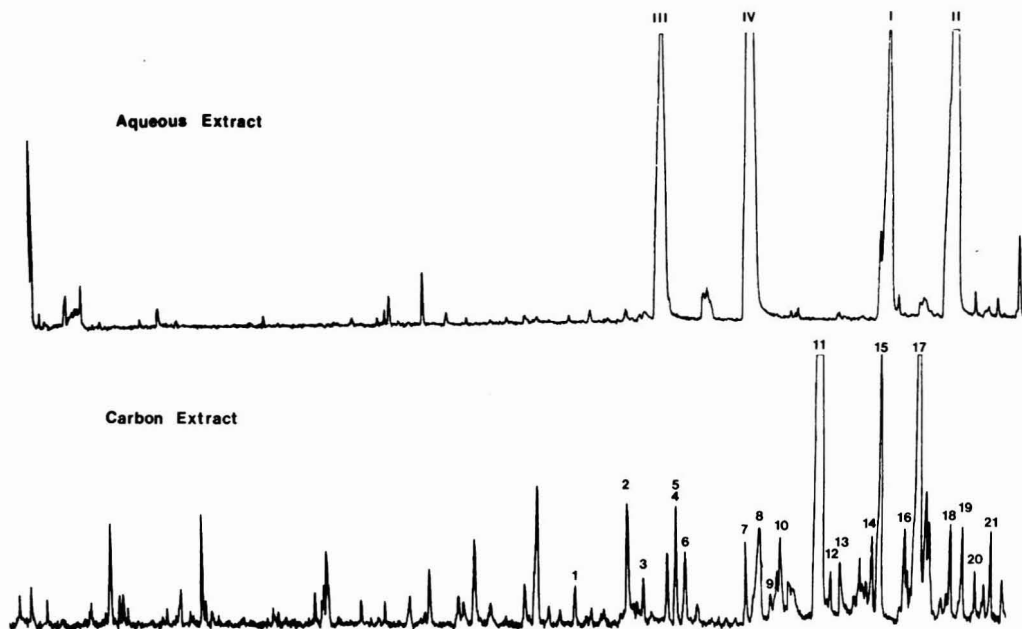


Figure 4. Total ion current chromatogram of the vanillic acid/chlorine influent. The labeled peaks correspond to the compounds in Figure 3 (top). TIC chromatogram of carbon that received vanillic acid and chlorine influent. The numbered peaks are identified in Table II (bottom).

approximately 2 min and passed into a carbon column. The chromatogram (Figure 4) of the influent to the column had four large peaks for vanillic acid and its three chlorination products, while that for the extract of the carbon at the inlet to the column had many more peaks. The numbered peaks are tentatively identified in Table II. Many of the peaks could be assigned to either a methoxy derivative of a polyphenol or a hydroxyquinone. For example, peak 3 could be trimethoxybenzene or dimethoxyquinone since the molecular weight of both compounds is 168 and the mass spectral fragmentation patterns are similar.

In order to facilitate compound identification, a portion of the extract was silylated. Mass spectra from the silylated extract were compared to spectra from the methylated extract, and structures of 17 compounds that were identified are shown in Table III. In addition to vanillic acid (m), two monochlorovanillic acid isomers (o, p), and the two chlorinated methoxyphenols (a, e), a variety of hydroxylated benzenes and quinones were found. There was evidence of three quinone products, a hydroxymethoxyquinone (b), its chlorinated derivative (g), and a dihydroxymethoxyquinone (i). There were two products that were polyhydroxybenzene derivatives; a trihydroxybenzene (h) and its monochloro derivative (k). There were several products that could be either methoxyhydroxybenzenes or hydroxyquinones (c, d, f, j, and l). Finally there were a hydroxyvanillic acid (n) and a trihydroxybenzoic acid (q).

By use of two derivatization procedures, silylation and methylation, the gross structure of particular molecules could often be more rigorously assigned. For example, the methylated product of compound (n) in Table III was identical in molecular weight with methylated syringic acid; it could not be readily determined if any of the substituents on the aromatic ring in the original molecule were methoxy groups prior to methylation. The silylated compound had a molecular weight of 400, corresponding to a

Table II. Compounds Identified in the Soxhlet Extract of the Carbon Receiving Vanillic Acid/Chlorine Influent



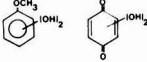
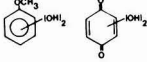

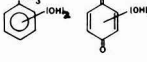



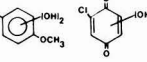

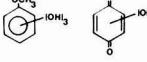





| compound  | mol wt |
|---|--------|
| 1. monochloromethoxyphenol <sup>a</sup>                 | 172    |
| 2. trimethoxyhydroxybenzene or dimethoxyhydroxyquinone  | 184    |
| 3. trimethoxybenzene or dimethoxyquinone                | 168    |
| 4. dichloromethoxyphenol                                | 206    |
| 5. chlorotrimethoxybenzene or chlorodimethoxyquinone    | 202    |
| 6. tetramethoxybenzene or dimethoxyquinone              | 198    |
| 7. monochlorodimethoxyquinone                           | 202    |
| 8. trimethoxybenzene or dimethoxyquinone                | 168    |
| 9. tetramethoxybenzene or trimethoxyquinone             | 198    |
| 10. trimethoxyhydroxybenzene or dimethoxyhydroxyquinone | 184    |
| 11. vanillic acid (methylated)                          | 196    |
| 12. dichloro compound (largest peak at mol wt 179)      |        |
| 13. vanillic acid (mono derivative)                     | 182    |
| 14. methyltrimethoxybenzoate                            | 226    |
| 15. monochlorovanillic acid                             | 230    |
| 16. unknown   | 206    |
| 17. methyltrimethoxybenzoate                            | 226    |
| 18. anthracene (internal standard)                      | 178    |
| 19. methyltrimethoxybenzoate                            | 226    |
| 20. methyltetramethoxybenzoate                          | 256    |
| 21. methylchlorotrimethoxybenzoate                      | 260    |

<sup>a</sup> Molecular weights are presented for the fully or partially methylated compounds.

tris(trimethylsilyl) derivative of a methoxy aromatic acid. One silyl group was attached to the carboxylic functional group, and the remaining two had reacted with phenolic hydroxyls. Therefore, the parent acid had one methoxy group and two hydroxy groups prior to derivatization.

Predominant reactions appear to be decarboxylation of the aromatic ring, hydroxylation of the aromatic ring, demethylation of methoxy substituents, oxidation to

Table III. Structures of Compounds Found in the Methylated and Silylated Extract of Carbon Receiving Chlorine and Vanillic Acid

| Compound   | MW <sup>1</sup> | MW <sup>2</sup> |
|--|-----------------|-----------------|
| a.    | 172             | 230             |
| b.    | 168             | 226             |
| c.    | 168             | 284             |
| d.    | 168             | 284             |
| e.    | 206             | 264             |
| f.    | 168             | 284             |
| g.    | 202             | 260             |
| h.    | 168             | 342             |
| i.    | 198             | 314             |
| j.   | 202             | 318             |
| k.  | 202             | 376             |
| l.  | 198             | 372             |
| m.  | 196             | 312             |
| n.  | 226             | 400             |
| o.  | 230             | 346             |
| p.  | 230             | 346             |
| q.  | 226             | 458             |

<sup>1</sup> The molecular weight of the methylated derivative.

<sup>2</sup> The molecular weight of the silylated derivative.

quinones, and chlorine substitution. Larson and Rockwell (15) observed that decarboxylation of a phenolic acid did not occur without substitution of chlorine at the leaving position. Reactions on carbon proceed quite differently from reactions in aqueous solution since nonchlorinated decarboxylation products were found in the extract.

Sarkanen and Dence (12) reported that demethylation of aromatic methoxy groups can occur by reaction with molecular chlorine in aqueous solution. They reported that demethylation of 4,5-dichloroveratrole could not be accomplished by HOCl in solution at pH 5.4 and stated that the reaction with Cl<sub>2</sub> appeared to be catalytic in nature. On activated carbon, demethylation occurred when HOCl was the predominant species.

One possible explanation for the differences between the extract of the influent solution and the activated carbon is related to the concentration and extraction procedures. The aqueous solutions were extracted by passing at least 10 L of acidified solution through an XAD-2 bed while the carbon samples were Soxhlet extracted for 24 h. Chriswell et al. (18) compared activated carbon with XAD-2 resin as an adsorbent for concentrating organic compounds and concluded that the resin was more effective for nine compounds including phthalate esters, most aromatic compounds, and pesticides. Carbon was more effective for alkanes; neither sorbent was particularly effective for acidic compounds. Thus varying selectivities and recoveries of the adsorbents for organic compounds may have caused the differences noted in the extracts.

An experiment was conducted to rule out this possibility. A sample of 25 L of vanillic acid solution was reacted with aqueous free chlorine for approximately 2 min with the conditions previously given. The solution was reduced with an excess of sodium sulfite and divided into two equal portions. Half of the solution was applied to an XAD-2 column and the other half was applied to a 4-g GAC column. The XAD-2 was eluted with methanol-methylene chloride, and the GAC was Soxhlet extracted for 24 h.

The same compounds were recovered by using the two extraction procedures, although different amounts were recovered with the two methods. There was a greater recovery of vanillic and monochlorovanillic acid from the GAC and comparable recoveries of the two phenolic decarboxylation products. It was not determined whether the low recovery of the acids from the XAD-2 was due to incomplete adsorption or incomplete elution from the resin. Mass chromatograms of 184, 198, and 226 molecular weight, corresponding to the methoxy-substituted benzenes or quinones reported in Table II, were constructed for each extract but none of these compounds were found. This indicates that these compounds were formed by the reaction with free chlorine at the carbon surface but not in aqueous solution in the absence of carbon.

### Conclusions

Activated carbon promoted the reaction of free chlorine at pH 6 with phenolic acids to produce a variety of oxidized products that were not produced by the reaction of chlorine in aqueous solution in the absence of carbon. These products include a variety of polyphenols and quinones that were produced by decarboxylation of the aromatic ring, hydroxylation of the aromatic ring, demethylation of methoxy substituents, oxidation to quinones, and chlorine-substitution reactions. It was demonstrated that the products were formed as a result of chlorination at the carbon surface and were not an artifact of the carbon extraction procedure. Previously we reported a similar work with humic acid and chlorine on GAC (9). Apparently the dihydroxy and chlorinated dihydroxybenzenes

recovered from the carbon in that work may have resulted from reactions similar to those reported here.

Reactions of chlorine and organic compounds on activated carbon have several environmental implications. The quinones and polyphenols formed on the carbon surface are of interest since they are toxic to aquatic plants (19) and participate in redox reactions in the environment. Quinones have also been shown to be toxic to blue-green algae (20) and to inhibit the photosynthesis of green algae (21).

The columns in these experiments were run for only a short period of time, and many oxidized compounds were found in the inlet to the bed. It would be expected that these compounds could be displaced further into the column during the life of the bed and eventually pass into the effluent. Although outside the scope of the present study, it would be interesting to observe the conditions under which displacement could occur and the concentrations and biological properties of the effluent organic compounds.

This work also has implications for carbon-extraction analysis. The extraction of carbon to determine the previous history of influent organic compounds to a bed may lead to erroneous results if an oxidant such as free chlorine has also been applied to the column. New compounds may have formed on the carbon through the reaction of the oxidant and adsorbed organic compounds.

Only one class of compounds was used in this study. It was shown that significant reactions did occur, and thus the extent of reaction of aqueous chlorine with other common organic compounds and the influence of pH, temperature, carbon type, and oxidant type on the reaction merit further work.

**Acknowledgments**

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**Zeolite A Hydrolysis and Degradation**

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■ The aqueous solution degradation of zeolite A, Na<sub>12</sub>(SiO<sub>2</sub>AlO<sub>2</sub>)<sub>12</sub>·27H<sub>2</sub>O, was studied by measuring the uptake of acid and the solubilization of silicon and aluminum with time at various pH values in the range 3-9. Sodium and calcium forms of zeolite A were studied under various fixed-volume and flow-through conditions in distilled water, model environmental systems, and actual sewage media. Zeolite A degradation products were characterized by scanning electron microscopy, infrared spectra, density measurements, oxygen adsorption, ion microprobe analysis, selected-area electron diffraction, X-ray diffraction, and X-ray fluorescence. The results are explained on the basis of an incongruent dissolution mechanism that is initiated by proton exchange and followed by silicic acid release, possibly yielding a mixture of gibbsite, Al<sub>2</sub>O<sub>3</sub>·3H<sub>2</sub>O, and halloysite, Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>.

Sodium zeolite A is a synthetic aluminosilicate increasingly used as a builder in laundry detergents. The

material is an insoluble ion exchanger which softens washwater by exchanging Ca<sup>2+</sup> and to a lesser extent Mg<sup>2+</sup> for Na<sup>+</sup>. When slurried in distilled water, sodium zeolite A raises the pH to 10-10.5 due to limited hydrolysis and the resultant formation of NaOH (1). It cannot be exchanged to the proton form in the presence of water without collapse of its crystalline framework (1-3). In strong acid media it dissolves completely (4).

Zeolite A is distinguished from other zeolites by its Al/Si ratio of 1:1. This places it in the same chemical class as certain feldspars whose degradation pathways and end products have been well characterized. The feldspar anorthite, stoichiometrically identical with calcium zeolite A, weathers to kaolinite (5), as do certain proton-exchanged zeolites under hydrothermal conditions (4).

The purpose of this work was to understand the degradation of zeolite A in natural water environments, to characterize the degradation products, and to relate zeolite A degradation to other aluminosilicate weathering reac-

tions. The approach was to measure acid uptake of zeolite A in various aqueous solutions differing in zeolite concentration, pH, and content of dissolved inorganic salts and chelating agents. Samples recovered from these studies were characterized by various techniques to determine the transformations that had accompanied acid uptake. Finally, zeolite A samples from a sewage-treatment plant study were examined in order to confirm the results of the laboratory systems.

### Experimental Section

**Materials.** Sodium zeolite A, denoted  $\text{Na}_{12}(\text{SiO}_2\text{-AlO}_2)_{12}\cdot 27\text{H}_2\text{O}$  or NaA, was commercial quality material. Anal. Calcd.: 12.6, Na; 32.9,  $\text{SiO}_2$ ; 32.3,  $\text{AlO}_2$ ; 22.2,  $\text{H}_2\text{O}$ . Found: 12.5, Na; 32.0,  $\text{SiO}_2$ ; 33.2,  $\text{AlO}_2$ ; 21.1,  $\text{H}_2\text{O}$ . Particle size distribution was determined by the Andreasen pipet method (6). The mass median equivalent spherical (Stokes' law) diameter was  $2.85\ \mu\text{m}$ , with 80% of the particles having diameters between 2 and  $6\ \mu\text{m}$ . The external surface area was found by nitrogen adsorption to be  $1.9\ \text{m}^2/\text{g}$ . The ion-exchange capacity was determined by analysis of the washed solids recovered from a dilute slurry of NaA exposed to a concentrated solution of  $\text{CaCl}_2$ . The measured exchange capacity was  $6.90\ \text{mequiv/g}$  of anhydrous material as compared to the theoretical value of  $7.04\ \text{mequiv/g}$ .

Calcium zeolite A, CaA, was prepared by multiple exposures of NaA to 1 M  $\text{CaCl}_2$  solution, followed by washing until chloride was absent. When the resultant zeolite was dissolved in acid and analyzed by atomic absorption spectroscopy, the measured Ca/Al mole ratio was 0.52, which is equal to the expected 0.50 molar ratio within experimental error. The Na content was negligible. Lead zeolite A, PbA, was prepared from CaA by repeated 24-h exposures to 0.05 M  $\text{Pb}(\text{NO}_3)_2$ . This resulted in total replacement of  $\text{Ca}^{2+}$  by  $\text{Pb}^{2+}$ . The analyzed Pb/Al mole ratio was 0.50. Both CaA and PbA retained the original crystalline structure of zeolite A as determined by X-ray diffraction and infrared absorption measurements.

All other chemicals, except for sodium tripolyphosphate (STP), were of reagent grade. STP was commercial  $\text{Na}_5\text{P}_3\text{O}_{10}\cdot 6\text{H}_2\text{O}$ .

**Apparatus and Analytical Methods.** The acid consumption of zeolite A was studied under two different sets of conditions: a fixed-volume approximation and an infinite-bath approximation. In the fixed-volume experiments a suspension of zeolite A was maintained at a constant pH with a Sargent Model D continuously recording automatic titrator in the pH-stat mode, using 0.1 N HCl. Dilution due to acid addition was always less than 5%. Reproducibility is estimated to be within about 2%.

A flow-through design was used to simulate infinite-bath conditions. In this system a zeolite A slurry was stirred in a closed Millipore filter reservoir into which  $\text{N}_2$ -sparged solutions were fed by a peristaltic pump at the rate of 1.5 mL/min and from which effluent (free of solids) was continuously extracted through a  $0.22\text{-}\mu\text{m}$  filter by gentle aspiration to maintain a constant 0.5-L cell volume. The thermostated filter reservoir was kept at constant pH by means of a Radiometer PHA943 titrator and ABU12 autoburet with a continuously recording REA1112 recorder. In these experiments, either 0.01 or 0.1 N HCl was used as titrant. Reproducibility of these experiments is estimated to be within 10%.

Silica analyses were performed either by atomic absorption or by the silicomolybdate blue method (7). Aluminum was determined by atomic absorption or by a colorimetric method using 8-hydroxyquinoline (8). The atomic absorption spectrophotometer was a Perkin-Elmer

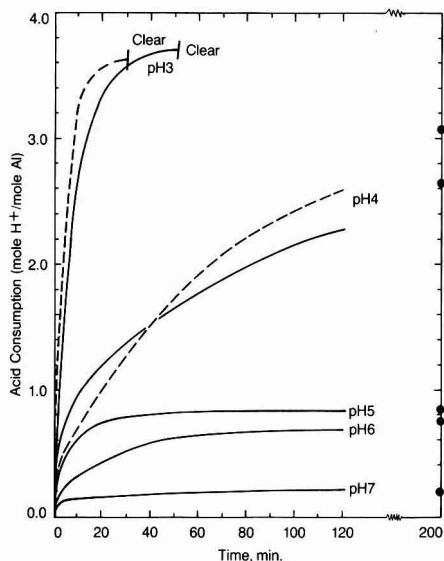


Figure 1. Acid consumption measurements for NaA (—) and CaA (---) at various pH values in a fixed volume of distilled water.

Model 403. IR spectra were obtained with a Perkin-Elmer 621 spectrophotometer. The X-ray emission data were obtained with a Philips 19010011 X-ray fluorescence unit, and the X-ray diffraction measurements were made with a Norelco XRG 5000 X-ray generator. Both X-ray measurements used a Norelco data control and Processor Model 130-125-00 for data readout. Gas-adsorption measurements were performed with Models 2100 and 2200 Micromeritics adsorptionometers.

Densities of hydrolyzed zeolite samples were determined by a flotation technique using chloroform and either tetrabromoethane or tribromoacetaldehyde blended at known concentrations until a suspension of zeolite in the solvent mixture could not be separated from solution by centrifugation. At this point the densities of the solvent and the zeolite were equal and the density of the solvent was calculated.

### Results and Discussion

**Acid Uptake.** Figure 1 shows the uptake of acid with time by 0.5 g/L (hydrated basis) of either the sodium or calcium form of zeolite A in fixed-volume aqueous suspensions at constant pH. The plots suggest that the zeolite takes up acid by two processes. At pH 5, 6, or 7 the presence of a plateau below 1 mol of  $\text{H}^+$ /mol of Al suggests simple ion exchange. Actually, this acid uptake results from concurrent ion exchange and hydrolysis reactions which lead to irreversible alterations in the zeolite crystal structure, as shown later. At pH 3, more than 1 equiv of acid is consumed per mol of aluminum, and the zeolite completely dissolves. The additional acid, up to 3 mol of  $\text{H}^+$ /mol of Al, is required to convert aluminum to the +3 ion.

Results from the corresponding CaA experiments at pH 5, 6, and 7 fell below the pH 7 NaA curve and are not shown. This low acid uptake occurs because the combination of the zeolite with a divalent ion is thermodynamically more stable than the combination with a monovalent ion. In contrast, at pH 3, the calcium form takes up acid faster than the sodium form. This is attributable to the

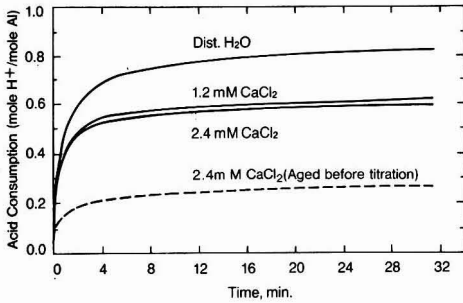


Figure 2. Acid consumption of NaA (—) and CaA (---) in a fixed volume of distilled and hard water at pH 5.

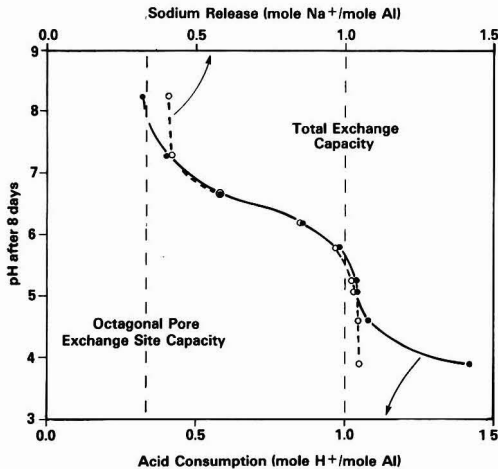


Figure 3. Acid consumption (—) and sodium release (---) by 1 g/L NaA in a fixed volume of distilled water as a function of pH.

larger pores (4) of CaA, which allows more rapid escape of the dissolution end products than from NaA.

Figure 2 shows the uptake of acid by fixed-volume 0.5 g/L suspensions of NaA at pH 5 in solutions of 1.20 or 2.40 mM  $\text{CaCl}_2$ . These concentrations correspond to median (7 grain/gallon) and high (14 grain/gallon) hardness levels for U.S. tapwater. The dashed curve, showing the result when titration was delayed 30 min, is identical with that obtained when preexchanged CaA was titrated immediately. Under these conditions, the Na/Ca exchange is complete within 30 min. At times less than 30 min, the uptake of acid is partly inhibited by the presence of excess  $\text{Ca}^{2+}$ . This inhibition is explained by the relative mobilities of the two ions. While  $\text{Ca}^{2+}$  forms the more stable zeolite, it is not able to reach the sites for ion exchange as rapidly as the  $\text{H}^+$  ion.

Additional fixed-volume acid consumption experiments are summarized in Figure 3. Instead of continuously controlling the pH during these experiments, it was adjusted at 0, 4, 20, 28, and 96 h to target values (pH 3.5, 4.2, 4.7, 5.0, 5.5, 6.0, 6.5, 7.0, 8.0). This technique appears to differentiate between two crystallographically different types of exchange sites present in NaA (1). Breaks in the acid consumption curve occur near 0.33 and 1.0 mol  $\text{H}^+$ /mol of Al. These breaks correspond to the known proportion of hexagonal (oxygen six ring) and octagonal (oxygen eight ring) exchange sites in NaA (1) and suggest that the sodium ions in the octagonal pore exchange

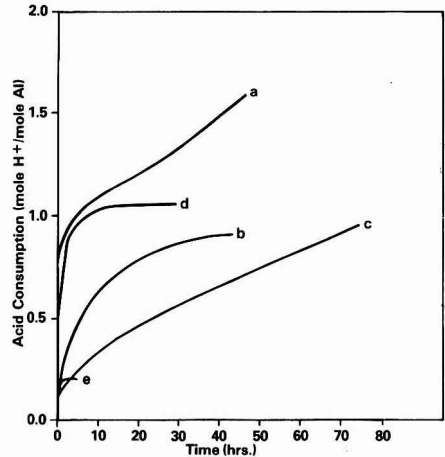


Figure 4. Effect of pH, concentration, and experimental design on the acid consumption of NaA (curves a-d, flow-through design; curve e, fixed volume): (a) pH 5, 10 g/L; (b) pH 7, 10 g/L; (c) pH 8, 10 g/L; (d) pH 7, 1 g/L; (e) pH 7, 0.50 g/L.

sites—one-third of the total—are more readily displaced by protons.

A rough estimate of the relative  $\text{H}^+/\text{Na}^+$  affinity for the hexagonal exchange sites can be obtained from Figure 3 by noting the pH at which half of these exchange sites have been proton substituted (mol of  $\text{H}^+$ /mol of Al = 0.67). At this pH (6.5), the proton concentration is  $3 \times 10^{-7}$  M while the calculated sodium solution concentration is  $5 \times 10^{-3}$  M. Thus, protons are able to compete equally with sodium at approximately  $10^{-4}$  the concentration.

Also displayed in Figure 3 is a plot of the sodium released from the zeolite as a function of pH. The correspondence of the sodium release to the acid consumption curve shows that proton exchange is the predominant acid-consuming reaction. Only in solutions of low pH where aluminum solubilization begins does the acid consumption significantly exceed sodium release.

Results from flow-through acid consumption experiments are shown in Figure 4. The flow-through design moderates the accumulation of sodium, hence minimizes competition from this source that would tend to reverse proton exchange. This procedure also helps to more realistically approximate the concentration of degradation products expected in the environment (9). In fixed-volume experiments, by contrast, unrealistically large amounts of reaction products result from the high concentration of zeolite used. The importance of this effect is apparent from a comparison of curves d and e. In the flow-through experiment depicted in curve d, acid consumption was much greater than for a similar fixed-volume experiment depicted in curve e and shown previously in Figure 1. Also, as curve a indicates, acid consumption greatly exceeds 1 mol of  $\text{H}^+$ /mol of Al at pH 5, unlike the fixed-volume case, which plateaued at  $\sim 0.8$  mol of  $\text{H}^+$ /mol of Al. However, this particular flow-through design only partially eliminates the effect of accumulated reaction products. Thus, reduction of the NaA concentration by an order of magnitude (compare curves b and d) still resulted in an increase in acid consumption.

Predictably, as the pH was decreased, protons competed more successfully for the exchange sites, just as in the fixed-volume experiments. Compare curves a, b, and c run at pH 5, 7, and 8, respectively. The competing cations in

**Table I. Characterization of the Filtered Sewage Used as an Influent for a pH-stat Hydrolysis Experiment**

| chemical species                        | concn, mM   | method                         |
|---|---|--------------------------------|
| orthophosphate                          | 0.126   | phosphomolybdate blue (11)     |
| orthophosphate + hydrolyzable phosphate | 0.168   | phosphomolybdate blue (11)     |
| total phosphate                         | 0.174   | phosphomolybdate blue (11)     |
| anionic surfactant (as HLAS)            | 0.008 (=2.7 ppm)                                      | methylene blue method (12)     |
| sodium                                  | 2.4 (=56 ppm)   | atomic absorption spectroscopy |
| potassium                               | 0.26 (=10 ppm)  | atomic absorption spectroscopy |
| calcium                                 | 0.70 (=28 ppm = 4.1 grains of CaCO <sub>3</sub> /gal) | atomic absorption spectroscopy |
| available (uncomplexed) calcium         | 0.32 (=13 ppm = 1.9 grains of CaCO <sub>3</sub> /gal) | calcium selective electrode    |
| magnesium                               | 1.2 (=28 ppm = 7.1 grains of CaCO <sub>3</sub> /gal)  | atomic absorption spectroscopy |
| manganese                               | trace <sup>a</sup>                                    | emission spectroscopy          |
| tin                                     | trace <sup>a</sup>                                    | emission spectroscopy          |
| bismuth                                 | trace <sup>a</sup>                                    | emission spectroscopy          |
| aluminum                                | trace <sup>a</sup>                                    | emission spectroscopy          |
| iron                                    | minor <sup>b</sup>                                    | emission spectroscopy          |
| copper                                  | trace <sup>a</sup>                                    | emission spectroscopy          |
| nickel                                  | trace <sup>a</sup>                                    | emission spectroscopy          |
| barium                                  | trace <sup>a</sup>                                    | emission spectroscopy          |
| strontium                               | trace <sup>a</sup>                                    | emission spectroscopy          |
| monomeric silicate                      | 0.306 (=18.4 ppm)                                     | silicomolybdate blue (7)       |
| total silicate                          | 0.313 (=18.8 ppm)                                     | silicomolybdate blue (7)       |

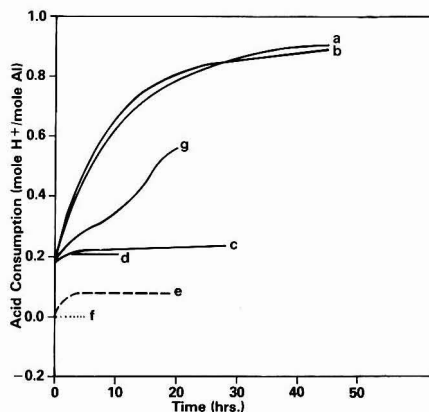
<sup>a</sup> Approximately 0.000 01-0.01 mM. <sup>b</sup> Approximately 0.01-0.05 mM.

this case are the sodium ions released by the proton-exchange reaction.

Ion-exchange competition was examined further under flow-through conditions at pH 7 by using 10 g/L of zeolite A. As Figure 5 indicates, an increase in the cation concentration or the addition of cations with higher binding affinities reduced the rate and extent of proton exchange. Curves a-c show the results of three experiments differing only in the influent concentration of NaCl. Curve b, based on a concentration that might be found in freshwater, is very similar to the distilled-water results in curve a. An increase in the NaCl concentration by a factor of 80 (to approximately 1/25th the concentration in seawater) caused a large decrease in acid consumption by NaA (curve c). As curve d shows, a much lower concentration of calcium (1.75 mM) caused similar reduction in acid consumption, due to the greater affinity of calcium for the exchange sites.

When zeolite A was exchanged to more stable cation forms, less proton exchange occurred. Curves a, e, and f in Figure 5 depict flow-through experiments that differed only in the initial cation form of the zeolite. At pH 7 no detectable acid consumption occurred in 5 h with lead zeolite A due to the high affinity of lead for the exchange sites. Calcium, which has an exchange constant intermediate between lead and sodium (10), allowed an intermediate degree of acid uptake. Comparison of curves d and e shows that preexchange of the zeolite to the calcium form is more effective in preventing proton exchange than is the presence of calcium in the test solution, in agreement with results shown in Figure 2.

Results from a flow-through experiment using raw sewage are shown in curve g. The sewage was prefiltered through a 0.45- $\mu$ m Millipore filter and preserved with sodium azide. Characterization of this sample is given in Table I. Of the cations found, calcium was judged to be the most effective in competing with protons for the exchange sites due to its high concentration relative to the other multivalent cations present. Since sewage is known to contain complexing agents other than phosphate species, the characterization of the complexing agents in Table I is only partial. Only 46% (1.9/4.1 grain/gallon) of the total calcium was measurable by a calcium-selective electrode and therefore considered to be available to compete for the zeolite A exchange sites. Considering these factors, the rate of acid consumption shown in curve g appears

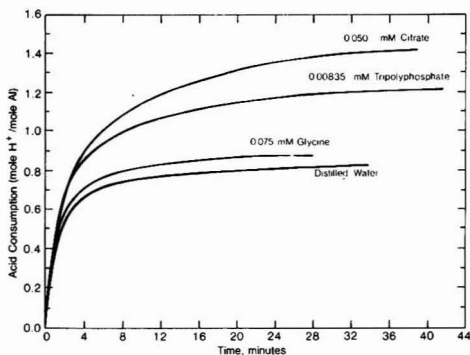


**Figure 5. Effect of solution composition and zeolite form on the acid consumption of 10 g/L of zeolite A at pH 7 (solid curves, NaA (—); CaA (---); PbA (····)); (a) distilled water; (b) 0.22 mM NaCl; (c) 17mM NaCl; (d) 1.75 mM CaCl<sub>2</sub>; (e) distilled water; (f) distilled water; (g) filtered raw sewage.**

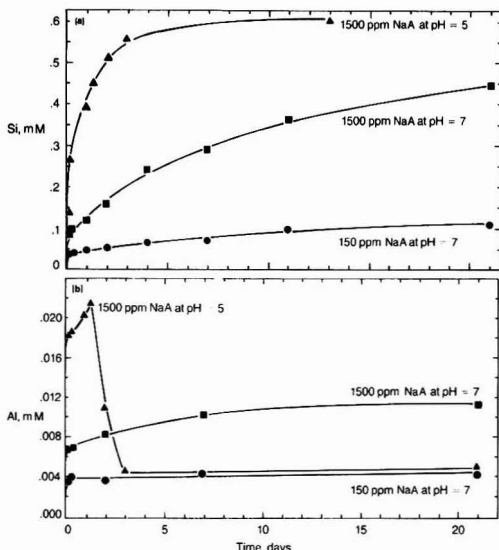
reasonable. This curve was corrected for the acid required to adjust the filtered sewage to pH 7, but there may still be some contribution to the acid consumption measurement from chemical and/or biological reactions in the sewage.

So that the effects of chelators in sewage could be investigated, a series of fixed-volume experiments was performed in solutions containing 0.050 mM sodium citrate, 0.008 35 mM sodium tripolyphosphate, or 0.074 mM glycine. These three chelators were chosen on the basis that they or similar materials had previously been employed as model compounds in sewage effluent simulations (13). In this study, the concentrations of the three chelators are somewhat lower than in the previously reported model study. Results are shown in Figure 6.

Comparison to the distilled water curve shows that the amount of acid consumption by zeolite A was increased by the addition of the complexing agents. This increase occurred in large part because the complexing agent solubilized some of the otherwise insoluble aluminum in the degradation products. This solubilization process was confirmed by observing an increase in the quantity of



**Figure 6.** Acid consumption of NaA in a fixed solution volume at pH 5 in the presence of  $\text{CaCl}_2$  and glycine, sodium tripolyphosphate, and sodium citrate.

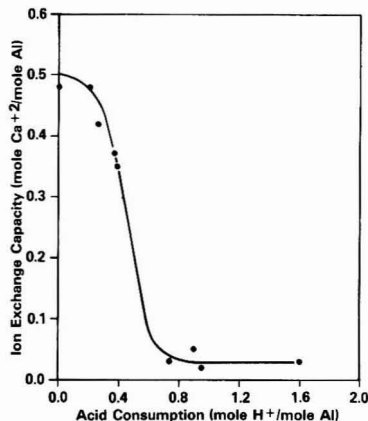


**Figure 7.** Solubilization of (a) silicon and (b) aluminum from NaA in fixed volume experiments.

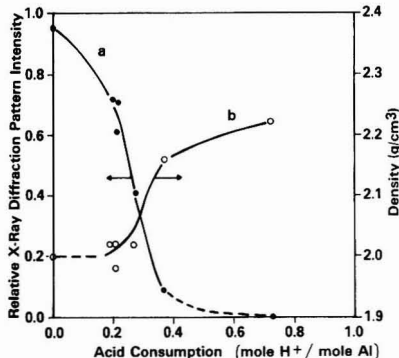
aluminum dissolved in these experiments.

In general, chelators will promote the degradation of zeolite A both by reducing the effective cation concentration competing with protons for exchange sites and by solubilizing aluminum from the zeolite.

**Dissolution of Silicon and Aluminum.** Measurements of silicon and aluminum solubilization under fixed-volume, constant pH conditions are summarized in Figure 7. Two concentrations of zeolite dispersions were used, 1.5 and 0.15 g/L. If all of the zeolite had dissolved, the 1.5 g/L dispersion would have given solution concentrations of 8.2 mM Al and 8.2 mM Si, while the more dilute dispersion would have given one-tenth these concentrations. As Figure 7 indicates, about 7% of the available silicon eventually dissolved from the more concentrated dispersion, while 13% dissolved from the more dilute dispersion. Even for the pH 5 experiment, the silicon in solution is substantially below the amorphous  $\text{SiO}_2$  precipitation threshold of 2.0 mM (15). In contrast, at pH 5 the concentration of aluminum in solution rose rapidly at first and then declined, indicating occurrence of an



**Figure 8.** Ion-exchange capacity of partially hydrolyzed zeolite A as a function of acid consumption, based on 10 g/L of zeolite A.



**Figure 9.** Changes in zeolite A crystallinity (curve a) and density (curve b) during pH 7 hydrolysis as a function of acid consumption.

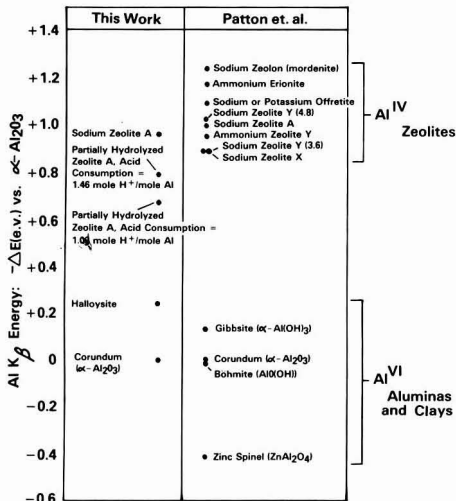
aluminum hydrous oxide or hydroxide precipitation reaction. No indications of precipitation were noted at pH 7, where aluminum is more soluble. At both pHs silicon release exceeded aluminum release, suggesting that an incongruent dissolution process was occurring and that a new aluminosilicate was very likely being formed. Similar data were obtained by analysis of the effluent from the reservoir in the flow-through experiments.

**Characterization of Degradation Products.** Calcium-exchange capacities of reaction products as a function of acid consumption are shown in Figure 8. The exchange capacity of unreacted zeolite approaches the theoretical level of 0.5 mol of  $\text{Ca}^{2+}$ /mol of Al. As acid consumption occurs, exchange capacity is lost. The plateau at low acid consumption levels indicates that initial proton substitution is reversible. However, once a significant fraction of the proton substitution has occurred, the process becomes irreversible.

Electron microscopy revealed that most of the partially hydrolyzed solids recovered from both the fixed-volume and flow-through experiments maintained the overall appearance of intact zeolite A, with slight evidence of erosion or crumbling at the edges, at worst. Nevertheless, the solids were completely amorphous upon examination by X-ray diffraction.

When a 10 g/L slurry of zeolite A was maintained at pH 5 in a flow-through experiment, the crystals became totally amorphous to X-rays in less than 5 min. Crystallinity was





**Figure 10.** Aluminum  $K\beta$  energy levels for various samples obtained in this work compared to published results (18).

lost more gradually, but similarly, at pH 7. A plot of the data is shown in Figure 9. The loss of crystallinity corresponds to the decrease in ion-exchange capacity shown in Figure 8. After approximately 4 h, 40% proton exchange had occurred, and the material had become amorphous.

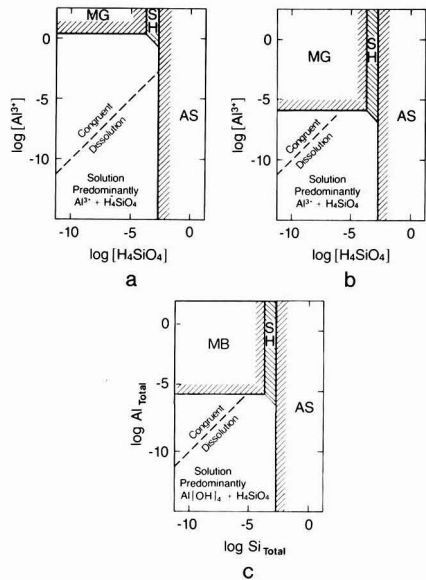
One sample of amorphous material was also analyzed by selected-area electron diffraction (a technique more sensitive to residual crystallinity) and found to be similarly amorphous. This indicated that the zeolite A structure was totally disrupted even though electron micrographs showed little morphological change.

The densities of these same partially hydrolyzed zeolite samples were determined and are also plotted in Figure 9. Since the density of a zeolite is dependent on the cation that occupies the exchange sites, proton exchange—in the absence of any other process—would decrease the density. As Figure 9 indicates, the density increased with proton consumption, suggesting that the structural transformation accompanying hydrolysis produced a solid less "open" and cagelike than intact zeolite A.

Confirmation of this hypothesis was provided by void fraction measurements using liquid oxygen. The measured void fraction for zeolite A before hydrolysis was 0.30. This compares well with the literature value of 0.33 (4). The void fraction of an acid-degraded sample of zeolite A was only 0.004.

Ion microprobe analysis was used to evaluate the compositional uniformity of an amorphous, partially hydrolyzed zeolite A sample. Three individual cubes were analyzed, and each showed a larger Al/Si ratio near the surface than in the interior of the cube. After penetrating to a depth of 200 Å—about 1% of the average particle size—the Al/Si ratio became constant. This confirmed the observations that silicon is preferentially dissolved during the hydrolysis reaction, leaving an aluminum-enriched surface on the zeolite crystal.

The IR spectra of the solids recovered from the flow-through experiments were quite distinct from that of intact zeolite A (16). Very sharp zeolite A bands at 550 and 378  $\text{cm}^{-1}$  were observed to disappear completely, the very sharp T-O bending band at 464  $\text{cm}^{-1}$  was broadened, and the asymmetric stretching band was broadened and shifted



**Figure 11.** Predominance diagrams for zeolite A alteration at (a) pH 3, (b) pH 5, (c) pH 7. Abbreviations: MG, microcrystalline gibbsite; MB, microcrystalline bayerite; SH, synthetic halloysite; AS, amorphous silica.

from 995 to 1025  $\text{cm}^{-1}$ . Diffuse new bands appeared at approximately 865 and 670  $\text{cm}^{-1}$ . This is the region in which vibrations involving hydroxyl groups and octahedral cations appear, such as found in Wyoming and Woburn montmorillonites (17). These features were found to be independent of the pH at which spectra were taken.

Figure 10 is a plot of  $K\beta$  X-ray emission-energy shifts measured for zeolite A, two partially hydrolyzed zeolite A samples, and the clay halloysite, all relative to corundum. Some results from a previous study by Patton and co-workers (18) are also given. This figure clearly shows that hydrolysis is accompanied by a definite shift toward the X-ray emission-energy characteristic of octahedral coordination for aluminum, although the shift was not proportional to the amount of acid consumption.

Halloysite, kaolinite, bayerite, and gibbsite all possess octahedral Al coordination, densities greater than 2.0  $\text{gm}/\text{cm}^3$ , and exchange capacities less than 0.02 equiv/mol of Al (19, 20). Thus, as hydrolysis occurs, the unique zeolite A structure is destroyed, and the characteristics of the transformed solid approach those of common, naturally occurring minerals.

**Fate of Zeolite A.** Data were obtained after long-term aging of some of the samples prepared in this study for comparison with aluminosilicate weathering data (21). Specifically, soluble silicate and aluminum concentrations were determined as a function of pH after 883 days of aging slurries prepared by adding 1.5 g of zeolite A to 1 L of  $\text{H}_2\text{O}$ . These slurries were periodically adjusted with dilute hydrochloric acid to targeted pH values. (The initial acid consumption measurements are reported in Figure 3.) Since the aluminum and silicate levels in these samples could each potentially reach several hundred mg/L, the dissolution process was expected to be incongruent at all pHs studied. This can be seen from the predominance diagrams in Figure 11, which are based on the equilibrium constants in Table II (5, 21). The figure shows it was also expected that the solutions would eventually yield hal-

Table II. Equilibrium Relationships for 25 °C

| material                     | pH  | equilibrium   | log K |
|------------------------------|-----|---|-------|
| 1. amorphous silica          | 3-8 | $\text{SiO}_2(\text{s}) + 2\text{H}_2\text{O} \rightleftharpoons \text{H}_4\text{SiO}_4$  | -2.70 |
| 2. microcrystalline gibbsite | 3-5 | $\text{Al}(\text{OH})_3(\text{s}) + 3\text{H}^+ \rightleftharpoons \text{Al}^{3+} + 3\text{H}_2\text{O}$  | 9.35  |
| 3. microcrystalline bayerite | 6-8 | $\text{Al}(\text{OH})_3(\text{s}) + \text{OH}^- \rightleftharpoons \text{Al}(\text{OH})_4^-$  | 1.28  |
| 4. synthetic halloysite      | 3-5 | $\frac{1}{2}\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4(\text{s}) + 3\text{H}^+ \rightleftharpoons \text{Al}^{3+} + \text{H}_4\text{SiO}_4 + \frac{1}{2}\text{H}_2\text{O}$           | 5.04  |
| 5. synthetic halloysite      | 6-8 | $\frac{1}{2}\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4(\text{s}) + \frac{1}{2}\text{H}_2\text{O} + \text{OH}^- \rightleftharpoons \text{Al}(\text{OH})_4^- + \text{H}_4\text{SiO}_4$ | -2.49 |

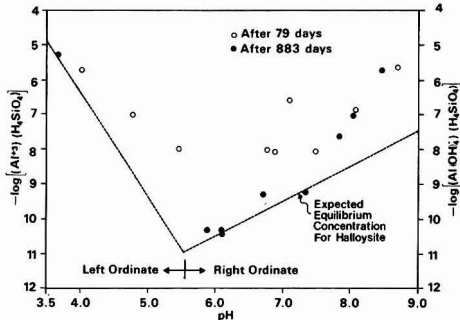
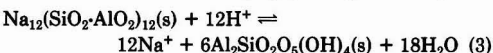
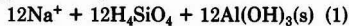
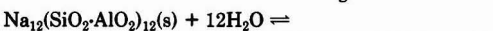


Figure 12. Relationship between silicic acid, soluble aluminum, and pH for partially hydrolyzed zeolite A suspensions compared to halloysite equilibria (21).

loysite, as do many other supersaturated solutions of aluminum and silicate (21).

Figure 12 shows a plot of the expected concentration of soluble aluminum and silicon based on halloysite equilibria (solid lines) and the results of these experiments. Six of the nine samples are in reasonable agreement with halloysite equilibria after 883 days. The three most alkaline samples deviate from the prediction because zeolite A hydrolysis is slower in alkaline media. These three samples still contained traces of intact zeolite A when filtered solids were examined by X-ray diffraction analysis after 883 days, while the other six samples were amorphous.

In summary, the changes in physical and chemical properties accompanying the hydrolysis of zeolite A are consistent with the reactions 1-3 leading to the formation



of halloysite, denoted  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ . Reaction 3 is the sum of reactions 1 and 2. Essentially the same reaction is expected to occur for the calcium form of zeolite A.

Evidence for the hydrolysis of zeolite A under real environmental conditions was provided by analysis of sewage samples obtained in a previous study involving a residential area in which many households used a detergent product containing zeolite A (22). Although the concentration of

zeolite A in the influent sewage was 7-17 mg/L, microscopic examination of the suspended solids in the mixed liquor revealed relatively few cubic solids. Several of the cubes thought to be partially hydrolyzed zeolite A were severely eroded while others appeared unchanged. Individual cubic particles were also studied by selected-area electron diffraction. Most were completely amorphous; the remainder were identified as zeolite A, but they generated diffuse diffraction patterns, indicating partial structural disruption. These data confirm the degradation of zeolite A in a sewage matrix.

Acknowledgments

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## Occurrence of Brominated Alkylphenol Polyethoxy Carboxylates in Mutagenic Wastewater Concentrates

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■ Removal and formation of mutagenic activity during advanced wastewater treatment were investigated by using the *Salmonella typhimurium* strain TA100. The activity of direct acting mutagens appeared to increase at the re-carbonation stage, where 6-10 mg/L of chlorine was added. Subsequent activated carbon treatment removed activity effectively but was apparently ineffective in removing precursors. Final chlorination typically with 25 mg/L of chlorine led to the reoccurrence of mutagenicity. Organic concentrates obtained by XAD-8 adsorption were separated by liquid-solid chromatography on silica gel. Mutagenicity was consistently found in the methanol fractions, which were further examined by GC/mass spectrometry. These fractions contained primarily carboxylic acids including brominated and nonbrominated alkylphenol polyethoxy carboxylic acids (BrAPECs and APECs). APECs were brominated during chlorination. Correlation between the occurrence of mutagenicity in the methanol fraction and the formation of BrAPECs suggested potential mutagenicity of these brominated compounds. However, preliminary experiments failed to confirm this hypothesis.

### Introduction

An increasing number of communities in the arid Southwest and elsewhere are facing immediate or predicted water shortages. The pressing need for additional water has led to several large-scale research projects to evaluate ground-water recharge with treated wastewater as an alternative to augment ground-water supplies (1). In Orange County, Southern California, Water Factory 21 (WF 21), which is operated by the Orange County Water District, has been treating secondary municipal effluent for ground-water recharge since 1976 (2). The effluent of WF 21 is injected directly into a freshwater aquifer to prevent seawater intrusion. The potential of using highly treated wastewater for potable purposes led to a study to assess the reliability of the performance of WF 21 (3-6). Among the water-quality characteristics evaluated were those included in the primary drinking water standards, general organic and inorganic parameters, viruses, and trace organic contaminants. The removal of a broad spectrum of organic pollutants including chlorinated and non-chlorinated hydrocarbons, phenols, and carboxylic acids has been determined (5, 6). However, only a small fraction of the total organic content has been specifically characterized, and questions remain as to the composition and significance of the unknown fraction. In this report we evaluate organic concentrates of WF 21 effluents with respect to their mutagenic activity as determined by the Ames *Salmonella*/microsome test (7).

Many mutagens have been shown to be carcinogens, and their presence in water is therefore considered a potential public health hazard (8). The occurrence of mutagens has been documented in secondary and tertiary treated

wastewater effluent (9-12), in drinking water (13-15), and in the effluent of paper pulp mills (16-21). The fact that mutagens may accumulate in fish (21) and in sediments (16, 22) indicates that the discharge of mutagens could be significant even at low levels. The origins of environmental mutagens are manifold; for example, byproducts of dye manufacturing (22), petroleum-derived hydrocarbons (23), diesel exhaust (24), certain pesticides (25), industrial solvents (13), and byproducts of water chlorination (8, 13) have been shown to be mutagenic. Mutagens belong to a broad variety of compound classes including nitroaromatics, polynuclear aromatics, nitrosamines (26), resin acids (20), volatile halogenated hydrocarbons (13), and chlorinated aldehydes (27).

The knowledge of the chemical properties of the mutagens present in advanced treated wastewater is limited at present, and no specific treatment technology is applied to remove them. However, it has been indicated that activated carbon (AC) adsorption (9), sulfite dechlorination (15, 19), biological treatment (18-20), and storage at high pH (19) reduce mutagenicity produced by chlorination. Some of the mutagenicity formed during chlorination appears to be associated with relatively nonvolatile compounds (15, 20, 21, 28), but none of the organics identified so far has been potent enough to account for the total activity detected in the samples. Apparently the residues causing the mutagenicity have not been detected with the analytical procedures applied.

Mutagenic concentrates of drinking water and of advanced wastewater treatment (AWT) plant effluent have been characterized in detail by combined gas chromatography/mass spectroscopy (GC/MS) (9, 29), but definitive conclusions as to the identity of the mutagens involved could not be drawn. In an effort to isolate specific mutagenic compounds, Tabor and Loper separated fractions by high-performance liquid chromatography (HPLC) to assay for mutagenic activity (30). Repeated separation and testing led to the isolation of a compound that was suggested to be a polychlorinated ether. Numerous compounds have been identified in mutagenic paper-pulp mill concentrates (16, 17, 20, 21), many of them chlorinated. The list of compounds identified includes aliphatic and aromatic hydrocarbons, phenols, aldehydes, quinones, and various classes of carboxylic acids. Polychlorinated acetone isomers identified in paper-pulp mill effluents were recently shown to be direct-acting, alkali-labile mutagens (27).

So that organic residues in biological assays could be tested, various enrichment procedures have been employed. Kopfler et al. used reverse osmosis (RO) to concentrate and isolate gram quantities from large samples up to 15 m<sup>3</sup> in size (31). Baird et al. developed a resin sampler for processing samples up to 200 L (12). In the studies on mutagenicity in drinking water reviewed by Loper (14), adsorption by Amberlite XAD resins (Rohm

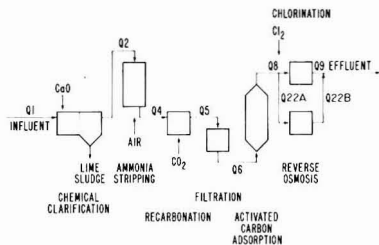


Figure 1. Schematic of WF 21 (this study period).

and Haas, Philadelphia) was the preferred concentration method, and 1–20-L samples were tested.

This study summarizes mutagenicity data obtained during a one and a half year study on WF 21 effluents. Organics were concentrated by adsorption on XAD-8, ion-exchange resins, ultrafiltration, and gaseous purging (6). Only in concentrates from XAD-8 were we able to detect mutagenicity; in all other concentrates, the response was negative. The samples tested were up to 1 gallon in size. In this report we emphasize the data obtained from XAD-8 concentrates and discuss the chemical characterization of the mutagenic extracts.

### Experimental Section

**Water Factory 21.** WF 21 is an advanced wastewater treatment facility (2) which treats 0.66 m<sup>3</sup>/s secondary effluent from an activated-sludge treatment plant. Figure 1 shows a schematic of the plant and indicates the sampling locations. The influent (Q1), was treated by high-lime treatment (Q2), ammonia stripping (Q4), re-carbonation with the addition of 6–10 mg/L of chlorine for algae control and nitrogen removal (Q6), dual-media filtration, and granular AC adsorption (Q8). One-third of the AC effluent underwent reverse osmosis (RO) (Q22B); the rest was disinfected with chlorine, typically 25 mg/L (Q9). A detailed description of the plant and its performance has been given previously (2–6). Composite samples of 1 L and 1 gallon were taken by WF 21 personnel and shipped to the Stanford University Water Quality Research Laboratory by air freight, where they were received on the same day and refrigerated for up to 4 days until analyzed.

**Extraction and Concentration.** Methanol (MeOH), dimethyl sulfoxide (Me<sub>2</sub>SO), acetonitrile, methylene dichloride (MeCl<sub>2</sub>), and ethyl ether were "distilled in glass" quality and used as received (Burdick and Jackson, Muskegon, MI 49442). Clean water (MQ water) was produced by a MilliQ water-purification system (Millipore Corp., Bedford, MA 01730). A diagram of the concentration and fractionation procedure developed is depicted in Figure 2. Samples were acidified to pH 2 with concentrated hydrochloric acid. After pH adjustment, the chlorinated 1-L samples were purged with nitrogen for 2 h and the 1-gallon samples for 6 h to remove free chlorine (18). Amberlite XAD-8 was purified as described by Leenheer and Huffman (32). The XAD-8 columns were packed in acetone in preparative chromatography columns (9 × 250 mm) (Altex, Berkeley, Ca 94710) to 20 mm below the top. After packing, 1 L of water was passed through the columns, followed by two cycles of 100 mL of 0.1 N hydrochloric acid and 0.1 N sodium hydroxide. After a final rinse with 100 mL of water, the columns were ready for use.

The samples were forced through the columns from the

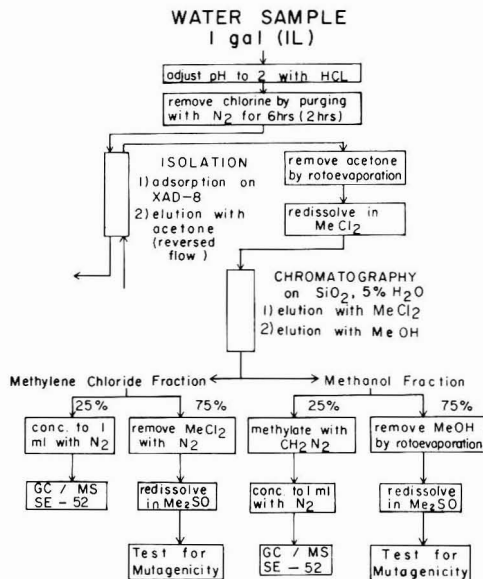


Figure 2. Concentration and fractionation scheme.

sample bottles by means of high-purity nitrogen and specially fabricated adapters (6). A nitrogen pressure of 10 psi resulted in a flow rate of approximately 8 mL/min. After the sample passed through the column, nitrogen was used to push the residual water out. Then an adjustable plunger was inserted into the column, and 50 mL of acetone was pumped through in reversed direction by means of a one-stroke metering pump (Model IVEK, ALLTECH, Deerfield, IL 60015) at the rate of 1–2 mL/min. Acetone and residual water were removed from the extract by rotoevaporation at 50 °C (thereby losing the volatiles). The concentrate was redissolved in 5 mL of acetone and divided into portions for mutagenic testing and chemical characterization.

**Mutagenic Testing.** The fractions intended for mutagenic testing were evaporated to dryness and redissolved in either 1 or 2 mL of Me<sub>2</sub>SO. Extracts were tested for mutagenicity by SRI International, Menlo Park, with the procedure developed by Ames, Yamasaki, and McCann (7). Aliquots of 50, 100, 200, and 400 μL were applied per plate. Negative controls were run with 100 μL of Me<sub>2</sub>SO. Positive controls without metabolic activation (MA) were run with sodium azide (NaN<sub>3</sub>); positive controls with MA were run with 2-anthramine. Initial blanks were run with MQ water. Then procedural controls were obtained by extracting the pre-cleaned XAD-8 columns with acetone. These extracts obtained from several columns were combined and tested along with the samples. An experiment was performed in which distilled water containing 5 mg/L of chlorine was passed through the columns without prior dechlorination in order to verify that residual chlorine did not produce mutagens during adsorption.

An extract was considered to be mutagenic (positive) when (i) a positive dose-response relationship was observed and (ii) when the number of revertant colonies at the highest dose exceeded the average background value by at least 100%. The net-revertant number (NR) was calculated by subtracting the average background value (determined with 2–4 doses of 100 μL of Me<sub>2</sub>SO) from the number of revertant colonies observed. The NR concen-

tration (NR/L) was calculated from the positive slope of the NR-dose relationship by linear regression after considering appropriate concentration factors.

**Silica Gel Chromatography.** Fractions of the extract intended for chemical characterization were evaporated to dryness and redissolved in 200  $\mu\text{L}$  of  $\text{MeCl}_2$ . The concentrate was then transferred to the top of a  $0.5 \times 10$  cm silica gel column packed in  $\text{MeCl}_2$ . The silica (80-200 mesh, J. T. Baker, Phillipsburg, NJ 08865) was deactivated with 5% w/w water prior to use. A first fraction was eluted with 10 mL of  $\text{MeCl}_2$ . After passing 2 mL of 25% MeOH in  $\text{MeCl}_2$  through the column, a second 10-mL fraction was eluted with MeOH. The combined MeOH eluates constituted the second fraction. Both fractions were concentrated to 1 mL under a stream of nitrogen purified with a Gas Purifier (Alltech Associates, Arlington Heights, IL 60004). Typically 25% of each concentrate was set aside for GC/MS analysis. The remainder was evaporated to dryness, redissolved in  $\text{Me}_2\text{SO}$ , and submitted for mutagenic testing.

**Methylation.** The MeOH fractions were derivatized with diazomethane prior to GC/MS analysis. Diazomethane was produced from Diazald (*N*-methyl-*N*-nitroso-*p*-toluenesulfonamide, Aldrich Chemical Co., Milwaukee, WI 53233) by using a Diazald kit. Approximately 2.15 g (10 mmol) of Diazald were transferred to a 250-mL round flask along with a magnetic stirring bar, followed by the addition of 30 mL of ether. As the round flask was cooled in an ice-water bath, the Diazald was stirred into solution, and 13.0 mL of a 0.81 N solution of potassium hydroxide in 95% ethanol was slowly added. Upon completion of the addition, the flask was allowed to warm to room temperature, and the ethereal diazomethane solution was slowly distilled into the dry ice cooled receiving flask.

The fractions to be methylated were evaporated to dryness under a nitrogen stream and redissolved in 1 mL of a 1:1 (v/v) ether-methanol solution. Methylation was accomplished by adding an excess ( $\sim 3$  mL) of reagent solution. After mixing, the sample was allowed to sit overnight at room temperature. Prior to GC/MS analysis, the sample was reconcentrated to  $\sim 100/\mu\text{L}$ .

**GC/MS Analysis.** GC/MS analyses were done on a Finnigan 4000-INCOS system (Finnigan, Sunnyvale, CA 94086). The GC was equipped with a Grob-type injector (E. M. Becker Co., Bala Cynwyd, PA 19004) and a 50-m (0.3 mm i.d.) fused silica capillary column coated with SE-52 (J & W Scientific, Rancho Cordova, CA 95670), which was connected directly to the mass spectrometer. A 2- $\mu\text{L}$  sample of extract was injected splitless for 36 s. The temperature program used was 50  $^\circ\text{C}$  isothermal for 3 min and then increased to 300  $^\circ\text{C}$  at a rate of 3  $^\circ\text{C}/\text{min}$ . The injector temperature was set to 260  $^\circ\text{C}$ ; the interface oven and the transfer line were set to the maximum temperature of 300  $^\circ\text{C}$ . The mass spectra were acquired under the following conditions: ion source temperature, 220  $^\circ\text{C}$ ; electron energy, 70 eV; electron current, 0.5 mA; preamplifier setting,  $10^{-7}$  A/V. Mass spectra were acquired in the multiple-ion detection mode at a rate of one scan/2 s, mass range 35-235 in 0.666 s (3.3 ms/amu) and mass range 236-430 in 1.222 s (6.3 ms/amu).

**GC/Triple Stage Quadrupole MS Analysis.** A Finnigan triple-stage quadrupole (TSQ) mass spectrometer was used, coupled to a Finnigan 9610 Model GC. The GC was equipped with a 6-ft column packed with 3% OV-1 on 60/80 mesh Chromosorb W A/W. A daughter ion experiment was performed with the first mass spectra in the positive-electron-impact (EI+) mode (33). For collision-activated decomposition (CAD) the nitrogen pressure

in the collision cell was adjusted to 2.35 mtorr; the collision energy was 12 V. A 2- $\mu\text{L}$  extract was injected at 120  $^\circ\text{C}$ , and then the temperature was increased at a rate of 5  $^\circ\text{C}/\text{min}$  to 250  $^\circ\text{C}$ . Injector and interface were set at 250  $^\circ\text{C}$ ; the flow rate was 16 mL/min.

**GC/High-Resolution (HR) MS Analysis.** A MAT 711 instrument was used, which was interfaced to a Hewlett-Packard 7610-A GC by means of a Watson-Biemann separator. The GC was equipped with a 6-ft column ( $1/8$  in. i.d.) packed with 3% OV-17 on Chromosorb Q 80/100 mesh. The resolution was 5000. The mass spectra were acquired from 500 amu downward to 40 amu at a rate of 8 s/decade. The extract (3  $\mu\text{L}$ ) was injected at 100  $^\circ\text{C}$ , and then the temperature was increased at a rate of 4  $^\circ\text{C}/\text{min}$  to 300  $^\circ\text{C}$ .

**Preparation of Brominated Alkylphenol Polyethoxy Carboxylate Test Mixture (BrAPECs).** "tert-Octylphenol polyethoxylate" (3 mol of ethylene oxide units (ETO)/molecule) was purchased from Chem Service, West Chester, PA 19380. For bromination approximately 400 mg of the alkylphenol polyethoxylate (APE) was dissolved in 20 mL of glacial acetic acid. To this solution was added 160 mg of elemental bromine dissolved in 5 mL of glacial acetic acid (34). After the reaction mixture stood overnight, excess bromine was destroyed by adding 0.1 N sodium thiosulfate solution. Then 200 mL of water was added and the solution was extracted two times with 100 mL of ether. The combined extracts were dried over anhydrous sodium sulfate, filtered, and concentrated to about 10 mL. For oxidation, i.e., conversion of the alcohol into the corresponding carboxylic acid, 10 mL of Jones reagent (0.4 mol of potassium dichromate in 700 mL of 2 M sulfuric acid) was added to an APE and a BRAPE solution (35). The solution was warmed at 60  $^\circ\text{C}$  for 2 h, then diluted with 25 mL of water, and extracted two times with 50 mL of ether. The combined extracts were washed three times with 100 mL of water. After being washed, the ether extract was dried, filtered, and concentrated. Half of it was set aside for Ames testing, and the other was used for chemical characterization.

## Results

**Mutagenic Response of Concentrates.** The net reversion rate/L (NR/L) was used to compare the mutagenic activity at different locations and in different fractions. So that an estimate for the significance of quantitative comparisons could be obtained, the data obtained from running negative and positive controls were statistically evaluated. The average of all background reversion rates observed with 100  $\mu\text{g}/\text{L}$  of  $\text{Me}_2\text{SO}$  was 110 ( $n = 48$ ); the coefficient of variation was 26%. Data from plates run simultaneously were less variable. Within a set, the coefficient of variation was only 12%. A similar observation was made for the positive controls obtained with 1  $\mu\text{g}$  of  $\text{NaN}_3$ . When tested within a set, the coefficient of variation was 5%. However, the number of total inversions induced by  $\text{NaN}_3$  fluctuated considerably over the study period. The mean value was 497, the coefficient of variation was 32%, and the observed values ranged from 227 to 706. Therefore, caution must be exercised when data obtained at different times are compared.

The initial experiments were designed to establish a procedure suitable for routine monitoring. XAD-8 resin was used as the adsorbent and both TA98 and TA100 were used as tester strains. The effect of metabolic activation was tested with concentrations of samples from the plant influent (Q1) and from the two plant effluents (Q9 and Q22B). These data are summarized in Table I.

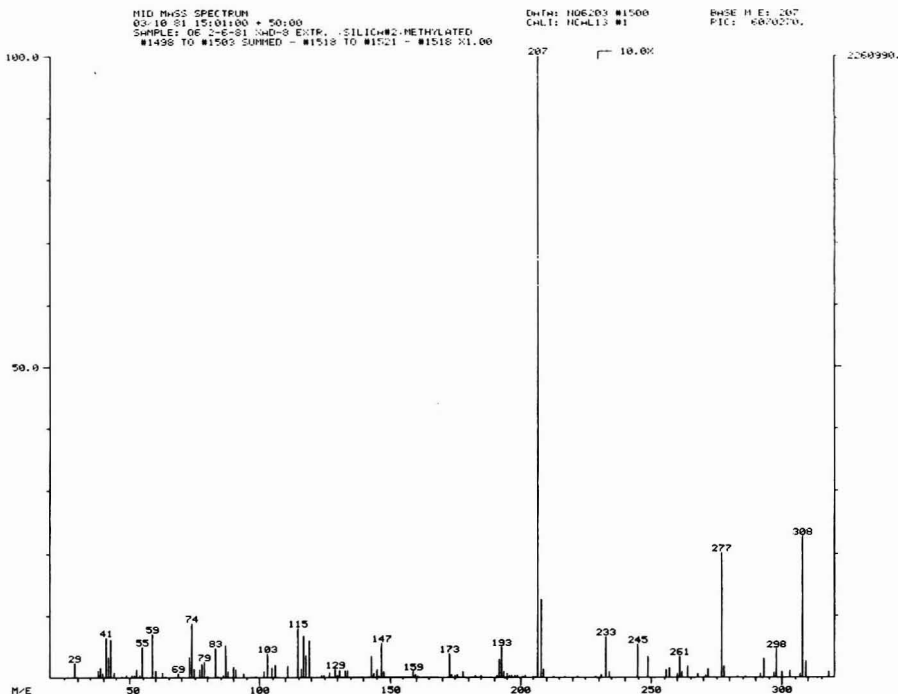


Figure 3. Mass spectrum of a representative APEC compound of the 207 group.

Table I. Mutagenic Activity at Q1, Q9, and Q22B against TA98 and TA100, without and with Metabolic Activation, in Net Revertants/L<sup>a</sup>

|             | sample   | TA98 |     | TA100 |      |
|-------------|----------|------|-----|-------|------|
|             |          | -MA  | +MA | -MA   | +MA  |
| influent    | Q1       |      |     |       |      |
|             | 12/25/79 | 280  | 0   | 1240  | 360  |
|             | 12/31/79 | 290  | 0   | 670   | 320  |
| Cl effluent | Q9       |      |     |       |      |
|             | 12/25/79 | 130  | 0   | 820   | 420  |
|             | 12/31/79 | 650  | 0   | 2480  | 1110 |
|             | 4/14/80  | 150  |     | 1190  |      |
| RO effluent | Q22B     |      |     |       |      |
|             | 12/25/79 | 0    | 0   | 0     | 0    |
|             | 12/31/79 | 0    | 0   | 0     | 0    |
|             | 1/25/80  | 0    | 0   | 0     | 0    |

<sup>a</sup> -MA, no metabolic activation; +MA, with metabolic activation; 0, no activity above detection limit.

The data suggest that the mutagens present in Q1 and in Q9 were detectable with both strains TA100 and TA98. In contrast, the organics present in Q22B did not induce activity in either strain. Several characteristics of the mutagenicity observed were similar to those reported in chlorination-stage effluents of pulp-mill effluents (16-21) and in chlorinated drinking water (15): the reversion rate was higher in TA100 than in TA98 and was reduced by MA. In TA100 the reduction was approximately 50%, and in TA98 it was 100%.

For evaluation of the impact of individual processes in more detail, concentrates from various stages of treatment were tested. MA was discontinued at this point because most mutagens present appeared to be direct acting. TA100 was selected for further investigations because of its high reversion rates.

Table II. Mutagenic Activity against TA100 at WF 21 Sampling Locations, Extracted with XAD-8 (Acetone Eluate)<sup>a</sup>

| date    | location       |    |    |          |    |      |      |
|---------|----------------|----|----|----------|----|------|------|
|         | Q1             | Q2 | Q4 | Q6       | Q8 | Q9   | Q22B |
| 4/25/80 | 970            |    |    |          |    | 500  |      |
| 5/01/80 | 1080           |    |    |          |    | 830  |      |
| 5/22/80 | T <sup>b</sup> |    |    |          |    | 540  | 0    |
| 5/28/80 |                |    |    | 2360 (T) | 0  | 2400 | 0    |
| 6/17/80 |                |    | 0  | 570      | 0  | 1620 |      |
| 6/21/80 |                |    | 0  | 2260     | 0  | 1840 |      |
| 6/27/80 | 0              | 0  |    | 1080     |    |      |      |
| 7/04/80 | 0              | 0  | 0  |          |    | 610  |      |

<sup>a</sup> Net revertants/L. <sup>b</sup> T, toxicity.

The data indicating mutagenic activity at seven treatment stages of WF 21 are summarized in Table II. During the period April 25 to July 4, 1980, eight sets of samples were tested. Only two of the five influent samples tested were positive during this period, one showed signs of toxicity, and two were negative. At Q6 all samples tested were positive, with activities ranging from 570 to 2360 NR/L. No Q8 sample was found to be positive, but mutagenicity reappeared at Q9 where all samples tested were positive. In the chlorinated effluent, the activities ranged from 500 to 2400 NR/L.

In three instances direct quantitative comparison of Q6 and Q9 was possible. In two cases (May 28 and June 21, 1980) the activities at Q6 and Q9 were remarkably close, whereas in the sample set taken June 17, 1980, the activity appeared to be significantly higher in Q9 in spite of activated-carbon adsorption between Q6 and Q9. This suggested that precursors were not removed completely and that perhaps the chlorination conditions were gov-

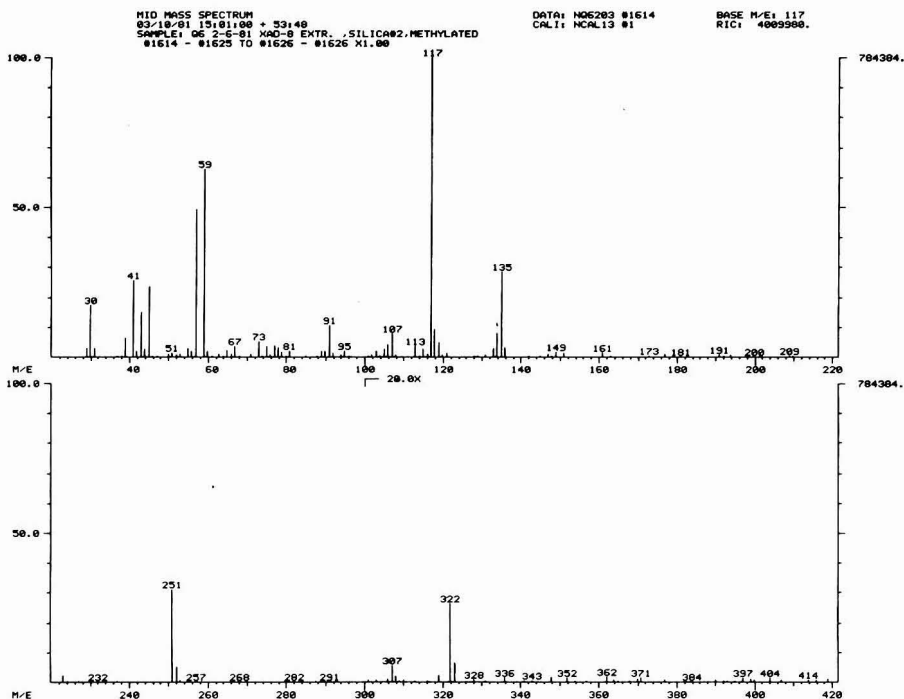


Figure 4. Mass spectrum of a representative APEC compound of the 117 group.

erning the amount of activity produced.

**Mutagenic Response of Fractions.** The XAD-8 concentrates were separated into nonpolar and polar fractions by silica gel chromatography. A nonpolar fraction was eluted with  $\text{MeCl}_2$ , and a more polar fraction was eluted with MeOH. An unfractonated aliquot of the XAD-8 concentrate was tested along with the corresponding  $\text{MeCl}_2$  and MeOH subfractions. Samples were taken from Q6, Q8, and Q9, where the impact of chlorination was most easily observed. The results are summarized in Table III. In all cases the mutagenicity present in the unfractonated controls appeared in the MeOH fractions, whereas the fractions eluted with  $\text{MeCl}_2$  were negative. In the set taken January 26, 1981, activity was not detected in the controls but was detected after fractionation at low levels. This suggested inhibition of activity by materials separated in the  $\text{MeCl}_2$  fraction. The activity detected in the MeOH fraction of Q8 (January 26, 1981) was the only case where weak activity appeared to break through the activated carbon columns.

**Chemical Characterization of Active Fractions.** Methylated MeOH fractions were subjected to GC/MS analysis for chemical characterization. Numerous peaks were detected, most of which appeared to be carboxylic acids. Manual (36, 37) and computer-assisted mass spectra comparisons suggested the presence of the methyl esters of the following acids: dehydroabietic acid and other unidentified compounds with similar spectra, fatty acids, toluenesulfonic acid, benzoic acid, and clofibric acid. Clofibric acid, which has previously been found in wastewater, is a metabolite of the drug clofibrate (38, 39). However, the largest group of constituents belonged to a complex mixture of brominated and nonbrominated compounds. On the basis of their spectra, two main groups

Table III. Mutagenic Activity (in NR/L) against TA100 in XAD-8 - Acetone Concentrates and  $\text{MeCl}_2$  and MeOH Subfractions

|  | date     | location | XAD-8<br>con <sup>a</sup> | $\text{MeCl}_2$ | MeOH             |
|--|----------|----------|---------------------------|-----------------|------------------|
|  | 8/12/80  | Q6       | 3040                      | 0               | 930              |
|  |          | Q9       | 2910                      | 0               | 3100             |
|  | 10/10/80 | Q9       | 970                       | 0               | 550              |
|  | 11/25/80 | Q8       | 0                         | 0               | 0                |
|  |          | Q9       | 0                         | 0               | 0                |
|  | 12/9/80  | Q6       | 3710                      | 0               | T <sup>b,c</sup> |
|  |          | Q8       | 0                         | 0               | 0                |
|  |          | Q9       | 370                       | 0               | 1590             |
|  | 1/26/81  | Q6       | 0                         | 0               | 420              |
|  |          | Q8       | 0                         | 0               | 210              |
|  |          | Q9       | 0                         | 0               | 550              |

<sup>a</sup> Unfractonated XAD-8 concentrate. <sup>b</sup> Questionable positive response. <sup>c</sup> T, toxicity.

could be distinguished. The first group (the 207 group), which eluted between 45 and 60 min, had spectra with a base peak of  $m/z$  207. The spectrum of the main peak of this group is depicted in Figure 3. The second group (the 117 group) eluted between 55 and 70 min and had spectra with a prominent fragment at  $m/z$  117. The spectrum of the largest peak of this pattern is given in Figure 4.

A fraction of the 117 group appeared to contain bromine, as was suggested by the presence of characteristic isotope clusters. The degree of bromination appeared to vary widely from sample to sample but clearly increased at the chlorination stages. The spectra of these compounds appeared to belong to either of two subgroups, one characterized by a cluster at  $m/z$  210-216 (the 213 group) and one by a cluster at  $m/z$  200-206 (the 203 group). In Fig-

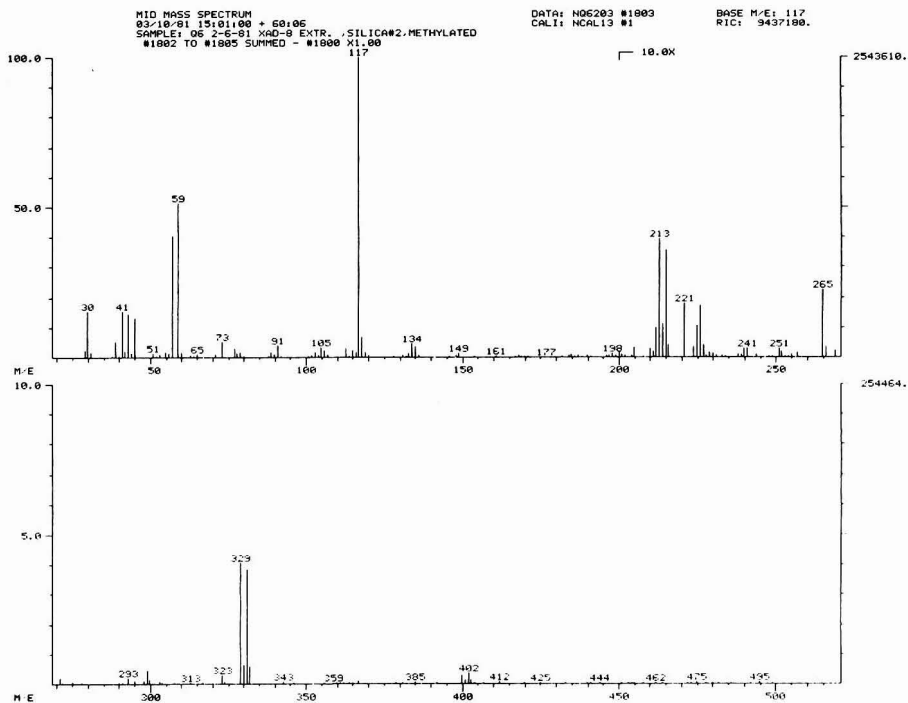


Figure 5. Mass spectrum of a representative BrAPEC compound of the 213 group.

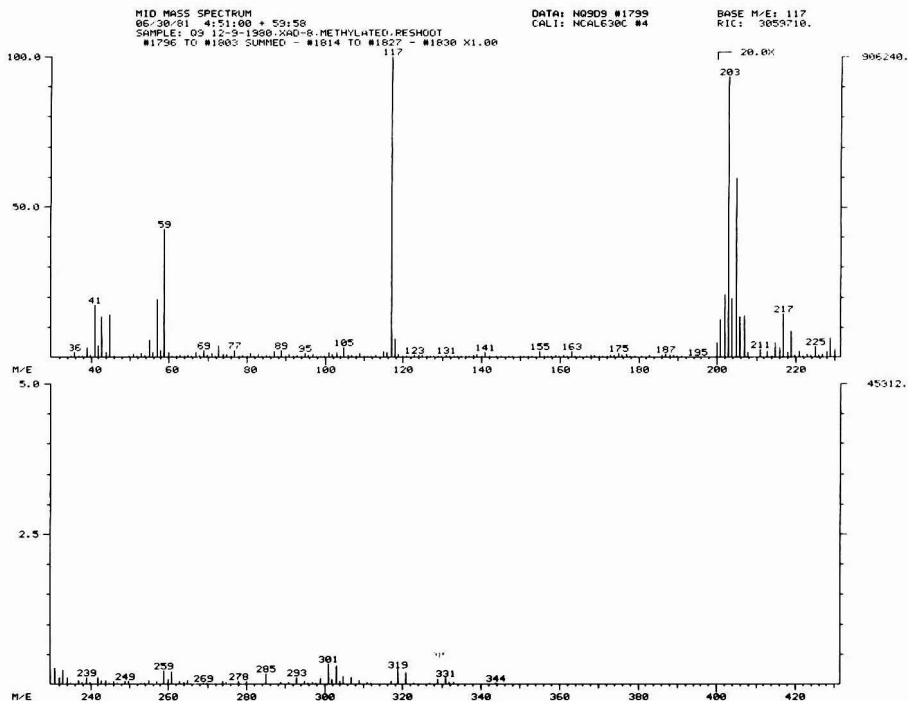


Figure 6. Mass spectrum of a representative BrAPEC compound of the 203 group (Br tentative).



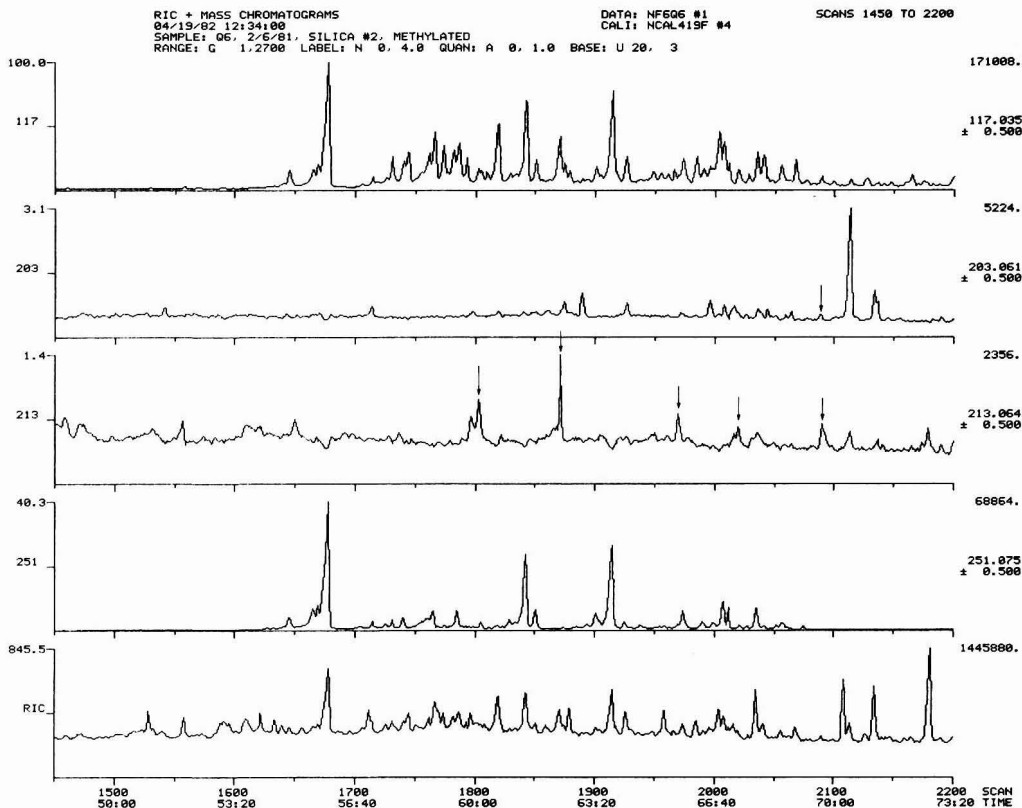


Figure 7. Mass chromatograms  $m/z$  117, 203, 207, 213, 251, and reconstructed ion current (bottom) of methylated MeOH fraction; extract of Q6 February 6, 1981. Brominated peaks are marked.

ures 5 and 6 typical spectra of both groups are presented. For characterization of the unknown mixture, mass chromatograms  $m/z$  117, 207, 203, 213, and 251 appeared to be suitable. Figure 7 shows these mass chromatograms along with a reconstructed ion current chromatogram of the methylated MeOH fraction of Q6 (February 6, 1981). In this sample the compounds are mostly unbrominated; trace amounts of brominated compounds occur between scans 1800 and 2100 (213 group) and at scan 2089 (203 group).

The spectra of these groups were absent in commercially available spectra compilations (36-37) but seemed to match very closely spectra of compounds detected previously in mutagenic concentrates of the Palo Alto Water Reclamation Facility (PAWRF) (9). This prompted us to undertake a new effort to elucidate their structure and to reexamine previously acquired high-resolution spectra. A 1-L sample of (PAWRF) chlorinated secondary effluent (sample C, February 27, 1979) had been extracted with  $\text{MeCl}_2$  ( $3 \times 20$  mL) at pH 2. The methylated extract was then subjected to GC/MS and GC/HRMS. A scan was acquired in which some of the typical fragments were present. In Table IV the exact masses of these fragments are given along with matching elemental compositions and relative intensities.

The HRMS data suggested that the cluster at 400/402 consisted of  $\text{C}_{19}\text{H}_{29}\text{O}_4\text{Br}$ . The cluster at 329/331 ( $\text{C}_{14}\text{H}_{18}\text{O}_4\text{Br}$ ) appeared to originate from a loss of a pentyl group. Other fragments detected were  $m/z$  117 and the

Table IV. Exact Masses, Relative Abundance, MMU Error, and Suggested Elemental Composition of Major Fragments

| mass     | % area | MMU error | composition   |
|----------|--------|-----------|---|
| 41.0385  | 7.8    | -0.652    | $\text{C}_3\text{H}_5$                                  |
| 43.0561  | 5.2    | 1.349     | $\text{C}_3\text{H}_7$                                  |
| 57.0340  | 1.8    | -0.073    | $\text{C}_3\text{H}_5\text{O}$                          |
| 57.0705  | 17.1   | 0.087     | $\text{C}_3\text{H}_7\text{O}$                          |
| 59.0471  | 11.8   | -0.567    | $\text{C}_3\text{H}_7\text{O}$                          |
| 117.0563 | 100.0  | 1.175     | $\text{C}_3\text{H}_5\text{O}_3$                        |
| 134.0759 | 3.5    | 2.742     | $\text{C}_3\text{H}_{10}\text{O}$                       |
| 135.0802 | 2.9    | 1.034     | $\text{C}_3\text{H}_{11}\text{O}$                       |
| 329.0342 | 41.2   | -8.176    | $\text{C}_{14}\text{H}_{18}\text{O}_4$ $^{79}\text{Br}$ |
| 331.0391 | 34.9   | 2.233     | $\text{C}_{14}\text{H}_{18}\text{O}_4$ $^{81}\text{Br}$ |
| 400.1243 | 5.8    | -0.608    | $\text{C}_{19}\text{H}_{29}\text{O}_4$ $^{79}\text{Br}$ |
| 402.1187 | 6.4    | -4.194    | $\text{C}_{19}\text{H}_{29}\text{O}_4$ $^{81}\text{Br}$ |

cluster  $m/z$  134/135, which were matched to  $\text{C}_3\text{H}_5\text{O}_3$  and  $\text{C}_3\text{H}_{10}\text{O} + \text{H}$ , respectively. Fragment 59.047 was matched to  $\text{C}_3\text{H}_7\text{O}$ , fragment 43.056 to  $\text{C}_3\text{H}_7$ , and 41.038 to  $\text{C}_3\text{H}_5$ . However, the two clusters present in the low-resolution spectra suspected to contain bromine,  $m/z$  200-210 and  $m/z$  210-216, were missing in the HRMS scan. It was therefore suspected that the HR mass spectrum was incomplete and possibly consisted of overlapping spectra of two closely eluting GC peaks. The slow scan time (8 s) and the insufficient resolution of the packed column may have been inadequate for analysis of the complex mixture at hand.

The crux of spectrum identification was fragment  $m/z$

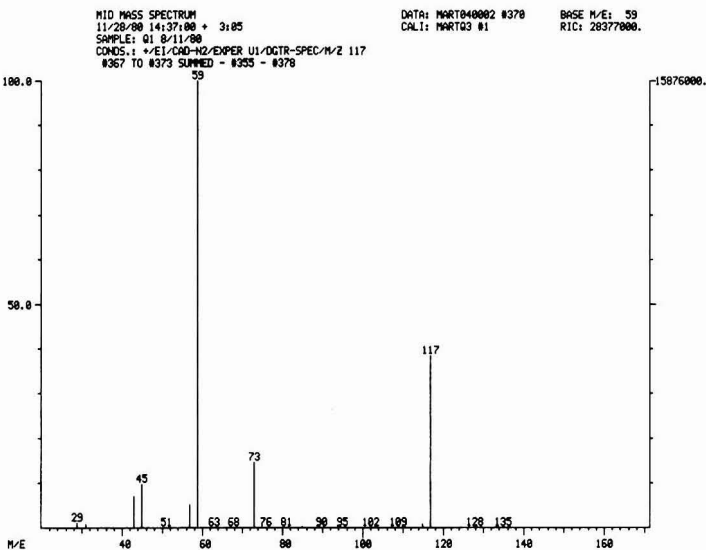


Figure 8.  $EI^+$  daughter-ion spectrum of fragment ion  $m/z$  117.

117. For aid in structural elucidation, an  $EI^+$  daughter-ion experiment was conducted with GC/TSQ MS. Figure 8 depicts the daughter-ion spectrum of fragment  $m/z$  117 produced by CAD with  $N_2$ . It indicates that this fragment loses neutral fragments of mass 44 and 58, resulting in the fragment ions  $m/z$  73 and 59, respectively. These losses were tentatively assigned to  $C_2H_4O$  and  $C_2H_4OCH_2$ , which leaves  $C_2H_3O_2$  for  $m/z$  59. This is consistent with the elemental composition of a methylated carboxyl group. By assignment of the loss of 71 from the apparent molecular ions 322 and 400 to a pentyl group and by recognition of the aromatic and phenolic elements of the spectrum, structures I and II depicted in Figure 9 could be proposed. The relatively high intensity of  $m/z$  135 was taken as an indication of the presence of two methyl groups (or an ethyl group) at the  $\alpha$ -carbon in the aliphatic side chain. The fragmentation patterns proposed in Figure 9 may explain the presence of the major fragments. For the group with  $m/z$  207 as a base peak no HRMS or TSQ MS data was available, and these spectra are consequently less understood. A structure of type III is suggested as a possibility. There appeared to be three reasons for the great complexity of the mixture. The presence of compounds differing in their apparent molecular weight by 14 amu indicated the presence of a series of homologues. The presence of compounds differing in their apparent molecular weight by 44 suggested the presence of compounds having side chains with different numbers of ETO units. The presence of compounds with the same apparent molecular weight but with slightly different GC retention times and with similar spectra suggested the occurrence of differently branched alkyl side chains.

So that spectra of compounds similar to those proposed in Figure 9 could be studied, commercially available alkylphenol polyethoxylates (APEs) were converted to the alkylphenol polyethoxy carboxylates (APECs) and brominated alkylphenol polyethoxy carboxylates (BrAPECs). The APE standard used was specified by the supplier as "polyethoxylated *tert*-octylphenol" with three ETO units per molecule. But GC/MS analysis indicated that a mixture of APEs were present, with the number of ETO

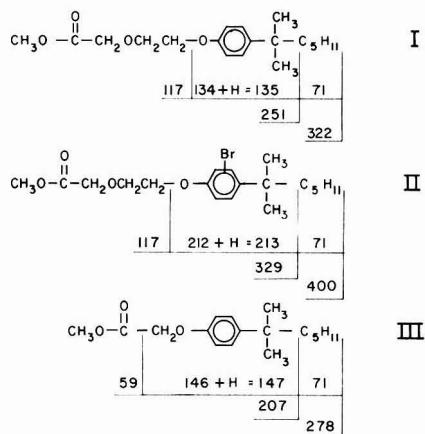


Figure 9. Proposed structures of APEC and BrAPEC compounds representative of 117 group (I), 213 group (II), and 207 group (III); fragmentation is tentative.

units/molecule ranging from one to greater than three. Spectra apparently belonging to the 207 group and the 117 group (Figures 10 and 11) were found in the APE mixture after oxidation. Visual comparison of the spectra suggested that the compounds produced chemically were of the same type as those present in the standard mixture. Bromination followed by oxidation of the APE mixture produced compounds with spectra similar to those found in the concentrates. Figure 12 depicts a spectrum matching closely the one depicted in Figure 5. Chemically produced methylated BrAPEC mixture was coinjected with an extract, and it was observed that BrAPECs with apparent MW of 400 coeluted. This seemed to confirm that the mixture produced chemically contained the same or closely related compounds as the extracts. Further characterization of the composition of the complex APEC and

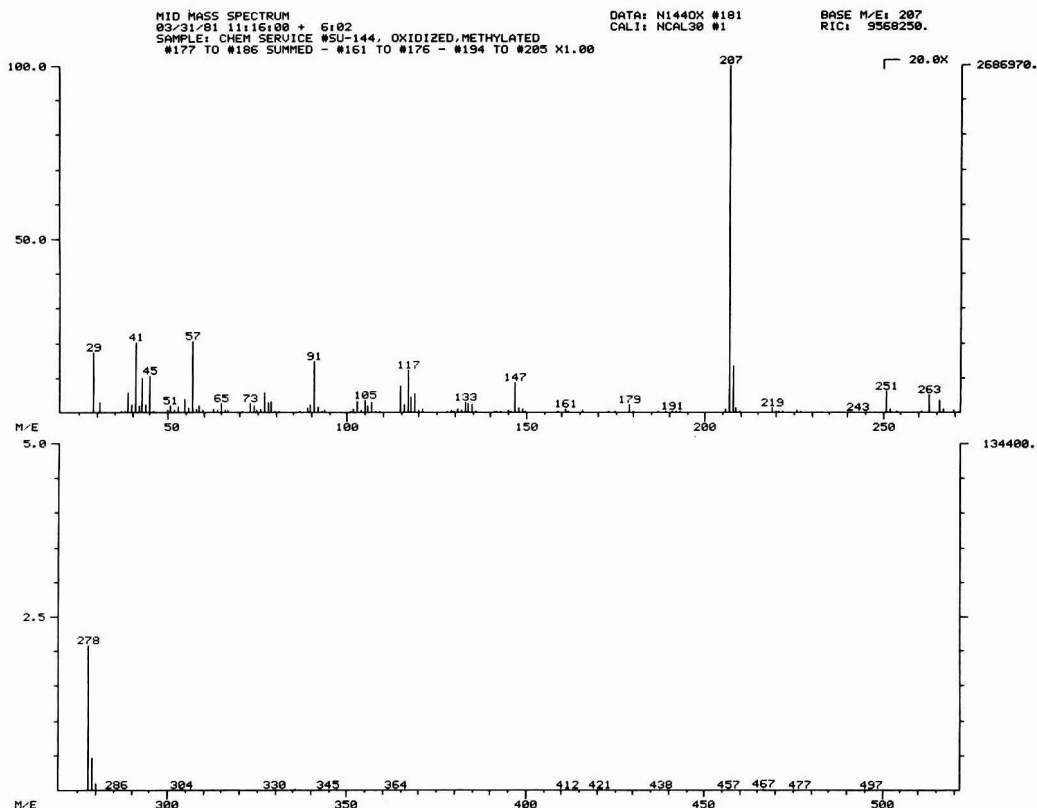


Figure 10. Spectrum of compound found in the chemically oxidized APE mixture apparently belonging to the 207 group.

BraPEC mixture present in the water extracts was beyond the scope of this work.

**Mutagenic Response of BraPECs.** Because of the prevalent occurrence of the APEC and BraPEC compounds in the mutagenic fraction, an attempt was made to relate their presence to the mutagenicity data. BraPECs were clearly products of chlorination, and it was suspected that they were the cause of the mutagenicity in the chlorinated samples. In Table V we present an attempt to correlate qualitatively the occurrence of mutagenicity with the occurrence of BraPECs.

Nonbrominated isomers detected with MC 207 and 251 were present in both Q8 and Q6 samples tested. Their presence in Q8 indicated that they were breaking through the activated-carbon column. They were not found in either of the Q9 extracts, however. No BraPECs were detected in the Q6 sample taken on December 9, 1980, where the mutagenic response was questionable (two values above twice background, but toxicity and no dose-response). However, BraPECs of the 203 type were present in Q9, where a clear mutagenic response was observed. In the second set BraPECs were present in Q6 (203 and 213 type) and Q9 (203 type), which were both positive, but were absent in Q8, which was negative. This indicated that bromination of APECs occurred during chlorination and suggested that BraPECs produced the observed mutagenic response.

For further exploration of the BraPECs as potential mutagens, the mixture prepared in the laboratory was subjected to Ames testing. It did not produce a mutagenic

Table V. Qualitative Correlation between Mutagenic Response and the Presence of APEC and BraPEC Isomers

| date   | sample | muta-<br>gen-<br>icity | 207 <sup>a</sup> | 251 <sup>a</sup> | 203 <sup>b,c</sup> | 213 <sup>b</sup> |
|--------|--------|------------------------|------------------|------------------|--------------------|------------------|
|        |        |                        | 12/9/80          | Q6               | T <sup>d</sup>     | +                |
|        | Q8     | 0                      | +                | +                | 0                  | 0                |
|        | Q9     | +                      | 0                | 0                | +                  | 0                |
| 2/6/81 | Q6     | +                      | +                | +                | +(w) <sup>g</sup>  | +(w)             |
|        | Q8     | 0                      | +(w)             | +(w)             | 0                  | 0                |
|        | Q9     | +                      | 0                | 0                | +(w)               | 0                |

<sup>a</sup> Indicative of APECs. <sup>b</sup> Indicative of BraPECs.  
<sup>c</sup> Bromine substitution suggested. <sup>d</sup> Questionable positive response; T = toxicity. <sup>e</sup> + = characteristic indicated was present. <sup>f</sup> 0 = characteristic indicated was absent.  
<sup>g</sup> Weak.

effect but was toxic at higher doses. In another experiment, the XAD-8/acetone extract of a 1-gallon Q6 sample (sampled May 20, 1981) was split into two halves, A and B. A was tested as previously; B was redissolved in 10 mL of 0.1 N NaOH. The next day, the organics were reextracted by using the XAD-8 adsorption method. The extract was split into two portions, one for Ames testing and one for chemical characterization. Comparison of the responses to A and B revealed that treatment of B with base apparently destroyed the mutagens that gave a positive response in A. However, comparison of the MC 213 profiles in A and B did not indicate an observable difference, and in both A and B the 203 profile was absent. These

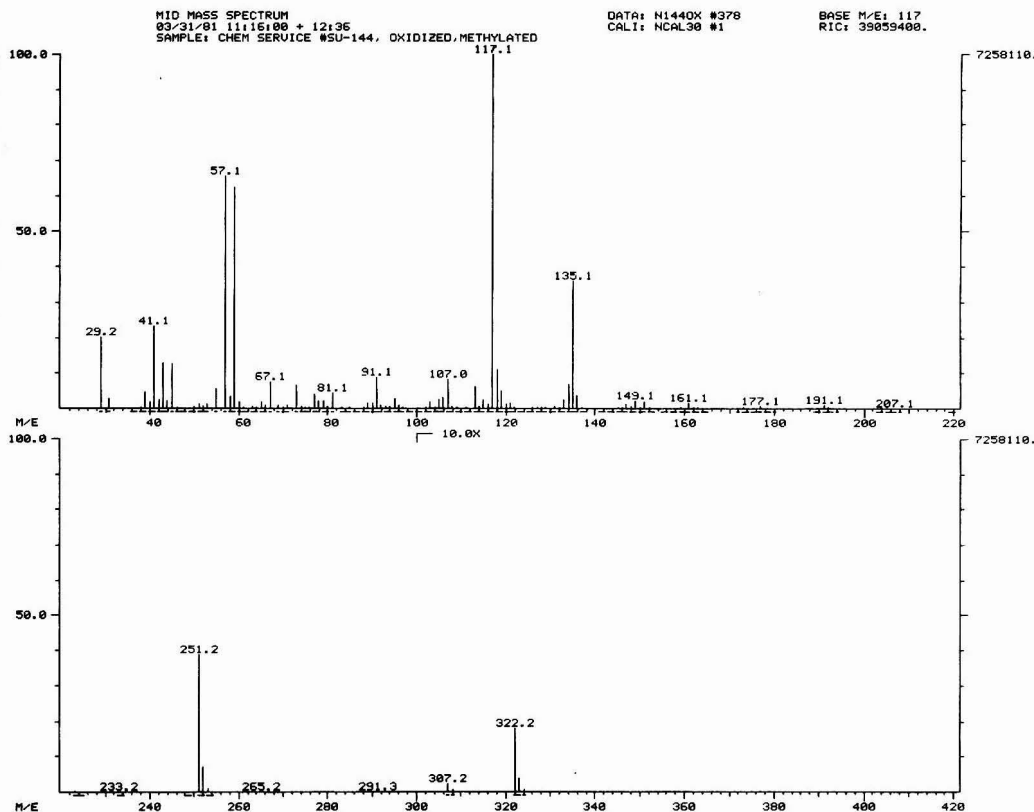


Figure 11. Spectrum of compound found in chemically oxidized APE mixture apparently belonging to the 117 group.

two experiments seemed to counter the hypothesis that the mutagenicity observed at Q6 and Q9 was due to BraPEC compounds detected with MC 203 and 213.

#### Discussion and Conclusions

WF 21 received a secondary effluent in which direct-acting mutagens were detected intermittently. Our data suggest that the mutagens present in the influent were removed or destroyed during treatment, as indicated by the absence of mutagenicity in the activated carbon and reverse-osmosis effluents. WF 21 influent also appeared to contain precursors that were converted into direct-acting mutagens during chlorination. Increased activities were found at Q6, where chlorine was added for algae control and nitrogen removal. The mutagens formed there were removed during subsequent AC adsorption. In the AC effluent, only one marginal case of activity was detected. However, the precursors were not sufficiently removed by AC adsorption, as was indicated by the reoccurrence of mutagenicity during final chlorination for disinfection. By and large, activity appeared to be as strong or stronger in the final chlorinated effluent as in the chlorinated recarbonation basin effluent. None of the RO effluent samples tested exhibited a mutagenic response. Because the RO effluent was not chlorinated, it is not known whether the precursor materials were removed by RO.

The nonvolatile mutagens formed during chlorination at WF 21 appeared to be associated with rather polar or surface active materials. Analysis of the mutagenic fraction

revealed the presence of a variety of organic acids, APECs and BraPECs being the major constituents. In Q1, the concentrations of the major components were estimated to be in the 100  $\mu\text{g/L}$  range. A significant fraction of each major component was removed during treatment, but significant quantities, probably in the  $\mu\text{g/L}$  range, remained even after AC adsorption.

The fact that BraPECs were formed during chlorination suggested that these compounds were involved in producing a mutagenic response. But preliminary experiments with chemically produced BraPECs did not support this hypothesis. Thus the coincidence of mutagenicity and BraPECs might have been accidental. Various reasons could explain this apparent discrepancy: (i) the chemically produced mixture did not reflect the mixture found in the mutagenic fractions, (ii) the difference in halogenation conditions might have led to different products (for instance small amounts of side-chain brominated products might have been formed under plant chlorination conditions), or (iii) the active compounds were not detected with the analytical procedure used. Clearly, an evaluation of these questions is complex and requires much more study.

APEs, from which APECs and BraPECs are suspected to derive, have been detected previously in wastewater effluents (40, 41) but are not presently being monitored as such in the environment (42). Little is known about their health and environmental significance, and only limited data are available pertaining to their occurrence and fate in the environment. APEs are presently in use

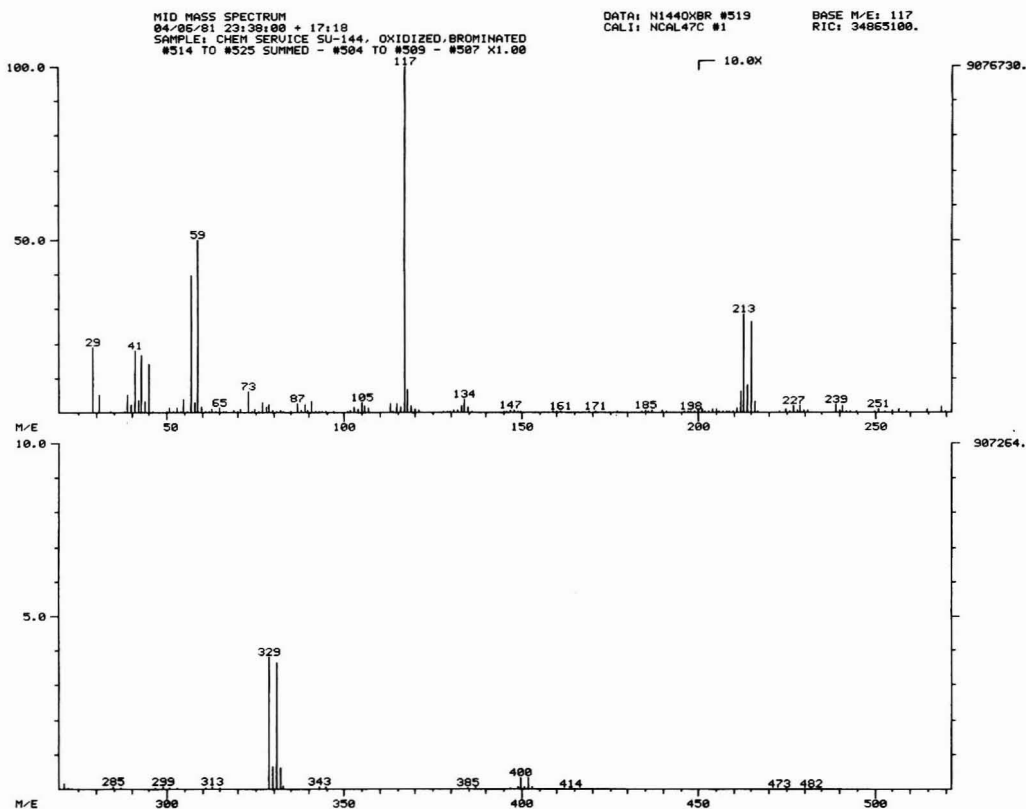


Figure 12. Spectrum of compound found in the chemically oxidized brominated APE mixture apparently belonging to the 213 group.

as industrial and domestic surfactants. The current amount of APEs produced is not known, but in 1962 about 50 000 tons were used in laundry-detergent formulations (43). APEs are reported to undergo primary biodegradation during activated sludge treatment and trickling filter sewage treatment (42), but it is known that APE residues are rather recalcitrant, particularly when the hydrophobic alkyl groups are highly branched (43). Long-chain APEs (10 ETO) were shown to undergo biological degradation to short-chain APEs (1-2 ETO) by adapted microorganisms in a laboratory investigation (44), but ultimate biodegradation is known to be very slow (45). It also seems likely that bromination (and chlorination if it should occur) will render these molecules even more refractory and more lipophilic. Both of those characteristics are likely to cause greater persistence in the environment and possibly accumulation in the food chain. It seems necessary to address these questions as well as the public health significance of these residues in more detailed studies.

The fact that brominated but not chlorinated species were detected is interesting. It suggests the presence of highly reactive brominating agents in the chlorinated water, possibly bromine ( $\text{Br}_2$ ), bromine chloride ( $\text{BrCl}$ ), or bromine hypochlorite ( $\text{BrOCl}$ ). Most studies of chlorination effects in the past have been directed toward chlorinated byproducts (8). The facts that all brominated haloforms are mutagenic (13) and that aromatics appear to be preferentially brominated during wastewater chlorination suggests that bromine incorporation into organic materials should receive more attention.

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# NOTES

## A Survey of Discharges from a Natural Gas Drilling Operation in Lake Erie

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■ We mapped turbid discharge plumes from a Canadian gas drilling rig by continuous-flow nephelometry and measured the concentrations of selected inorganic and organic constituents in the plumes. The buoyant surface plumes were from ~600 to 1500 m long, with a maximum width of ~250 m and areas less than 25 ha. Maximum total suspended solids in the discharge plumes were usually less than 5.0 mg/L and were rapidly dispersed when discharging ceased. Sodium, magnesium, sulfate, and chloride were diluted to ambient lake-water levels within 50 m of the drilling rig. Volatile hydrocarbons were <25 µg/L and dispersed quickly. Methane and ethane were enriched in the discharge plume but dispersed rapidly with increasing distance from the rig.

### Introduction

Canada has produced natural gas from offshore Lake Erie wells since 1956. Presently, more than 1100 wells have been drilled and about 450 are producing natural gas or awaiting connection to an underwater collection system (1). Similar development in U.S. waters has been prevented by state bans on natural gas drilling in Lake Erie. However, in 1977 New York and Pennsylvania lifted existing bans and Ohio allowed their ban to expire in 1978, signaling a willingness to allow natural gas exploration. Currently, an environmental impact statement is being completed by the U.S. Environmental Protection Agency and the U.S. Army Corps of Engineers to guide development of the legal framework necessary to begin natural gas exploration in United States waters.

This report describes a field investigation of the discharges from a Canadian offshore natural gas drilling operation in Lake Erie. The study was conducted in conjunction with preparations of the environmental impact statement.

### Methods

The drilling site was located at 42°35'12" N by 80°35'36" W, approximately 5.8 km southwest of Port Burwell, Ontario, and 5.0 km offshore. Water depth at the site was 16 m. The lake bottom at the site was firm and level, and the sediment was composed of coarse sandy material overlying glaciolacustrine clay.

The drilling operation was conducted by the Canadian firms Consumers' Gas Co. and Underwater Gas Developers Ltd. The drilling rig used was the *Mr. Neil*, a jack-up rig capable of drilling in water of 25 m maximum depth and 2440 m maximum drilling depth. The normal time required for the *Mr. Neil* to complete a gas well is 4-5 days. The operation includes the following phases: (1) jack-up

into the drilling position; (2) surface hole drilling and casing; (3) drilling to total depth (i.e., the gas-bearing formation); (4) well completion. The field study occurred primarily during phases 2 and 3 when drilling fluids and cuttings were discharged to the lake. The drilling fluid utilized during these phases was Lake Erie water that was circulated through the wellbore. Drilling mud (a suspension used to aid drilling performance) was occasionally circulated through the wellbore, but it was returned to shipboard tanks after use and not discharged to the lake.

The *Mr. Neil* arrived at the drill site at 2225 on 28 May 1979, and began operations immediately. The well produced commercial quantities of gas and was completed on 2 June 1979. The operation sequence is thoroughly described by Ferrante et al. (1).

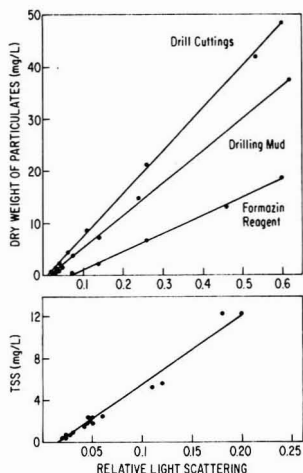
The field study focused on mapping the turbid discharge plume from the drilling operation and comparing chemical characteristics of plume samples with samples from the rig discharge and undisturbed reference stations in the lake. Field sampling was accomplished with a small, fast-work boat equipped with a Mini-Ranger III navigation system, continuous-flow nephelometry apparatus, and water-sampling equipment.

The nephelometry apparatus was a Turner Designs Model 10-035 fluorometer fitted with a high-pressure continuous-flow nephelometry kit that meets specifications recommended by American Public Health Association (2). The nephelometer was nulled daily to a reading near zero by passing particle-free water (0.2 µm filtered Lake Erie water) through the instrument. A calibration curve was prepared to convert the relative light-scattering signal from the nephelometer to the dry weight of total suspended solids. The dry weight of total suspended solids (TSS) was determined in lake-water samples of known light-scattering intensity that were collected at undisturbed reference stations and in the discharge plumes. TSS was measured by filtering the particulate material from 1-L water samples on washed and preweighed 0.45-µm Gelman Metricel filters, drying the filters to constant weight at 60 °C, and then reweighing the filters on an analytical balance. The light scattering-TSS relationship was also determined with three other mixtures of suspended particles to evaluate the performance of the nephelometer. Serial additions of a 400 NTU formazin reagent (3), drilling-rig discharge, and drilling mud were cycled separately through the nephelometer while operating in a closed-loop mode. After each addition, light scattering was recorded and the reference suspension sampled to determine the dry weight of TSS as described above.

During drilling operations, the turbid discharge plumes were surveyed by nephelometry and mapped by coupling the nephelometry data with sampling-location information provided by the Mini-Ranger III navigation system and Polaris bearings from the support R/V *Roger R. Simons*, anchored nearby. Surface water (0-2 m) was continuously

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**Figure 1.** Light scattering/dry weight relationship for three different reference suspensions (upper) and the light scattering/TSS relationship for water samples (lower) collected in the discharge plume and at reference stations.

supplied to the nephelometer by a towed submersible pump. The vertical distribution of TSS was periodically sampled by lowering the submersible pump through the water column to within 1 m of the bottom.

Triplicate samples of drilling mud and undiluted drilling-rig discharge were analyzed by emission spectrometry for an extensive suite of elements to evaluate their potential for increased concentrations in the discharge plumes. Although drilling mud was not discharged, it was included in these analyses to aid its identification in the event of an accidental spill. The elements included Ag, Al, B, Ba, Be, Bi, Ca, Co, Cr, Cu, Fe, K, Li, Rb, Cd, Mg, Mn, Mo, Na, Ni, Pb, Sb, Si, Sn, Sr, Ti, V, Zn, Zr, La, and Y. Details of these analyses are presented by Ferrante et al. (1). From this suite, Mg and Na were selected for determination in the plume samples. These elements occur at high concentrations in the discharge samples, and they serve as indicators of the behavior of chemical species associated with the particulate and dissolved fractions, respectively, of discharged materials. Sulfate and chloride were also determined because they occurred at high concentration in the drilling-rig discharge.

The plume chemistry survey was conducted on 31 May when drill cuttings were being discharged to the Lake. After completion of a nephelometric survey to determine the plume dimensions and heading, triplicate water samples for chemical analysis were collected at 6 locations along the longitudinal axis of the plume and at the reference stations (Figure 1c). These samples were analyzed for Mg, Na, chloride, sulfate, volatile hydrocarbons, and carbon tetrachloride extractable hydrocarbons (CTEH). Mg and Na were measured by atomic absorption analysis (1, 3). Sulfate and chloride were measured with a Dionex Model 14 ion chromatograph and checked gravimetrically (1, 3). The volatile hydrocarbons methane, ethane, and propane were determined by gas chromatography (4, 5). Carbon tetrachloride extractable hydrocarbons were measured on Beckman Model 4260 and Digilab FTS20 infrared spectrometers (1).

### Results

The least-squares regression relationship between the dry weight of TSS ( $Y$ ) in lake water samples and the

light-scattering intensity ( $X$ ) measured by nephelometry on the same samples was  $Y = -1.16 + 67.66X$ ;  $r^2 = 0.96$  (Figure 1). All the TSS data presented in this report are based on this conversion. Similar linear relationships were observed with the three other reference suspensions (Figure 1). The relationships for lake-water samples and drill-rig discharge samples were identical, indicating that the nephelometer accurately measured TSS levels in the discharge plumes. Since the usual measuring unit for turbidity is the nephelometric turbidity unit (NTU) based on formazin reagent, the second abscissa on Figure 1 was prepared for conversion purposes. This was done by assigning the known NTU values per unit of light scattering, observed in the formazin reagent dilution series, to the equivalent light-scattering values observed in the field samples.

A predrilling survey to determine the background level and distribution of TSS at the drill site showed low levels of TSS (less than or equal to 0.4 mg/L) with very little variation in the concentration and spatial distribution. This provided excellent conditions for the detection of turbid discharges from the drilling operation. Similarly, daily surface transects between the drilling rig and the reference stations showed no changes in the background concentrations of TSS throughout the study period.

As drilling to total depth commenced, drill cuttings were removed from the wellbore by circulating Lake Erie water through the drill string. The turbid mixture was pumped up to the rig and discharged into the lake through a submerged discharge pipe. Dispersion of the drill cuttings began at the point of discharge and a sorting of particle sizes occurred as a result of differential net settling velocity and currents. The coarsest cuttings likely settled quickly to the bottom, while the finer materials deposited at increasing distance from the discharge. The finest material appeared to rise to the lake surface, producing a buoyant surface plume of turbid water.

Vertical nephelometry profiles of the water column under the plume showed the detectable surface plume extended downward to a maximum depth of only 4 m. The buoyant surface plumes were tracked and mapped twice from 1535 to 1630 and from 1800 to 2000 on 30 May and once from 1430 to 1510 on 31 May 1979. The two initial mappings (A and B in Figure 2) showed surface plumes that drifted eastward approximately 600–1500 m before dispersing to background TSS values (less than or equal to 0.4 mg/L). These plumes achieved maximum widths of approximately 200 m and included areas of approximately 10–25 ha. The TSS concentrations ranged from 0.4 to 1.2 mg/L. The third plume (C in Figure 2) traveled only about 320 m before dispersing to the background TSS level; it covered only ~3.5 ha. Although this plume was much smaller than the other two, the TSS levels were higher. The maximum was 5.3 mg/L of TSS, measured approximately 25 m downcurrent from the rig discharge.

The plume chemistry survey showed that the concentrations of Na,  $\text{SO}_4$ , and Cl were not elevated in the 31 May discharge plume at distances >25 m (Table I). These constituents apparently dispersed quite rapidly after discharge, since their concentrations at distances >25 m were approximately equal to the concentrations measured at the reference stations. Mg concentrations at 25 m from the drilling rig were significantly higher than at other locations in the 31 May discharge plume and the reference stations. However, Mg rapidly declined to ambient lake-water levels throughout the remainder of the plume, suggesting that the area exposed to elevated Mg levels was small (less than 1 ha).



Table I. Concentrations of Sodium, Magnesium, Sulfate, and Chloride at Midpoint of Transect across Plume C on 31 May, in the Drilling Discharge Fluid, and at the Reference Stations on 31 May

| sample designation    | dist from discharge, m | Na <sup>a</sup> | Mg <sup>b</sup> | SQ <sub>4</sub> <sup>2-a</sup> | Cl <sup>-</sup> |
|-----------------------|------------------------|-----------------|-----------------|--------------------------------|-----------------|
| MN 14 <sup>c</sup>    |                        | 272.0           | 618.0           | 265.0                          | 605.0           |
| Plume Transects       |                        |                 |                 |                                |                 |
| 1a (2 m)              | 25                     | 7.5             | 8.8             | 21.6                           | 18.9            |
| 1b (2 m)              | 25                     | 7.5             | 8.9             |                                |                 |
| 2a (2 m)              | 100                    | 9.9             | 8.7             | 22.3                           | 18.6            |
| 2b (2 m)              | 100                    | 10.1            | 8.3             |                                |                 |
| 3a (2 m)              | 200                    | 10.0            | 8.4             | 22.5                           | 19.0            |
| 3b (2 m)              | 200                    | 10.0            | 8.4             |                                |                 |
| 4a (2 m)              | 330                    | 9.9             | 8.3             | 22.0                           | 19.0            |
| 4b (2 m)              | 330                    | 10.0            | 8.4             |                                |                 |
| 5a (2 m)              | 140                    | 10.1            | 8.5             | 22.3                           | 19.0            |
| 5b (2 m)              | 140                    | 10.2            | 8.3             |                                |                 |
| 6a (2 m)              | 160                    | 10.2            | 8.1             | 22.3                           | 19.1            |
| 6b (2 m)              | 160                    | 10.0            | 8.2             |                                |                 |
| Reference Stations    |                        |                 |                 |                                |                 |
| R <sub>1</sub> (2 m)  |                        | 10.0            | 8.3             | 22.7                           | 19.6            |
| R <sub>2</sub> (2 m)  |                        | 9.8             | 8.3             | 22.9                           | 19.5            |
| R <sub>1</sub> (14 m) |                        | 10.2            | 8.3             | na <sup>d</sup>                | na              |
| R <sub>2</sub> (14 m) |                        | 9.9             | 8.3             | na                             | na              |
| drilling mud          |                        |                 |                 | 28.4 × 10 <sup>4</sup>         |                 |

<sup>a</sup> Filtered. <sup>b</sup> Unfiltered. <sup>c</sup> Undiluted drilling discharge fluid from the Guelph Formation. The Na value for the unfiltered sample was 282.0; the Mg value for the filtered sample was 49.3. <sup>d</sup> na = not available.

Table II. Concentrations of Volatile Hydrocarbons at Midpoint of Transects across Plume C on 31 May and at Reference Stations on 31 May

| sample designation    | concn, µg/L |        |         |
|-----------------------|-------------|--------|---------|
|                       | methane     | ethane | propane |
| Plume Transects       |             |        |         |
| 1a (2 m)              | <10         | <1     | <3      |
| 1b (2 m)              | <10         | <1.3   | <3      |
| 2a (2 m)              | 21          | 4.6    | <3      |
| 2b (2 m)              | 19          | 3.7    | <3      |
| 3a (2 m)              | 15          | 4.6    | <3      |
| 3c (2 m)              | 15          | 3.0    | <3      |
| 4a (2 m)              | <10         | 1.3    | <3      |
| 4b (2 m)              | <10         | 1.6    | <3      |
| 5a (2 m)              | 13          | 1.1    | <3      |
| 5b (2 m)              | 13          | 2.0    | <3      |
| 6a (2 m)              | 10          | 1.9    | <3      |
| 6c (2 m)              | 12          | 1.7    | <3      |
| Reference Stations    |             |        |         |
| R <sub>1</sub> (2 m)  | <10         | <1     | <3      |
| R <sub>2</sub> (2 m)  | <10         | <1     | <3      |
| R <sub>1</sub> (14 m) | <10         | <1     | <3      |
| R <sub>2</sub> (14 m) | <10         | <1     | <3      |

The analyses of volatile hydrocarbons showed minor increases of methane and ethane in the 31 May plume as compared to reference station levels (Table II), but the increases were generally less than a factor of 2 above ambient. Methane and ethane declined rapidly at distances greater than 100 m from the rig. A low concentration of methane (<10 µg/L) was observed at the station nearest the rig, but a higher concentration (~20 µg/L) occurred 100 m downcurrent. This suggests that low-density components of the subsurface discharge were rising to the surface between 25 and 100 m downcurrent. This hypothesis is supported by the nephelometry data and a plume modeling effort by Dettmann (6), but data on the distributions of inorganic chemicals in the plume do not show this effect.

Table III. Concentrations of Carbon Tetrachloride Extractable Hydrocarbons in the 31 May Plume, in the Discharge Fluid, at the Reference Stations and near the Rig after Drilling Was Completed on 31 May

| sample designation | concn, µg/L |
|--------------------|-------------|
| CC <sup>a</sup>    | 128         |
| CC <sup>a</sup>    | 138         |
| MN 23 <sup>b</sup> | 894         |
| Plume Transects    |             |
| 1a                 | 48          |
| 1b                 | 48          |
| 2a                 | 37          |
| 2b                 | 43          |
| 3a                 | 44          |
| 3b                 | 42          |
| 4a                 | 79          |
| 4b                 | 60          |
| Reference Stations |             |
| R <sub>1</sub>     | 48          |
| R <sub>2</sub>     | 64          |

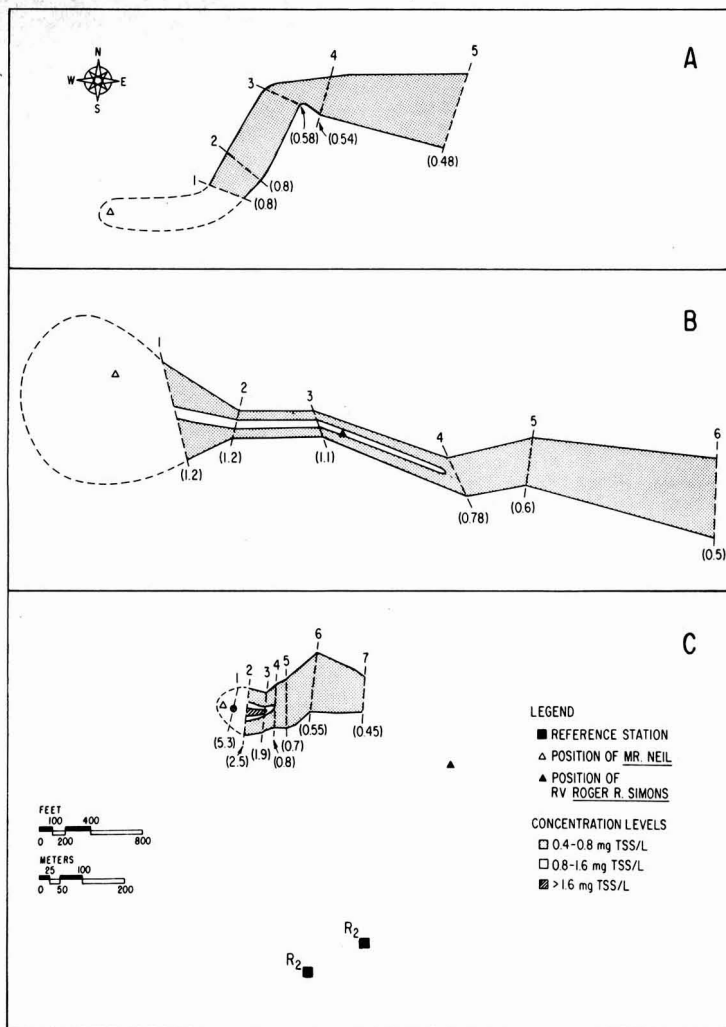
<sup>a</sup> In-lake sample collection within 100 m of the rig, about 3 h after drilling was completed. <sup>b</sup> Undiluted drilling discharge from the Grimsby Formation.

The distribution of CTEH in the plume may also support the hypothesis of a rising plume of low-density materials (Table III). A comparison of the concentrations of CTEH in the 31 May plume and reference station samples showed no increase of extractable hydrocarbons due to rig discharges at the time of sampling. However, 3 h after drilling and discharging ceased, at 0912 on 1 June, measurable increases of CTEH were observed in samples collected ~100 m downcurrent from the discharge. The average concentration of CTEH in these samples was 133 µg/L, an increase of ~2.4 over reference station samples.

### Discussion

High concentrations of suspended solids in aquatic ecosystems can alter fish behavior (7) and metabolism (8), reduce photosynthetic rates of indigenous phytoplankton (9), and reduce feeding rates and numbers of zooplankton (10, 11). NAS (9) suggested that a high level of protection for aquatic communities is provided when TSS do not exceed 25 mg/L. The highest TSS concentration measured during the drilling study was 12.6 mg/L, measured in a water sample collected at the surface within 5 m of the subsurface discharge plumes, which posed no threat to aquatic life in the water column since the concentrations generally averaged less than 5.0 mg/L, the plume areas were small (less than 50 ha), and TSS dispersed to background levels very quickly after discharging ceased.

Deposition of drill cuttings on the lake bottom could potentially affect the benthic community. The estimated amount of drill cuttings discharged to the lake from this wellbore was ~5.0 × 10<sup>4</sup> kg, based on wellbore dimensions and the density of crustal rock material. If all the discharged cuttings settled uniformly over an area of ~100 ha (estimated by summing surface plume areas), mass sedimentation would be ~5 mg/cm<sup>2</sup>. This represents a small fraction (less than 5%) of the natural annual mass sedimentation rate determined for Lake Erie (12). This calculation suggests that effects on the benthic community may be minor and limited to a small area around the discharge pipe, where maximum deposition occurred. However, the potential for impacts would also depend on the concentration of toxicants in the deposited material and on whether or not sediments actually accumulate at the drill site. Most drill sites are in shallow water where



**Figure 2.** Spatial distributions of turbid discharge plumes in the surface water. Plumes A and B were mapped on 30 May between 1535 and 1630 and between 1800 and 2000, respectively. Plume C was mapped on 31 May between 1430 and 1510 and simultaneously sampled for chemical constituents at midpoints of transects 1-6. Numbers in parentheses are maximum concentrations of TSS along transects.

no mass sedimentation occurs, suggesting that sediment from drilling would be dispersed over a much larger area than estimated above.

Since elevated concentration of Mg, Na, SO<sub>4</sub>, an Cl were limited to an area within 50 m of the drilling rig, the potential for environmental impacts on the lake due to these constituents appears minor. The biological impacts of the small addition of volatile hydrocarbons discharged to the lake during drilling also appear minimal since the concentrations measured represent only a small fraction of levels previously reported in some areas of Lake Erie (13, 14). The largest single source of methane in Lake Erie is probably biogenic release from anaerobic decomposition of organic material in bottom sediments (15).

The elevated levels of CTEH measured at the study site after discharging ceased may not have resulted from this drilling operation. Zapotosky and White (14) showed considerable variability in the background CTEH levels

in their survey of the whole lake; at numerous locations the concentrations exceeded 200 µg/L. The potential for environmental impacts of CTEH components cannot be overlooked, however, since they can be accumulated and transferred through the food chain in aquatic systems (16).

Based on our observations during the drilling of this well, the potential for impacts on water quality and aquatic biota by discharges from open-cycle natural gas drilling, where the circulating fluid is the ambient lake water and the use of drilling fluid additives are limited, appears low and likely limited to a mixing zone located within a few hundred meters of the drilling operation.

*Acknowledgments*

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**Biotransformation of PCB by Natural Assemblages of Freshwater Microorganisms**

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■ Natural mixed-microbial populations in lake water were found capable of oxidizing 2-chlorobiphenyl but not 2,4'-dichlorobiphenyl. No evidence was found to indicate that these populations were able to oxidize a PCB mixture 54% chlorine by weight. Oxidation of 2-chlorobiphenyl resulted in the accumulation of two biotransformation products, chlorobenzoic acid and chlorobenzoylformic acid (chlorophenylglyoxylic acid). The results indicate that biodegradation of PCB congeners may result in the accumulation of environmentally stable chlorinated biotransformation products in aquatic environments.

Introduction

A number of reports have cited the ability of isolated heterotrophic bacteria to grow on and in some cases degrade polychlorinated biphenyls (PCB) (1-7). There are also reports that natural assemblages of microorganisms are capable of PCB biodegradation (8-12), but little information exists on the environmental biodegradative fate of PCB. Chlorinated biodegradation products have been suggested for trichlorobiphenyl in marine samples (8). A recent report has suggested that the terminal fate of p-chlorobiphenyl in a marine environment is mineralization accompanied by accumulation of benzoic acid (13). The objective of this brief report is to demonstrate that an alternate fate for PCB exists in aquatic environments.

Problems associated with assessing the biodegradative fate of PCB in the environment are numerous and relate to low solubility, volatilization, photodecomposition, and sorption/desorption to living organisms and particulate

matter. In addition, the position and degree of chlorination of the numerous congeners in commercial PCB mixtures, such as Aroclor 1254, modulates the biorecalcitrance of the PCB substrate. Consequently, gas-liquid chromatographic analysis of residual PCB following routine biodegradation assessment for removal of the substrate from terrestrial or aquatic samples is inexact and can only yield information pertaining to the potential interaction of the PCB with biotic components of a natural sample. As an example of this point, Table I represents a preliminary examination of PCB removal from aquatic samples exposed to PCB. These data are based on residual PCB quantitation using a previously described biodegradation assay, hexane extraction, and electron-capture GC analysis for PCB (14, 15). These results indicate a significant interaction of PCB with microbial populations present in a variety of temporally and spatially segregated samples from Center Hill Reservoir, TN (16). These data and the gas chromatographic profiles from which they are generated do little to assess the actual fate of PCB.

In a further attempt to delineate the fate of PCB, the ability of microbial populations to mineralize PCB to CO<sub>2</sub> was investigated. Some 10-mL Center Hill Reservoir samples were placed in 70-mL serum bottles to which 10 μL of repurified (Florasil column chromatography) [U-<sup>14</sup>C]PCB (New England Nuclear, Boston, MA; 31.3 mCi/mmol, 54% chlorine by weight in mixture) in acetone was added. The reaction vessels were supplemented with 10 mg of prewetted powder XAD-4 resin (Supelco Inc., Bellefonte, PA) to inhibit PCB volatilization. (Preliminary experiments indicated that XAD-4 resin had no effect on microbial growth and that naphthalene was mineralized in the presence of XAD-4 resin in the same experimental system.) <sup>14</sup>CO<sub>2</sub> liberated from the PCB substrate was collected in a center-well NaOH CO<sub>2</sub> absorber. The ex-

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Table I. Aroclor 1254 Biodegradation in Center Hill Reservoir Samples, 1977<sup>a</sup>

| site | % PCB degradation in samples taken |                        |           |           |           |           |
|------|------------------------------------|------------------------|-----------|-----------|-----------|-----------|
|      | Feb                                | Mar                    | Apr       | June      | Aug       | Dec       |
| 1    | ND <sup>b</sup>                    | 62.6 ± 10 <sup>c</sup> | 53.5 ± 7  | 70.3 ± 14 | ND        | ND        |
| 2    | 13.8 ± 7                           | 35.0 ± 7               | 18.8 ± 15 | 51 ± 28   | ND        | 43.6 ± 9  |
| 3    | ND                                 | 47.7 ± 33              | 37.4 ± 18 | 69.8 ± 18 | ND        | ND        |
| 4    | 6.8 ± 10                           | 11.4 ± 11              | 66.7 ± 30 | ND        | 42.4 ± 21 | 37.3 ± 19 |
| 5    | 47.7 ± 28                          | 10.8 ± 33              | 41.5 ± 39 | 53.8 ± 6  | ND        | 69.8 ± 8  |
| 6    | ND                                 | 81.2 ± 16              | 71.2 ± 20 | 70.4 ± 36 | ND        | ND        |

<sup>a</sup> Values expressed as % PCB degradation relative to sterile controls, one month incubation at 25 °C. <sup>b</sup> Not determined. <sup>c</sup> ± 1 standard deviation calculated from triplicate replication.

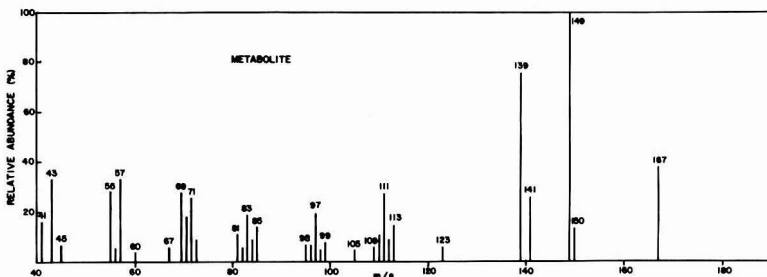


Figure 1. Mass spectrum of chlorinated metabolite tentatively identified as chlorobenzoylformic acid isolated from Center Hill Reservoir water amended with 2-chlorobiphenyl (peaks at  $m/e$ , 167, 150, and 149 represent a phthalate contaminant).

perimental samples and autoclaved sterile control and acetone control samples were incubated for various time intervals up to 96 days at room temperature in the dark. Under the experimental conditions used, no <sup>14</sup>CO<sub>2</sub> was detected throughout the entire incubation period, indicating that for complex mixtures of PCB, mineralization was insignificant with respect to adsorption, volatilization, and cellular accumulation, which occur kinetically at a much faster rate (17).

Based on the results of other studies (1-4, 8, 18-22), if metabolic transformation of PCB were occurring, various chlorinated acidic products should accumulate in samples exposed to PCB. For analytical purposes, high concentrations of two lesser chlorinated biphenyls were employed to determine if biodegradation was occurring with accumulation of refractory metabolites. Center Hill Reservoir samples were placed in 1000-mL cotton-stoppered Erlenmeyer flasks, each containing 50 mg of Celite, a diatomaceous earth. The flasks were dosed with a 10-mL acetone solution of 2-chlorobiphenyl or 2,4'-dichlorobiphenyl (Analabs Inc.), purified by Florisil column chromatography, at a final concentration of 40 mg L<sup>-1</sup>. Sterile control samples and experimental samples were incubated at 25 °C in the dark for 3 and 8 months, respectively, for the mono- and dichlorobiphenyl. Following incubation, the samples were adjusted to pH 1.5 with concentrated HCl and twice extracted with pesticide grade ethyl acetate (Fisher Scientific Co.). The extracts were combined, reduced to a 10-mL volume by vacuum rotoevaporation, and further reduced to 1 mL by evaporation with N<sub>2</sub> gas. Chemical standards and extracts were spotted on LQF Chromoflex, fluorescent thin-layer chromatography plates (Kontex, Vineland, NJ). Plates were developed in benzene/methanol/acetic acid (90:9:1 v/v) and viewed under ultraviolet light. Spots were removed and dissolved in ethyl acetate for analysis by a computerized direct-probe mass spectrometer (Hewlett-Packard 5980A; electron impact, 70 eV).

Components of the 2,4'-dichlorophenyl extract migrated as a single yellow spot,  $R_f$  0.91, on TLC as compared to the

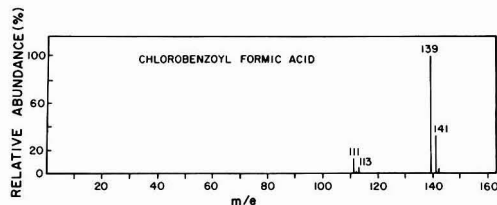


Figure 2. Mass spectrum of authentic chlorobenzoylformic acid.

parent substrate,  $R_f$  0.99. This component was resolved as two peaks by mass spectrometry (MS); the first was identified as 2,4'-dichlorobiphenyl ( $M^+$ ,  $m/e$  222) and the second was an unidentified peak containing no chlorine atoms ( $M^+$ ,  $m/e$  278)—this latter peak was tentatively identified as a phthalate based on a matching with the NIH library of reference mass spectra. It is most likely that the phthalate is a laboratory contaminant.

The extracts of the 2-chlorobiphenyl samples were resolved as three components,  $R_f$  0.98, 0.68, and 0.54. The first component ( $R_f$  0.98) comigrated with the 2-chlorobiphenyl standard and was confirmed by the mass spectrum ( $M^+$ ,  $m/e$  188). The second component ( $R_f$  0.68) demonstrated molecular ions at  $m/e$  139 and 111 with characteristic chlorine doublets and was tentative identified as chlorobenzoylformic acid from the mass fragmentation pattern (Figure 1). This identification was confirmed by mass spectra comparison with a benzoylformic acid standard (Aldrich Chemical Co.) and a chemically synthesized chlorobenzoylformic acid (23) (Figure 2) and by IR and NMR spectra. The third component ( $R_f$  0.54) comigrated with chlorobenzoic acid on TLC. This identification was confirmed by MS ( $M^+$ ,  $m/e$  156) and comparison to a chlorobenzoic acid standard (Analabs Inc.) (Figure 3). No attempts were made to determine the isomeric forms of either the chlorobenzoylformic acid or the chlorobenzoic acid.

The results of the studies reported here indicate that chlorobenzoic acids can be expected to accumulate during

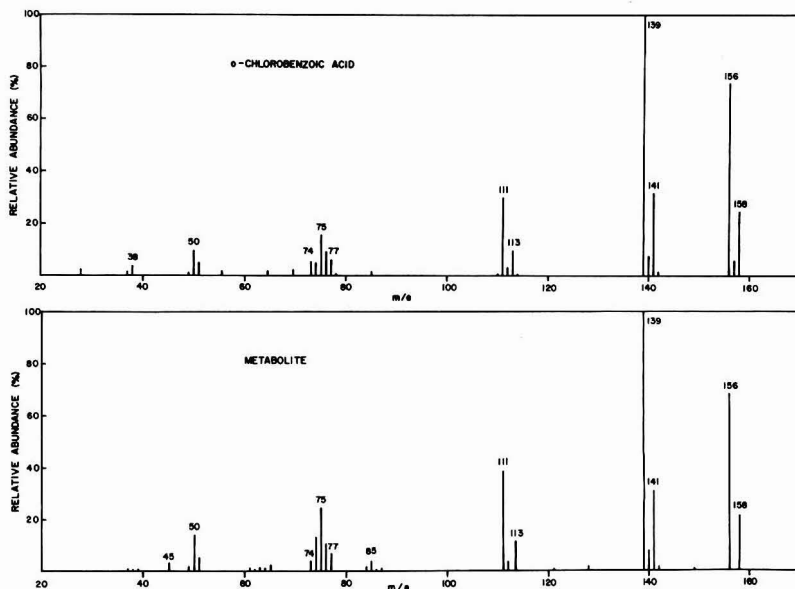


Figure 3. Mass spectra of *o*-chlorobenzoic acid standard and the metabolite isolated from Center Hill Reservoir water amended with 2-chlorobiphenyl.

the degradation of the lesser chlorinated biphenyls in the environment. These results validate the predictions from pure culture studies demonstrating chlorobenzoic acids as stable PCB biodegradation products. The isolation of chlorobenzoylformic acid (chlorophenylglyoxylic acid) as a biotransformation product of 2-chlorobiphenyl by natural aquatic microbial communities is a novel observation. Chlorobenzoylformic acid was postulated as a possible product resulting from the ortho fission of a chlorobiphenyl-2,3-diol (18). It may also hypothetically arise through a 3,4-meta fission of the chlorobiphenyl-2,3-diol, a mechanism proposed for the oxidation of biphenyl (21), and the oxidation of a chlorophenylpyruvic acid intermediate to the chlorobenzoylformic acid. However, these mechanisms have received little support in the literature, and the 1,2-meta fission of biphenyl-2,3-diol as proposed by Catelani et al. (22) has received general acceptance. Reports of the isolation of benzoylbutyric acid resulting from the oxidation of biphenyl (19) and a chlorobenzoylpropionic acid from the oxidation of chlorobiphenyl (20) as well as our results support the 1,2-meta ring-fission mechanism with sequential oxidation of the ring-fission products to chlorobenzoic acids.

These results support the hypothesis that aquatic ecosystems have detectable potential for PCB biodegradation. Since the Center Hill Reservoir environment appears to be free of PCB contamination, it is suggested that PCB-contaminated environments will demonstrate a greater potential for biodegradation as microbial populations respond to selective pressure. This biodegradation potential can result in the environmental accumulation of stable chlorinated degradation products.

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## CORRESPONDENCE

### Critique of "Petroleum and Marine Fishes: A Review of Uptake Disposition and Effects"

SIR: I am concerned by the selective presentation of data in the article "Petroleum and marine fishes: a review of uptake disposition and effects" (Malins, D. C.; Hodgins, H. O. *Environ. Sci. Technol.* 1981, 15, 1272). The state of knowledge in this area seems to have been subjected to a rather selective filter, and I am fearful of the picture that might be painted by a novice (concerned citizen, research manager, funding agency, etc.) upon reading this feature review. The authors state that it was not their intent to deal comprehensively with the overall subject of the fate and effects of petroleum in the marine environment. This is fair enough, but even considering effects on fish, the presentation of data was quite selective and derogates the extensive data base that is presently available.

One of the major aims of the article was to present an overview on the "current state of knowledge" of the effects of petroleum on marine fish, presumably addressing concerns on the possible impacts of petroleum contamination of the marine environment by oil spills, blowouts, etc. Given such an avowed aim, it is not realistic at this juncture in oil-spill research to dwell upon a few select studies (with, I might add, a seemingly inordinate indulgence toward activities in the authors' own laboratory). Research on the probable impacts of oil on fish and other marine life has been ongoing at an intense pace in many countries for over a decade, and some thousands of papers (recent estimates by German scientists) have already been published. (Radiation is probably the only other environmental concern that has received similar attention.) This vast literature, the fruits of a worldwide community of scientists, covers many biological disciplines and forms the basis for the current perceptions on the relative hazards of petroleum to marine life. The draconian images of the probable impacts of oil that were so popularly painted by many scientists just a few years ago and accepted in good faith by the public have fortunately weathered away. The present review draws upon many of these old apparitions and does not lend justice to the variety of literature that can lead to a more "balanced" understanding of the potential of petroleum for harmful impacts on fish or other animal populations.

Considering the available literature, none of the major areas of concern have been addressed in a reasonable manner.

For instance, considerable coverage has been given to hydrocarbon uptake and metabolism with implications for the appearance of such adverse toxicological endpoints as mutagenicity/carcinogenicity, resulting from the enzymatic formation of reactive byproducts. There has already been considerable work in this general area, and how can one presently reflect on the special topic of petroleum hydrocarbon mutagenicity without addressing the negative studies that have appeared in the literature. Also, why should one bypass such general literature as that dealing with hydrocarbons as anticarcinogens or more specifically

the antimutagenic effect of petroleum hydrocarbons on benzo[a]pyrene, a compound whose toxicological potential has been extensively discussed in the review. More important, however, is the precept of perspective. Even if fractions of petroleum were converted into reactive mutagenic byproducts, how could one presently fail to stress the relative importance (in terms of inputs) of anthropogenic sources of petroleum hydrocarbons versus well-recognized sources of mutagenic hydrocarbons (besides benzo[a]pyrene) from combustion and even natural sources. No such comparable potential, in terms of either mutagenic potency or inputs, has been indicated for petroleum hydrocarbons. Such perspectives would seem to be extremely important at this juncture.

It is presently insufficient to stress that oil is a toxic substance and fish can be affected by exposure. Toxicologists never cease to remind us that all compounds, natural as well as anthropogenic, have, in the absolute sense, a toxicity potential that depends on dose as well as exposure. One must always remain cognizant of the fact that oil, because of extensive subsurface seepage over wide areas of the world oceans, remains part of the evolutionary experience of marine animals and cannot be included under the same genre of concern as trace levels of man-made contaminants. (Similar considerations must be extended to other natural sources of toxic hydrocarbons such as those originating from plants or produced by natural combustion processes.) It is the episodic high dosages of petroleum, acute or chronic, upon which we have to pass judgment, and the present body of literature permits the introduction of a degree of perspective on the potential of such events for environmental harm. Linking concentrations to impacts, it now seems reasonable to state that adverse effects *may possibly* be found in fish in the immediate area of a spill or blowout (if the fish do not simply swim away). Considering the present data base, however, it would be extremely difficult to formulate tenable hypotheses to indicate substantial impacts on fish or any other animal populations. Isn't this already commonly accepted?

A well-recognized exception for potential harm is shoreline stranding of large amounts of oil, but even here it has to be realized that, under most circumstances, effects would be localized, impacting stationary or relatively immobile species and not fish. Even in terms of shoreline fouling (admittedly, an esthetic affront), it would appear difficult to dramatize the effects of the worst spills as having any more potential for biological damage than a few miles of paved road in terrestrial environments. Even a small city the size of St John's has a hundred miles of paved roads. This may be a crude but probably apt analogy, if we want to introduce a degree of perspective.

Attention is drawn to the presence of elevated concentrations of hydrocarbons in sediments. Point sources of such high concentrations of hydrocarbons can be found in urban associated harbors and estuaries, but these localized hot spots are indicated to be mostly contaminated by runoff and atmospheric sources. Petroleum should not be generally invoked as a major contributor of hydrocarbon contamination in such "hot-spot" areas. Also, I would add that considering either concentrations or effects, petroleum hydrocarbons are probably the pollutants of least concern

in most urban associated waters.

A large amount of circumstantial evidence indicates that high concentrations of sediment hydrocarbons would likely be required before one could expect fish populations to be adversely affected. There is no discussion of this important area in the review. In relation to laboratory studies, the authors discussed the uptake of hydrocarbons from sediments but failed to mention the specific studies carried out with flatfish, in which adverse effects markedly decreased in animals exposed to as much as 2000 ppm of oil in sediments. I am not aware of any oil development, blowout or spill area in which one-tenth or one-hundredth of this concentration is known to contaminate any significant area of offshore marine sediments. As previously indicated, the localized mixing of oil and sediment in intertidal waters is probably the only scenario where such high levels of petroleum hydrocarbons could be realized to any extent.

The authors invoke effects on fish reproduction, which it is true would be generally accepted as having special ecological significance. I would add that there is no circumstantial evidence, from the large variety presently available, to support such a hypothesis. Also, the authors did not discuss laboratory studies in which attempts to induce reproductive effects in fish by feeding very high concentrations of oil in food (0.1%) for prolonged periods were negative.

The section in which the authors imply that the most significant impact of oil on marine fish would likely stem from the special sensitivity of larvae is woefully inadequate. The sensitivity of fish larvae to oil (which probably simply reflects surface area/volume relationships) has been especially well documented by European workers. The caveat, however, which is commonly recognized, lies in translating larval effects into impacts on fish populations. No mention is made in the review of the general theories or of fishery models that address larval mortality effects and stock recruitment mechanisms in fish. Generally speaking, it is indicated that large numbers of young yolk sac larvae would be destroyed before effects would be detected in adult fish populations. And it is presently difficult to envisage how single oil-spill events would have the dosage potential to impact large proportions of most larval populations. Even the specific modeling studies that have addressed such oil/larval and oil/phytoplankton impacts were not mentioned in the review. One model states that "on average, or even at worst, the impact of offshore oil pollution on fisheries will be negligible or small, much less than factors such as over-exploitation or unsuccessful stock recruitment." I suggest that the current "state of knowledge" of putative impacts on larvae can hardly be addressed without covering the available literature a little more carefully.

A case is made for further studies on petroleum hydrocarbon metabolism. The authors mention that besides reviewing the current "state of knowledge" of the effects of petroleum on fish, their other aim was to indicate "direction that should be taken for future research." Presumably, this is deemed a critical research area that is needed to "fill existing gaps" so we can make "balanced judgments" about the impact of petroleum on fish and other marine life. Considering the knowledge that is already available in this area (one prominent American investigator has estimated the number of scientists working in the general area of aromatic hydrocarbon metabolism/mutagenesis to a number over a thousand) and considering the relative importance of petroleum vs. other known sources of toxic hydrocarbons from natural as well as combustion sources, it is presently difficult to visualize

the social benefits of a special focus on petroleum hydrocarbons from either a practical or a fundamental research perspective. In relation to reactive metabolite formation and environmental mutagenesis/carcinogenesis, an area that the authors discuss rather extensively, surely the present evidence indicates a minor or negligible potential from petroleum spills vs. a major potential from other sources of hydrocarbons. (Neither may be of any significance in the real world.) Are the authors suggesting that we should catalog the metabolites of the 10,000 plus compounds present in petroleum? If not this many, how many, and with how many species before we would be in a position to make the all important "balanced" judgments on hydrocarbon metabolite toxicity. In relation to fundamental science, I certainly support all creative efforts that might provide major insight into, for instance, molecular mechanisms of toxication/detoxication, but caution must always be exercised in selecting any area of research as being preeminent. There presently seems to be little scientific rationale for selective focusing on the metabolism of petroleum hydrocarbons over hydrocarbons from other sources, from either a fundamental or a practical viewpoint.

Glib statements are made about possible interactions between petroleum and other pollutants such as PCBs, pesticides, and heavy metals. This is an area that should be approached very prudently because of the great potential for endless obfuscation. Consider effects that might be invoked at just one level, the level of mutagen metabolism. For instance, at the moment we have a good appreciation of the primary metabolites formed from representative aromatic hydrocarbons such as benzo[a]pyrene. A few studies have indicated how the ratios of various metabolites may be changed and how this may influence mutagenic potential. The general principle of interactive effects is important, but the possibility for "interactions" between single and multiple substrates as well as any other compounds administered in sufficient dosages to the test tube or animal are, of course, endless. Consider the major effort that would be required given the academic exercise to delineate the interactive effects (one tissue and one fish species) of petroleum hydrocarbons, singly and in various combinations, on benzo[a]pyrene metabolism *in vitro*. The combinations are such that investigations on a relatively few of the 10,000 plus compounds present in petroleum would lead us into experimental trials greater than Avogadro's number ( $6 \times 10^{23}$ ). At what point in such enzymatic studies might we be able to suggest that we have looked at the requisite combinations to make "balanced judgments" on the possible interactive effects of various petroleum compounds on benzo[a]pyrene metabolism? This is not necessarily whimsy—there are no limits on how far the interactive effects conundrum may be "logically" extended.

Scenarios of the possible interactive effects of hydrocarbons, PCBs, heavy metals, etc. in the natural environment should have been discussed more critically. It is true that some heavily polluted harbors and estuaries are believed to contain more fish with "tumors" and other diseases compared to fish from cleaner regions. (The converse has also been demonstrated for some diseases.) As previously noted, however, such polluted conditions have little to do with petroleum contamination. Moreover, the literature is also quite weak (considering the large variety of cytotoxicity, mutagenicity, and carcinogenicity studies available) in being able to indicate a major potential for either petroleum hydrocarbons, PCBs, or pesticides in marine animal tumor (or other) problems in "hot-spot" polluted areas. Much more tenable hypotheses can be formulated from consideration of the high levels of sewage

and other natural runoff compounds commonly found in these environments.

The authors attempted to review the "state of knowledge" on the effects of petroleum on fish and to "give directions that should be taken in future research." The presentation of data was quite selective for each topic covered, and clearly what was omitted was of paramount importance for a balanced presentation of our current understanding of potential impacts. Petroleum was also too often introduced as a pawn or proxy toxicant to situations that should have been discussed much more critically. The authors advocated more studies on petroleum hydrocarbon detection and metabolism as the "direction that should be taken for future research." Given the present state of knowledge in this area, as well as the rather undefined limits as to its importance from either a practical or a fundamental viewpoint, it is difficult to see how such studies can presently be placed in a priority category.

The authors eschew the importance of "filling in the existing gaps" in knowledge so we can make "balanced judgments" about the effect of petroleum on fish. I wish this ideal of balancing had been practiced to a much greater degree in this exercise. I am quite familiar with the authors' research interests and activities, and they could and should have presented a better perspective, considering the information available. It is especially important to make balanced presentations in general "semipopular" overviews, since they are often the only types of literature read by concerned citizens, decision makers, funding agencies, etc.

For a balanced appraisal (in my viewpoint) of potential oil pollution problems, as well as convincing arguments for future research directions, the reader is referred to a recent Royal Commission Report prepared by British concerns.

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SIR: Dr. Payne's principal criticism appears to be that we have presented a biased selection of the available literature on petroleum in the marine environment, ignoring and derogating "the extensive data base that is presently available." We stand accused, as a result of this alleged bias, of having fostered and perpetuated "The draconian images of the probable impacts of oil that were so popularly painted by many scientists just a few years ago."

We have to wonder about the care with which Payne read our article. As a case in point, the subheading on the first page reads as follows: "In the laboratory, petroleum causes certain adverse effects on marine fish. However, definitive information generally is lacking about the biological effects of petroleum in the marine environment."

This is the perspective we have, and this is the perspective we portrayed through the representative papers described in the review article—hardly a "draconian" image of the probable impact of oil!

In the course of his critique, Payne makes the astonishing indictment that "Considering the available literature, none of the major areas of concern have been addressed in a reasonable manner." We point out that this view was obviously not held by three experts in petroleum

fate and effects research who were acknowledged by name (*Environ. Sci. Technol.* 1981, 15, 1278) for having read and commented on the article for technical accuracy before publication.

In another astonishing statement Payne alleges "Considering the present data base, however, it would be extremely difficult to formulate tenable hypotheses to indicate substantial impacts on fish or any other animal populations." This simply is not a defensible position. One example that refutes this concerns sea-bird mortalities in areas of oil spills. Completely tenable hypotheses have been formulated concerning potentially massive population impacts from petroleum blowouts in arctic staging and nesting areas in which a substantial percentage of North America's populations of certain species of these birds congregate (Barry 1976, Milne and Smiley 1976). And, of course, myriad other such tenable hypotheses can be formulated. This is not to say that marine ecological disaster is probable. A major impact would appear to require a special combination of unfortunate circumstances.

Payne claims that even the worst oil spills would not have "any more potential for biological damage than a few miles of paved road in terrestrial environments." We will not respond in detail to this statement. We do draw attention, however, to the conclusions formed by a group of internationally renowned scientists in response to a comparable position taken by Wyman (1978) in a letter to *Science*. Wyman maintained that surveys of major oil spills revealed that the affected areas "fully recovered in a surprisingly short time." The respondents concluded: "We disagree with the claim, although it reflects current mythology." They pointed out that petroleum can remain for prolonged periods in marine environments and that there is "evidence for persistent physiological and community disruption for at least a decade following oil spillage."

Payne indicates that high concentrations of hydrocarbons can be found in urban-associated harbors and estuaries, but these are "indicated to be mostly contaminated by runoff and atmospheric sources." He goes on to say that "Petroleum should not be generally invoked as a major contributor of hydrocarbon contamination in such "hot-spot" areas." There is, in fact, contrary evidence. May we direct Dr. Payne's attention to a paper by Hoffman et al. (1981).

In this paper, Hoffman et al. state: "Comparison of the 665 metric tons/year input of hydrocarbons with other sources of oil to the Narragansett Bay watershed suggests that urban runoff is a major source of hydrocarbons (~40%) to Narragansett Bay and its tributaries" (Hoffman, in press).

These authors also, based on a number of assumptions, derive projections "that 66 000 tons of petroleum hydrocarbons are discharged annually into U.S. coastal waters via runoff and 198 000 tons are discharged on a worldwide basis."

The impacts of these inputs on the marine environment are of course not at all clear, but such sources cannot be simply written off as inconsequential.

Payne contends that "offshore marine sediments do not contain 2000 ppm oil or even one-tenth or one-hundredth of the concentration." Although the term "offshore" is ambiguous, we remind Payne that his claim most certainly does not apply to coastal waters, where hydrocarbon concentrations in sediment have been shown to often substantially exceed 2000 ppm after oil spills (Clark and MacLeod 1977).

Payne appears to believe that the effects of petroleum



on fish reproduction and on early developmental stages would have important ecological significance except that there is no evidence that any such effects translate into impacts on fish populations. We agree that there is great difficulty in differentiating pollutant effects from the large degree of natural variation that occurs in fish and other animal populations. A reasonable and objective approach is not one, however, that says: We can't determine whether or not oil has an effect, therefore it has no effect.

This question of reproductive effects and their translation to populations leads directly to another subject that Payne has raised: the concept and utility of modeling studies. We believe that this is an area that is a vital moving front in ecological research and a direction that must be taken. Unfortunately, pollutant/marine fish modeling studies have largely been published in data reports or in semitechnical literature. Payne, in his discussion of modeling, relates that "One model states that, on the average, or even at worst, the impact of offshore oil pollution on fisheries will be negligible or small . . ."

It should be emphasized that other models have been applied to derive other interpretations. One modeling study that presents another perspective (*Sea Technol.* 1981, Nov, 52-53) was conducted by a Rhode Island based engineering consulting firm, Applied Science Associates (ASA), and was a cooperative venture with researchers from the University of Rhode Island. The model addressed the impacts of potential oil spills on Georges Bank cod, haddock, herring, and yellowtail. This model infers first-order direct impacts of oil on a commercial fishery through hydrocarbon-induced egg and larval mortality. The following quotes from the brief news article are illustrative:

"Results of the present study on Georges Bank indicate maximum impacts for cod on the order of 20% of one year's catch lost due to a major 30 day spring blowout releasing 5 thousand tons of petroleum per day, according to ASA. Because of growth dynamics within the adult population, the study estimates that this loss will be distributed over the 5 years following the spill, with a maximum reduction on the order of 6%, or 1.4 thousand metric tons of cod.

The magnitude of the impacts depends on a complex interaction between spill location and timing, the spatial and temporal spawning distribution, and the hydrodynamics of the area."

We point out that this volume of oil is not unrealistic in terms of petroleum inputs such as the *Amoco Cadiz* spill, that this is an open-ocean impact, that it is based on egg and larval mortality, that the impact is for only one species, and that the estimated maximum effect is not negligible.

Payne asks whether "we should catalog the metabolites of the 10000 plus compounds present in petroleum?" Obviously not! He seems to miss the point. The fact is that substantial evidence indicates that metabolites are toxic to animal systems. Thus, the ability to detect and evaluate certain potentially toxic metabolites is essential to the overall assessment of the fate and effects of petroleum on marine life. Such studies also form an essential basis of understanding for the rational development of methods for analyzing potentially toxic transformation products in abiotic as well as biotic marine samples.

The claim that petroleum hydrocarbons are probably pollutants of least concern in most urban associated waters is only speculation. We do recognize that coastal and estuarine environments near urban areas contain complex mixture of hundreds of xenobiotics so that the potential

effects of petroleum components, per se, are largely masked. Payne expresses concern about the problem of interactions among these myriad chemicals. He states "there are no limits on how far the interaction effects conundrum may be 'logically' extended." We could be led "into experimental trials greater than Avogadro's number ( $6 \times 10^{23}$ )." This is an unreasonable perspective, as is the implication that studies of interactions between petroleum components and other chemicals in marine environments are not realistic or even important. Although the technical problems are formidable, progress is being made in understanding interactions among chemicals and their biological effects in marine environments. Studies have been conducted with mixtures of individual compounds, model systems, and "extracts" from environmental samples. The results show promise, and on the basis of a number of investigation, a wide range of biological effects have been attributed to interactions among environmental chemicals in aquatic life, to include synergism and antagonism between petroleum components and other xenobiotics (Verma et al. 1981, Von Westernhagen et al. 1979, Malins and Collier 1981).

For the perhaps now thoroughly confused nonspecialist, we offer these thoughts. Present evidence supports the concept that petroleum in the marine environment does not reflect the "doomsday" potential claimed by some a few years ago. However, exposure of some species and developmental stages to petroleum and its derivatives under certain environmental conditions clearly can result in substantial damage to marine life. Although the work reported to this time is extensive on certain aspects of fate and effects of petroleum, much of it is of limited utility for definitely demonstrating and quantitatively evaluating petroleum effects—particularly subtle and long-term effects. Nevertheless, progress has been and is continuing to be made in these areas. Whether or not petroleum entering the marine environment will have substantial or minimal impact depends on interactions among complex variables that are only now beginning to be understood.

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## Comment on "Estimating Equilibrium Adsorption of Organic Compounds in Activated Carbon from Aqueous Solution"

SIR: In his recent article entitled "Estimating Equilibrium Adsorption of Organic Compounds in Activated Carbon from Aqueous Solution" (*ES&T* 1981, 15, 812), Dr. Arbuckle compared three methods for predicting relative adsorbability: solvophobic theory, Polanyi theory, and the net adsorption energy approach. We direct the attention of your readers to recent significant developments and applications of the solvophobic ( $c\phi$ ) theory that render Dr. Arbuckle's evaluation obsolete. We would also like to reiterate certain fundamental problems with both the Polanyi theory and the net adsorption energy approach that one of us (G.B.) discussed in a recent interview in *ES&T* (1, 2).

The  $c\phi$  theory, like most theories, has developed through several stages. From its early stages, when Taft, Hammett, and steric parameters were used to correlate adsorption (3), the theory has now jelled into a comprehensive theory incorporating all known thermodynamic interactions (4, 5). Details on how to calculate each interaction from physical-chemical parameters found in handbooks are outlined in the literature (4-6). Unfortunately, Dr. Arbuckle used the first version of the  $c\phi$  theory for the comparison in his paper. This is in spite of the fact that a comprehensive analysis of the most recent version was published in summary 10 months prior to the publication of his paper (2).

Several comments are necessary in answer to Dr. Arbuckle's criticisms of the  $c\phi$  theory. With the exception of the solute eccentric factor and cavity surface area, all of the required physical properties may be found in standard references such as the CRC Handbook of Chemistry and Physics (7). A listing of eccentric factors may be found in ref 8 or other sources. Molecular surface area may be estimated from liquid density and molecular weight or obtained from a computer program available from the Indiana University chemistry-computer library (9). Thus, in principle, the  $c\phi$  theory does not require inaccessible parameters. As of now, it is true that separate correlations have only been developed for each family of compounds or homologous series. This does not, of course, preclude later incorporation of correction factors directly related to functional polarity for the development of universal correlations. The  $c\phi$  theory is not restricted to small compounds, as Dr. Arbuckle suggests. It has been applied externally to macromolecules such as DNA and proteins (10-12).

In regard to the two other theories that are discussed in Dr. Arbuckle's paper, your readers would be interested in the following fundamental problems with each. The basic problem with the "thick compressed film theory" (or "Polanyi adsorption potential theory", as it is often called) is that the original physical model of a three-dimensional film has been questioned and rejected by many scientists, including none other than Polanyi himself (13). Associated with this is the problem of defining or measuring the adsorbate density, which is needed for plotting the characteristic curves (1). Quoting Dr. M. Manes, "Thus far no good predictive method has been found for estimating the adsorbate densities" (14). Belfort has shown recently that the Polanyi and ideal adsorption theory based on Gibb's adsorption isotherm have similar thermodynamic structure (15).

One of us (G.B.) has recently presented a detailed

analysis and criticism of the quasi-theoretical net adsorption energy approach (2). Suffice it to mention that the arbitrary choice of the relative values for the acid and base solubility hydrogen bonding parameters is without theoretical justification. See Table IV in Dr. Arbuckle's paper in which these arbitrary values are assigned and then used for calculating the net adsorption energy.

The usefulness of the  $c\phi$  theory extends beyond that of a purely predictive tool. It can provide a comprehensive framework for considering specific contributions to aqueous phase adsorption, leading to an improved understanding of the entire process.

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SIR: The purpose of my article was not to determine which model gives the greatest insight into adsorption but to determine which could be most readily used by engineers to estimate equilibrium loadings on activated carbon. An empirical model would have been acceptable if the parameters needed were readily available; of course I would rather use a theoretically based model, and therefore I evaluated the three models selected without regard to their validity. As for the solvophobic method, I did state that it may give insight into adsorption phenomena (insight we may be not be able to obtain from other methods). Also,

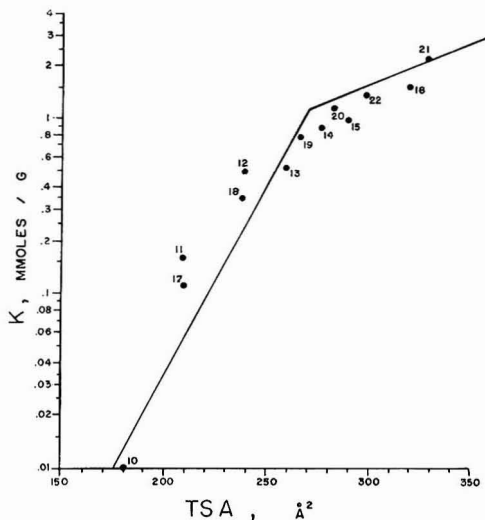


Figure 1. Solvophobic curve with actual data.

I did use the first version as noted, but my article was submitted before publication of the most recent solvophobic version—this is indicated by the received date published with the article. I have reevaluated the solvophobic theory by correlating the total solute cavity surface area (TSA) with loading in a manner similar to Altshuler and Belfort (1), and since the TSA calculation procedure was not readily available, Altshuler and Belfort graciously provided TSA's for the 22 compounds of interest. So that their approach could be made more widely applicable, two changes were made (2): (1) the alcohol data were used to generate a predictive curve for the other four families of compounds (rather than obtaining a separate curve for each family, which would require too much data); (2) two straight lines were used to fit the data (rather than using a single line, which indicates a compound's size may be limiting its access to part of the adsorbent's surface). The predictive line from the alcohol data and the loadings for the 13 additional compounds indicate that the solvophobic method can be used to predict loadings (Figure 1) and that larger compounds can be handled, which was not the case for the first version. This method does not predict loadings as well as the Polanyi and net adsorption energy methods,

as indicated by the square of the difference between actual and predicted values (2):

| method                | (actual - predicted) <sup>2</sup> ,<br>(mmol/g) <sup>2</sup> |
|-----------------------|--|
| solvophobic           | 0.6721   |
| Polanyi               | 0.4665   |
| net adsorption energy | 0.1803   |

(Note: the improvement in the net adsorption energy method's value over my *ES&T* article is due to the use of a log-log plot rather than the arithmetic plot.) In spite of the arbitrariness of the net adsorption energy approach, it still predicts single-point equilibrium loadings best for this data, even though from a theoretical standpoint it is least satisfactory. The Polanyi method (or A. L. Meyers and S. Sircar's theory of correspondence (3)) would seem to offer the most potential for use in column modeling, since a complete isotherm is obtained. Others have reported on the successful application of the Polanyi method, particularly to bisolute systems (4).

A better understanding of adsorption phenomena is needed and studies should continue in this area, but we must not sit back and wait for an acceptable theory and model. As engineers we must try to use what is presently available and try to provide information for others to use as an aid to design and as a screening process to save valuable laboratory time.

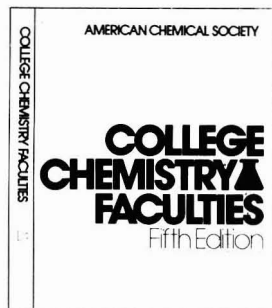
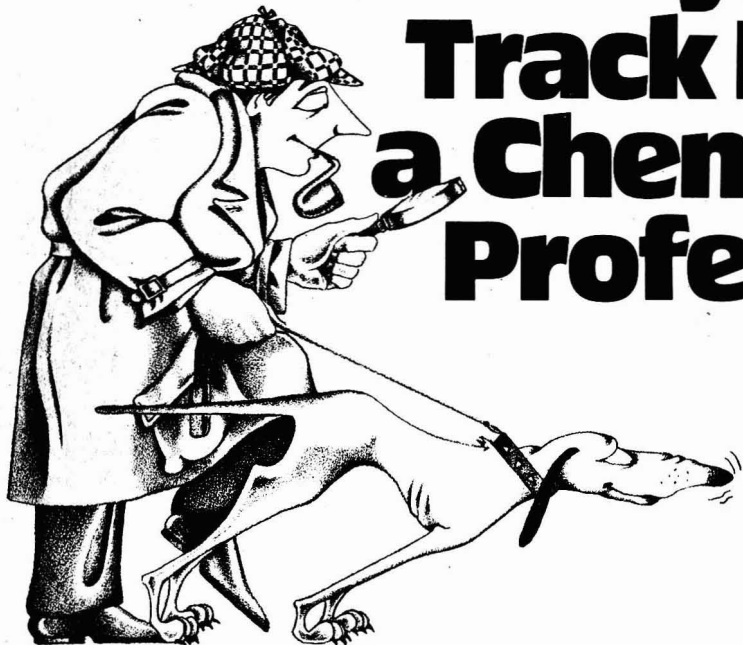
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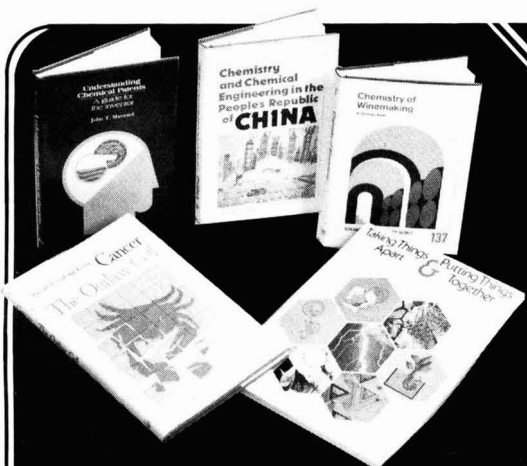
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