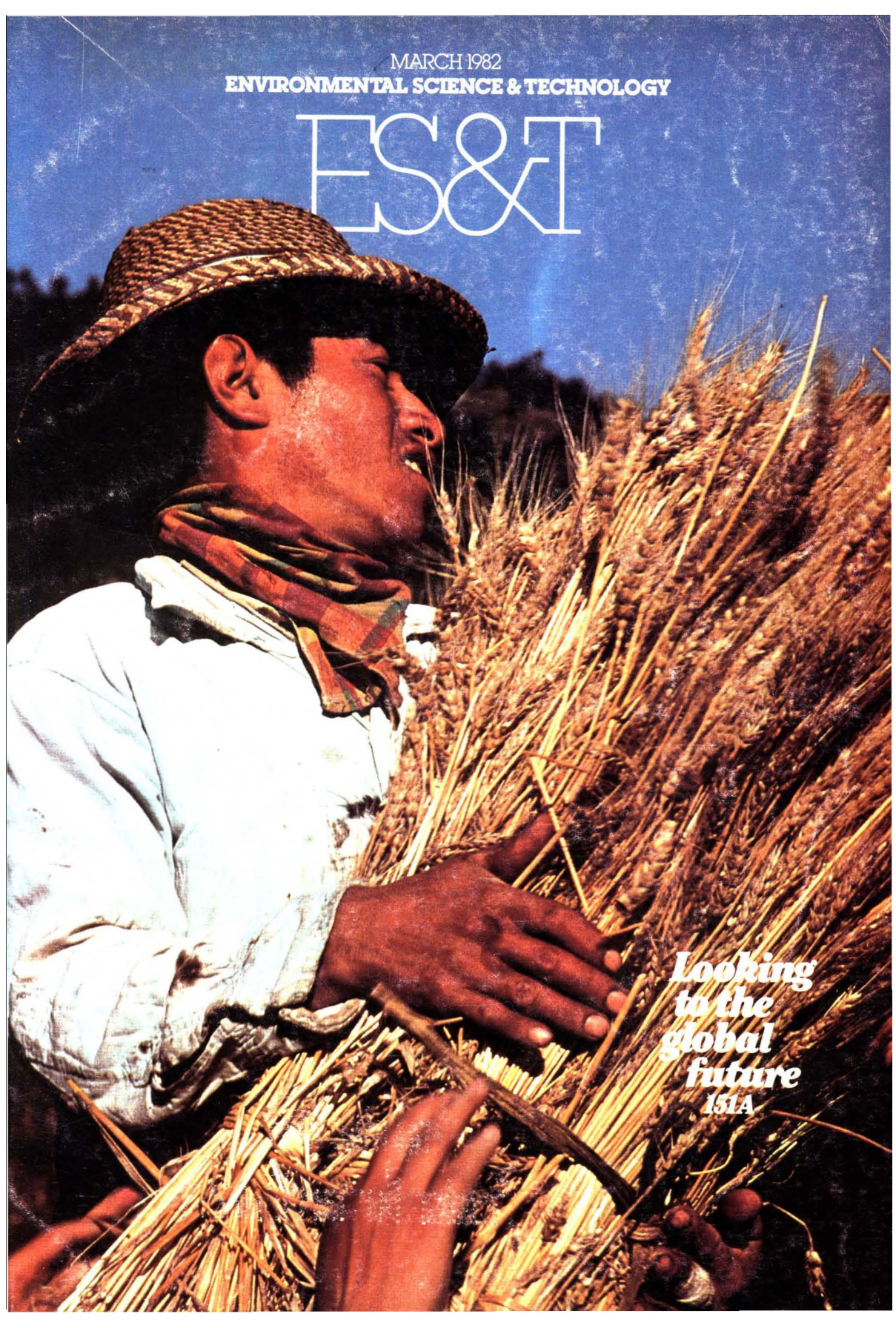


MARCH 1982  
ENVIRONMENTAL SCIENCE & TECHNOLOGY

ES&T

A photograph of a man in profile, wearing a wide-brimmed straw hat and a white long-sleeved shirt with a colorful patterned scarf. He is smiling and looking towards the right, where a large field of golden wheat is visible. The background is a clear blue sky. The overall scene is bright and sunny, suggesting a rural agricultural setting.

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151A

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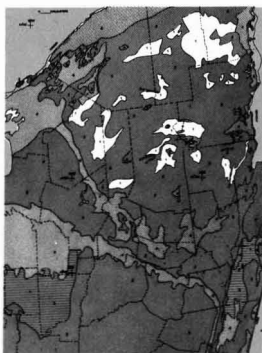
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### Environmental Science & Technology

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## Guidelines for GC/MS identification

The advent of GC/MS technology and the availability of commercial instruments at reasonable costs have produced an avalanche of data on the occurrence and distribution of trace organic contaminants in the environment. From the point of view of industrialists, utility managers, and federal agency personnel, this trend has the potential for increasing regulatory pressures. From the point of view of editors, the explosion of research interest in this subject and the resulting proliferation of manuscripts that claim identification of organic chemical structures is producing certain quality control problems.

The editorial problem is related to the fact that GC/MS instruments are sensitive and sophisticated and inevitably produce large quantities of data that may or may not have meaning. The responsibility for arranging and interpreting data in scientifically acceptable form is under the control of the instrument operator and the manuscript author. The responsibility of scientific journals is to urge adoption of reasonable guidelines and policies guaranteeing that minimum quality standards are followed with regard to data presentation and interpretation. To begin this process in *ES&T*, I suggest the following guidelines for the presentation and interpretation of GC/MS data. We will follow these guidelines with all research manuscripts on an interim basis from the present time through December 1982. During this time, I welcome any comments you may have with regard to these guidelines. Based upon our experience in the next few months and communications from you, an iterated form of these guidelines will appear in the January 1983 Editorial Policy Statement.

Our most general guideline is for the presentation of sufficient analytical detail in the experimental section to enable another researcher to duplicate the work. In terms of hardware and operating conditions, this minimally includes specification of type and source of columns, carrier gas and flow rate, operating temperature range, mode of ionization, scan cycle time, ion source temperature, and model of mass spectrometer used.

If the purpose of the work is to identify structures of organic components in mixtures, then the provision of good quality electron ionization (EI) spectra are minimally required to employ the description of "tentative structural assignment" to a component, if these data match library spectral data or literature sources. Currently employed matching procedures (computer or manual) are somewhat subjective; therefore, authors should present evidence of their matching criteria. If these "tentative structural assignments" are supported by additional data such as chemical ionization (CI), accurate mass ( $\pm 0.005$  amu), or retention data, then the description "confident structural assignment" may be used. Only when an authentic specimen of the proposed structure is obtained and its EI, CI, and retention data are shown to match those of the component within experimental error can the description "confirmed structural assignment" be employed.

It is desirable that authors strive to report only confirmed structural assignments. If authentic compounds are not available to researchers, it may be necessary to synthesize them. For the time being, *ES&T* will accept structural assignments at each of these three levels of confidence.

Even for components for which no computer or manual matching exists, it is desirable to provide as minimal data EI, CI, and retention data (e.g., Kovats index), which is readily obtainable by almost all GC/MS users. In this case, the component would be described as "unidentified" but the data would be available in the literature for the use of others. The most important need at present is to be able to distinguish easily the level of confidence in presented literature data.

*R F Christman*

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# ES&T LETTERS

## The lead debate

Dear Sir: Scientific debate continues about the existence and interpretation of subtle effects of lead, notwithstanding the conclusions reached by Mr. Budiansky (*ES&T*, Vol. 15, No. 3, 1981, p. 243). Low-level exposure and minimal neurobehavioral effects of lead are difficult to quantify and isolate from a multitude of confounding variables. Dr. Needleman reminds us that six governmental agencies are each trying to prove a particular point about lead. Are we to assume that all investigators are biased towards the interests of their funding sources, or rather, and as I would hope, that scientific work should be judged on its own merits? The broad and unsupported allegations Dr. Needleman makes (*ES&T*, Vol. 15, No. 11, 1981, p. 1250) of bias in studies supported by industry may justly do

more to discredit the accuser than the accused.

### Sidney Lerner, M.D.

Institute of Environmental Health  
Associate Clinical Professor of  
Environmental Health  
University of Cincinnati, College of  
Medicine  
Cincinnati, Ohio 45267

Dear Sir: In a recent issue you published a letter by Dr. Herbert Needleman (*ES&T*, Vol. 15, No. 11, 1981, p. 1250) that illustrates quite clearly why the lead debate has been clouded with emotional overtones that obscure the scientific elements of the debate. Dr. Needleman discredits the work of others on the basis of support from industry-derived funds. He, in effect, accuses scientists so funded of dishonesty by association. Fortunately,

this approach to the evaluation of science is rare—at least in my experience.

I have in recent years received some funds from the lead industries to support investigations of the health effects of occupational lead exposure. Some of this work has been presented at an NIH-sponsored symposium (by invitation) and some has been published in the *Journal of Occupational Medicine*. Acknowledgments as to industry support have been clearly indicated in both cases. No one has ever suggested that the work is tainted thereby; but I presume Dr. Needleman thinks it is, if he is at all consistent in his approach to the evaluation of scientific literature.

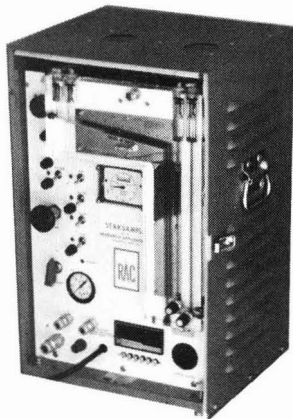
In my dealings with lead industry sponsors (I.L.Z.R.O.), there has never been any interference with my freedom to report data as I wished. Further, I.L.Z.R.O. continues to fund our studies in spite of the fact that findings published to date clearly indicate that the health of some lead workers has not been adequately protected.

### Paul B. Hammond, D.V.M., Ph.D.

Professor of Environmental Health  
Institute of Environmental Health  
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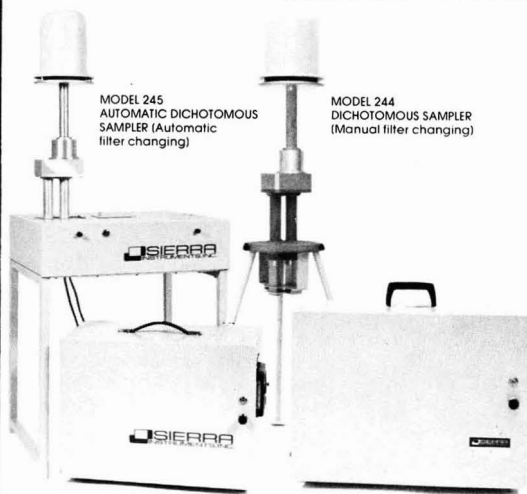
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CIRCLE 32 ON READER SERVICE CARD

## INTERNATIONAL

**Transition to alcohol and other bio-fuel "will prove possible for Brazil, on balance,"** predicts Robert Goodrich of the Southern Research Institute (Birmingham, Ala.). But it will be "a slow, costly, arduous process," he warned. However, without its "Proálcool" program, Brazil would have perhaps only 67% of its necessary transportation fuel, for example. "Proálcool" provides loans at advantageous interest rates to help recover agricultural and distillery projects costs. Whether that would work in more developed countries, Goodrich does not judge. There is also a new program, "Proóleo," aimed at making substitute fuels for diesel vehicles.



Kates: did CFC survey

**The national responses of six countries to the chlorofluorocarbon (CFC) problem** were surveyed and a wide range of responses were found. Robert W. Kates and Thomas E. Downing of Clark University, Worcester, Mass., conducted the survey. They found that Sweden and the U.S. were quick to control CFCs; the U.K. and France have been slow; and West Germany and the Netherlands fall somewhere in between. These six countries produce 75% of the world's CFCs. Kates and Downing believe that environmental attitudes, approaches to decision making, and the economics of produc-

tion can account for the range of responses.

## WASHINGTON

**EPA Administrator Anne M. Gorsuch is reported to have plans to fire** between 800 and 1500 headquarters staff beginning in March in order to cut the total headquarters staff to between 2085 and 2785 by June 30, 1982, down from the equivalent of 5298 employees when President Reagan came into office. One-half to two-thirds of the reduction would be accomplished by squeezing present employees out of their jobs. Under Civil Service rules, for every person fired, 1.5 people are downgraded, shifted to temporary status, or shifted involuntarily to a different, usually less desirable job. In addition, the EPA staff is quitting at a rate of 32% a year. By June 1982, it is estimated that about 80% of EPA's headquarters staff will have been driven out, fired, or demoted. Because of the high attrition rate, there is no need to fire any employees in 1982 to be at or below this year's employment ceiling. The firings in 1982 will bring the number of employees down to the low levels of the proposed 1983 budget. Administration officials justify the reduction in staff on the grounds of "management efficiencies" or "reorganizations." Firing civil servants in 1982 to accommodate a 1983 budget not yet submitted to Congress is illegal.

**The White House has formed a cabinet-level work group to look at** the issue of acid rain and provide advice to the Cabinet Council on Resources and Environment. The work group will keep abreast of acid rain research and evaluate new information to determine whether it sheds new light on the administration position. Some observers felt the work group was

formed because the administration realizes that the acid rain issue is a serious one and because of the possibility that acid rain-control legislation may be passed by the Senate.

**The Occupational Safety and Health Administration (OSHA) launched a review** of the policy it uses to decide whether a workplace chemical may cause cancer. The agency will also look at the methods it employs to determine which potential carcinogens should be reviewed first and the means used to protect workers from them. Present policy says that chemicals shown to cause cancer in one kind of animal should always be listed as potential human carcinogens. Rejecting the idea of a threshold level, it also states that any dose of a potential carcinogen should be considered dangerous. James Foster, an OSHA spokesman, said no changes were proposed in nine existing or proposed OSHA standards regulating exposure to such chemicals as lead, arsenic, and asbestos. The current policy reconsiderations are designed to incorporate such new developments as the Supreme Court's benzene decision.

**An Office of Technology Assessment staff paper on long-range transport** of air pollutants has concluded that acid rain-control decisions made in the immediate future probably will have to be based on subjective regional perceptions of risks and cost of control rather than hard information on effects. The staff paper does not make policy recommendations, but notes that "both the costs of potential damages and the costs of controls have been estimated to be in the range of billions of dollars annually." The paper suggests that postponing controls may result in increased resource damage that may take "years to recover [from] after pollution is reduced." It estimates the annual costs of acid deposition

damage in the eastern U.S. in billions of dollars. The paper concludes that "even stringent pollution controls on SO<sub>2</sub> might not greatly affect the economics of coal-fired boilers because of the current cost advantage of coal as compared to oil."

**A poll of congressmen and state governors indicates an ambivalent attitude** toward nuclear energy. The poll was conducted by David Aviel of California State University (Hayward). On the one hand, the majority of respondents placed nuclear energy low on their priority list of energy sources, yet felt that federal appropriations for nuclear energy R&D should be increased. A majority believed that the safety record of nuclear energy is adequate, yet also wanted to increase the level of federal regulation. Most respondents also felt that the accident at Three Mile Island had no effect on their attitude toward nuclear energy.

**A General Accounting Office (GAO) report finds pitfalls** in the Interior Department's new accelerated offshore leasing program. The report raises a number of questions about Interior's ability to accommodate large increases in lease offerings at the same time appropriations and budgets are being reduced. The GAO report also points out that Interior has not evaluated all likely effects of an expanded program and urges more environmental analysis and reductions in the size of areas offered for sale. In response to a recent court decision, Interior is preparing a document that provides a more detailed balancing of environmental and energy issues, according to agency official Alan Powers.

## STATE

**A federal court ruled that the psychological health** of neighboring residents must be accessed before the Three Mile Island Unit 1 reactor is relicensed by the Nuclear Regulatory Commission. It was the first time psychological stress factors had been cited by a federal court in an environmental dispute. Unit 1 was shut down for routine maintenance and refueling when Unit 2 ran out of control on March 28, 1979. NRC has not permitted Unit 1 to resume operation since that time. However, before the

court decision, NRC had been planning to relicense it, perhaps in February.

**A first conviction of a corporation under Superfund** occurred as Ralston Purina Company pleaded guilty to criminal violations of Superfund, the Refuse Act, the Clean Water Act, and the Comprehensive Environmental Response, Compensation, and Liability Act. Ralston Purina was fined \$62 000 for discharging 18 000 gallons of hexane, used in extracting oil from soybeans, into the sewer lines in Louisville, Ky. The discharge led to explosions in the sewer system.

## SCIENCE

**The photochemical syntheses of nitrous oxide (N<sub>2</sub>O)** and, from this, other oxides of nitrogen, take place in the upper atmosphere, according to physicists Edward C. Zipf of the University of Pittsburgh and Sheo S. Prasad of the California Institute of Technology's Jet Propulsion Laboratory. Previous models assumed that all oxides of nitrogen found in the upper atmosphere originated at the earth's surface. These physicists propose that N<sub>2</sub>O is produced in the mesosphere by possibly two pathways. These mechanisms would increase the amount of N<sub>2</sub>O expected at 50 km above the earth's surface by 39% and at 70 km by 192%.

**Biological effects of chemically dispersed oil on marine shellfish** will be assessed by Battelle (Richland, Wash.), under the sponsorship of Exxon Production Research Co. Fate and effects will be determined, as will impacts on coastal ecosystems. The agent under test is a dispersant that breaks oil into microscopic particles that are diluted by ocean currents and wave action, and then biodegraded. Trays of oil and sediment or dispersed oil and sediment are placed in intertidal basins; clams grow in them; clams are also grown in sediment only, as a control. Effects on clams, dungeness crabs (which eat clams), and other organisms will be determined after 3-12 months.

**Toxic chemicals could cause human behavioral and mental as well as physical problems**, Bambi Batts Young of the Center for Science in the Public Interest told the American Association for the Advance-

ment of Science. She said that lead, for instance, could cause distraction, vagueness, and intelligence declines. However, Bernard Weiss of the University of Rochester said that lead is so widespread that no one is lead-free; thus, it is impossible to set up a controlled experiment on effects of small doses, he added. Ellen Silbergeld of the National Institutes of Health said that the brain may have receptors for chemicals previously thought to affect only other body parts.

## TECHNOLOGY

**Slow-rate land treatment "generally reduced" levels of pollutants in wastewater** below corresponding levels typically found in secondary treatment effluent, according to EPA's Office of Environmental Engineering and Technology (Washington). Such effects were studied for about 50 pollutants, with soil, crop tissues, and groundwater sites receiving wastewater for 10 or more years. Most of the wastewater was municipal. Crops took up much of the nitrogen and phosphorus, although some nitrate did leach out and exceed EPA drinking water standards in groundwater. In most cases, pathogens seemed to be attenuated below detection limits.



*Solar collector being tested*

**A solar collector that, even in cloudy weather, "promises to be highly effective,"** has been invented at General Electric's Research and Development Center (Schenectady, N.Y.). According to GE, tests indicate that the hot-air collector can accumulate three times more heat

during a northern U.S. winter than comparable flat-plate collectors can. The device has a cover made of clear vacuum tubes, a "super-insulating" plastic foam body, and a special heat-absorbing fiber. GE says that it can be made of common materials, maintain temperatures above 180 °F needed to operate absorption-type air conditioners for summer cooling, weigh 3 lb/ft<sup>2</sup>, and be competitive in cost.

**"Gold in that thar dry fog?"** Some are seeking it in dust thrown up by operations at old, worked-over gold mines. The dust is blown down by micron-sized water droplets created by ultrasonic bombardment. The ultrasonic approach was developed by Sonic Development Corp. (Mahwah, N.J.). Gold can be extracted from the settled dust. Because of the present high price of gold—about \$375 as of January, as opposed to \$35 not many years ago—Sonic estimates that the system's payback is "virtually immediate."

**PCB-contaminated oil was burned in a utility boiler** by the GCA Corporation at the Northeast Utilities Middletown, Pa., generating station, and no measurable amounts of PCBs, polychlorinated dibenzofurans, or polychlorinated dibenzop-dioxins were present in the boiler emissions. The destruction rate of PCBs was found to be at least 99.998%. The actual rate may be greater, but detection is hampered by the instrumental limit of 1.2 µg.

**A "Three-Mile-Island"-type accident is believed impossible with a pool-type breeder reactor**, Argonne National Laboratory says. The reason given is that natural convection currents in the pool (of liquid sodium) "can protect the core from serious overheating, even if *all* the sodium pumps fail," Argonne believes. The laboratory has its Experimental Breeder Reactor II (EBR-II) in southeastern Idaho, which it says is the longest-operating breeder in the world. Argonne studies have also shown that in the event of a fuel leak, "leached fuel cannot accumulate to block sodium flow or threaten safe operation." However, a major effort is aimed at leak detection and stoppage.

**Converting sewage sludge and garbage into "useful products" with cost recovery benefits** is the objec-

tive of a waste treatment system developed by RECO Industries, Inc. (Richmond, Va.). According to the firm, the RECO/Dano system recovers ferrous metals, produces a stabilized nutrient compost for landscaping and soil reclamation, and reduces landfill needs. The key is the "Bio-Stabilizer," which combines biological and mechanical processes, and can handle an average 100-tpd throughput with 20% solids. After processing, coarse materials are screened out, and compost (from the finer matter) is made by aerobic methods.

**The Savannah River defense radioactive waste management facility got "a clean bill of health"** from a National Research Council (NRC) panel. Its current interim storage poses no threat to public health, and should function safely until permanent storage methods come on line, the NRC believes. In fact, the panel said that the feasibility of storage in bedrock beneath the Savannah River facility site should be studied. However, the NRC also noted that it did not endorse the bedrock disposal approach, and that all other alternatives should also be considered.

## INDUSTRY

**A National Society of Professional Engineers (NSPE) award went to the Garrett Turbine Engine Co.** (Phoenix, Ariz.) for a fluidized-bed/closed gas turbine power system, which can be coal-fired. A "first" is the use of air-lubricated bearings in a highly recuperated closed-cycle gas turbine. Pressures can be raised to 10 atm, giving 10 times the power of an equivalent open-cycle engine. Efficiency actually *increases* slightly at reduced power levels. Waste heat recovery is accomplished with recovery heat exchangers in the exhaust stack, and replacing the cooler in the working gas loop. Air is the working fluid.

**Polychlorinated biphenyls (PCBs) do not initiate cancer**, according to a recent Chemical Manufacturers Association (CMA) study. It says: "In spite of over 50 years of use, no causal relationship has been established for any specific type of cancer, nor has it been proved that the incidence of cancer mortality has increased." According to the study, PCBs have at most a weak promot-

ing activity for cancer and present only slight mutagenic and reproductive risks. No significant adverse health effects except for dermatitis and chloracne were found; these were reversible after discontinuing the exposure. CMA believes the study provides justification for the current PCB standard for 50 ppm.



*McCracken: sponsoring wind energy*

**Cooperation with entrepreneurs to develop a new wind energy resource** is a program undertaken by Southern California Edison (SCE, Rosemead, Calif.). A series of small turbines in the wind-swept Tehachapi Mountains generate power, Frank McCracken, SCE's director of research and development, says. The utility signed a long-term contract with Zond Systems Inc., an alternate energy firm in the Tehachapis, to supply this wind-generated power. With a first-stage budget of almost \$3 million, Zond is installing 40-50 of its 25-50-kW turbines. Estimates are that these 40-50 units could produce up to 4.7 million kWh/y for 800 residential customers.

**How is innovation affected by the Toxic Substances Control Act (TSCA)?** According to the Chemical Specialties Manufacturers Association (CSMA, Washington), TSCA resulted in a decline of more than 25% in new substance development, with small businesses being hit hardest. A major factor in this decline is the premanufacturing notification (PMN) for EPA whose costs for filing "far exceed simply the time consumed in the paperwork itself; again, particularly affecting small businesses." CSMA says that its members plan 12-49% cutbacks in new product development, mainly because of PMN costs, and sees increased small business failure and decreased competition as possible outcomes.

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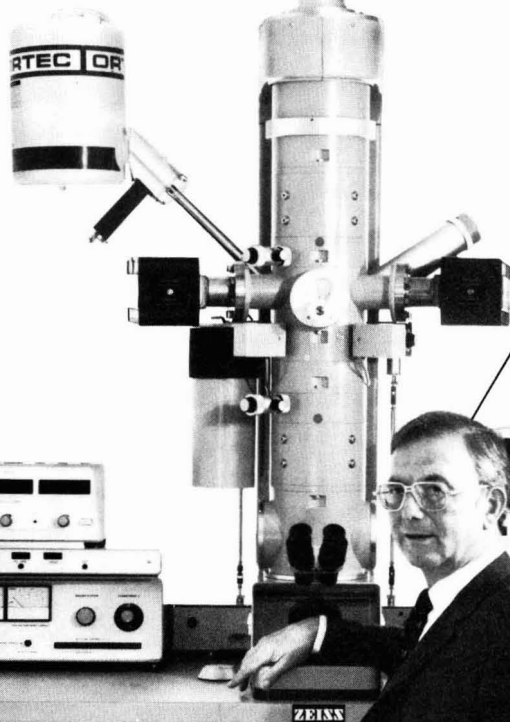
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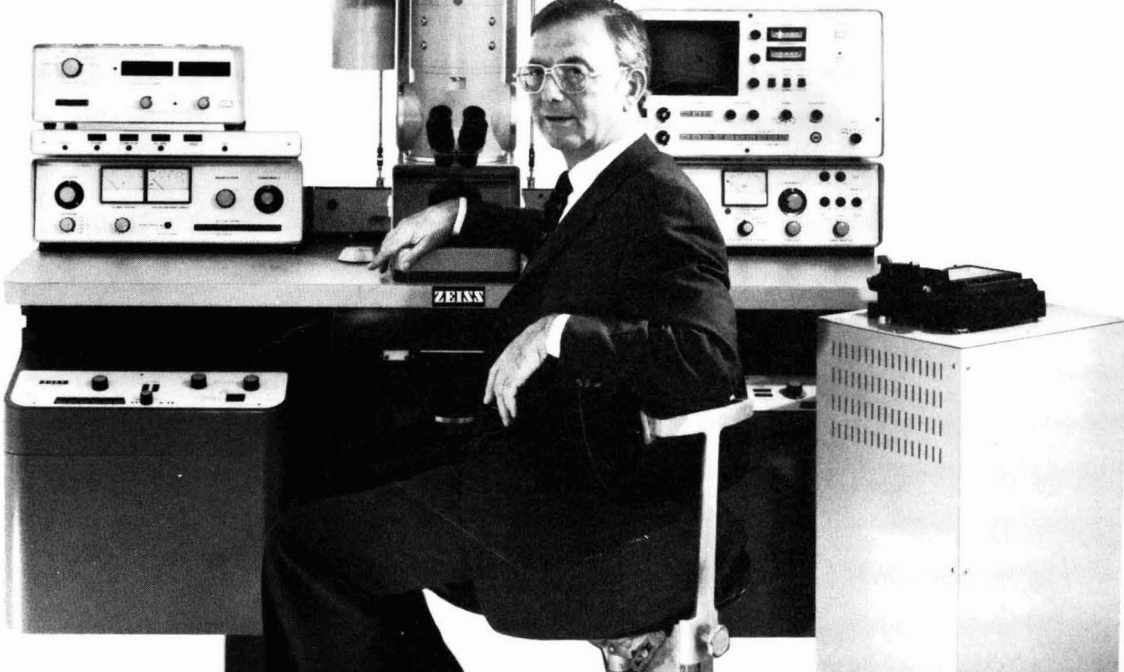
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# The Global 2000 Report to the President

*In which direction—beneficent or malign—  
are the global trends going for the environment,  
natural resources, and population?*

In his 1977 environmental message to Congress, President Carter directed the Council on Environmental Quality and the Department of State, working in cooperation with other agencies, to make a study of the probable changes in the world's population, natural resources, and environment through the end of the century.

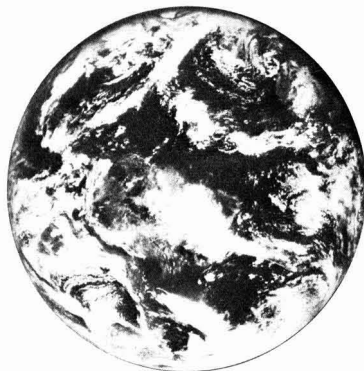
This was the beginning of what was a three-year effort to look at these issues and resulted in a massive three-volume publication that has been translated into many languages and sold half a million copies. It was the first time the U.S. government studied natural resources, population, and environment from a long-term global perspective and attempted to make connections among them.

The conclusions of the study are summarized in the following two paragraphs:

*"If present trends continue, the world at 2000 will be more crowded, more polluted, less stable ecologically, and more vulnerable to disruption than the world we live in now. Serious stresses involving population, resources, and environment are clearly visible ahead. Despite greater material output, the world's people will be poorer in many ways than they are today.*

*"For hundreds of millions of the desperately poor, the outlook for food and other necessities of life will be no better. For many, it will be worse. Barring revolutionary advances in technology, life for most people on earth will be more precarious in 2000 than it is now—unless the nations of the world act decisively to alter current trends."*

These statements, strong as they



are, have generated much controversy. At the January meeting of the American Association for the Advancement of Science (AAAS), four sessions were devoted to the Global 2000 Report. Several of the authors gave updates on what had been learned in certain areas since the report was written. In one session, criticisms were made of the report and of its implications, and one panel considered the effects this report should have on education. In some ways the debate between those who essentially agree with the report and those who disagree is similar to the age-old debate between doomsday prophets and "cornucopians," and goes back to Malthus and probably beyond.

## Population

In the section on population, as in most topics of the Global 2000 Report, high, medium, and slow growth projections are made. All three predict that if present trends continue, the increase in the world population will be of unprecedented magnitude, and the world will gain many more people in

the next 25 years (1.88–2.22 billion) than it acquired in the last quarter century (1.56 billion). The medium growth projection forecasts that the world's population will grow from 4 billion in 1975 to 6.35 billion in 2000, an increase of more than 50%, while the rate of growth will decline only marginally from 1.8–1.7% per year. The poorest countries will experience 90% of this growth and by the year 2000 will have 78–80% of the world's population compared to 72% in 1975.

Samuel Baum of the U.S. Census Bureau, one of the original authors of the Global Report who spoke at the AAAS meeting, said there is no reason to expect that the problems projected in the report will be altered. He also said that since 1977, when the projections were prepared, many countries have taken censuses or released new data on fertility and mortality. The latest census figures have changed the predictions for some individual areas. For example, Africa would grow somewhat faster and Latin America somewhat slower; but the world population is still predicted to reach the same figure as in the Global Report.

## Per capita income

The Gross National Product (GNP), which represents the total goods and services available to a society, is also discussed in the Global 2000 Report. GNP per capita is expected to increase by about a third. In some areas such as in the great populous nations of south Asia—Pakistan, India, and Bangladesh—little or no growth in per capita GNP is projected, while in some developing countries, especially in Latin America, the GNP

per capita is expected to rise substantially. The large gap that already exists between the rich and poor nations will widen. The authors of the report caution, however, that projecting GNP is extremely difficult because it is dependent on so many variables. They say that the GNP data are particularly subject to error for the less developed countries because the contributions of the traditional sector cannot be accurately represented.

### **Food supply**

If food were distributed uniformly, the world would probably be able to feed itself adequately in the year 2000. The Global Report forecasts a 90% increase in total food production for the 1970–2000 period, which translates into a 10–15% per capita rise. However, the bulk of the increase will probably go to countries that already have relatively high per capita consumption. The real price of food is projected to rise 30–115% over 1969–1971 prices, and in most cases food will go only to those individuals who can afford to pay for it or grow it themselves. The per capita consumption of food in South Asia, the Middle East, and the less developed countries (LDCs) of Africa is expected to improve little, if not actually decline below present inadequate levels. The World Bank estimates that because of rapid population growth, the number of malnourished persons in LDCs could increase from the current figure (400–600 million) to as many as 1300 million by the year 2000. The Global Report also states that in 2000, each arable hectare will have to support 4.0 persons instead of the current 2.6 persons (first half of 1970), and this will be accomplished through the increased use of fossil fuels, irrigation, and pesticides.

At the AAAS meeting, another of the original authors of the Global Report, Patrick M. O'Brien of the U.S. Department of Agriculture said that appreciably more of the world's resources will have to be used, and more extensively, to meet demand in 2000. In other words, additional land, water, fuel, and fertilizer will have to be devoted to food production. He also pointed out that trends since 1978 had changed sufficiently to suggest somewhat slower growth in the demand for food than expected and smaller per capita gains, but that recent developments tended to "support the general themes highlighted in the chapter" on food and agriculture.

Throughout history, there have been hunger and malnutrition somewhere in the world. However, as National

Academy of Sciences past President Phillip Handler observed: "The character of malnutrition has changed markedly in the last 40–50 years. The classical deficiency diseases—beriberi, scurvy, pellagra, rickets, sprue—have almost disappeared. . . . Instead, there is marasmus and kwashiorkor, both forms of general protein calorie insufficiency and iron deficiency anemia. . . . Malnutrition now reflects lack of food, not lack of scientific understanding." It is interesting to note that more people are malnourished today than the total population of the earth prior to about 1650.

Another factor that will make it difficult to feed the population of the year 2000 is that it will be a somewhat older population than that of today. As a population ages, the food requirements increase sharply. Also higher incomes in some parts of the world will cause eating habits to shift to a more diversified diet—from one of starches and cereals to one that includes meat and other animal products. This kind of diet is more expensive and requires a larger amount of grain to sustain it. It is expected that many parts of the world will increase their dependence on the U.S. as a source of supply.

### **Environmental aspects**

The Global Report states that the race to provide food for a rapidly growing world population will have, and already is having, harmful effects on the environment. Improper farming practices are increasing erosion and depleting the nutrients of topsoils. In summary, this report noted: "Evidence is accumulating that agricultural and grazing lands in parts of Africa, Asia, the Near East, and Latin America are already under such heavy stress that they simply cannot be expected to retain their present productivity through another two decades of intensifying human and animal population pressure." In LDCs there has been a great increase in the number of free-ranging animals; this has led to overgrazing, one of the leading causes of desertification. It is already a serious problem in Rajasthan, India, where sharp increases in the amount of land under cultivation have reduced available pasture land.

Even in the U.S., soil erosion is a current problem, although it has not resulted in a decline in overall productivity. In 1975 soil losses on U.S. crop land amounted to almost 3 billion tons, an average of about 9 tons per acre, according to the Department of Agriculture Soil Conservation Service. It has been estimated that soil losses must be cut in half if crop production

is to be sustained indefinitely.

In order to increase food production in LDCs by the year 2000, much greater use of pesticides will be needed. The other more modern and more costly methods of integrated pest management (the use of natural enemies, crop rotation, sterilization, and hormones to eradicate pests) will probably be too expensive for these countries. However, the heavy use of pesticides always results in the development of pesticide-resistant pests. Consequently, these are expected to cause considerable problems, especially because the world is expected to rely more and more on monocultures (single species), which means that an entire crop being grown in many different countries could become vulnerable to a single resistant pest.

Irrigation will also have to be used much more extensively by 2000 if food production goes up as expected. By 1990, the irrigated area of the world is projected to rise from 223 million to 273 million hectares. It is estimated that about half of all the irrigated lands of the world have already been damaged by salinization, alkalization, and water logging. Damaged land can often be repaired; but the repair is expensive, and much of the injury has occurred in LDCs—countries which can least afford to remedy it. In Pakistan, for example, out of a total of 15 million hectares of irrigated land, about 11 million suffer from salinity, water logging, or both. Soil degradation from irrigation is expected to continue in many areas unless irrigation practices are changed.

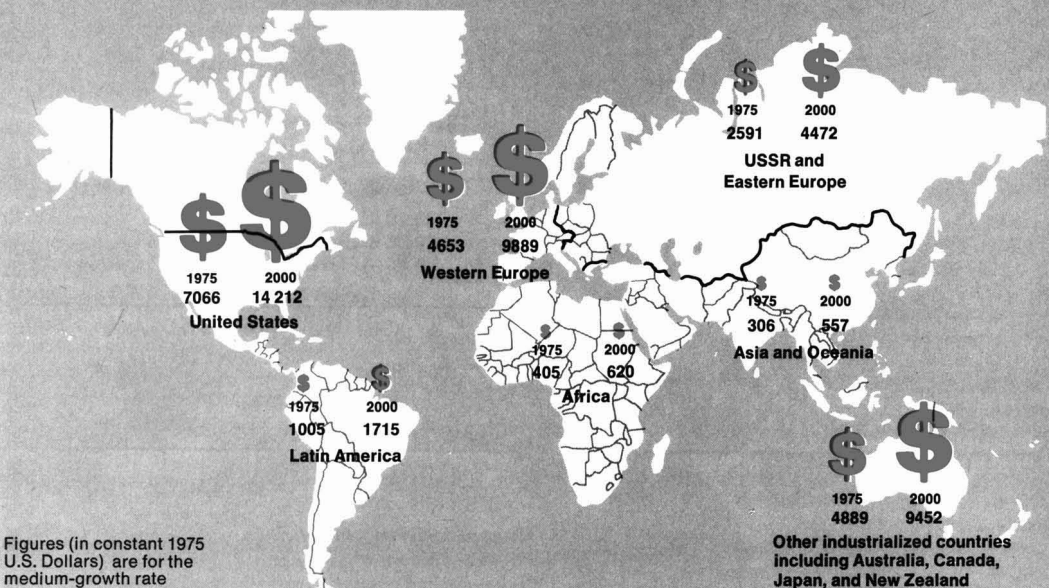
### **Deforestation**

One of the most serious problems that has resulted from the effort to expand crop growing areas has been deforestation. It has also been caused by logging operations and the building of highways when forests are cut down along the roads. However, in tropical areas where forests are being cut at a rapid pace, logging and farming usually go hand in hand. Loggers take out the large trees and are followed by farmers who burn the rest of the vegetation and begin to grow crops. If there is only sparse population in the area and no farmers follow the logging operation, reforestation is usually left to chance.

One of the authors of the Global Report, Bruce Ross-Sheriff of the Office of Technology Assessment, said at the AAAS meeting that there is controversy about the exact rate of deforestation, but no disagreement about the severity of the tropical forest resource problem. This report states:



## Per capita gross national product by regions, 1975 and 2000



Figures (in constant 1975 U.S. Dollars) are for the medium-growth rate

Source: The Global 2000 Report to the President.

“Twenty-two years ago, forests covered over one-fourth of the world’s land surface. Now forests cover one-fifth. Twenty-two years from now, in the year 2000, forests are expected to have been reduced to one-sixth of the land area.” This statement may be somewhat exaggerated. A 1981 Food and Agricultural Organization (FAO) publication states that the tropical deforestation rate in Latin America is 0.64%, 0.61% in tropical Africa, and 0.60% in tropical Asia, which means that tropical deforestation is going on at about half the rate indicated in the Global Report.

Even if these FAO rates sound rather low, they do not mean that rapid deforestation is not taking place in certain countries. In Haiti, for example, only 9% of the original forests remain. Thailand has lost forests so rapidly that even the most optimistic estimates of the rate of destruction offer no hope of significant forest stands beyond 1993. For the countries of The Ivory Coast and Nigeria on the west coast of Africa, the situation is also serious. More than 70% of the forest area The Ivory Coast had at the beginning of the century has already been cleared. In Central Africa the situation is not alarming, except for Zaire and Cameroon, and in Eastern Africa deforestation is severe only in Madagascar. Nearly two-thirds of the

original area of tropical moist forest has already been converted to other purposes in India, Sri Lanka, and Burma.

Another study points out the seriousness of the tropical forest problem. A 1980 National Academy of Sciences report states that an area of tropical lowland forest about the size of Delaware is permanently converted to other forms each week, and an area about the size of Great Britain every year. This report goes on to say that “no more than scattered remnants of undisturbed tropical lowland forest are likely to survive into the 21st century,” chiefly in western Brazilian Amazonia and Central Africa.

### The creation of barren land

If extensive areas of tropical forest are converted to crop land on a sustainable basis, then deforestation might cause species extinctions and timber losses, but allow food production to be permanently expanded. Some areas, such as parts of the Amazon basin, can be and are being used for modern agriculture with appropriate soil technology. Much tropical forest land, however, is not suitable for raising crops, especially not on a continuous basis.

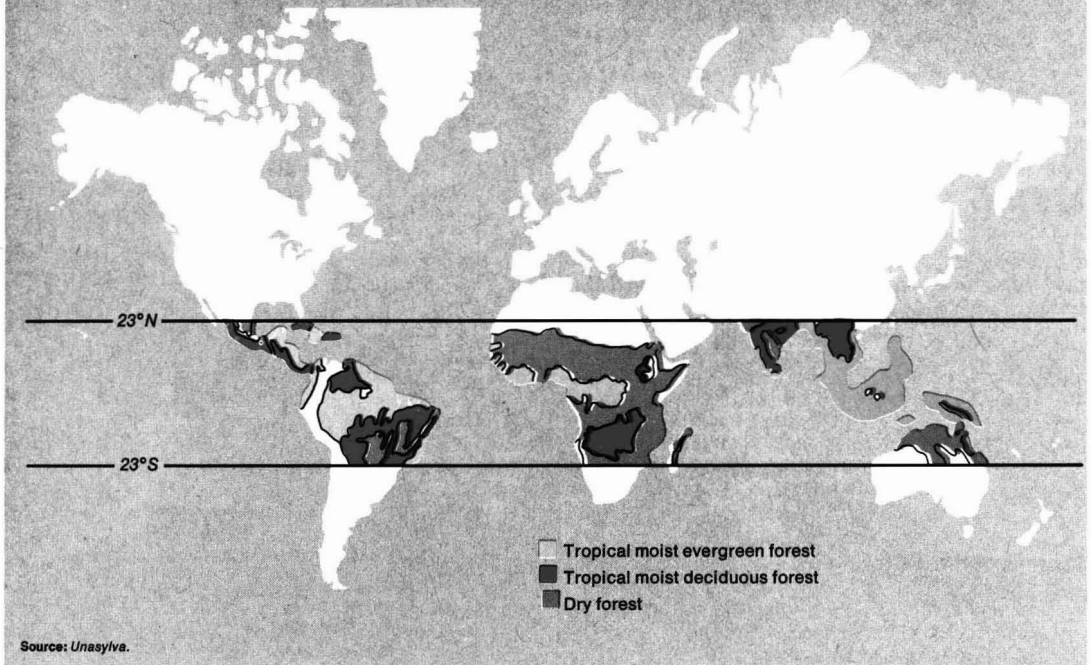
In many tropical forests, most plant nutrients are held in the diverse flora of the forest itself. If the forest is

standing, dying plants fall and decompose and the enormous mass of vegetation quickly recaptures the nutrients. If the forest is cut, burned over, and planted with crops, the nutrients are quickly washed off or deeply into the soil by the heavy rains and out into the streams and rivers. Many of these forest soils can maintain crops for no more than two or three years at a time, and no system is now in use that will sustain their productivity. After two or three years of cultivation, tropical forest soils often lose their ability to support crops or forest. If the land is allowed to lie fallow for about a decade while a secondary forest grows back, the species composition is often different and biological diversity much more limited.

In some tropical forest areas, a shift and burn method of agriculture has been practiced for centuries. After clearing, the land is burned, and crops are grown for a year or two. Then the land is allowed to lie fallow for about a decade while a degraded forest develops. After this the whole process is repeated. With this method, crops can be grown. In recent years, however, farmers have shortened the fallow periods in many areas because the populations have expanded so rapidly. The result has often been barren land.

In addition, the environmental effects of deforestation in tropical areas

## Tropical forests of the world



are flooding, increased erosion, decreased water supplies, and sometimes drought. The loss of forest may also increase temperatures. According to the Global Report: "When the forest is razed, the heat that has fueled the evaporation-transpiration process instead raises the air temperature, usually to the detriment of seed germination, plant survival, . . . and human comfort." In addition, the loss of forest can cause an increase in atmospheric dust that some climatologists believe can prevent moist air from rising and inhibit precipitation.

### Loss of species

Probably the most serious environmental effect of deforestation in tropical areas is an increased rate of species extinction (see *ES&T*, Vol. 16, No. 2, 1982, p. 94A). The Global Report states that "the rain forest areas modified by deforestation can be expected, with few exceptions, to include a negligible number of the species that were present in the virgin forests." Many tropical forests contain species that not only do not exist outside of these forests, but are unique to that particular area. Madagascar's forests, for example, contain species found nowhere else, which represent a museum of the cretaceous and paleocene biota of Africa. A majority of tropical forest species can exist only in a pri-

mary forest, and they regenerate very poorly. Tropical moist forests are believed to be the most complex and perhaps the most fragile ecosystems in nature.

If deforestation continues at the present rate, many species will be lost and a large portion of those lost will never have been described or catalogued. According to a recent NAS report, about two-thirds of most species of organisms exist in the tropics and these number about 3 million. Only about one-sixth of these are known to science at the present time. The report goes on to say that "it is not unrealistic to suppose that, within the next two decades, as many as a million species of plants and animals could disappear in the tropical forests."

There are some signs that efforts to hinder deforestation will increase in the future. At the recent AAAS meeting, Ross-Sheriff pointed out that since 1978 international development agencies began to turn from industrial forestry to agroforestry. For example, AID "increased its budget for vegetative-cover activities from \$1.8 million in fiscal year 1978 to \$25 million in fiscal year 1981." The World Bank and the U.N., among others, are likewise "expanding agroforestry work."

Thailand has taken strong measures to stop its cutting in national forests. However, when farmers and loggers

are remote from the seats of government, it is not known whether LDC authorities will have sufficient control to keep them from destroying the forests. Ross-Sheriff pointed out that "there is no reason to think that the Global Report's best-case scenario [for deforestation] can be achieved."

Temperate deforestation has not been as rapid as tropical deforestation. The temperate forests in some countries have probably expanded recently. However, the U.S. forests have changed significantly in the last few years. Many acres of natural hardwood forest have been converted into rapidly growing forest plantations, a type of crop land.

The Global 2000 Report discusses several other subjects such as water supplies, energy supplies, fisheries, and nonfuel minerals. The environmental effects of the projections are also covered. There is no area in which serious problems are not foreseen.

### Assessment

The AAAS session criticizing the Global Report offered a wide variety of observations. Several scientists who were not authors of the original report, such as Julian Simon and S. Fred Singer, took issue with certain data reported. Many criticisms were made on the basis of the theory that if trends have been improving in certain areas

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over the last 200 years, these developments will continue. Most of the trends cited concerned improvements in life within the U.S., such as longer life expectancies, declining death rates, decreases in the number of sick days in industry, growth in the amount of corn produced per acre. The observations presented may be true, but most of them are not global trends, and many are unrelated to the material presented in the Global Report. One panelist stated that there was no reason to believe that the earth did not have the capacity to support tens of billions of people. Garrett Hardin, author of "Tragedy of the Commons," pointed out that the trends of the past 200 years are not nearly as important as the trends of the past 25 years and that what we see taking place before our eyes is even more important. The basic conflict expressed at the AAAS meeting seemed to be between those who believe the earth has nearly unlimited resources to support a continually expanding number of people, and those who think the resources are limited and that we have almost exhausted the planet's capacity to support life in a satisfactory way.

To those who say that past trends in this country indicate what the world's future will be, we might compare the earth to a ship sailing in a foggy sea with poor navigational instruments. The trip might seem good for centuries and many trends could seem positive; but if cliffs cannot be clearly seen, eventually and quite suddenly the ship might collide with them. The question is whether we as a nation or world have radar that is accurate enough to detect dangers around us and whether we will see them in time and have the courage and conviction to avert disaster.

—Bette Hileman

#### Additional reading

"Research Priorities in Tropical Biology"; National Research Council, National Academy of Sciences; Washington, 1980.

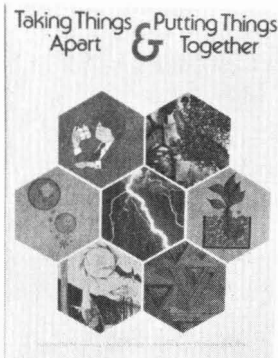
"Global Future: Time to Act." Report to the President on Global Resources, Environment, and Population, The Council on Environmental Quality and the U.S. Department of State, January 1981.

"The World's Tropical Forests: A Policy, Strategy, and Program for the United States." Report to the President by a U.S. Interagency Task Force on Tropical Forests, Department of State, May 1980.

"Conversion of Tropical Moist Forests"; National Academy of Sciences: Washington, April 1980.

"The Global 2000 Report to the President," Council on Environmental Quality and the Department of State: Washington, 1980; Vols. 1, 2, and 3.

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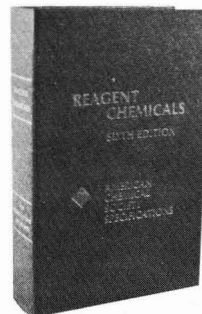
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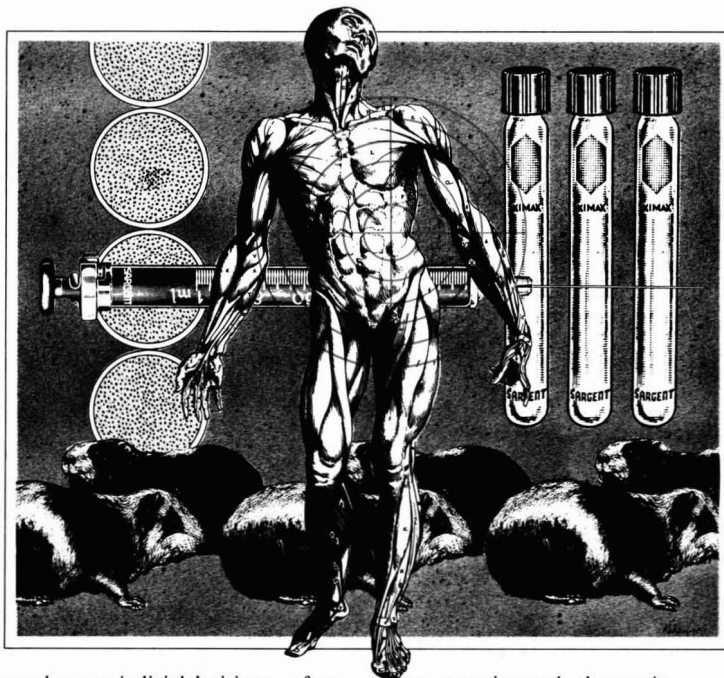
*Participants at a Washington seminar suggested ways that peer-reviewed scientific data could balance value judgments and legislative and regulatory fiat as a basis for*

## Environmental quality standards development

"What are desirable characteristics of environmental quality standards?" and "What considerations should be involved in the development of these standards?" are questions that have been asked in various forms for at least two decades. So far, no one seems to have come up with answers that satisfy everybody, and probably no one ever will. However, what is heard increasingly is that such standards should be based far more upon objective scientific or technological data that would stand peer review, and less upon value judgments or subsequent legislative, regulatory, and judicial fiat.

Nevertheless, value judgments, such as a perception of the need for public health protection, less polluted air, "fishable" or "swimmable" waters, and the like, must be regarded as stimuli to which standard-setting is a response. Difficulties and controversy arise when, in reply to demands for regulations for given pollutants aimed at achieving such values, virtually inflexible standards are set that are based on "worst case" reports and projections. As a result, standards could be set at a number taken, on the basis of these reports and projections, to be below a point at which the slightest adverse effect might be expected to occur. There is often little or no opportunity for hard scientific scrutiny or assessment of the efficacy of these standards.

Proposing a reason for these difficulties, Edward Burger of the Georgetown University Medical Center (Washington) explained that "for many reasons, the fund of scientific information available in any particular case is often exceedingly thin." Thus, "Decisions about regulations and standards are taken 'almost always under conditions of uncertainty,'" he said. Moreover, government agencies must proceed with regulatory activity and standard-setting in response to citizen pressure, legislative



mandates, or judicial decisions—often by a legislatively or judicially mandated deadline—regardless of the availability of plausible scientific data to justify these standards.

### Deriving a risk figure

Burger ascribed the paucity of scientific support for standards to the situation that "the main purpose of scientific observation is to test a narrowly defined hypothesis, and expand the frontiers of understanding about the natural order of things." Such observations, and the experiments from which they stem, have "almost never been designed to aid governmental regulation [or any other policy purpose]," he added.

The practical problem, then, becomes one of "translation," as Burger put it. By "translation" he meant "combining results of a series of dis-

parate experimental observations—animal laboratory, clinical, and epidemiological," for example, "to derive a numerical figure of risk to human health," which might justify a given standard. This translation process, he added, has not been considered in any systematic fashion. One result is that "changes in biochemical or physiological function [such as liver enzyme activity or lung action], brought about by exposure to a substance, have sometimes been [hastily] deemed impairments to health. Also, adaptive changes in function have been considered synonymous with pathological changes," Burger observed.

Exposure to ozone is an example. There is no *single* biological response, but a *series* of effects, such as cellular changes, blood changes, effects on preexisting diseases, and numerous others. The magnitude of such changes

can range from no effect, through adaptive and pathological, to life-threatening. Burger pointed out. However, they may vary from person to person, animal to animal, and body function to body function.

How, then, does one set a single standard for ozone when the concept of a fixed threshold level of exposure may be called into question because of all these differences? Again, maybe by using a number below which any effect of any kind is detected, especially if a law or judge's order says that this must be done.

#### A mix of reality

Perhaps the long-argued question of environmental standards and their scientific plausibility would not have raised so much of a brouhaha were it not for the economics involved. However, standards mean regulations—volumes of them—on the federal level alone, not to mention those of state and local governments. These regulations affect the financial situations of businesses and individuals, often adversely. Moreover, there has seldom been any solid consensus as to what the dollars spent for compliance buy in terms of human and environmental health and welfare.

To address these and other pertinent matters, the American Academy of Environmental Engineers (AAEE) and George Washington University sponsored the Seminar on Development and Assessment of Environmental Quality Standards, held in Washington in mid-December. Keynoting the seminar with a quotation from a U.S. Agency for International Development report, Abel Wolman of Johns Hopkins University (Baltimore, Md.) pointed out that standards "are not acts of God, although they sometimes appear to have become engraved in granite. [Environmental] standards contain a mix of epidemiological and empirical reality, and no inconsiderable number of value judgments."

Since at least 1940, Wolman has been calling for the consideration of standards in two categories: one involves *methods* for diagnostic applications; the other entails principles or concepts. One may recall that he chaired the first committee that made a report to Congress on pollution in the mid-1930s (*ES&T*, April 1968, p. 256).

In the first category, which can include chemical analysis, for example, standardization presents few problems. The uniformity and interchangeability of instrumentation, technical language, analytical protocols, and the like, can be considered *objectively*, and



Wolman: objectivity vs. subjectivity

#### Seminar objectives

The AAEE/George Washington University seminar's objectives were to shed more light on areas of concern, such as:

- establishment of mandated (environmental) goals
- development of risk/benefit estimates with respect to health, economics, and other measures of the "quality of life"
- assessment of sampling, analytical, and other uncertainties associated with these estimates
- scientific, technical, economic, political, and other considerations involved in the standards decision-making process.

More than 80 people attended the seminar.

The American Academy of Environmental Engineers, founded in 1955, now has about 2300 members. To become an AAEE member, one must

- be a graduate of an accredited school of engineering
- be a registered professional engineer
- have a minimum of eight years of experience in his or her field
- go through a written examination plus an oral interview to determine applicable qualifications and experience.

Alternatively, if a prospective member has 15 years of valid experience, the written examination may be waived, but the interview and a sponsor are required.

The AAEE Awards Banquet takes place on March 15. Its executive director is Ralph Graber, P.E., who can be reached at P.O. Box 269, Annapolis, Md. 21404; (301) 267-9377, or (202) 261-1820.

be scientifically validated, Wolman said.

In the second category, the standardization of principles or concepts "introduces to the element of judgment the element of *subjectivity*, which must loom large in final decisions." For instance, if a standard for a given chemical is set through legislative, regulatory, or judicial fiat, especially when it is based solely on value judgments, "the scientific basis, or even the logic for its setting could be open to question, doubt, and confusion," Wolman has been warning for many years.

He acknowledged that value judgment "is often a valid factor" in arriving at final standard-setting decisions. His hope was that future decision making would have a "much greater scientific and technological input. Value judgment," Wolman said, "should not be used as an escape clause for acting in ignorance."

#### Beating the drums

Perhaps the prime value judgment involved in standard-setting is the protection of public health. But suppose, under the rubric of public health, regulatory agency personnel are directed to search scientific literature and experimental evidence to find the lowest level, over a given averaging time, at which *any* adverse health effect for a given substance had ever been reported. The next step may be to use this very lowest value as a basis for standard-setting. Along this line of argument, Georgetown's Burger suggested that this approach was used in developing certain air standards during the early 1970s. As examples, he cited justifications for doing away with tetraethyl lead in gasoline as well as development of standards for automotive emissions.

Could a parallel situation develop with respect to water quality standards? One example considered was trichloroethylene (TCE). Raymond Loehr, director of environmental studies at Cornell University (Ithaca, N.Y.), reminded the seminar that because of federal legislative fiat, criteria (followed by standards) must be developed for the chemical.

At least two laws affect TCE. The Clean Water Act (CWA) says that water quality criteria and effluent limitations for receiving waters must be established. The Safe Drinking Water Act (SDWA) calls for the promulgation of a maximum contaminant level (MCL).

Loehr said that, so far, EPA has not issued standards for this compound under the CWA. But legally, at least,

standards must come in the form of technology-based effluent limits. TCE is a "priority pollutant," and thus must meet the requirements of "best available technology." Just to meet monitoring, record-keeping, and reporting requirements, sampling, separation, extraction, and analysis by a chromatographic method might be needed; even costlier techniques may be called for in some circumstances.

On the SDWA front, Loehr noted that EPA is planning to issue an Advance Notice of Proposed Rule Making for MCL values this year. However, whether that particular notice will include TCE is not yet certain.

One of the reasons for "beating the drums" for maximum contaminant level standards for TCE is that it is alleged to be carcinogenic (particularly the "technical" grade; Loehr said that evidence implicating *pure* TCE "was less convincing." Thus, some impurity may be the culprit). For an adult human being weighing 70 kg, consuming 2 L/day of water, and eating an average of 6.5 g/day of fish, or about 2.4 kg/y (take 50% of these values for a child) he pegged the lifetime incremental increase of cancer risk for the substance, with a concentration of 27 µg/L, at 1 case in 100 000, or 1 in 10<sup>5</sup>.

Alleged carcinogen or not, TCE figured in the closure of at least one drinking water supply well. Its water showed 300–500 µg/L of the chemical, Loehr said.

### Rationale for a standard

Since fear of cancer leads to public demands that standards be set, one would ask, "Can TCE actually cause

### Criteria vs. standards

At a meeting of the Water Pollution Control Federation held last March, *criteria* were defined as "narrative and numerical [scientific] descriptions of the level or concentration of a pollutant, that produces particular environmental effects when the pollutant is discharged to receiving waters." On the other hand, *standards* are "combinations of desired uses and water quality criteria aimed at protecting those uses in a given body of water." Presumably one can substitute other media for water. *Criteria* are not enforceable under the law; *standards* are.

"Criteria are not [water] quality standards, and in themselves have no regulatory effect. However, they may become standards when adopted by a state through rule-making procedures, or when promulgated by EPA," Kenneth Mackenthun, vice president of Enwright Laboratories, Inc. (Greenville, S.C.), pointed out. In this case, Mackenthun was referring to EPA's powers under Section 303 of the Clean Water Act, and discussing the history of the development of standards for dissolved oxygen.

human cancer?" Toxicologist Edward Calabrese of the University of Massachusetts said that TCE is believed to cause tumors in mice. "But," he added, "are mice or rats [or any animal models] 'signposts' for humans, and can we extrapolate from them" in order to arrive at a standard?

Calabrese predicts that one could

ultimately have a hard time making such an extrapolation hold water scientifically. "Look at the wide intra-human differences," he reminded the seminar. "Imagine how many more interspecies differences there are!" For instance, humans do not synthesize vitamin C; rats and dogs do (so do sheep—as much as 10 g/day). Humans have gall bladders; rats do not, Calabrese pointed out. A shaved rat's skin permeability is much greater than that of a human. And even *within* the rodent family, mice show about half of the anticarcinogenic enzyme activity of rats. Because of these and other differences, it is probably safe to say that extrapolations of TCE cancer risk assessments from mice or rats to humans must be fraught with uncertainty.

Presumably on the basis of rodent models, TCE human cancer risk figures were cited as 1 in 10<sup>5</sup> if 27 µg/L is present in drinking water, and 1 in 10<sup>6</sup> if 2.7 µg/L is present. Calabrese asked how confidence-worthy such figures may be if, for example:

- In mice or rats, TCE itself is not active, but requires bioactivation to be transformed into an "ultimate" carcinogen.

- The extent of such bioactivation is directly proportional to retention time in the animal's body, and does not take into account anticarcinogenic activity.

- The TCE biochemical pathway in humans is probably even less understood than it is in rodents; in any event, one cannot ascertain it directly, since humans are not used as experimental animals for carcinogenicity tests.

If the foregoing cancer risk numbers

### Standards development: more suggestions

VPI's Cairns had several more suggestions for the development of standards, which he felt would make them more defensible:

- Since a single standard "will not apply to all types of ecosystems, or regions of the country," federal and even state standards should include provisions for adaptation to local conditions.

- Exactly *what* environmental qualities are being protected should be explicitly stated in the standards documents applying to them.

- Scientific/engineering evidence on which standards are based should be gathered in a systematic fashion, rather than merely compiled from professional journals and in-house documents.

- The predictive or estimated environmental concentration or fate of a chemical should be explicitly stated; this should include chemical partitions, secondary and tertiary transformation products, persistence, and other pertinent data, which should be closely coupled with that of biological tests. In that way, an overall hazard estimate could be prepared.

- Statistical analyses showing confidence limits, and other evidence of the soundness of data upon which standards are based, should be included in all criterion documents.

- All literature examined when the standards document was prepared should be listed (as it is in criteria documents), *even if a decision was made not to use that information.* Also,

indications of what literature passed peer review should be included.

- For a basic EPA criterion document, an indication of whether or not the EPA Science Advisory Board or one of its appointed committees endorsed it should be included.

What is perhaps a principal problem with standards development was expressed by Wolman in this wry manner: "The late George C. Whipple judiciously commented that 'a regulatory edict, both in law and philosophy, should establish the minimum for safety, rather than the maximum of hope.' The latter approach is perhaps the symbol of regulatory practice of the last decade, if any uniformity is discernible among the responsible agencies."



present problems, it should follow that maximum contaminant level standards developed from these numbers may be on shaky scientific ground. Suppose, however, a standard of, say, 1.5  $\mu\text{g}/\text{L}$  is promulgated. One might ask whether its basis was hard scientific knowledge, or the belief that the public is entitled to "health protection" to the point of attempting to mandate an aim for "zero risk." While a goal of "zero risk" is probably scientifically, technologically, and economically unattainable, the concept certainly has broad political appeal.

### Single-species testing

The practice of extrapolating mouse data to humans or ecosystems gives trouble to John Cairns, Jr., of Virginia Polytechnic Institute and State University (VPI, Blacksburg). "Prediction of effects from [one] level of biological organization to another—for example, from single species to ecosystems—is not a scientifically sound practice. However, most testing, which would result in measures that the public assumes will protect ecosystems, is based almost entirely on single-species toxicity assays," he said.

Cairns noted that for developing criteria (the precursors of standards), EPA normally requires acute and chronic single-species laboratory testing. But results from such laboratory toxicity tests "may be quite different from responses in the real world. If validation in field studies is not possible, a microcosm should be used," he suggested.

In nature, usually, "environmental quality mediates the toxic response of aquatic organisms to most potential environmental pollutants," Cairns observed. He proposed that to some extent, at least, these responses in nature could be simulated or modeled in a microcosm.

When existing environmental quality plays a role in ecosystem response to pollutants, "standards should contain some estimate of the recovery time of ecosystems likely to be damaged if, for example, a spill or a naturally-occurring phenomenon takes place. This estimate would provide some guidance to enforcement officials in determining frequency of monitoring, development of early warning systems, and the like," Cairns said.

### A middle ground?

Cairns also suggested that "standards should be considered provisional until their efficacy has been validated in a scientifically justifiable manner." Maybe this concept could provide a sort of middle ground. On the one

hand, the public demands standards that it believes will help to achieve certain perceived societal values (for example, health protection, "fishable/swimmable" water, or other). On the other hand, standards set more for political than for scientific reasons can cause considerable economic and social displacement, while leading to little progress toward the goals they were established to achieve.

Value judgments and legislative and regulatory activity stemming from them might point out the directions in which criteria determinations and standard-setting should go, and man-

date actions in those general directions. Any standards set would be provisional, and therefore flexible and subject to revision, and could be unenforceable during the time prior to finalization. Valid scientific assessments could then indicate, say, environmental and health risk values for given contaminants, and where final standards should be set. These final standards would serve as the basis of regulations providing the maximum risk reduction for the dollars that society may see fit to make available for this purpose.

—Julian Josephson

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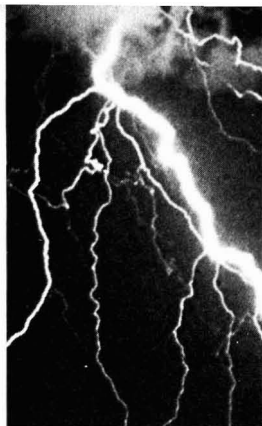
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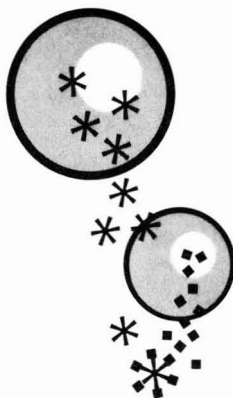
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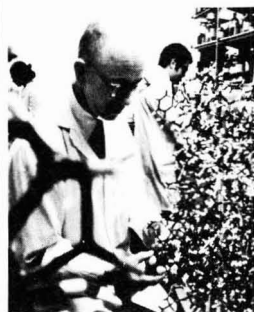
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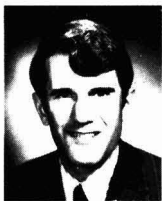
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## EPA seeks to amend Clean Water Act



**Michael R. Deland**  
*ERT, Concord, MA*

Both the Clean Air and Clean Water acts are currently awaiting reauthorization and amendment by Congress. While often heated debate over the Clean Air Act has swirled for many months around Congress, the administration, and special interest groups, meaningful discussion on the Clean Water Act (CWA) is just now beginning to surface. Last year, during the early deliberations on the air act, EPA was basically a bystander. The agency did circulate 11 general "principles," but it left the formulation of specific details and legislative language to individual congressmen and industrial and environmental representatives.

Sensing that this lack of leadership contributed to the chaos, EPA has adopted a different, more aggressive, posture on the CWA. By preparing and circulating a detailed issue paper on possible amendments, and by pledging to submit legislative language to Congress this month, EPA has seized the initiative, leaving Congress, industry, and environmental groups in a reactive posture.

### The EPA position

In a recent letter to Congress, EPA Administrator Anne Gorsuch stated that the CWA "is good and fundamentally sound . . . without a need for major or extensive revision," except "in those few areas where obvious statutory problems have emerged." Yet many of the issues addressed by EPA in its draft paper go to the heart of the act and could precipitate "major revisions."

Among the more basic issues is the approach to water quality goals and standards. Deputy Administrator John Hernandez has assumed the role of lead agency spokesman since an Assistant Administrator for Water has yet to be confirmed. He recently stated that existing water quality standards are too stringent and are based on aquatic life and human health effects criteria of "questionable" validity. He feels that a number of the standards are "extremely conservative," in some instances as a result of "statistical maneuvering" by earlier EPA researchers. To correct this problem the agency offers a number of options: seasonal use designations, encouraging states to adopt criteria on a site-specific basis, and reviewing the criteria for technical validity.

A second major issue is the "pretreatment" section of the current act that requires EPA to establish general and categorical pretreatment standards for direct discharge of industrial pollutants into publicly owned treatment works (POTWs). On the assumption that the requirements are too cumbersome and that POTWs may be removing greater amounts of heavy metals and toxic organics than originally anticipated, the agency has set forth two options. Either option would retain the basis of the existing program. The first would impose categorical toxic requirements only in cases where local programs are inadequate to meet water quality standards. The second option would allow waivers to be granted upon demonstration of adequacy of the POTW.

Another area of EPA concern is technology-based industrial effluent limitations. The agency notes that only one "best available technology" (BAT) guideline has been issued, and questions whether industry will have sufficient time to meet the July 1, 1984, statutory deadline. One proposal is to extend the compliance dates to three years from the date of promulgation of a given guideline, while another provides for a system of waivers.

Changes in the National Pollutant Discharge Elimination System (NPDES), the basic permitting scheme of the current act, are also planned. In her letter to Congress, Gorsuch noted that approximately 38 000 NPDES permits will expire in 1982, including over 3000 major industrial permits. The overwhelming resource demands the reissuance of these permits would impose on the agency could be reduced by several methods. They include extending the life of permits from the present five years to 10, adopting a permit-by-rule approach in place of the existing case-by-case permitting, or by reducing the requirements for delegation of the program to the states.

One major area EPA has not yet addressed is the Section 404 permit program under which the Army Corps of Engineers issues permits for dredge and fill disposal. This could be a key omission since Senator John Chafee (R-R.I.), the Chairman of the Senate Subcommittee on Environment and Pollution, is insisting Section 404 be addressed; the Army Corps also appears to be pressing for amendment.

### Prospects for change

Thus far there has been little by way of formal reaction to EPA's various options from either the industrial or environmental communities or from Congress. Whether Congress amends the CWA this session is still problematical. To a large degree this depends on whether EPA first is able to obtain support for its proposals from the remainder of the administration, in particular from the Army Corps of Engineers and the Regulatory Reform Group. Secondly, EPA must be able to produce finely honed legislative language that can provide a foundation for the deliberation of the congressional committees. Finally, the agency proposals must be couched so as to not stimulate intractable opposition. The next several months will reveal whether EPA can prompt Congress to "streamline" the act this session.

# Effects of acid precipitation

*Recent studies suggest that ecosystems susceptible to acidification occur over the entire length of the Appalachian Mountains and certain other regions of the East*

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**Norman R. Glass**

*U.S. Environmental Protection Agency  
 Corvallis, Ore. 97333*

**Dean E. Arnold**

*Pennsylvania Cooperative Fishery Research Unit  
 University Park, Pa. 16802*

**James N. Galloway**

*University of Virginia  
 Charlottesville, Va. 22903*

**George R. Hendrey**

*Brookhaven National Laboratory  
 Upton, N.Y. 11973*

**Jeffrey J. Lee**

*U.S. EPA  
 Corvallis, Ore. 97333*

**William W. McFee**

*Purdue University  
 West Lafayette, Ind. 37907*

**Stephen A. Norton**

*University of Maine  
 Orono, Me. 04443*

**Charles F. Powers**

*U.S. Environmental Protection Agency  
 Corvallis, Ore. 97333*

**Danny L. Rambo**

*Northrop Services, Inc.  
 Corvallis, Ore. 97333*

**Carl L. Schofield**

*Cornell University  
 Ithaca, N.Y. 14853*

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The U.S. is turning increasingly to coal to meet the nation's energy requirements. One major reason for this shift is the availability of vast coal reserves along with a well-developed technology for coal combustion. Other

reasons are this country's lack of control over foreign petroleum supplies and the problems associated with nuclear power, such as greater cost and long, unpredictable time periods required for nuclear power plants to gain approval through the political process and meet regulatory licensing prerequisites (1).

Acid precipitation, including dry deposition, is now widely recognized, if not universally accepted, as coming from pollution-caused strong acid precursors that result from the burning of fossil fuels. Because power plants and other major users of natural gas and oil may be required to convert to coal, sulfur and nitrogen emissions from power plants will probably increase even if the best available control technology is used on both new and old facilities. Transportation and industrial combustion and processes also emit significant quantities of both nitrogen and sulfur oxides.

Owing to the ubiquitous nature of the pollution sources contributing to acid precipitation and the ease with which the emissions are carried by moving air masses, acid precipitation has become widespread. These same reasons make it difficult, if not impossible, to establish a quantitative link between specific acidification problems and specific point sources of pollution. Most of the northeastern U.S. and some of Ontario, Quebec, Nova Scotia, and Newfoundland, as well as portions of the upper Midwest, the Rocky Mountains, and the West Coast, now receive strongly acidic precipitation (2, 3). Serious symptoms of acidification have been documented in New York's Adirondack Mountains, far removed from any industrial activity (4). Many areas of New En-

gland and Appalachia characterized by relatively insoluble bedrock, thin soils, and poorly buffered waters show signs of acidification. Similar conditions are found in northern Minnesota, Wisconsin, and Michigan, a region with comparable sensitivity.

## Current status of acidity

Although precipitation is most acidic in the northeastern U.S., the geographic extent of the problem encompasses the Southeast and portions of the Midwest and Far West. All states east of the Mississippi are affected to some degree (5). Rainfall is considered acidic if the pH falls below 5.6, the normal equilibrium value of carbon dioxide and water. In north-central California and near Los Angeles, precipitation with pH averaging between 4.0 and 5.0 is common (6, 7); mean values below 5.0 appear to be the norm for the Puget Sound basin and the west slopes of the Cascade Mountains near Seattle-Tacoma (8). Rainfall with pH below 4.0 is increasingly frequent in the Southeast (9, 10).

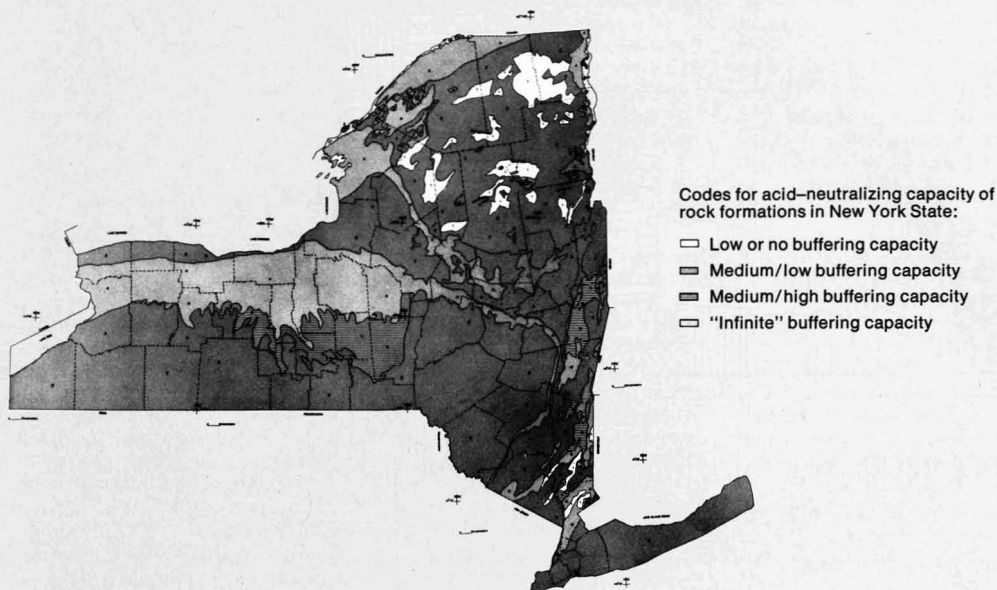
In contrast, between January 1980 and February 1981 precipitation over a pristine site in western Oregon had an average pH of 5.5, with a range of 4.5-6.4. The low reading coincided with the deposition of volcanic ash following an eruption of Mount St. Helens, Washington (8). Except for readings taken during that event, the lowest pH observation at this site was 4.9.

## Concern about effects

A growing body of evidence suggests that acid rain adversely affects public welfare. Such evidence consists of the loss of fish and other aquatic life from

FIGURE 1

Generalized sensitivity map for New York, based on bedrock geology



acidified higher altitude lakes and headwater streams, increased leaching of nutrient cations from the soil, possible reductions in crop and forest productivity, and the release of heavy metals or nutrients from rocks, soils, and lake and stream bottom sediments. Other adverse effects are the release of copper and lead from water pipes into drinking water supplies and corrosion of materials such as limestone buildings, monuments, statuary, and automobile finishes.

There is enough qualitative evidence of environmental injury to cause concern over the scope, magnitude, and rate of change of the acid precipitation phenomenon. In order to understand this phenomenon, we need to know the sources, atmospheric chemical transformations, and transport of the precursors of acid rain so that any contemplated regulatory strategy can be based on quantitative demonstrations of losses due to pollutant deposition.

**A short-term assessment**

Before beginning a major long-term research effort, it was important to ascertain the scope of the acid precipitation problem. A short-term program was initiated by the Environmental

TABLE 1

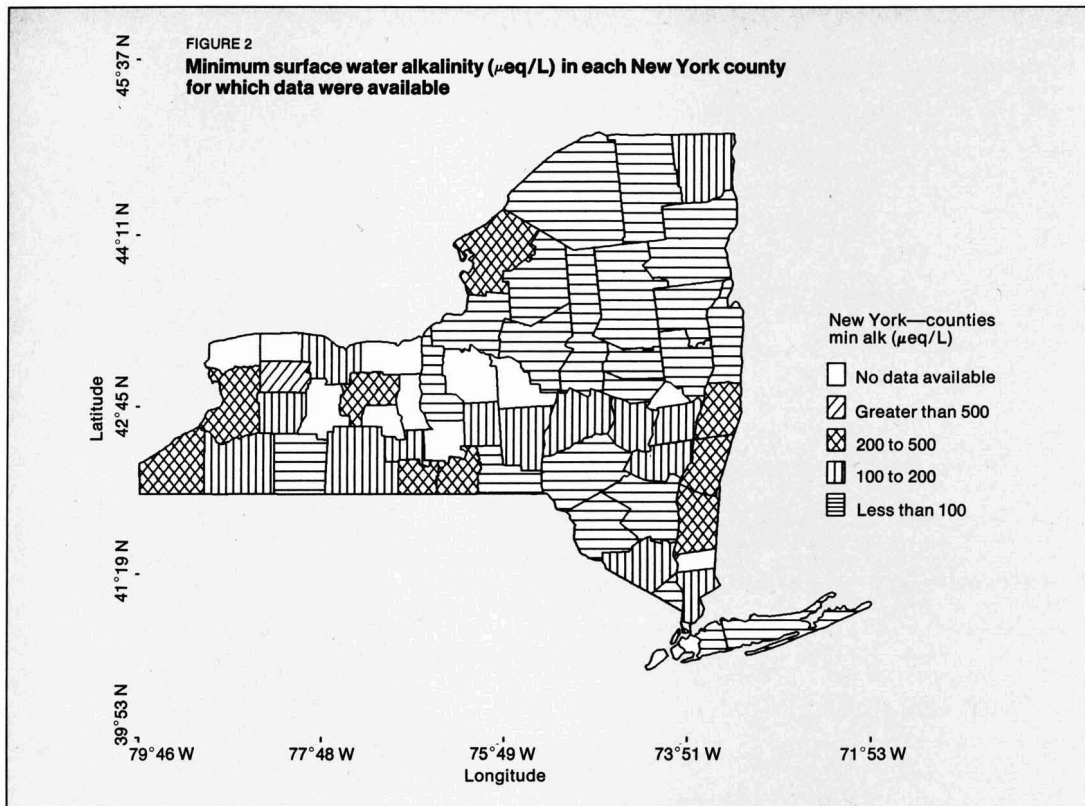
**Classification of rock formations according to their ability to neutralize acid**

- Type I** — Low or no buffering capacity, overlying waters very sensitive to acidification (granite/syenite, granitic gneisses, quartz sandstones, or equivalents)
- Type II** — Medium to low buffering capacity, acidification restricted to first and second order streams and small lakes (sandstones, shales, conglomerates, high grade metamorphic to intermediate volcanic rocks, intermediate igneous rocks, calc-silicate gneisses)
- Type III** — High to medium buffering capacity, no acidification except in cases of overland runoff in areas of frozen ground (slightly calcareous, low grade intermediate to mafic volcanic, ultramafic, glassy volcanic rocks)
- Type IV** — "Infinite" buffering capacity, no acid precipitation effect of any kind (highly fossiliferous sediments or metamorphic equivalents, limestones, dolostones)

Protection Agency in April 1979 to survey the extent of the effects of acid precipitation on the environment and assemble available knowledge useful in structuring a long-term research effort. Another purpose of the short-term program was to summarize and synthesize existing data that could be incorporated into an EPA criteria document on the effects of SO<sub>x</sub>/particulate matter. Criteria documents are written to provide a scientific and technical basis for promulgating air quality standards.

In the short-term program the following tasks were undertaken:

- Areas of the eastern U.S. that are geologically sensitive to the impacts of acid precipitation were evaluated and mapped.
- Soils in the eastern U.S. were appraised and mapped on the basis of sensitivity to acid precipitation.
- Historical changes in stream water chemistry in Pennsylvania were examined and compared with changes in fish populations.
- The effects of simulated sulfuric



**TABLE 2**  
**Expected alkalinity (in  $\mu\text{eq/L}$ ), annual change in alkalinity, and the level of significance ( $p$ ) for these time-trend coefficients in the nine northernmost New York counties<sup>a</sup>**

Rock type	I	II	III	IV
Predicted 1980 alkalinity	94	67	254	403
Annual change in alkalinity	-12.4	-11.3	-3.5	+2.5
$p$	<0.01	<0.01	0.09	0.05

<sup>a</sup> The multiple regression equation derived was:  $\text{alkalinity} = 42397 + 2.49y - 11731R - 6000I_{G1} + 3522I_{G2} - 14.9I_{G1}y - 13.8I_{G2}y - 6.0I_{G3}y$ ;  $y$  = calendar year;  $R$  = rock type (I, II, III, or IV);  $I_{G1}$ ,  $I_{G2}$ , and  $I_{G3}$  are indicator variables for rock type I, II, and III, and were given values 0 or 1;  $r = 0.69$ .

acid rain on yields and foliage of major U.S. crops were assessed.

- The effects of simulated sulfuric acid rain on model hardwood forests and their soils were studied.

These tasks were conducted over an eight-month period in 1979 and resulted in a series of reports published in the EPA Ecological Research Series (11, 12, 13, 14, 15). In addition, three related reports have appeared in the literature (2, 16, 17). The reader is directed to these publications for more detail than is present in the following discussion.

The work on the sensitivity of bedrock, soils, and surface waters was performed for all states east of the Mississippi River. Data on bedrock and soil distribution and characteristics are especially plentiful for New York, allowing a reasonable coverage of that state with respect to sensitivity. A large body of data (nearly 4000 observations) on surface water alkalinity in New York is available to illustrate how reliable bedrock geology is as a predictor of sensitivity to acid deposition. Therefore, in this paper, we focus on New York to exemplify the pur-

poses and results of EPA's short-term sensitivity studies. Data from Pennsylvania and Virginia show effects on streams. Studies of the impacts of acid precipitation on crop yields and model forest ecosystems are, of course, generic and apply to no particular state or region.

#### Bedrock geology and acidification

Soils and bedrock are considered the principal factors controlling regional sensitivity to acidification. While predicting the susceptibility of a particular lake or stream to acidification might require detailed analyses of these factors for an upstream watershed, less detailed information is needed for a larger area such as a county or state. In most regions currently known to be affected by acid precipitation, soils are shallow and derived primarily from local bedrock. Thus, analysis of the regional distribution of rock types and the relationships between rock type and water quality should help identify regions of greatest sensitivity.

Although the bedrock in some areas is uniform, for example the Canadian Precambrian Shield, geologic heterogeneity is more common. Igneous rock

masses normally have maximum dimensions less than 10 km. Folded/faulted metasedimentary/sedimentary rocks rather than being widely distributed may appear at only a single point (as a single rock outcrop), whereas flat-lying sedimentary rocks may cover wide areas that are occasionally broken up by other topographic features. Small amounts of limestone in a drainage basin exert an overwhelming influence on water quality in terrains that otherwise would be highly vulnerable to acidification.

Consequently, in the regional analysis of sensitivity, areas with intimate mixtures of rock of varying acid neutralizing capacity were classified according to the more influential rock types. Geologic terrain was analyzed on the scale used by the most recent state geologic maps, and rock formations were evaluated according to their potential buffering capacities as indicated in Table 1. Using this classification, maps were developed for the eastern U.S. by tracing the boundaries of all geologic formations, eliminating boundaries between contiguous formations with comparable buffering ability, smoothing boundaries between formations with dissimilar buffering capacities, and finally, deleting small areas of rock with low-buffering capacity. Regions considered sensitive to acidification are dominated by Type I and Type II bedrock, with little or no Type IV. A generalized sensitivity map for New York State is shown in Figure 1. The age of New York bedrock ranges from about 1.1+ billion years (the Precambrian Adirondack Massif) to ~350 million years (Devonian). There are minor amounts of younger rocks.

The Adirondack area, generally north of latitude 43° in the eastern part of the state, contains highly folded, faulted, and metamorphosed rocks. Granitic gneisses (Type I) are common, rendering this area sensitive to acidic precipitation.

East of the Hudson River Valley, bedrock is of older Paleozoic age and variable composition (Types I-IV) and is generally nonsensitive. The Mohawk River Valley and the westerly extension of this low area are underlain by flat-lying calcareous rocks, also rendering this region insensitive. West of the Hudson River and south of the Mohawk River Valley the soil is underlain by flat-lying rocks, many of which have only slight acid neutralizing capacity. On a broad scale, this area is slightly sensitive.

Data on the chemistry of surface waters for all states in the study area

were collected from various federal, state, and local agencies; maps of minimum alkalinity were prepared including each county for which data were available. The map for New York appears in Figure 2. Alkalinity, which is determined by the weathering of base cations from the watershed, is a convenient measure of the total buffering capacity of water, and hence can be used as an indicator of how susceptible a lake or stream is to acidification.

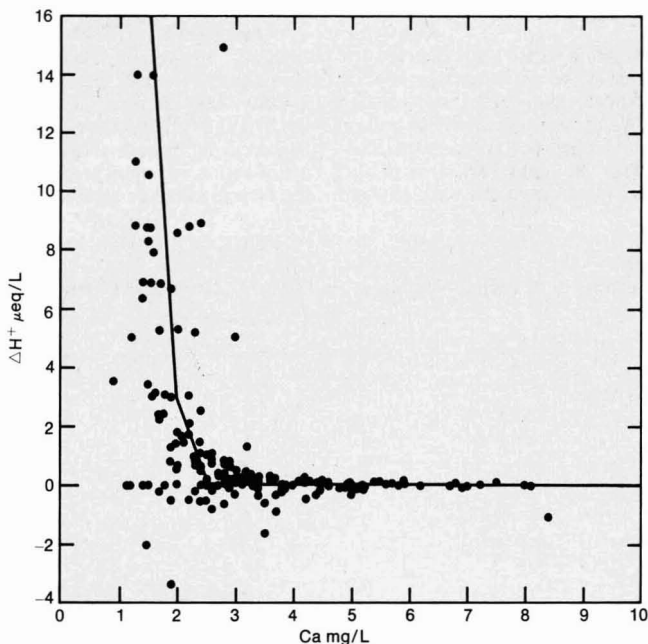
There is a strong correlation between the concentrations of calcium, or calcium plus magnesium, and alkalinity (18). In New York State, the most recent alkalinity measurements from 731 sites were compared to the bedrock type of each site. Both alkalinity and calcium were found to be significantly related to rock type. However, the correlation coefficients were low, which undoubtedly reflects the fact that site-specific variables, particularly soils, were not considered (Table 2). In many areas, such as Long Island, New York, soils are so thick

that bedrock becomes an irrelevant factor in surface water chemistry.

The nine northernmost counties of New York include the Adirondack Mountains, a region where acidification of surface waters by acid deposition is known to occur. Large areas of these nine counties are underlain by rock types I, II, and IV, with small areas of Type III rock also present. Soils of this region are generally thinner than in the rest of the state, so that the influences of the bedrock are likely to be more pronounced. Alkalinity data collected from these counties over the period 1960 to 1980 were analyzed. The data were adjusted for both seasonal and long-term trends, the rock type of each station was identified, and the data from all stations were regressed on rock type (assuming the buffering ability of each rock type was indicated by its numerical value, I through IV) and time. This analysis found that alkalinity is lower for rock types I and II than for types III and IV, and that alkalinity decreases over time in areas where the bedrock is

FIGURE 3

**Observed (•) and predicted (—) hydrogen ion concentration of 176 Adirondack lakes sampled in the periods 1929-1934 and 1975-1979, in relation to calcium levels measured in the latter period<sup>a</sup>**



<sup>a</sup> Predicted  $H^+$  concentration is based on current mean  $SO_4$  level of 6 mg/L and assumed historical  $SO_4 \leq 4$  mg/L. The observed  $H^+$  concentration is determined from Hellige colorimetric pH measurements made in the same manner in both time periods, after correction of Hellige measurements by regression against calibrated pH meter measurements (meter  $pH = 1.13 \times \text{Hellige } pH - 0.83$ ,  $R^2 = 0.92$ ). Data from Schofield (1977) and Pfeiffer and Festa (1980).

more sensitive (Table 2). Time trend analyses including all stations were also conducted for each of the four rock types. The results are shown in Table 2 as annual changes in alkalinity. Note that changes associated with types I, II, and III were negative.

#### Surface water sensitivity

Measurements of lake calcium concentrations obtained by Schofield, Pfeiffer, and Festa provide a more detailed regional perspective on the sensitivity of Adirondack lakes to acidification (19, 20). Lakes containing less than 2.5 mg/L calcium were considered sensitive. The majority of these waters are currently in a chronic or transitional state of acidification and are found in the headwaters of the major drainage basins in the western Adirondacks. This acidification threshold is based on the relationship between hydrogen ion concentration measurements made in the years 1929-1934 and 1975-1979 and calcium levels observed in the latter period. Figure 3 shows this relationship when increased sulfate and constant calcium levels are assumed over the ~50-year interval between pH measurements. These observations lend support to the predictive capability of the model proposed by Henriksen, which suggests that lake acidification is analogous to strong acid titration on a regional scale (18).

Attention was also directed to streams in two states representative of the Appalachian region. In Virginia, headwater streams situated over a variety of bedrock types in the Shenandoah National Park area of the Blue Ridge Mountains were charac-

terized and sampled during the summer of 1979. Streams on the eastern slopes of the mountains flowing over Precambrian metamorphic formations had pH values near neutrality and alkalinities of about 200  $\mu\text{eq/L}$  or a bit higher. Western slope streams, however, lie in clastic bedrock formations and are characterized by low alkalinities (about 10  $\mu\text{eq/L}$ ) and average pH values in the 5-6 range. There was thus a direct relationship between geology and surface water sensitivity as defined by alkalinity. The western slope streams would be critically sensitive to both short- and long-term acidification processes.

#### Historical changes in surface waters

To document past changes in streams situated on bedrock and soils of different sensitivities, an analysis of temporal trends in stream sensitivity was performed. Acidification by precipitation in undisturbed, upland surface waters was examined in the White Mountains of New Hampshire and the Blue Ridge Mountains of North Carolina (17). The pH and alkalinity of samples taken from both areas in the summer of 1979 were compared to those taken in North Carolina in the early 1960s and in New Hampshire in the late 1930s. These parameters had declined significantly over the sampling intervals. Results were confirmed by comparing recent measurements of calcium, magnesium, sodium, and potassium to those of bicarbonate alkalinity. This comparison confirmed the hypothesis that some acidification has occurred in both areas and that acidification was more pronounced in the New Hampshire waters.

In Pennsylvania, from state stream surveys and state university records, a large number of stream sampling sites were identified for which alkalinity or pH data existed at two different times, at least one year apart. An analysis of this information appears in Table 3. The average time span between early and recent data was 8.5 years. Of 314 sites, 107 showed a decrease in pH, alkalinity, or both, and 207 increased or showed no change. Losses of fish species occurred in both categories of streams, but at a greater rate in those showing decreased pH/alkalinity (57% vs. 38%). Decreases in pH or alkalinity were not clearly associated with generalized bedrock or soil types, with physiographic provinces, or with particular river basins. In general, sampling locations with decreased pH or alkalinity were on the lower order, higher altitude headwater streams.

Increases in pH and alkalinity are not unexpected in larger, higher order streams subject to cultural influences and siltation. Lime in runoff from cultivated areas, or in waste treatment plant effluents, for example, would raise both pH and alkalinity. Likewise, gains in the number of fish species are probable in passing from headwater to downstream conditions, where a variety of warmwater, more eutrophic-oriented forms can appear. It is more difficult, however, to rationalize apparent long-term shifts toward increased acidity. In the examination of the Pennsylvania stream records, sampling sites showing evidence of acid mine drainage were eliminated, leaving acid deposition as the most likely cause of the reduced pH and alkalinity values indicated by the data.

TABLE 3  
Summary of water chemistry and fish records for 314 Pennsylvania stream locations<sup>a</sup>

Stream group and measurement	Number of usable observations	Mean of first <sup>b</sup> observations	Standard deviation	Mean of latest <sup>b</sup> observations	Standard deviation	Streams where the number of fish species:		
						Decreased	Increased	No change
All streams								
pH <sup>c</sup>	312	6.28	5.41	6.35	5.57	81	74	20
Alkalinity (ppm CaCO <sub>3</sub> )	294	40.8	41.8	40.4	42.9	(46%)	(42%)	(12%)
Number of fish species	175	10.5	5.3	10.9	5.4			
Streams with decreasing pH or alkalinity								
pH <sup>c</sup>	107	6.99	6.72	6.37	5.84	41	22	8
Alkalinity (ppm CaCO <sub>3</sub> )	101	39.8	34.4	26.0	29.8	(58%)	(31%)	(11%)
Number of fish species	71	10.0	5.3	9.1	5.2			

<sup>a</sup> These data were located in various data files by Arnold et al. (1980).

<sup>b</sup> The least time between first and latest observations was one year; average was 8.5 years.

<sup>c</sup> Mean pH calculated by converting all values to H concentration, averaging, and converting back to pH.



For further detail, see (13).

Likens et al. estimated the average annual pH of precipitation in Pennsylvania to be less than 4.3 (5). More recent, unpublished data from independent rain analyses by D. E. Arnold, J. A. Lynch, and others indicate that the annual average pH of Pennsylvania precipitation is now about 4.0, with some events as low as 3.2. Because most of Pennsylvania's "woodland trout streams" have very low alkalinity, there is strong concern that precipitation at such low pH levels will soon overwhelm the buffering capacity of such waters, resulting in serious harmful effects on fish populations.

### Soil mapping

Existing information on the chemical characteristics of eastern U.S. soils was surveyed to develop maps delineating areas according to the sensitivity of their soils to acidic precipitation. Sensitivity was defined by the fraction of exchangeable cations that could be leached from the upper 25 cm of soil by 25 years of 100 cm/y precipitation with an average pH of 3.7. This degree of hydrogen ion loading would exceed 10% of the cation exchange capacity (CEC) for a slightly sensitive soil and

25% of the CEC for a sensitive soil. (For a discussion of cation exchange capacity, see 21.) The following parameters were considered in estimating sensitivity:

- total buffering capacity or CEC provided primarily by the clay and soil organic matter
- base saturation of that exchange capacity that can be estimated by the pH of the soil
- management system imposed on the soil, whether cultivated and fertilized or limed, or renewed by flooding

or other additions

- presence or absence of carbonate minerals in the soil profile.

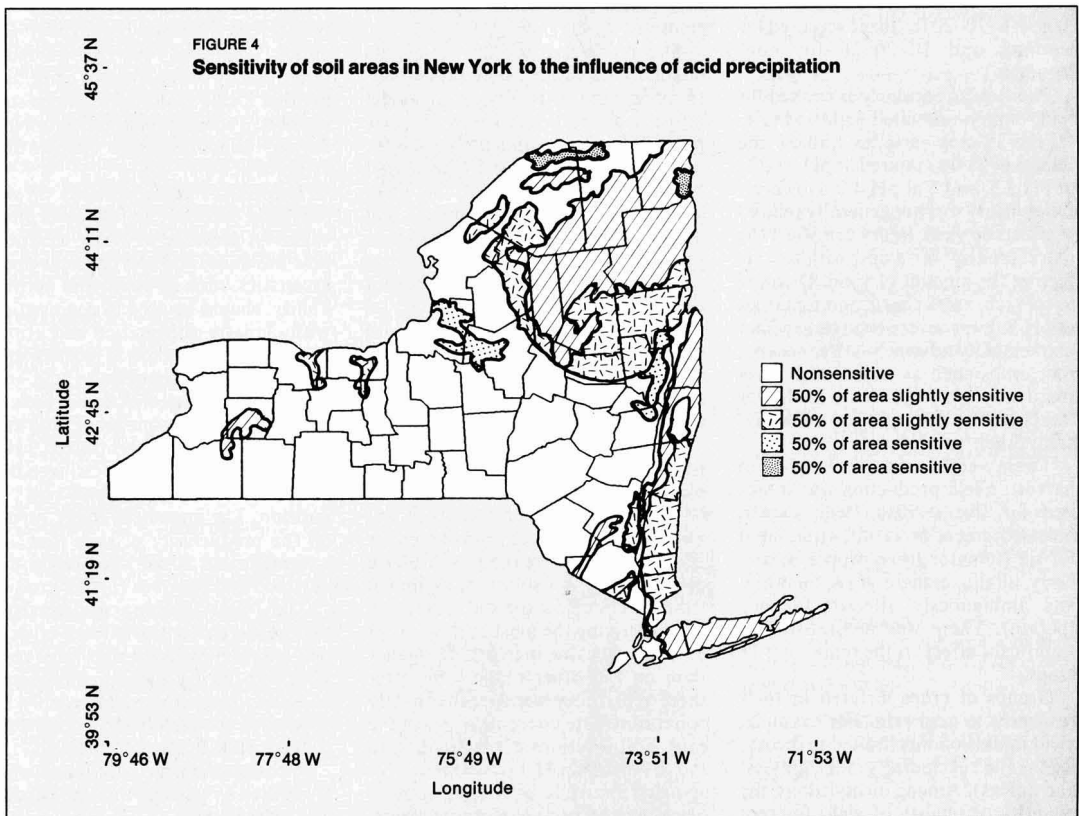
From these considerations, three classes of soil sensitivity were established (Table 4).

Using these criteria, we prepared maps showing regions with different soil sensitivity. (For further detail, see 12.) The northeastern states include large regions of slightly sensitive and sensitive areas with nonsensitive areas interspersed. In New York (Figure 4), the sensitive areas are concentrated in

TABLE 4  
Soil sensitivity to acid precipitation <sup>a</sup>

Sensitivity	Cation exchange capacity (CEC) meq/100 g	Other relevant conditions
Nonsensitive	Any value	Free carbonates present or subject to frequent flooding
		or
	>15.4	None
Slightly sensitive	$6.2 \leq \text{CEC} \leq 15.4$	Free carbonates absent; not subject to frequent flooding
Sensitive	<6.2	Free carbonates absent; not subject to frequent flooding

<sup>a</sup> Sensitivity is predicted from the chemical characteristics of the top 25 cm of soil and cation input.



the Adirondack region, where most of the soils are derived from coarse, noncalcareous glacial till or sandy outwash deposits. Significant sensitive areas also lie east of the Hudson River and on Long Island. The soil ratings are intended to locate areas most likely to be sensitive to acid loading and should not be interpreted as areas that are currently being damaged.

### Crop sensitivity

Studies of the effects of acid precipitation on major farm crops comprised a comparison of the relative foliar or yield sensitivities of crops to simulated sulfuric acid rain. This was a preliminary step toward an economic assessment of the effect of acid precipitation on crops in general.

Potted plants were grown in the field in chambers and exposed to simulated sulfuric acid rain (pH 3.0, 3.5, or 4.0) or to a control rain (pH 5.6). Simulated rain was applied at an average rate of 6.7 mm/h, 1.5 h/day, 3 days/wk, for a total of 30 mm/wk. Supplemental irrigation with well water (pH 7.5) was provided according to individual pot needs, as determined visually. Thus, soil moisture content was similar among pots. Plants were grown in sandy loam soil amended with peat moss (7.7 kg/m<sup>3</sup>) and fertilizer (624 g/m<sup>3</sup>); 6-20-20 fertilizer was used for legumes and 10-20-20 for non-legumes.

Plants were regularly examined for foliar injury associated with acid rain. Of the 35 crop varieties studied, the foliage of 31 was injured at pH 3.0, 28 at pH 3.5, and 5 at pH 4.0. However, foliar injury was not generally related to effects on yield. Injury can affect the marketability of crops without affecting the amount of yield. Damage to spinach, swiss chard, and tomatoes at pH 3.0 was severe enough to affect marketability adversely. Also, because root crops such as radish and beets frequently are marketed with leaves attached, the disfiguration could decrease their value.

Twenty-eight crops were grown to harvest. Yield production was inhibited for five (radish, beet, carrot, mustard green, broccoli), stimulated for six (tomato, green pepper, strawberry, alfalfa, orchard grass, timothy), and ambiguously affected for one (potato). There was no statistically significant effect on the remaining 15 crops.

Groups of crops differed in their responses to acid rain. For example, yield inhibition was limited to dicotyledons (i.e., excluding grains, grasses, and onions). Among dicotyledons, the quantity or quality of yield for root

crops (radish, beet, carrot) was most adversely affected, followed by leaf (mustard green, spinach, chard, lettuce, tobacco), cole (broccoli), and tuber (potato) crops. Legumes (alfalfa) and fruit crops (tomato, pepper, strawberry) were more frequently stimulated by acid rain. Grain crops (oats, wheat, barley) were least sensitive to acid rain, while some monocotyledonous forage crops (grasses) were more productive under acid rain conditions. (For a more detailed discussion of results, see 14.)

### Forest leaching effects

Before reaching the forest soil, precipitation percolates through the forest canopy and litter layer. Rain that falls through the canopies of deciduous trees and leaches through hardwood litter layers tends to have higher pH values, higher Ca and Mg concentrations, and a lower volume than incident rain. Any study of the effects of acid precipitation on forest soils must consider the differences in quality and quantity between the incident precipitation and the actual input to the soil, the litter leachate. Similarly, any study of biological processes in forest litter or soil must consider the chemical environment as determined by the litter leachate or soil solution.

Lee and Weber studied the effects of simulated sulfuric acid rain on nutrient cycling in two types of model hardwood forest ecosystems (15). As part of this study, simulated rainwater was regularly collected above and below the canopy, below the litter layer, and at two depths in the soil during a period of more than three years. While the chemistry of the rain that fell through the canopy was not very different from the chemistry of the incident rain, the litter leachate (the input to the inorganic soil) had consistently higher concentrations of calcium and magnesium, and higher pH, than the acid rain.

For the first six months, sulfate adsorption by the soil prevented any apparent differences in sulfate, calcium, or magnesium concentrations of soil solutions among plots receiving either acid or control treatments. Sulfate concentrations of solutions extracted from 20 cm below the soil surface on plots receiving the most acid rain (pH 3.0) then became increasingly higher than on the other plots until, after three years, they were approximately equal to sulfate concentrations in the rain. Soil solutions corresponding to the pH 3.5 and pH 4.0 treatments responded similarly with a lag time of one year and two years, respectively,

after exposure to simulated acidic precipitation was begun. Increased calcium and magnesium concentrations and lowered pH in 20-cm soil solution occurred simultaneously with increased sulfate concentrations. At a depth of one meter, no acid rain-related effects were evident even after 3.5 years of exposure to pH 3.0 sulfuric acid rain.

Comparisons of the data with the predictions of a computer simulation model developed by Reuss indicated that soil properties obtained under laboratory conditions can be used with established relationships to predict cation concentrations in soil solutions associated with increased anion concentrations from acid rain (22).

### Short-term program implications

Results from this series of short-term studies have extended our awareness of the potential scope of acid precipitation effects in this country. With respect to geological and hydrochemical sensitivity, attention in the past has been largely directed to the Northeast, where the problem was first perceived. Acid precipitation is now known to occur in all the states east of the Mississippi River. Our studies suggest that ecosystems susceptible to acidification are widespread and are found over the entire length of the Appalachian range. Sandy coastal regions constitute another locale that appears to be susceptible; a recent investigation in New Jersey supports this observation (23).

Theoretical considerations of soil buffering capacity, sulfate adsorption capacity, presence of easily weatherable minerals, and soil physical characteristics, such as depth and permeability, should be used in conjunction with climatic information and atmospheric deposition data to identify soils most likely to be sensitive to acid precipitation. Regions that do not receive agricultural amendments of lime and fertilizer should be scrutinized first; the effects of lime and fertilizer undoubtedly outweigh those of acid deposition. The impact of acidic inputs on the productivity of soils that are naturally acid is not adequately understood and deserves further study.

The forest leaching studies show that research on the effects of acid precipitation on forest soils must consider both the dry and wet components of acidic deposition and can only be conducted adequately in an ecosystem context, specifically considering:

- changes in precipitation chemistry caused by passage through canopy and litter layer

- effects of altered soil solution chemistry on uptake of chemicals by plants

- effects on soil biological processes such as decomposition, nitrogen fixation, nitrification, sulfur oxidation/reduction, etc.

- effects on weathering of minerals

- the role of sulfate adsorption by the soil in controlling the chemistry of the soil solution.

Research on perennial crops, forest productivity, and unmanaged ecosystems must extend over several years. Scientists in Scandinavia have initiated forest productivity studies that are planned to last decades. If the forest soil leaching study cited here had not spanned more than three years, significant long-term effects on mineral nutrient mobility would not have been observed. Many ecological processes occur over decades rather than in just one or two years. Thus, it is important to match the study period carefully to the process or system being investigated.

In lakes and streams bounded by poorly buffered soils, symptoms of acidification generally appear more rapidly than in those located in well-buffered areas. However, the interrelationships of bedrock, soils, and surface waters with respect to acidification and its effects still need to be elucidated.

The crop survey results indicate that annual plant productivity and yield can be directly altered by sulfuric acid precipitation. There is an urgent need to test perennial crops, orchard crops, and managed forest species. Because acid rain contains sulfuric and nitric acid, both must be incorporated into future test regimes.

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**Norman R. Glass (left)** is the director of the EPA's Terrestrial Research Division at the Corvallis Environmental Research Laboratory.

**Dean E. Arnold (right)** is a research fishery biologist with the U.S. Fish and Wildlife Service and leader of the Cooperative Fishery Research Unit at Pennsylvania State University.

**James N. Galloway (left)** is assistant professor of environmental sciences at the University of Virginia.

**George R. Hendrey (right)** is head of the Terrestrial and Aquatic Ecology Division at Brookhaven National Laboratory.

**Jeffrey J. Lee (left)** is a research environmental scientist at EPA's Environmental Research Laboratory, Corvallis.

**William W. McFee (right)** is professor of soils and director of the Natural Resources and Environmental Science Program at Purdue University.

**Stephen A. Norton (left)** is professor and chairman of the Department of Geological Sciences at the University of Maine at Orono.

**Charles F. Powers (right)** is a research biologist with the EPA Environmental Research Laboratory at Corvallis, Ore.

**Danny L. Rambo (left)** is a scientist with Northrop Services, Inc. and a technical information specialist for EPA's acid deposition research.

**Carl L. Schofield (right)** is a senior research associate with the Department of Natural Resources at Cornell University.

# Microbial removal of hazardous organic compounds

*Within certain broad limitations, many microorganisms not previously considered useful for biological waste treatment could be applied to the removal of anthropogenic substances*

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**Hester Kobayashi**  
Sohio Research Center  
Cleveland, Ohio 44128

**Bruce E. Rittmann**  
Department of Civil Engineering  
University of Illinois at  
Urbana-Champaign  
Urbana, Ill. 61801

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The presence of man-made (anthropogenic) organic compounds in the environment is a serious public health problem. Sixty-five classes of such chemical compounds are considered hazardous, and among them, 114 organic compounds have been designated by the U.S. Environmental Protection Agency (EPA) as priority pollutants (1). The presence of these compounds appears to be attributable largely to inadequate disposal techniques (2), which have caused contamination of water and soil. Accidental generation of such compounds during treatment processes, such as the generation of chloroform during chlorination (3), is another source of water pollution. Existing legislation to control and regulate the entry of hazardous chemicals into the environment includes the Safe Drinking Water Act (SDWA), the Clean Water Act (CWA), the Toxic Substance Control Act (TSCA), and the Resource Conservation and Recovery Act (RCRA). The public health danger of anthropogenic compounds and the enforcement of the pertinent laws and regulations require that considerable effort be placed upon reducing or eliminating environmental intrusion and persistence of hazardous organic compounds.

In numerous cases, biological treatment can eliminate hazardous compounds by biotransforming them into innocuous forms, degrading them

by mineralization to carbon dioxide and water, or anaerobically decomposing them to carbon dioxide and methane. Many compounds, however, are not removed efficiently by existing biological treatment techniques, either because they are metabolized very slowly, or because they are resistant to microbial attack under prevailing environmental conditions.

Under the support of the Advanced Environmental Control Technology Research Center at the University of Illinois and the U.S. EPA, we conducted an in-depth evaluation of the potential for microorganisms to remove anthropogenic organic compounds, mainly priority pollutants and related compounds. The evaluation indicates that use of properly selected populations of microbes, and the maintenance of environmental conditions most conducive to their metabolism, can be an important means of improving biological treatment of organic wastes. One major theme is that microorganisms not normally associated with biological waste treatment have potential advantages when the removal of anthropogenic compounds is the goal. A broadened perspective into what constitutes biological treatment opens promising new areas of research and application.

## Biodegradability

In contrast to naturally occurring compounds, man-made compounds are relatively refractory to biodegradation. One reason is that organisms that are naturally present often cannot produce the enzymes necessary to bring about transformation of the original compound to a point at which the resultant intermediates can enter into common metabolic pathways and be completely mineralized.

The required transformation steps

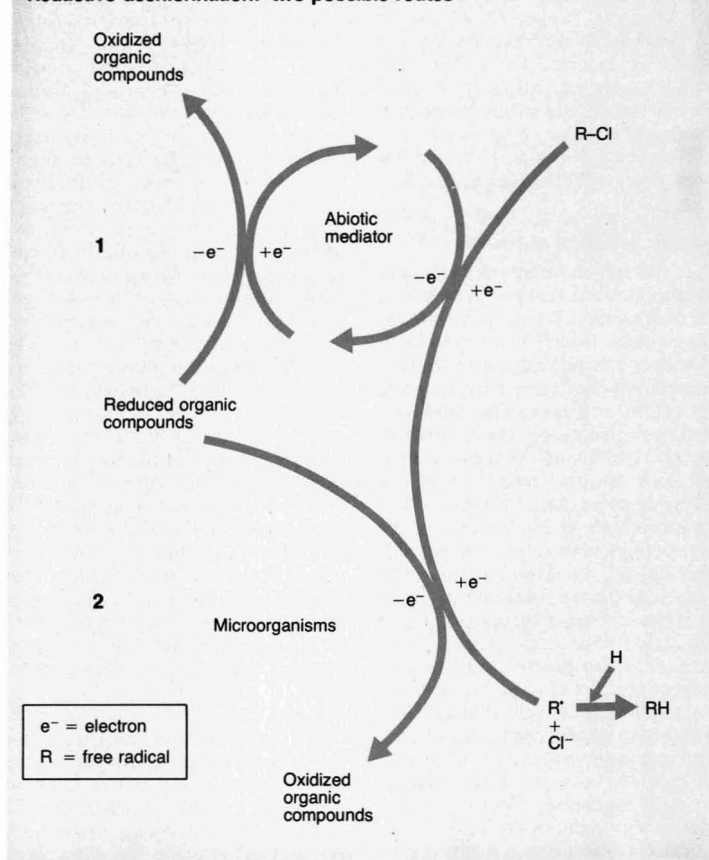
to initiate biodegradation are fairly well known, and can be found in general reviews by Dagley (4), Alexander (5), Evans (6), and Matsumura and Benezet (7). Attempts to generalize the relationships between chemical structure and biodegradability have led to lists of chemical substituents that, when attached to organic parent compounds, make the compounds persistent. These lists include amines, methoxy, sulfonates, and nitro groups; chlorine, substitutions in the meta position in benzene rings, ether linkages, and branched carbon chains (8). In addition, larger molecules are generally considered less degradable than smaller ones. However, so many exceptions to these generalizations exist that such rules should be considered only as broad guidelines.

Many environmentally important man-made compounds are halogenated, and halogenation is often implicated as a reason for persistence. The list of halogenated organics includes pesticides, plasticizers, plastics, solvents, and trihalomethanes. Chlorinated compounds are the best known and most studied because of the highly publicized problems associated with DDT, other pesticides, and numerous industrial solvents. Hence, chlorinated compounds serve as the basis for most of the information available on halogenated compounds.

Some of the characteristics that appear to confer persistence to halogenated compounds are the location of the halogen atom, the halide involved, and the extent of halogenation (8, 9). The first step in biodegradation, then, is sometimes dehalogenation, for which there are several biological mechanisms (10).

Again, simple generalizations do not appear to be applicable. For example, until recently, oxidative pathways were

FIGURE 1  
Reductive dechlorination: two possible routes



mostly believed to be the typical means by which halogenated compounds are dehalogenated. At present, anaerobic, reductive dehalogenation, either biological or nonbiological, is now recognized as the critical factor in the transformation or biodegradation of certain classes of compounds (11-15). Compounds that require reductive dechlorination are common among the pesticides, as well as halogenated one- and two-carbon aliphatic compounds. Chlorinated benzenes and PCBs, however, appear to be attacked only under aerobic conditions (16-18).

Reductive dehalogenation involves removal of a halogen atom by oxidation-reduction, as illustrated in Figure 1, which is a modification of the scheme presented by Isaac and Matsumura (11). In essence, the mechanism involves the transfer of electrons from reduced organic substances via microorganisms or a nonliving (abiotic) mediator, such as inorganic ions (for example,  $Fe^{3+}$ ), and biological products (for example, NAD(P), flavo-

vin, flavoproteins, hemoproteins, porphyrins, chlorophyll, cytochromes, and glutathione). The mediators are responsible for accepting electrons from reduced organic substances and transferring them to the halogenated compounds. The major requirements for the process are believed to be available free electrons and direct contact between the donor, mediator, and acceptor of electrons. Significant reductive dechlorination is reported to occur only when the oxidation-reduction potential ( $E_h$ ) of the environment is 0.35 V and lower (11); the exact requirements appear to depend upon the compound involved.

Evidence for abiotic mediators of environmental significance were shown by Matsumura (19), who used flavoproteins derived from blue-green algae, and Miskus (20), who found a relationship between plankton concentration and reductive dechlorination. The flavoproteins are produced in all living cells, and can become available as the cells die. It is proposed that

chlorinated pesticides sorb onto cells in the water column, and in the sediment with them. As the cells decay, the proximity of the free electrons from the decaying organic matter, the mediators, and the chlorinated compounds make conditions ideal for reductive dechlorination to occur.

Examples of biological reductive dehalogenation are well documented, especially for pesticides and halogenated aliphatics. A particularly interesting case is the reductive dechlorination that occurs in algae. In algae, the dechlorination process may be a nonenzymatic photochemical transformation, and may occur through absorbance of light energy by photosensitive compounds, which then transfer electrons to the insecticide molecule (7). Numerous cases of apparent photochemical transformation are reported in the literature (7, 21, 22).

The emphasis in studies of biodegradation of compounds arising from human activity has been largely on aerobic, oxidative processes because they are best known, and because aerobic techniques are relatively simple compared to anaerobic culture methods. Another reason for their widespread use is that aerobic processes previously have been considered the most efficient and generally applicable (4). However, aerobic treatment requires transfer of oxygen to the water, and can create copious amounts of sludge; both aspects often are energy-intensive and expensive. By comparison, anaerobic processes reduce or eliminate both of the major operating expenses of an aerobic system. Thus, anaerobic microbial processes are energy-efficient, and can enhance certain critical reactions, such as reductive dehalogenation, nitroreduction, and reduction of sulfoxides (11).

Although simple studies using pure cultures of microorganisms and single substrates are valuable, if not essential, for determining biochemical pathways, they cannot always be used in predicting biodegradability or transformation in more natural situations (5, 8, 16, 23, 24). The interactions among environmental factors, such as dissolved oxygen, oxidation-reduction potential, temperature, pH, availability of other compounds, salinity, particulate matter, competing organisms, and concentrations of compounds and organisms, often control the feasibility of biodegradation (16, 23, 25-28). The compound's physical or chemical characteristics, such as solubility, volatility, hydrophobicity, and

octanol-water partition coefficient, contribute to the compound's availability in solution (23, 28-32). Compounds not soluble in the water are not readily available to organisms for biodegradation.

Simple culture studies are similarly inadequate for predicting the fate of substances in the environment if there are many interactions between different organisms. First, substances that cannot be changed significantly in pure-culture studies often will be degraded or transformed under mixed culture conditions (16, 33-35). A good example of this type of interaction is cometabolism, in which a compound, the cometabolite, is not metabolized as a source of carbon or energy, but is incidentally transformed by organisms using other similar compounds. Second, products of the initial transformation by one organism may be subsequently broken down sequentially by a series of different organisms until compounds that can be metabolized by normal metabolic pathways are formed (5, 34, 36-38). An example is the degradation of DDT, which is reportedly mineralized directly by only one organism, a fungus; other organisms studied appear to cometabolize only the compound, resulting in numerous transformation products that subsequently can be used by other organisms. Pfaender and Alexander (39) illustrated the point by showing that *Hydrogenomonas* can metabolize DDT only as far as *p*-chlorophenylacetic acid (PCPA), while *Arthrobacter* sp. can then remove the PCPA.

One limitation encountered in biodegradation studies is that antagonistic interactions between organisms can inhibit biodegradation. Bacteria, for instance, are known to be the antagonist to fungi (26, 27). Another limitation is that they were performed with high concentrations of the organic substrate. In many instances involving contaminated water, hazardous compounds are already present at trace concentrations (for example,  $\mu\text{g/L}$ ), and effluent concentrations still lower may be desired.

Very low substrate concentrations pose two problems for biological treatment. The first problem is that the slow substrate utilization kinetics that occur with very low concentrations provide too little energy flux to sustain the microorganisms. Rittmann and McCarty (40-42) demonstrated that steady-state bacterial mass and substrate utilization declined to negligible quantities when the substrate concentration in a biofilm reactor ap-

proached a threshold value,  $S_{\text{min}}$ . Typical  $S_{\text{min}}$  concentrations for aerobic systems typically have been in the 0.1-1.0 mg/L range (42, 43), while the desired effluent concentrations are often 1  $\mu\text{g/L}$  or less. A second problem with trace concentrations is that they may be insufficient to induce the production of necessary enzymes. Tentative evidence for such behavior has been observed in three studies (25, 25a, 42a).

### Specific groups of organisms

In this section we consider groups of microorganisms that might be useful for treating specific types of man-made compounds. Table 1 lists examples of species or groups of organisms and the compounds they have been found to transform or attack. The conditions that prevailed during the observation or experiment (such as aerobic or anaerobic) are also noted in relative terms. In some cases, "aerobic" refers to incubation in air without added aeration; in such cases, it is possible that culture conditions varied from aerobic at the top of the culture vessel to microaerobic or even anaerobic at the bottom. The term "anaerobic culture" is also variable. It sometimes refers to culture in vessels filled to the top and simply capped; at other times it refers to anoxic conditions using a nitrogen atmosphere. In still other cases it refers to cultures grown under strictly ("fastidious") anaerobic conditions with reduced media.

Table 1 demonstrates that members of almost every class of man-made compound can be degraded by some microorganism. The table also illustrates the wide variety of microorganisms that participate in environmentally significant biodegradation reactions.

Table 2 is a list of characteristics that might be used for the selective culture of specific types of organisms. In other words, Table 2 indicates how the conditions can be made most favorable for the development of a desired type of microorganism.

**Actinomycetes.** Actinomycetes, a group of organisms morphologically similar to bacteria and fungi, are found in environments in which unusual compounds are encountered. They are known to attack a wide variety of complex organic compounds, including phenols, pyridines, glycerides, steroids, chlorinated and nonchlorinated aromatic compounds, paraffins, other long-chain carbon compounds, and even lignocellulose, which very few organisms can attack. The most commonly found actinomycete in aquatic

systems is *Nocardia*. *N. aramae* organisms occasionally are found proliferating in activated-sludge units where they appear to feed on lipids at the surface (44, 45). They are also found to grow under low nutrient conditions (oligotrophically), such as in distilled water (44-46). These organisms provide several advantages that make them attractive for use in wastewater treatment: sludge production lower than bacteria and fungi; wide temperature range, from psychrophilic to thermophilic; resistance to desiccation; and wide pH range.

Organic decomposition brought about by actinomycetes generally results in various metabolites that can be mineralized in the presence of other organisms. Thus, mixed-culture systems are a necessity when actinomycetes are used. The number of nitrogenous compounds actinomycetes can use is limited, and because their cell synthesis is low, most of the nitrogen in the substrate is liberated as ammonia. Also, low cell synthesis makes their population size generally small under natural conditions. Actinomycetes might be especially useful in treatment of contaminated soil where a composting technique would be practical.

**Fungi.** Selective cultures of some forms of filamentous fungi are of potential value in certain cases, since the fungi appear to have greater ability to degrade or transform hydrocarbons of complex structure or long chain length. Bacteria and yeasts, on the other hand, show decreasing abilities to degrade alkanes with increasing chain length (24). Organisms in two orders of fungi—Mucorales (such as *Cunninghamella*) and Moniliales (*Fusarium*, *Aspergillus*, *Penicillium*)—show the best potential (23). An example of this ability is the complete degradation of DDT by *Fusarium oxysporum*, a feat never observed with other microorganisms (see Table 1). Because they have nonspecific enzyme systems for aromatic structures, fungi (yeasts and filamentous) are believed to be capable of biodegrading PCBs better than bacteria can (23). However, fungal metabolism, in general, often results in incomplete metabolism. Hence, subsequent bacterial association for complete mineralization is necessary.

**Bacteria.** Examples of bacteria that have been reported to attack different kinds of artificial compounds are listed in Table 1. In many studies, species were not defined, but were given only by the source of the original inoculum, such as sewage or soil. The most com-

**TABLE 1**  
**Examples of anthropogenic compounds and microorganisms that can attack them**

Compound	Organism(s)	Condition	Remarks/products	Refs.
<b>Aliphatics (nonhalogenated)</b>				
Acrylonitrile	Mixed culture of yeast mold, protozoa bacteria; activated sludge	ae		33,77-79
<b>Aliphatics (halogenated)</b>				
Trichloroethane	Marine bacteria	ae		16
Trichloromethane	Sewage sludge	ae		80
Trichloroethane, trichloromethane, methyl chloride, chloroethane, dichloroethane, vinylidene chloride, trichloroethylene, tetrachloroethylene, methylene chloride, dibromochloromethane, bromochloromethane	Soil bacteria	an	Anoxic conditions	81
Trichloromethanes, trichloroethylene, tetrachloroethylene	Methanogenic (7) culture	an (8)		18
Trichloroethane, trichloromethane, tetrachloromethane, dichloroethane, dibromochloromethane, 1,1,2,2-tetrachloroethane, bis-(2-chloroisopropyl) ether, bromoform, bromodichloromethane, trichlorofluoromethane, 1,1-dichloroethylene, 1,2-dichloroethylene, 1,3-dichloropropylene, 1,2-trans-dichloroethylene	Sewage sludge	ae (?)		80
<b>Aromatic compounds (nonhalogenated)</b>				
Benzene	<i>Pseudomonas putida</i> (1)	ae		23
	Sewage sludge	ae		80
	Stabilization pond microbes	ae (?)		82
Toluene	<i>Bacillus sp.</i> (1)	an		83
	<i>P. putida</i>	ae		23
Nitrobenzene	Stabilization pond microbes	ae (?)		82
2,4-Dinitrotoluene	Stabilization pond microbes	ae (?)		82
	Activated sludge	ae		78, 79
2,6-Dinitrotoluene, di-n-butylphthalate, diphenylhydrazine	Sewage sludge	ae		80
Creosol	<i>Pseudomonas sp.</i> (1)			84
	<i>Aureobasidium pullulans</i> (4)	ae	Used as carbon and energy source	23
Phenol	<i>Pseudomonas</i> , <i>Vibrio</i> , <i>Spirillum</i> ; <i>ae</i>			85-87
	<i>Flavobacterium Chromobacter</i> , <i>Bacillus</i> , <i>Nocardia</i> (5)			
	<i>Chlamydomonas ulvaensis</i> (2) <i>ae</i>		Light also required	88
	<i>Phoridium fuveolarum</i> , <i>Scenedesmus basiliensis</i> (2) <i>ae</i>		Light also required	89
<i>Euglena gracilis</i> (2) <i>ae</i>				
	<i>Corynebacterium sp.</i> (1) <i>ae</i>			
<i>p</i> -Nitrophenol	Rumen microorganisms	an	<i>p</i> -Aminophenol by nitroreduction	11, 90
<b>Aromatic compounds (halogenated)</b>				
1,2-, 2,3-, 1,4-Dichlorobenzene; <i>p</i> -, <i>m</i> -, <i>o</i> -chlorobenzoate; 3,4-, 3,5-dichlorobenzoate, 3-methyl benzoate; 4-chlorophenol	Sewage sludge	ae		80
	<i>Pseudomonas sp.</i> (1), sewage	ae	Plasmid transfer led to ability to attack a number of these compounds simultaneously; sole energy and carbon source	91
	<i>Pseudomonas sp.</i> B13 (WR1)	ae		91, 92
Hexachlorobenzene, trichlorobenzene	Sewage sludge	ae		80
	Soil microbes	ae	2,6-, 2,3-Dichlorobenzene; 2,4- and 2,5-dichlorobenzene; CO <sub>2</sub> ; slow	94
1,2,3- and 1,2,4-Trichlorobenzene				
Pentachlorophenol	Soil microbes	an	tetra-, tri-, di-, and <i>m</i> -Chlorophenol (8)	11, 95
Monochlorophenol, monochlorobenzoate	<i>Nocardia</i> , <i>Mycobacterium</i> (5)	ae	Cometabolism	64

(continued)

TABLE 1 (continued)

Compound	Organism(s)	Condition	Remarks/products	Refs.
<b>Polycyclic aromatics (nonhalogenated)</b>				
Benzo(a)pyrene	<i>Cunninghamella elegans</i> (4)	ae	<i>trans</i> -7,8-Dihydroxy-7,8-dihydrobenzo(a)pyrene	24, 75, 96
	<i>Pseudomonas</i> sp. (1)	ae		16
	<i>Beijerinckia</i> sp. (1)	ae		23
Naphthalene	<i>Agmenellum</i> , <i>Oscillatoria</i> (3)	ae	1-Naphthol; <i>cis</i> -1,2-dihydroxyl-1,2-dihydronaphthalene; 4-hydroxy-1-tetralene	24
	<i>Anabaena</i> (3)			21, 97, 98
	<i>Cunninghamella elegans</i> (4)	ae	$\alpha$ -Naphthol, $\beta$ -naphthol, <i>trans</i> -1,2-dihydroxy-1,2-dihydronaphthalene; 4-hydroxy-1-tetralene; 1,4-naphthoquinone	23
	<i>Microcoleus</i> sp. (2), <i>Nostoc</i> sp., <i>Coccochloris</i> sp., <i>Aphanocapsa</i> sp., <i>Chlorella</i> sp., <i>Dunaliella</i> sp., <i>Chlamydomonas</i> sp., <i>Cylindrotheca</i> sp., <i>Amphora</i> sp. (2)	ae	light required; ability to breakdown this compound is common among algae	21
	<i>Pseudomonas</i> , <i>Flavobacterium</i> , <i>Alcaligenes</i> , <i>Corynebacterium</i> , <i>Aeromonas</i> , <i>Flavobacterium</i> (1), <i>Nocardia</i> (5)	ae		16
	Stream bacteria	ae	Stream at coal coking site	99
Pyrene	Stabilization pond organisms	ae (?)	Under static conditions	82
Fluoranthene	Sewage sludge	ae		80
Anthracene	Stream bacteria	ae	Stream at coal coking site	99
Phenanthrene	<i>Beijerinckia</i> (1)	ae	<i>cis</i> -3,4-Dihydroxy-3,4-dihydrophenanthracene	
Benzo(a)anthracene (BA)	<i>Cunninghamella elegans</i>	ae	3,4-; 8,9-; 10,11-Dihydro	100
Dibenzanthracene	Activated sludge	ae	Very slow, insignificant breakdown	16
Biphenyl	<i>Beijerinckia</i> B8/36	ae	<i>cis</i> -2,3-Dihydro-2,3-dihydroxybiphenyl	23
	<i>Oscillatoria</i> sp. (3)	ae	4-Hydroxybiphenyl	101
	<i>Pseudomonas putida</i> (1)	ae	Benzoic acid	102
<b>Polycyclic aromatic hydrocarbons (halogenated)</b>				
PCBs (mono- and dichlorobiphenyls)	<i>Pseudomonas</i> , <i>Vibrio</i> , <i>Spirillum</i> , <i>Flavobacterium</i>	ae	Biodegradation appears to be inversely related to extent of chlorination	16, 93, 103
	<i>Achromobacter</i>		High level dehalogenase, major end product CO <sub>2</sub>	
	<i>Chromobacter</i> , <i>Bacillus</i> (1), <i>Nocardia</i> (5)			
4-Chlorobiphenyl; 4,4-dichlorobiphenyl; 3,3'-dichlorobiphenyl	Fungi	ae	4-Chloro-4'-hydroxybiphenyl; 4,4'-dichloro-3-hydroxybiphenyl; chlorinated benzoic acid	23
<b>Pesticides</b>				
Toxaphene	<i>Corynebacterium pyrogenes</i> (1)	an		31
Heptachlorobornane	<i>Micromonospora chalybeata</i> (5)	ae		11
	Bovine rumen fluid (7)	an	Hexachlorobornane (8)	11
Lindane	<i>Chlorella vulgaris</i> (2)	ae (?)		
	<i>Chlamydomonas reinhardtii</i>	ae	Pentachlorocyclohexane (non-toxic) (8)	11, 15
	<i>Chlosteridium</i> sp., <i>Pseudomonas</i> (1)			
	Soil bacteria	an	$\gamma$ -3,4,5,6-Tetrachloro-1-cyclohexane, $\alpha$ -BHC (7)(8)	11, 15
	Sewage sludge	an		13
Dieldrin	<i>Anacystis nidulans</i> (3)	an	Photodieldrin	104
	<i>Agmeneloum quardiplicatum</i> (3)	an	Toxic epoxide moiety reduced to olefin	11
	<i>Pseudomonas</i> (1)			
	Rumen fluid (7)	an		11
	Actinomycetes	an/ae	Chlordene (8) chlordene epoxide (oxidation)	11



Compound	Organism(s)	Condition	Remarks/products	Refs.
DDT (1,1'-bis(p-chlorophenyl)-2,2,2-trichloroethane)	<i>Klebsiella pneumoniae</i> (1) <i>E. coli</i> , an <i>Aerobacter aerogenes</i> , <i>Pseudomonas</i> , <i>Clostridium</i> , <i>Proteus vulgaris</i>		More than 20 species of bacteria are reported to be able to reductively dechlorinate DDT. Aerobic conditions are sometimes reported but apparently do not promote much dechlorination. Anaerobically DDT goes mainly to DDD (TDE) while aerobically it appears to be transformed to DDE.	11, 15, 105, 106
	Sewage	ae	TDE & DBP major products	39
	Soil bacteria	an	7 possible metabolites, simplest reported was p-chlorobenzoate	12
	Rumen bacteria (7)	an	DDE, TDE, DDMU (8)	11
	Yeast	ae	TDE (8)	107
	<i>Trichoderma viridae</i> (4)	an	TDE, DDE (8)	15, 106
	<i>Fusarium oxysporum</i> (4)	ae	Complete mineralization; no DDT in 10-14 days	106
	<i>Mucor alterans</i> (4)	ae	Cometabolism	106
	<i>Cylindrotheca</i> , <i>Closterium</i> (2)	ae	DDE (slow) (9)	106
	<i>Dunaliella</i> (2)	ae	TDE, DDE, DDMS, DDOH (8)(9)	108
	Anaerobic sludge (7)	an	TDE rapid	13
	<i>Nocardia</i> , <i>Streptomyces</i> (5)	ae	DDE (9)	11
	<i>Hydrogenomonas</i> (1)	an/ae	10 Products, simplest was PCPA; 9 products, simplest was DBP	39
	Parathion	<i>Bacillus subtilis</i> , <i>Rhizobium</i> , <i>Chlorella pyrenoidosa</i> , soil bacteria	an	Nitroreduction to amino-parathion
Phorate sulfoxide	Soil bacteria	an	Sulfoxide reduction	11
Pentachloronitrobenzene (PCNB)	<i>Aspergillus niger</i> , <i>Fusarium solani</i> , <i>Glomerella congulata</i> , <i>Helminthosporium victoriae</i> , <i>Myrothecium</i> , <i>Penicillium</i> , <i>Trichoderma viridae</i> (4)	ae	Only during active growth	15
Methoxychlor	<i>Nocardia sp.</i> , <i>Streptomyces sp.</i> (5)	ae		15
	<i>Aerobacter aerogenes</i> (1)	ae/an	1,1-Dichloro-2,2-bis(p-methoxyphenyl)ethylene; 1,1-dichloro-2,2-bis(p-methoxyphenyl)-ethane	31
Acrolein	Site water (microbes)	ae	$\beta$ -Hydroxypropionaldehyde	105, 109
Aldrin	Site water (microbes)	ae	Dieldrin by epoxidation	105
	Sewage sludge	an	(8)	13
Endosulfan	Fungi, bacteria, soil actinomycetes	ae	Endosulfen (2), endodiol (1), endohydroether (5)	105, 110
Endrin	<i>Pseudomonas sp.</i> , <i>Micrococcus sp.</i> , yeast (4)	ae	Soil organisms, aldehydes and ketones with 5 to 6 chlorine atoms (1)	111
	Sewage sludge	an	(8)	13
Chlordimeform	<i>Chlorella</i> (2), <i>Oscillatoria</i> (3)	ae	4-Chloro- $\alpha$ -formotoluidiene, 4-chloro- $\alpha$ -toluidiene, 5-chloroanthranilic acid, n-formyl-5-chloroanthranilic acid, suspected mutagens	22
Kepone	Treatment lagoon sludge	an	(8), Cometabolism	112
Diuron	Mixed culture of fungi and bacteria; mineralization; single isolates ineffective	ae/an		34
<b>Nitrosamines</b>				
Dimethylnitrosamine	Rumen organisms (7)	an		60
	<i>Rhodopseudomonas capsulata</i> (6) an		Nontumorigenic product	57, 58
<b>Phthalate esters</b>				
DDT—(only p,p'-DDT considered here)	<i>Micrococcus</i> 12B	ae		113, 114
	Sediment-water	an	Nitrate respiration (anoxic)	83, 115
DDE (TDE)—1'-bis(p-chlorophenyl)-2,2-dichloroethane	(1) Bacteria		ae—aerobic (may be ae/an)	
DDE—1,1'-bis(p-chlorophenyl)-2,2-dichloroethylene	(2) Algae		an—anaerobic (either anoxic or fastidious)	
DBP—4,4'-dichlorobenzophenone	(3) Blue-green algae			
DDMS—1,1'-bis(p-chlorophenyl)2-chloroethane	(4) Fungi			
PCPA—p-chlorophenyl acetic acid	(5) Actinomycetes			
DDMA—1,1'-bis(p-chlorophenyl)-2-chloroethylene	(6) Photosynthetic bacteria			
DDOH—1,1'-bis(p-chlorophenyl)-2-hydroxyethane	(7) Consortium of anaerobics			
BHC—1,2,3,4,5,6-hexachlorocyclohexane	(8) Reductive dechlorination			
	(9) Dehydrochlorination			

TABLE 2

## Selective use of microorganisms for removal of different anthropogenic compounds

Microorganism	Selective characteristics <sup>a</sup>	Significance	Refs.
<b>Fungi</b>			
Yeast	pH < 5, ae-mae; high O <sub>2</sub> tension, pH < 5 moisture about 50%	Attacks and partially degrades complex compounds not readily metabolized by other organisms. Wide range of nonspecific enzymes	8, 23, 24, 46, 75, 84, 90, 96, 102, 116-131
Mold			
Algae	ae-mae; light: 600-700 nm; low carbon flux	Self-sustaining population, light is primary energy source, partially degrades certain complex compounds, photochemical reactions, oxygenates effluent, supports growth of other microbes, no aeration needed; effective in bioaccumulation of hydrophobic substances	11, 19, 20, 88, 98, 132
Cyanobacteria (formerly called blue- green algae)	ae-mae, an; light: 600-700 nm; low carbon flux	See algae	11, 19, 21, 30, 97, 98, 100, 104, 132
<b>Bacteria</b>			
Heterotrophs (aerobic)	ae; proper organic substrate, growth factors as required; Eh: 0.45 to 0.2 V	For many compounds degradation is more complete and faster than under anaerobic conditions. High sludge production	56, 133
Anaerobic (fastidious)	an; Eh: < -0.2 to -0.4 V	Conditions for abiotic or biological reductive dechlorination, certain detoxification reactions not possible under aerobic conditions; no aeration, little sludge produced	6, 11, 13, 14, 60, 134, 135
Facultative anaerobes	mae-an; Eh: < -0.2 V	No aeration necessary, reductive dechlorination possible	8, 11, 15, 56
<b>Photosynthetic bacteria</b>			
Purple sulfur	an (light), mae (dark); Eh: 0 to -0.2 V; S <sup>2-</sup> : 2 to 8 mM, 0.4-1 mM; light: 800-890 nm at 1000-2000 lux, high intensities near limit; low C flux	Self-sustaining population able to use light energy, conditions right for reductive dechlorination, no aeration	8, 51, 56, 136
Purple nonsulfur	an; Eh: 0 to -0.2 V; light: 800- 890 nm; low carbon flux	See purple sulfur bacteria, also nonspecific enzymes	6, 8, 51, 52, 54-58, 66, 136-143
Actinomycetes	ae, moisture: 80-87%, temp.: 23-28 °C, urea as nitrogen source	Universal scavengers with range of complex organic substrates often not used by other microbes	64, 87, 144, 145
Oligotrophs (may be from almost any group above)	ae; carbon flux of <1 mg/L/d; favorable attachment sites	Removal of organic contaminants in trace concentrations, many inducible enzymes for multiple substrates	61, 63, 146

ae = aerobic; mae = microaerophilic (<0.2 atm oxygen); an = anaerobic

<sup>a</sup> Possible characteristics for selection, not growth range.

<sup>b</sup> Specific examples in Table 1.

monly isolated organisms in areas of hydrocarbon contamination are heterotrophic bacteria represented by the genera *Pseudomonas*, *Achromobacter*, *Arthrobacter*, *Micrococcus*, *Vibrio*, *Acinetobacter*, *Brevibacterium*, *Corynebacterium*, and *Flavobacterium* (24). *Corynebacteria* found in aquatic environments in which unusual substrates are encountered are believed to be major agents for breaking down heterocyclic compounds and hydrocarbons. *Pseudomonas* appears to be the most ubiquitous, and able to adapt to many different man-made compounds. *Pseudomonas* seems to be readily adaptable to a combination of different forms of chlorobenzenes through what could be plasmid transfer of genetic material (Table 1).

**Phototrophic microorganisms.** The photosynthetic microorganisms of interest are the algae, cyanobacteria (formerly blue-green algae), and photosynthetic bacteria. These organisms are of potential importance in situations involving low concentration of nutrients, because they are able to obtain energy from sunlight and carbon by CO<sub>2</sub> fixation. Low substrate concentration is not a problem to these organisms. In addition, some of the cyanobacteria and photosynthetic bacteria are able to fix N<sub>2</sub>; hence, they can survive in situations in which the dissolved nitrogen concentration is inadequate to support bacterial growth.

In general, phototrophs do not promote complete degradation, but only

transformation. Hence, interactions with other organisms are important. The prolific growth of phototrophs will, however, promote growth of heterotrophic organisms because of metabolic products they form. If properly balanced by growth with bacteria, algae can bring about extensive biodegradation of compounds originating from human activity.

Table 1 illustrates that many algae and cyanobacteria are capable of transforming biodegradable anthropogenic compounds. They can transform certain compounds to the same extent as bacteria do. An example is the transformation of naphthalene by *Oscillatoria*.

*Dunaliella* is also of great interest, because it can transform DDT further

TABLE 3

## Bioaccumulation of anthropogenic compounds by different microorganisms

Microorganism	Compound	Refs.
<b>Fungi</b>		
<i>Aphanomyces euteiches</i> , <i>Fusarium solani</i> , <i>Pythium ultimum</i> , <i>Rhizoctonia solani</i>	DDT, dieldrin, PCNB (pentachloronitrobenzene)	30, 107, 147, 148
<i>Aspergillus</i> sp.	Toxaphene, methoxychlor, DDT	
<b>Actinomycetes</b>		
<i>Streptomyces albus</i> , <i>S. aurefaciens</i> , <i>S. griseus</i> , <i>S. viridochromogenes</i>	Dieldrin	149
<b>Bacteria</b>		
<i>Bacillus subtilis</i> , <i>Serratia marcesans</i> , <i>Agrobacterium tumefaciens</i>	DDT, dieldrin, methoxychlor	149, 150
<i>Aerobacter aerogenes</i>	DDT	150
<i>Flavobacterium harrisoni</i>	Toxaphene, methoxychlor	148
<b>Cyanobacteria (blue-green algae)</b>		
<i>Microcystis aeruginosa</i>	Benzene, toluene, chlorobenzene, 1,2-dichlorobenzene, nitrobenzene, naphthalene, 2,6-dinitrotoluene, phenanthrene, di- <i>N</i> -butylphthalate, pyrene	29
<i>Anacystis nidulans</i>	Malathion, carbaryl, parathion, DDT, aldrin, dieldrin	15, 30, 132
<i>Anabaena cylindrica</i>	Aldrin, dieldrin	30
<i>Nostoc muscorum</i>	Dieldrin	30
<b>Algae</b>		
<i>Chlorella</i>	Toxaphene, methoxychlor	30, 132, 148
<i>Chlorococcum</i> sp. <sup>a</sup> , <i>Dunaliella teriolecta</i> <sup>a</sup> , <i>Chlamydomonas</i> sp. <sup>c</sup> , <i>Thalassiosira</i> <i>pseudonana</i> <sup>b</sup> , <i>Porphyridium cruentum</i> <sup>d</sup>	Mirex	151
<i>Nitzschia</i> <sup>b</sup>	Mirex, methoxychlor, 2,4-DBE	132, 151
<i>Monoraphidium</i> <sup>b</sup>	Methoxychlor	132
<i>Euglena gracilis</i> <sup>c</sup> , <i>Scenedesmus obliquus</i> <sup>a</sup>	Parathion, DDT	15
<i>Cylindrothea closterium</i> <sup>b</sup>	DDT	15
<i>Selenastrum capricornatum</i> <sup>a</sup>	Benzene, toluene, chlorobenzene, 1,2-dichlorobenzene, nitrobenzene, naphthalene, 2,6-dinitrotoluene, phenanthrene, di- <i>n</i> -butylphthalate, pyrene	29

<sup>a</sup> Green alga.<sup>b</sup> Diatom.<sup>c</sup> Flagellate alga.<sup>d</sup> Rhodophyte.

than many bacteria can. Of particular significance is the fact that dechlorination to trichlorodiphenyl dichloroethene (TDE) occurs under what appear to be aerobic conditions. This observation suggests that photochemical reactions may be involved. Participation of photosystems in algae degradation of organics has also been suggested by the work of Cerniglia (21).

In addition to their potential use for breaking down organic compounds, phototrophic organisms are potentially valuable because of their ability to bioaccumulate hydrophobic compounds (Table 3). Although bioaccumulation is a characteristic shared by many different microorganisms, bioaccumulation by phototrophs offers the greatest potential for exploitation in treatment processes, because phototrophs can self-sustain relatively large populations without the presence of organic matter in concentrations

high enough to serve as carbon and electron donors. In addition, some of the algae (especially *Chlorella* and certain diatoms) can be manipulated physiologically to develop large lipid stores (47-49) into which hydrophobic compounds may be sequestered.

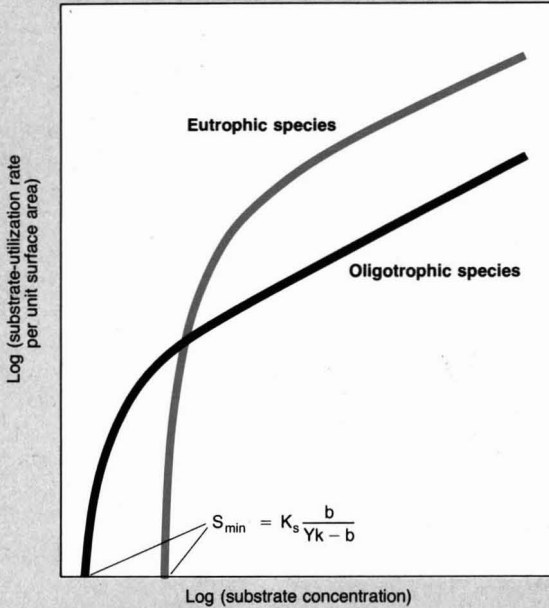
Cyanobacteria in general, and *Chlorella* among the green algae, are tolerant of pollution and low concentrations of dissolved oxygen. *Dunaliella*, which tolerate a wide salinity range, therefore are usable under conditions of variable salinity. Some of these organisms (particularly among the cyanobacteria) appear to be relatively simpler to manipulate genetically than bacteria (50).

Photosynthetic bacteria of particular interest are the purple sulfur (*Chromatiaceae*) and the purple nonsulfur (*Rhodospirillaceae*) bacteria (51). Knowledge of the metabolic capacity of these organisms is still not well established with respect to man-

made compounds; however, photosynthetic bacteria are known to be able to metabolize a wide variety of substances (46, 52). Examples are simple sugars, alcohols, volatile fatty acids, tricarboxylic acid (TCA) cycle intermediates, benzoates, and 1,3,5-trihydroxybenzene. They are also known to have a wide range of inducible enzymes, and are already used in wastewater treatment processes that treat a variety of organic compounds (53-55).

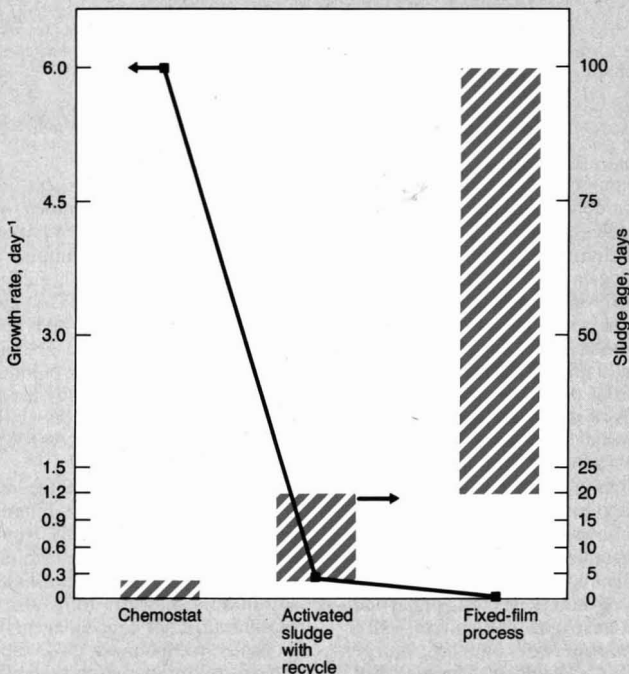
The *Chromatiaceae* are the most pollution-tolerant, and are found in waste treatment lagoons (56). Among the purple nonsulfur bacteria, at least one species, *Rhodospseudomonas capsulata*, is known to transform nitrosamines (tumor-causing agents) to innocuous compounds (57). Some purple nonsulfur organisms are able to grow microaerobically and anaerobically as phototrophs, but live as heterotrophs aerobically in the dark (56,

FIGURE 2  
Substrate utilization



The substrate utilization rate per surface area declines rapidly to zero as the substrate concentration approaches  $S_{\min}$ , which is defined by the kinetic parameters. An oligotrophic species has a large advantage at low substrate concentrations [after Rittmann and McCarty (41, 42)].

FIGURE 3  
Typical net cell growth and sludge ages<sup>a</sup>



<sup>a</sup>Net cell growth and sludge ages (cross-hatched bar graphs) for aerobic chemostat, activated-sludge, and biofilm-type processes show how cell retention by attachment allows the maintenance of the slowest growing organisms.

58). Photoheterotrophy (heterotrophic metabolism in the presence of light) is also a common mechanism. Because these organisms can grow anaerobically and require light, they are very simple to grow selectively, though they normally occur in small numbers in conventional waste treatment systems (56).

**Anaerobic bacteria.** Anaerobic decomposition of organic matter to carbon dioxide and methane involves interactions within consortia of fastidiously anaerobic bacteria. Although little is yet known about the exact species composition, especially in aquatic environments, and the multitude of interactions that occur, evidence suggests that at least four interacting trophic groups of bacteria are involved:

- hydrolytic bacteria that catabolize the major components of biomass, such as saccharides, proteins, and lipids
- H<sub>2</sub>-producing, acetogenic bacteria that catabolize products from the activity of the first group, such as fatty acids and neutral end products
- homoacetogenic bacteria that catabolize multicarbon compounds to acetic acid
- methanogenic bacteria (59).

The anaerobes require not only anoxic (oxygen-free) conditions, but also oxidation-reduction potentials of less than -0.2 V. We will refer to the entire association as "methanogenic consortia."

Methanogenic consortia can be obtained from anaerobic sediments, digesting sewage sludge, and rumen samples (from stomachs of ruminating animals, such as cattle). The specific collection site would depend upon the type of compounds to be treated and previous exposure to the compounds. The importance of using fastidious anaerobic consortia of organisms is illustrated by the types of detoxification reactions known to occur in the animal rumen, the best known of all anaerobic systems (60). These reactions include reductive dechlorination (or dehalogenation), possibly a limiting factor in degradation of certain compounds; nitrosamine degradation, a removal mechanism for a suspected carcinogen; reduction of epoxide groups in various compounds to olefins (60); reduction of nitro groups, as found in nitrophenol; and breakdown of aromatic structures.

In addition to the fastidious anaerobes, the organisms capable of living under anoxic, but not necessarily reduced, environmental conditions, as well as those capable of living facul-

tatively (aerobic/anaerobic) are also very important. These organisms, which occur in abundance in soil and sewage, are also found at sites where reductive dechlorination occurs.

**Oligotrophic bacteria (61-63).** Oligotrophic bacteria have been defined as organisms that can live under conditions of very low carbon flux (<1 mg/L/d) (63). These organisms do not comprise a special taxonomic grouping of organisms, but come from almost any group of bacteria or other chemotrophs. They are generally adapted to life under low nutrient conditions, but can readily be re-adapted to high nutrient conditions. Reverse adaptation to the low nutrient environment is, however, not readily achieved; therefore, oligotrophs are obtained only from low-nutrient environments.

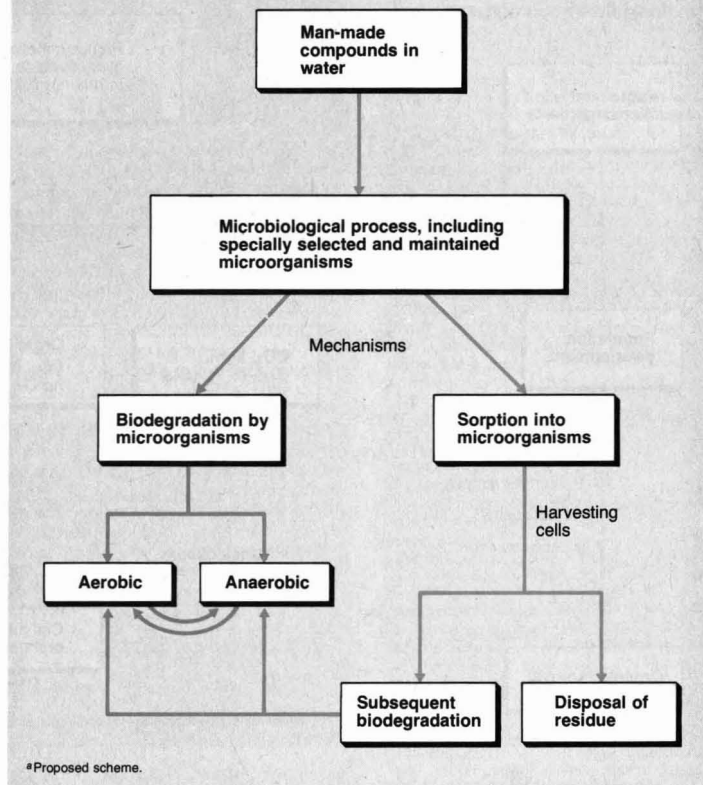
Oligotrophs generally have a high surface/volume ratio and high affinity for substrate. The minimum substrate concentration ( $S_{min}$ ) needed for measurable growth is lower than that required for eutrophic (high nutrient) organisms (Figure 2), but the maximum growth rate is also lower. Oligotrophic bacteria appear to prefer an attachment to a free-living existence, and are usually found living as biofilms. An important characteristic of these organisms is that they often appear to have multiple inducible enzymes, can shift metabolic pathways, and can often take up and use mixed substrates. A good example is a species of *Clostridium*, which was found to use 20 substrates.

Although oligotrophs are rather little known and relatively unstudied, they are potentially useful in the removal of trace concentrations of organic contaminants from water, or effluent from wastewater treatment processes. Normally, bacteria cannot grow and live under low-nutrient conditions because minimum maintenance conditions may not be met by the available nutrients. By contrast, oligotrophs among the *Actinomycetes* (*Nocardia*), *Coryneforms*, and *Mycobacteria* are especially interesting because they apparently are capable of the necessary control of their metabolism to survive for as long as 30 days under starvation conditions (64).

#### Selective use of microorganisms

Some of the major issues that must be faced in an attempt to improve biological treatment by use of selective types of organisms are population selection, development, and retention. The relative refractoriness of compounds must also be considered.

FIGURE 4  
Biochemical removal of man-made organic compounds from water<sup>a</sup>



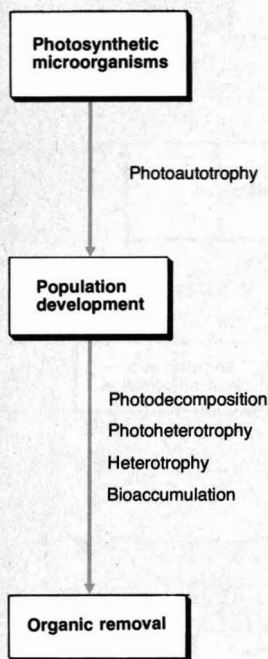
Although population selection can be based upon the use of various techniques of genetic engineering to develop the most desirable types of organisms, a practical method for assuring proliferation and maintenance of selected populations involves controlling environmental factors to encourage only the desired species. Table 2 indicates that pH, amount, and quality of illumination, nutrient availability, oxidation-reduction potential, and moisture content are key control parameters. The choice of factors that must be manipulated varies with the physiological needs of the organisms involved. The goals are to determine which organism carries out the limiting reaction, and to assure its proliferation. Consideration must also be given to the needs of the interacting organisms that may be involved. In some cases a series of biological reactors—each maintained under different environmental conditions—is required to provide the wide variety of microorganisms necessary for complete biodegradation.

Use of controlled environmental conditions to select for specific or-

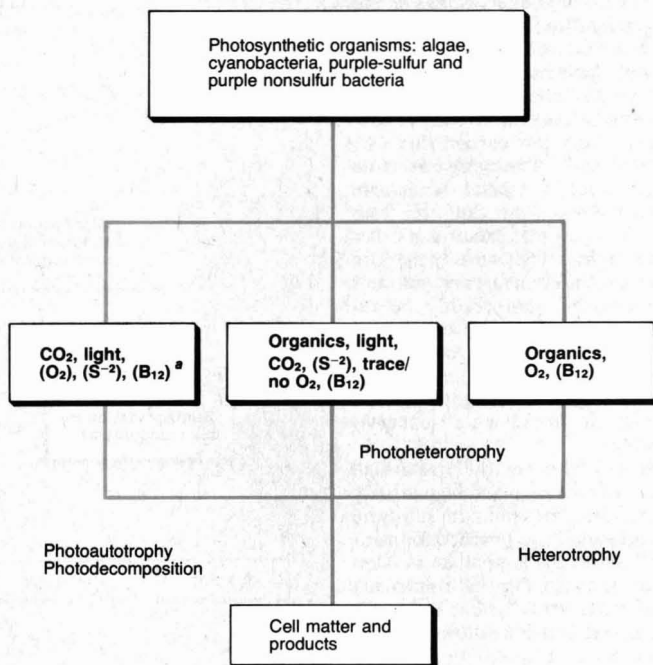
ganisms is not a new technique. It is, in fact, common practice in certain applications. The relatively standard wastewater treatment scheme for biological removal of nitrogen through sequential nitrification and denitrification is an example of such application in current practice (65). Controlled mixed cultures are already in limited use in Japan for treating selected industrial wastes with reactors comprising heterotrophic bacteria, photosynthetic bacteria, and algae (54-56). Selective culture treatment systems using purple nonsulfur bacteria to remove organic compounds (66) and green sulfur bacteria to remove hydrogen sulfide (67) from anaerobic digester effluents have also been described. The main concept needed for the biological removal of man-made organic compounds is that the types of microorganisms that can be useful, and their selective conditions, are diverse, extending beyond current practice.

Population retention is an important consideration, because the organisms may grow slowly, resulting in washout (total loss of the organism from the

**FIGURE 5**  
Removal of organic contaminants with photosynthetic microorganisms



**FIGURE 6**  
Mechanisms for photosynthetic organism growth



a ( ) indicates that the substance may or may not be required.

reactor), or takeover by other organisms. Fixed-film processes may be the best mechanism to assure population retention.

Evidence is widely available, showing that in fixed-film processes, the cell retention time is long compared to suspended growth processes (68, 69). Figure 3 illustrates how fixed-film processes foster long cell retention, and enhance growth of slow-growing microorganisms. Fixed-film populations are particularly advantageous when sorption is the main mechanism for the removal of a compound. One advantage of fixed-film processes is that they can provide cell concentrations of an order of magnitude higher than those found in suspended growth systems; a study of the partitioning of organic compounds into biomass indicates that efficient removal is possible only when the biomass concentration is large (68, 70).

For maximum advantage, fixed-film reactors must be designed to allow easy harvesting of the cells after the maximum sorption capacity has been reached. Since the primary requirement for the fixed-film process is that cells attach, it is fortunate that the ability to attach to surfaces appears to

be common among many microbes. However, some strains of the different species can attach more efficiently than others. Attachment is controlled by production of macromolecular substances, such as glycoproteins (71-73), which first must adhere to the surface before cellular attachment can take place. Because certain strains of microorganisms have greater potential to attach than others, selective techniques have recently been developed to screen for such mutants (74) and may prove to be a useful tool in selection of organisms for fixed-film use.

The biodegradability (or transformability) of different organic compounds to be treated must be taken into consideration in order to plan for selective use of organisms. In this discussion, we classify as readily degradable (transformable) those compounds that are altered significantly almost immediately after introduction to the biological system. Compounds that require much longer detention times, extending to several weeks, are relatively refractory. Refractory compounds are those that cannot be changed over a period of time practical for a waste treatment process.

Figure 4 gives a scheme for separating and treating compounds of the different categories. The degradable (transformable) compounds follow the left path and are treated directly in reactor(s), while the relatively refractory compounds are removed by sorption. Depending upon the character of the waste, the reactor(s) will be either aerobic or anaerobic, chemotrophic or phototrophic, or a series of several types. Removal by sorption to microorganisms of compounds not readily biodegraded can provide an extension of the detection time in a treatment system for relatively refractory compounds, can concentrate the substance, and can be a means to transfer compounds from one environmental condition to another without making it necessary to deal with the entire volume of wastewater. Once concentrated and removed from the water, refractory compounds can be disposed of by other means, such as incineration or burial. The relatively recalcitrant compounds can be effectively degraded if they are first sorbed. An example of such use is the sorptive removal from aerobic wastewater of compounds that undergo the necessary reductive dechlorination during sub-

sequent anaerobic digestion of the cells.

Photosynthetic organisms appear to be potentially valuable when initial sorption is required, because large populations can be readily developed, even under low organic nutrient conditions. A generalized scheme for use of photosynthetic organisms is presented in Figures 5 and 6. Cell populations would be initially developed by photosynthetic activity; sorptive processes would then operate bioaccumulating substances. In addition, heterotrophic activity (with or without the mediation of light), or reductive dehalogenation brought about by the phototrophs could biotransform the compounds. Once the initial, limiting reactions are performed by the phototrophs, products could be further biodegraded by other organisms.

### The state of the art

The use of novel microorganisms for biological treatment of man-made compounds is a new concept. A number of advancements are required before large-scale application is possible, among the most important of which is an improved knowledge of metabolic pathways for the biodegradation of specific compounds by different organisms. The metabolic capabilities of many microorganisms, in particular algae and oligotrophic bacteria, are poorly understood. Such knowledge is necessary if limiting reactions are to be determined, and the proper types of organisms selected for specific applications. More information about appropriate types of microorganisms to be selected and maintained in "real-world" treatment systems is needed, especially for the more novel microbial cultures. In order to develop special-purpose organisms by genetic manipulation, major advances in the understanding of the genetic structure of the many different types of organisms in nature are needed.

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**Hester Kobayashi** was a research associate with the Advanced Environmental Control Technology Research Center at the University of Illinois at Urbana-Champaign at the time this article was prepared. Kobayashi received her doctorate in environmental science from the School of Public Health at U.C.L.A., and she has B.A. and M.S. degrees from the University of Hawaii. Anaerobic systems and the use of photosynthetics are two key areas of her research. Kobayashi is now with the Sohio Research Center (Cleveland, Ohio).

**Bruce E. Rittmann** is assistant professor of environmental engineering at the University of Illinois at Urbana-Champaign. Rittmann has a Ph.D. degree in environmental engineering from Stanford University, as well as B.S. and M.S. degrees from Washington University. He has performed research in the areas of trace organics biodegradation and the kinetics of biofilms.

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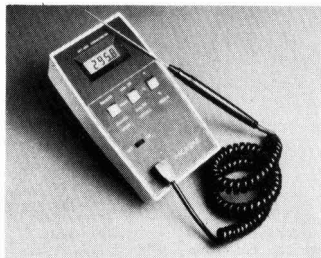
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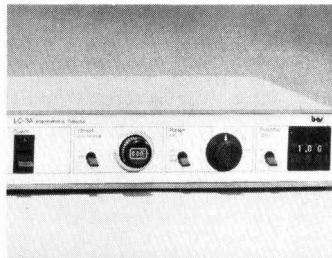
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*(continued on p. 189A)*

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High-speed evaporator suitable for residue analysis drives solvent from batches of 1-49 samples in 69 min. It is designed to conserve the nitrogen evaporating agent. The water bath temperature is adjustable from 35-70 °C. Organomation Associates 114

### Compact materials analyzer

Portable device provides direct concentration readouts of up to 32 elements in one measurement. Detects elements with atomic numbers 13 through 92 without sample preparation. Concentrations may range from 100 ppm-100% and the operating temperature range is from -20-40 °C. Columbia Scientific Industries 115

### Automatic gas analyzer

Uses an electrochemical cell system to measure gases such as SO<sub>2</sub>, NO<sub>x</sub>, oxygen, and CO at low ppm or percent levels. Provides immediate gaseous emission data so the effects of equipment changes can be observed as adjustments are made. Mogul 116



### Humidity and temperature indicator

Both portable and rack-mountable, the instrument provides analog d.c. voltage, d.c. current outputs, and set-point alarms as standard equipment. Multiple sensor systems are also available. The device covers a span of 5-99% RH with an accuracy of ±3% RH. The temperature span is -30-120 °F. General Eastern 117

### Digital temperature indicators

Accept any of seven thermocouple types and offer a choice of 13 temperature ranges from -180-1820 °C. An automatic detecting thermocouple notes breaks and prevents erroneous readout. Iveron Pacific 118

### Chemical structure search system

This system provides access to the DARC interactive structure and sub-structure search system and the QUESTEL bibliographic data bases. Any of over 5 000 000 defined chemical compounds can be selected by structure, identified by CAS registry number, and then searched by subject for appropriate bibliographic information. QUESTEL 119

### Spectroscopy detector

Used with fourier transform spectrometers, this accessory employs the photoacoustic spectroscopy technique to analyze samples that cannot be measured by conventional sampling accessories, i.e., foams, rubbers, minerals. Samples may be solid, liquid, or gaseous, and need minimal preparation. DIGILAB/Bio-Rad Laboratories 120

### Microprocessor-based control unit

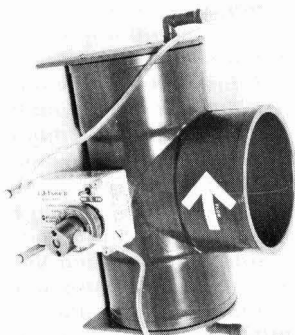
Designed to interface with Lear Siegler's transceiver, this control unit computes and displays stack exit opacity and optical density. It offers 10 measurement ranges, dual recorder outputs, multiple alarm detectors, calibration timing, and a variety of warning indicators. Lear Siegler 121

### LCD event counter

Panel-mounted counters can be programmed by the user for switch-contact closure inputs, d.c. logic input pulses, and a.c. signal inputs. Other features include logic controls such as count inhibit, reset, display hold, carry output, and over-range output. Textmate 122

### Amine analyzer

This accessory for the Varian 5000 Series liquid chromatographs analyzes primary amines eluting from an HPLC column. It consists of a fluorescence detector, a reagent pump, and an orthophthalaldehyde reagent kit. Varian Associates 123

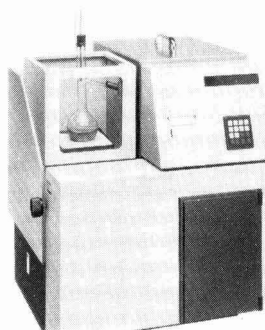


### Flow chambers

Calibrate groundwater flowmeters by determining hydraulic conductivity, linear velocity, and specific discharge for different pressure heads under constant flow conditions. Micrometer-adjusted flow produces velocities from 0.02-10 ft/d, suitable for silt to coarse sand soils. K-V Associates 124

### Electronic precision balance

Portable balance has a 24 kg capacity and reads to 1 g. A single control bar switches the balance on and off and resets the display to zero and tares. Integration time can be extended to overcome the effects of poor weighing conditions. Mettler Instruments 127



### Distillation unit

Microprocessor controlled unit contains an internal computer that monitors and controls the distillation process, calculates data, and prints test results on a roll of thermal paper. Except for the printer mechanism, there are only three moving parts. All parameters including range and temperature are programmed with a keyboard. Lab-Line Instruments 128

### NO<sub>x</sub> analyzer

This instrument detects concentrations in the 2-ppb to 5.0-ppm range and exhibits low zero and span drift. It exceeds all present EPA requirements for NO<sub>x</sub> monitors and may be operated without an attendant for at least seven days. Columbia Scientific Industries 129

### HPLC columns

These columns are used to analyze peptides, proteins, and oligonucleotide mixtures with molecular weights up to 150 000 (globular) and 300 000 (fibrous). Wide-pore silica gel allows effective permeation and partition of large bipolymers. The columns provide high resolution of complex protein mixtures in less than one hour. J. T. Baker Research Products 130

### Disposable filter holder

Suitable for the filtration of organics and HPLC solvents and samples, the syringe-mountable filter holder consists of a 0.5 µm pore size membrane filter sealed in a 30-mm diameter solvent-resistant polypropylene housing. The filter unit has a fast flow rate and can withstand pressures up to 150 psi. Schleicher & Schuell 131

# ES&T LITERATURE

**Instrument rental.** Catalog lists microprocessors, test sets, analyzers, generators, many other instruments of numerous makes for rent. Fully calibrated and guaranteed; meet NBS certification requirements. Continental Resources **151**

**PCB analyzer.** Bulletin describes PCB analyzer using gas chromatography (GC) to separate and detect PCBs, with electron capture and electrolytic conductivity detection. Can meet many analysis needs. Tracor **152**

**Ethylene oxide.** Application Data Sheet PAD Q8000-001 describes MIRAN analyzers that nearly instantly detect and measure ethylene oxide concentrations in ambient air, to meet OSHA regulations. Foxboro Analytical **153**

**Stable isotope amino acids.** Booklet lists wide selection of stable isotope-labeled amino acids with sharp price reductions brought about by a technological breakthrough. A bibliography is included. KOR **154**

**Laboratory water systems.** Brochure describes laboratory systems that can yield ultra-pure water "on demand." Quality assurance is provided. Technic **155**

**Air washer treatment.** Information discusses SUPERSPERSE 901, a dispersant for aiding in removal of deposits that foul industrial air washers. Disperses oil, lint, tobacco dust, other debris. Drew Chemical **156**

**Bearings.** Brochure, "Innovation," lists and describes many different types of bearings for mills, chemical uses, engineering, other applications, SKF Industries **157**

**Computer products.** Ordering guide lists a whole line of analog input/output boards, floppy discs, and other

products compatible with the 100 DEC LSI-11 computer system. ADAC **158**

**Metering pumps.** Capability brochure lists metering pumps able to handle liquids of almost any viscosity, as well as corrosive chemicals and abrasive particles. Waste treatment, chemical processing, many other applications. Milton Roy **159**

**Photomicrography.** Literature tells about H/I stand for supporting heavy cameras and projection heads to prevent vibrations when photomicrography is being done. Vibrations are not transmitted to microscope. Hacker Instruments **160**

**Flow/pressure control.** Applications handbook describes 109 successful product applications for pressure and flow control for gases and liquids. For monitoring, leak detection, other uses. Dwyer Instruments **161**

**Solar air collector.** Technical data sheet gives specifications on a new solar energy collector that uses air rather than a liquid. Company says that efficiency is high, and that the device can blend into most architectural schemes. Solar Shelter **162**

**Power conversion.** Catalog announces full line of products for a.c. to d.c. conversion, and many other electrical needs. Kinetics Control Systems **163**

**Hazardous material transport.** 1982 Fleet Forms & Supplies Catalog lists safety and personnel forms, bills of lading, hazardous materials compliance forms, other items meeting government requirements for hazardous material transport. J. J. Keller & Associates **164**

**Laboratory products.** Catalog lists full line of laboratory products for pollution control, science, industry, research, education, other needs, Lab Line Instruments **165**

**Graphic arts.** 1982 catalog lists microscopes, magnifiers, loupes, densitometers, other products needed in micrographic and graphic arts. Keyan Industries **166**

**Pressure transducer.** "Pressure Transducer Application Note 8" describes and reviews pressure transducers that can be used for precise measurement of liquid flow. MICRO SWITCH **167**

**Clarifiers.** Clarifier Bulletin No. 6301 describes high-performance clarifiers for treating wastewaters from the iron and steel, electronics, chemical, other industries. ERC/LANCY **168**

**Flame-retardant polyethylene.** Data bulletin describes EMPEE PE 113, a flame retardant polyethylene believed to offer same specifications as many other insulators, for example, but with cost advantages. Extrudability is "excellent," company says. Monmouth Plastics **169**

**Signal conditioners.** Catalog lists servo recorders that can include linearizing signal conditioners for various recording instruments. Chessell **170**

**Low-temperature incubators.** Bulletin No. 627 lists seven incubators, one of which accommodates 300 BOD bottles, that work in temperature ranges from  $-10^{\circ}\text{C}$  to  $60^{\circ}\text{C}$ . Fisher Scientific **171**

**Pumps.** Condensed catalog lists centrifugal, rotary, and sump pumps made of engineered plastics. Can handle difficult fluids from less than 1 to 1000 gpm. Vanton Pump & Equipment **172**

**Chloride analyzer.** Brochure describes procedures for measuring chloride in drinking water by the electrode method, from set-up through calibration and analysis, to maintenance. References are given. Orion Research **173**

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

**Laboratory products.** Brochure BR-437 lists centrifuges, recorders, balances, other products for many laboratory needs, including chromatography. Sybron/Brinkmann 174

**Laboratory products.** Catalog 82/83 lists items to meet supply needs of industrial, educational, and biomedical laboratories, pH equipment, incubators, photographic materials, other items featured. VWR Scientific 175

**Data handling.** Brochure describes meteorological, data acquisition, and data transmission equipment; some is solar-powered. Microprocessors are also featured. Climatronics 176

**Liners.** Brochure describes line of pond liners of 30- and 45-mil thickness. Pinhole-free, will not delaminate, are resistant to oxidation, ozone, ultraviolet light. Have uses in liquid pollution abatement, potable water storage. Burke Rubber 177

**Air monitoring.** Brochure describes filtration media for air sampling, monitoring, and analysis, which can

meet stringent standards. High efficiency collection. Schleicher & Schuell 178

**Water sampler coolers.** Refrigerators converted to precisely temperature-controlled water sampler coolers are described in flyer sheet. They are 2.2 and 6.5 ft<sup>3</sup>. Can be built-in or free-standing. Dayton-Walther 179

**Air quality services.** Brochure describes a full range of services in atmospheric sciences. Plume modeling, acid rain analysis, wind energy research, other capabilities available. Tetra Tech 180

**Chemicals.** 1982-83 catalog lists over 5000 chemicals, including reagents, dyes, monomers, polymers, biochemicals, other. Precision microscopes also listed. Polysciences 181

**Solar heating.** Brochure describes window-mounted solar heater that can heat individual residential rooms or equivalent spaces. Suggested retail price is \$499; there is a possible 40% tax credit. Solar Heat Conditioner, Inc. 182

**Particle size analysis.** Brochure describes Watson Image-Shearing Eye-piece for particle size analysis and other related measurements. Hacker Instruments 183

**Chromatographic connections.** Guide 744-81 discusses ferrules, which are tiny fittings indispensable for leak-tight chromatographic connections. Guide lists ferrules and related tools. Supelco 184

**Water control.** Issue of *ORANGE PEAL* focuses on two major sewage projects, in one of which is included the innovative use of ozonation. Rodney Hunt 185

**Quadrupole mass "spec."** Finnigan Topic 8160 discusses collision-activated decomposition experiments for a triple-stage quadrupole GC/MS/MS/DS. Paper was presented at 1981 Pittsburgh Conference. Finnigan MAT 186

**Chemical kits.** Bulletin CS-102 lists 63 types of lab chemical groupings available in kit formats. Examples are organic solvents, EPA water pollution standards, amino acids, many others. Chem Service 187

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CIRCLE 17 ON READER SERVICE CARD

**Lab safety.** Bulletin 202D addresses safety requirements and equipment for the laboratory. A bibliography of safety equipment literature and films is included. A full line of items is listed. Fisher Scientific **188**

**Water treatment.** Announcement invites subscriptions to *Water Treatment Report*, which reviews and abstracts hundreds of sources of information in the field. Afterwards, readers can dig further for what they really need. \$88/y. Technical Communications Associates **189**

**OSHA compliance.** Brochure announces occupational exposure guide that keeps an affected company up-to-date on OSHA regulatory requirements. Loose-leaf binding, with supplementation service available. Initial cost, \$95. J. J. Keller & Associates **190**

**Breathing apparatus.** Brochure describes Bendix Air 30 self-contained breathing apparatus for respiratory and eye protection in toxic, oxygen-deficient, or combustible environments. Bendix **191**

**Moisture titrations.** Bulletin No. 390A describes system that can titrate liquid, gas, or solid samples for moisture content in concentrations up to 100%. Automatic, highly reproducible. Fisher Scientific **192**

**Slow irrigation.** Publicity releases describe Leaky Pipe, a flexible buried pipe system for underground drip irrigation system. TREK Services **193**

**Chromatography.** Information available describes custom-synthesized high performance liquid chromatography (HPLC) phases and column packings. ES Industries **194**

**Incubators.** Brochure describes Heraeus incubators with precision electronic control of temperature, CO<sub>2</sub> and O<sub>2</sub> content, humidity, pH, and other factors, allowing an approximation of in vivo conditions. Tekmar **195**

**Mass spectrometer.** Announcement sets forth availability of Micromass 7070E mass spectrometer, exhibited at Pittsburgh Conference this year. VG Analytical Ltd., Tudor Rd., Altrincham, Cheshire WA14 5RZ, England (write direct)

**Earth science agencies.** 1981 edition, "Worldwide Directory of National Earth Science Organizations . . .," USGS Circular 834, by Wenonah Bergquist, et al., is available. Branch of Distribution, U.S. Geological Survey, 604 South Pickett St., Alexandria, Va. 22304 (write direct)

**Radioactivity standards.** Release of Dec. 10, 1981, announces availability of Standard Reference Materials for measuring/monitoring low-level radioactivity. Office of Standard Reference Materials, National Bureau of Standards, Washington, D.C. 20234 (write direct)

**Geothermal maps.** Geological maps show geothermal areas in state. Department of Natural Resources, Division of Geology and Earth Resources, Mail Stop PY-12, Olympia, Wash. 98504 (write direct)

**Vegetative filter standards.** Said to be economical for smaller feedlots. A. G. Taylor, Agriculture Advisor, Illinois Environmental Protection Agency, 2200 Churchill Rd., Springfield, Ill. 62706 (write direct)

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CIRCLE 1 ON READER SERVICE CARD



**Management of Toxic Substances In Our Ecosystems: Taming the Medusa.** Barney W. Cornaby, Ed. 186 pages. Ann Arbor Science Publishers, Inc., Butterworth, 10 Tower Office Park, Woburn, Mass. 01801. 1981. \$22.50.

The editor is with Battelle/Columbus Laboratories. The book offers an overview of toxic substances. It analyzes major issues in environmental toxicology, carcinogenesis, synergisms/antagonisms, animal-human extrapolation, chronic effects, and many other related matters.

**Modeling Wastewater Renovation.** I. K. Iskandar, Ed. xv + 802 pages. John Wiley & Sons, Inc., 605 Third Ave., New York, N.Y. 10016. 1981. \$55, hard cover.

This book provides an overview of modeling of soil water, virus transport, soil phosphorus, site selection and optimization, economics, research needs, and other pertinent subjects. Most models are "directly applicable to slow-rate land treatment, a method of wastewater application that is similar to an agricultural irrigation system."

**Plastics Waste: Recovery of Economic Values.** Jacob Leidner. viii + 317 pages. Marcel Dekker, Inc., 270 Madison Ave., New York, N.Y. 10016. 1981. \$39.50, hard cover.

This reference source addresses the plastics industry and processes, plastics waste origins and analysis, and various recovery methods. The idea is to recover feedstocks and energy from plastics waste reprocessing.

**Small Hydroelectric Projects for Rural Development: Planning and Management.** Louis J. Goodman, et al., Eds. xiv + 200 pages. Pergamon Press, Inc., Maxwell House, Fairview Park, Elmsford, N.Y. 10523. 1981. \$20, hard cover.

Small-scale hydropower is being considered as a fairly low-cost, renewable means of providing rural areas with electricity. Here is a look at how this can be done in different ways, with some case histories in China, the Philippines, New Zealand, and Hawaii. Policy and research issues are also discussed.

**Chemistry in Water Reuse.** Vol. 1. William J. Cooper, Ed. xv + 557 pages. Ann Arbor Science Publishers Inc., P.O. Box 1425, Ann Arbor, Mich. 48106. 1981. \$39.95, hard cover.

Actually, water is much reused now, since one town's discharge may, after downstream flow, end up in another town's water system. The impetus for reuse may be increased by scarcities of water in the future. This book addresses chemical controls needed for reuse, including monitoring, quality assurance, disinfection, toxic substances removal, and swimming pool needs.

**The Water Environment: Algal Toxins and Health.** Wayne W. Carmichael, Ed. xii + 491 pages. Plenum Press, 227 West 17th St., New York, N.Y. 10011. 1981. \$59.50, hard cover.

Algae, for instance, can cause seafood to be poisoned, and can subsequently cause human fatalities. Certain cyanobacteria might cause freshwater to contain contact poisons, or endanger drinking water supplies. Prospects are for a marked increase in this type of situation. Growing out of a conference on the subject, this book explains how and why.

**14th Oil Shale Symposium Proceedings.** James H. Gary, Ed. v + 433 pages. Colorado School of Mines Press, Golden, Colo. 80401. 1981. \$18, paper.

Might oil from shale help to cure America's imported petroleum problems without monumental environmental cost? That question is what the symposium examined, addressing processes, hazards, NO<sub>x</sub>, in situ reporting, EPA regulations, and numerous other topics. Ongoing research in the U.S. and abroad was also discussed, as were environmental controls.

**Microbial Degradation of Xenobiotics and Recalcitrant Compounds.** Thomas Leisinger, et al., Eds. xiv + 416 pages. Academic Press, Inc., Ltd., 24-28 Oval Road, London NW1 7DX, England. 1982. \$66.

Some man-made chemical waste compounds, or xenobiotics may be re-

fractory to microbial breakdown. They could present environmental dangers, however. This book looks at waste disposal problems, difficult compounds, what is presently degradable, and what progress toward developing microbes for the more refractory substances has been made. Strategies for strain isolation and management are proposed.

**RCRA/Hazardous Wastes Handbook.** 3rd ed. 600 pages. Government Institutes, Inc., 966 Hungerford Drive, No. 24, Rockville, Md. 20850. 1981. \$95, in binders.

This book comes in two volumes, and is updated. It discusses the latest regulations dealing with hazardous wastes, and is expandable to fit more information as new rules are printed in the *Federal Register*. Responsibilities of hazardous waste generators, carriers, and others involved are covered, as well as criminal liabilities. The first volume covers RCRA and regulations; the second has *Federal Register* applicable to the subject.

**Catalog on Air Pollution and Sampling.** The Mellvaine Company, 2970 Maria Ave., Northbrook, Ill. 60062. 1981. \$95, in three-ring binder.

This catalog is devoted entirely to air pollution monitoring and sampling products. It contains a product index, detailed descriptions of each company's product, and company brochures. Intermittent and continuous monitoring devices, meteorological instruments, analyzers, sampling devices, balances, chromatographs, and spectrophotometers are among the many items listed and described.

**Risks of Nuclear Energy and Low-Level Ionizing Radiation.** AMA Advisory Panel. 39 pages. Order Department OP-125, AMA Publications, P.O. Box 821, Monroe, Wis. 53556. 1981. \$4.50, paper.

This is a report to the Council on Scientific Affairs of the American Medical Association. It modifies a previous report of 1978. Major topics covered are electricity generation,

mine tailings, radiation exposure, health effects, risks of nuclear operations, and public perceptions of risk.

**NBS Standard Reference Materials Catalog, 1981-83 Edition (SP-260).** Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402. 1981. \$5.50. Ask for Stock No. 003-003-02382-5.

The present catalog describes nearly 1000 materials issued by the National Bureau of Standards Standard Reference Material (SRM) program (*ES&T*, December 1981, p. 1408). SRMs are certified for their chemical composition, or for a physical or chemical property. Listed materials are classified as Chemical Composition Standards, Physical Property Standards, Engineering Type Standards, Research Materials, and Special Reference Materials.

**Cost-Benefit Analysis and Environmental Regulations: Politics, Ethics, and Methods.** Daniel Swartzman, et al., Eds. 196 pages. The Conservation Foundation, 1717 Massachusetts Ave., N.W., Washington, D.C. 20036. 1982. \$11.50, paper.

Cost-benefit analysis took the limelight because of perceived inefficiencies, ineffectiveness, and expense of federal regulations. It can be helpful to decision making, but is subject to abuse, the Conservation Foundation observes. In some cases, cost-benefit requirements can unleash its own regulatory nightmare, according to the book, which explains how that might happen.

**Polycyclic Aromatic Hydrocarbons in Water Systems.** David J. Futoma, et al. 200 pages. CRC Press, Inc., 2000 N.W. 24th St., Boca Raton, Fla. 33431. 1981. \$54.95 (\$63.95, outside U.S.), hard cover.

Basic subjects covered include solubility studies, sampling and preconcentration, chromatographic analysis methods, and spectroscopic methods of analysis. Extraction, thin-layer and column methods, fluorescence, and other such topics are also examined closely.

**Environmental Risk Analysis for Chemicals.** Richard A. Conway, Ed. 576 pages. Van Nostrand Reinhold,

135 West 50th St., New York, N.Y. 10020. 1981. \$37.50, hard cover.

The author shows step-by-step how to determine a chemical's environmental risk. He explains how to spot early warning signs of potential problems in air, land, and water environments. Fate analysis, models or microcosms, and case studies involving applications of the principles set forth are among major subjects discussed.

**Chemical and Radiation Waste Litigation Reporter.** Neil J. Cohen, Ed. Periodical, monthly. Chemical & Radiation Waste Litigation Reporter, Suite 228, 4420 Connecticut Ave., N.W., Washington, D.C. 20008. \$975/y.

This periodical is aimed at legal counsel involved in such litigation. It goes over issues, cases, briefs, opinions, and many other documents encountered in legal work. Critical facts of a case are featured. Past issues have featured common law theory, several/strict liability, landowner liability, responsibility for cleanup and damages, and other such matters. Each issue normally contains more than 200 pages.

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CIRCLE 3 ON READER SERVICE CARD

**Water and Waste Treatment Data Book.** 14th ed. 160 pages. The Permutit Company, Inc., E 49 Midland Ave., Paramus, N.J. 07652. 1981. \$3.95, paper.

This book contains 91 sections of data with charts, tables, and formulas for practicing engineers. Data on water, pipes and fittings, chemical properties, waste treatment, and other topics are given.

**The Federal Yellow Book Directory.** Semiannual update. The Washington Monitor, Inc., 499 National Press Building, Washington, D.C. 20045. \$130 a year, loose-leaf binder.

When one deals with the federal government, it is good to know who does what job. This directory lists about 27 000 federal employees by organization, name, title, address, room, and phone number, as well as regional offices nationwide. It covers much of the executive branch. The aim is to have the user "reach the right office and the right person right away."

**The Human Impact: Man's Role in Environmental Change.** Andrew Goudie. 328 pages. The MIT Press, 28

Carleton St., Cambridge, Mass. 02142. 1982. \$22.50, cloth; \$10, paper.

This book traces current ideas concerning the interaction between human beings and nature. It also surveys human interference with environmental systems at various stages of development. Impacts on water, climate, soil, flora, and fauna, as well as the human being as a geomorphological agent are discussed. Case histories in Africa, the Middle East, Great Britain, and the western U.S. are covered.

**Radiofrequency and Microwaves.** 134 pages. WHO Publications Centre U.S.A., 49 Sheridan Ave., Albany, N.Y. 12210. 1981. About \$6, paper.

This World Health Organization book is Environmental Health Criteria 16. It discusses sources and conditions of exposure, monitoring instruments, biological effects, health effects in human beings, and many other related topics.

**Exposure Commitment Assessments of Environmental Pollutants.** Vol. 1, No. 2. MARC Report Number 25. 40

pages. Monitoring and Assessment Research Centre, the Octagon Building, 459A Fulham Road, London SW10 0QX, England. 1981. \$4, paper.

This volume contains summary exposure assessments for mercury, nickel, and tin. It discusses natural cycles, man-made sources, environmental considerations, metabolism, effects, literature critiques, and pathway analyses for each metal.

**Banbury Report 9: Quantification of Occupational Cancer.** Richard Peto, Marvin Schneiderman, Eds. 750 pages. Cold Spring Harbor Laboratory, Fulfillment Department, P.O. Box 100, Cold Spring Harbor, N.Y. 11724. 1981. \$89, cloth (\$106.80 outside U.S.).

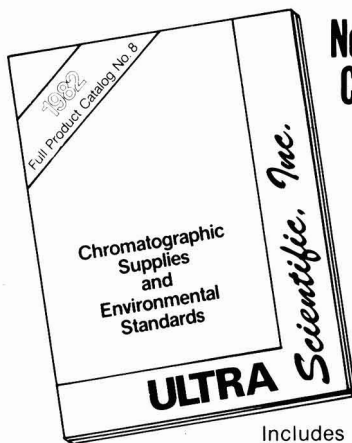
Here are presented various viewpoints concerning the contribution of occupation to overall cancer incidence. This book covers the role of asbestos exposure with respect to lung cancer and mesothelioma, along with data that can elucidate this relationship. Surveillance programs, case-control studies, identifying high-risk groups, and other such pertinent topics are discussed in detail.

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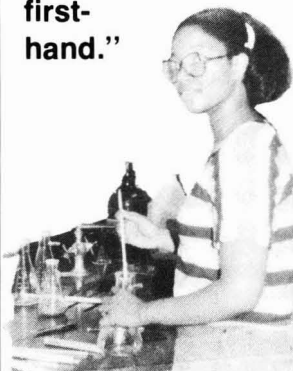
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## MEETINGS

**March 22-23** Houston, Tex.  
**Outer Continental Shelf (OCS) Conference.** The Energy Bureau, Inc.

*Write:* Paul N. Gilman, The Energy Bureau Inc., 41 East 42nd St., New York, N.Y. 10017; (212)687-3178

**March 22-23** Atlanta, Ga.  
**Fundamentals of Groundwater Quality Protection.** American Ecology Services, Inc. and Geraghty & Miller, Inc.

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

**April 4-7** Houston, Tex.  
**1982 Industrial Energy Conservation Technology Conference and Exhibition.** American Society of Civil Engineers, AIChE, and 11 other associations

*Write:* Texas Industrial Commission, P.O. Box 12728, Capitol Station, Austin, Tex. 78711

**April 5-7** Kansas City, Mo.  
**Wind and Solar Energy Technology.** American Society of Civil Engineers and others

*Write:* G. H. Stickney, College of Engineering, University of Missouri-Columbia, Columbia, Mo. 65211

**April 7-9** Park City, Utah  
**4th Annual RMCOEH Occupational and Environmental Health Conference: "Health Issues Related to Metal and Nonmetallic Mining."** The University of Utah

*Write:* K. Blosch, Rocky Mountain Center for Occupational and Environmental Health (RMCOEH), Building 512, University of Utah, Salt Lake City, Utah 84112; (801)581-5710

**April 12-14** Chicago, Ill.  
**13th Annual Spring Meeting of the Fine Particle Society.** Fine Particle Society

*Write:* Dr. Teoman Ariman, College of Engineering and Physical Sciences, University of Tulsa, Tulsa, Okla. 74104; (918)592-6000, Ext. 2575

**April 12-15** Dearborn, Mich.  
**D-22 Committee on Sampling and Analysis of Atmospheres.** ASTM

*Write:* Alice Cavallaro, ASTM, 1916 Race St., Philadelphia, Pa. 19103; (215)-299-5486

**April 13-15** New Orleans, La.  
**7th Annual Spring Workshop and Exposition.** The Association of Official Analytical Chemists

*Write:* Nicole F. Hardin, Food and Drug Administration, 4298 Elysian Fields Ave., New Orleans, La. 70122; (504)589-2471

**April 19-22** Milwaukee, Wis.  
**1982 Hazardous Materials Spills Conference.** U.S. Coast Guard, EPA, DOT, and CMA

*Write:* Hazardous Materials Spills Conference, Suite 700, 1629 K St., N.W., Washington, D.C. 20006; (202)296-8264

**April 19-23** Las Vegas, Nev.  
**Groundwater Management in Arid and Semi-Arid Regions.** American Society of Civil Engineers

*Write:* Helen J. Peters, ASCE, c/o California DWR, P.O. Box 388, Sacramento, Calif. 95802; (916)445-2182

**April 26-28** Minneapolis, Minn.  
**1982 TAPPI Environmental Conference.** Technical Association of the Pulp and Paper Industry

*Write:* Janet Crane, TAPPI, One Dunwoody Park, Atlanta, Ga. 30338; (404)-394-6130

## Courses

**March 19-23** Chicago, Ill.  
**Basic Principles of Chemical Engineering.** The Center for Professional Advancement

Fee: \$975. *Write:* The Center for Professional Advancement, Dept. NR, P.O. Box H, East Brunswick, N.J. 08816; (201)249-1400

**March 22-24** Madison, Wis.  
**Groundwater Quality Protection.** University of Wisconsin-Extension

Fee: \$330. *Write:* Philip R. O'Leary, Department of Engineering and Applied Science, University of Wisconsin-Extension, 432 N. Lake St., Room 701, Madison, Wis. 53706; (608)262-0493

**March 22-25** East Brunswick, N.J.  
**Industrial Waste Incineration Technology.** The Center for Professional Advancement

Fee: \$835. *Write:* The Center for Professional Advancement, Dept. NR, P.O. Box H, East Brunswick, N.J. 08816; (201)249-1400

**March 29-April 1** Washington, D.C.  
**The Systems Approach to Radiation Protection.** The George Washington University

Fee: \$685. *Write:* Director, Continuing Engineering Education, George Washington University, Washington, D.C. 20052; (202)676-6106

*continued on page 202A*

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**ENVIRONMENTAL SYSTEMS SCIENTIST:** The Great Lakes Environmental Research Laboratory of NOAA in Ann Arbor, MI seeks a Scientist or Engineer with a background in systems analysis or mathematical modeling. Research will involve: (1) determining means to maximize use of water resources while maintaining environmental quality, (2) assessing costs of environmental management, (3) developing information on risks associated with environmental decisions, innovative syntheses and interpretations of multidisciplinary environmental data will be the foundation of the research. Position is in the competitive service and will be filled either at GS-12 or GS-13 level with annual salary ranges of \$26,245-\$36,723 or \$33,586-\$43,666 respectively, based upon both superior or unique qualifications and existing rate of pay. **QUALIFICATIONS:** BS or higher degree in physical science, engineering, or mathematics. Candidates must also have 3 years of professional experience which has equipped them with the knowledges necessary to perform the above duties. One year of experience must have been comparable to the next lower grade in Federal service. Graduate education may be substituted in part for the experience requirements. **SELECTIVE FACTORS:** Experience in: (1) water related multidisciplinary studies, (2) computer techniques for data manipulation, and (3) systems analysis techniques or applied statistics. Additional technical information may be obtained from Dr. William C. Sonzogni, (313) 668-2249 or FTS 373-2249. **TO APPLY:** Current or former Federal employees should submit SF-17-1, CD-332, and OPM Form 1386. Forms may be obtained by calling (303) 497-6332 or FTS 320-6332. Other applicants should submit a CN-1300 package and Form 1386, both obtainable at nearest Office of Personnel Management. **ALL APPLICANTS MUST SUBMIT THEIR PUBLICATION RECORD AND SPECIFICALLY ADDRESS SELECTIVE FACTORS.** Applications should be submitted to NOAA/NTIA, Pers Svcs Div (R562), Attn: Mr. Mann, 325 Broadway, Boulder, CO 80303, Ref. Vac. No. NOAA/ERL 82-26. Applications must be received by April 9, 1982. AN EQUAL OPPORTUNITY EMPLOYER.

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Applicants to send vitae and names of three referees to Professor D. B. Botkin, Chairman, Environmental Studies Program, University of California, Santa Barbara, CA 93106. Closing date is March 31, 1982. The University of California is an Equal Opportunity/Affirmative Action Employer.

**ENVIRONMENTAL QUALITY AND HEALTH POSITION**

**UNIVERSITY OF CALIFORNIA, IRVINE:** The Program in Social Ecology, University of California at Irvine, invites applications for an Assistant Professor in a tenure track position, beginning September 1982. Candidates must be well trained in analytical or physical chemistry and have research interests in environmental chemistry and in the health implications of environmental contaminants. Doctoral training may be in chemistry, toxicology, environmental science or engineering, public health or medicine. The candidate must be capable of developing an independent research program within the environmental analysis (environmental quality and health) area of the Program in Social Ecology. The ideal candidate would have experience and/or interests in the public policy application of environmental research findings. The Program in Social Ecology is a multidisciplinary unit which grants the B.A., M.A., and Ph.D. degrees. Faculty include biologists, health specialists, lawyers, planners, psychologists and sociologists who conduct research on environmental and social problems. The campus is located 40 miles south of Los Angeles and five miles inland from the Pacific Ocean. Applications from all qualified candidates are welcome. Women and minorities are encouraged to apply. Candidates should submit a brief letter stating research interests and equipment needs, curriculum vita, and names and addresses of three references by March 31, 1982 to: Dr. Steven D. Colome, Chair/Search Committee, Program in Social Ecology, University of California/Irvine, Irvine, CA 92717. An Affirmative Action/Equal Opportunity Employer.

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**MEETINGS** (continued)

**March 29–April 2** Washington, D.C.

**Risk and Reliability Assessment Using Modern Methods of Fault Tree Analysis.** The George Washington University

Fee: \$760. *Write:* Director, Continuing Engineering Education, George Washington University, Washington, D.C. 20052; (202)676-6106

**March 29–April 2** Boston, Mass. **Fundamentals of Industrial Hygiene.** The Harvard School of Public Health

Fee: \$725. *Write:* Kathleen T. Fahey, Harvard School of Public Health, 665 Huntington Ave., Boston, Mass. 02115; (617)732-1171

**April 5–9** Atlanta, Ga. **Societal Cost of Energy Alternatives: Methodologies and Results.** The Georgia Institute of Technology

Fee: \$725. *Write:* Department of Continuing Education-R, Georgia Institute of Technology, Atlanta, Ga. 30332; (404)-894-2547

**April 15–16** Washington, D.C. **Environmental Law and Regulations Introductory Course.** Government Institutes, Inc.

Fee: \$495. *Write:* T. P. F. Sullivan, Government Institutes, Inc., 966 Hungerford Dr., No. 24, Rockville, Md. 20850; (301)251-9250

**April 19–21** Arlington, Va. **Environmental Regulation Course.** Executive Enterprises, Inc.

Fee: \$675. *Write:* Thomas J. Lombardi, American Seminars Institute, 1700 Ygnacio Valley Rd., Suite 220, Walnut Creek, Calif. 94598

**April 19–23** Chicago, Ill. **Laboratory Safety Course.** National Safety Council

Fee: \$450 (member), \$560 nonmember. *Write:* Sol Miller, Training Chairman, National Safety Council, 444 North Michigan Ave., Chicago, Ill. 60611; (312)527-4800

**April 26–27** Washington, D.C. **Energy Management: Controlling Energy Usage and Costs.** George Washington University

Fee: \$530. *Write:* Director, Continuing Engineering Education, George Washington University, Washington, D.C. 20052; (202)676-6106

**International**

**April 19–21** Berlin, Germany **International Recycling Congress.** IRC Secretariat

*Write:* Dr. James G. Abert, National Center for Resource Recovery, Inc., 1211 Connecticut Ave., N.W., Washington, D.C. 20036; (202)223-6154

**May 10–12** Marseilles, France **4th International Conference on Planning and Management of Water Resources for Industrial, Agricultural, and Urban Use**

*Write:* Secretariat de la Conference Societe des Eaux de Marseille, 25 rue Edouard Delanglade, 13006 Marseille, France

**Call for Papers**

**April 1, 1982 deadline**  
**Identification and Analysis of Organic Pollutants in Air.** Environmental Chemistry Division of the American Chemical Society

The conference will be held at the ACS meeting in Kansas City this fall, Sept. 12–17, 1982. *Write:* Dr. Lawrence H. Keith, Radian Corporation, P.O. Box 9948, Austin, Tex. 78766; (512)454-4797

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## Estimation of Inhalation Exposure to *N*-Nitrosodipropylamine during the Application and Incorporation of the Herbicide Trifluralin

Edgar W. Day, Jr.,\* Donald G. Saunders, James W. Mosler, Edward M. McKinney, Fred L. Powers, Richard D. Griggs, and Richard Frank

Lilly Research Laboratories, Division of Eli Lilly and Company, Greenfield, Indiana 46140

■ The discovery of *N*-nitrosodi-*n*-propylamine (NDPA), a volatile nitrosamine in the herbicide trifluralin, prompted an investigation into the possible exposure of field workers to the contaminant. The potential for inhalation of the nitrosamine during and following application of the herbicide was evaluated. Experiments were conducted in which personal air monitors were attached to workers while applying herbicide containing 2–6 ppm of NDPA. To more closely approximate the inhalation rate of field workers, additional experiments were conducted with high-volume pumps mounted on tractors and placed in treated fields. Sampling and analytical techniques are described. The results of these experiments demonstrated an extremely low level of exposure potential.

### Introduction

In September 1976, Fine et al. (1) reported on their discovery of the presence of volatile nitrosamines in certain pesticide formulations. The United States Environmental Protection Agency subsequently examined a number of pesticide products (2, 3) and observed *N*-nitroso compounds in several products, including a number of di-nitroaniline herbicides. One of the products analyzed was Treflan EC (trifluralin, Elanco Products Co., Division of Eli Lilly and Co.) which was found to contain approximately 150 ppm of *N*-nitroso-di-*n*-propylamine (NDPA). In conjunction with the initial observation (1, 4), no NDPA was detected in the air, water, or crops following application of Treflan to a tomato field.

NDPA has been shown to be carcinogenic in laboratory animals (5–8) and is thus a potential hazard to man. Data reported previously (9–11) indicated that consumers of crops grown in fields treated with NDPA-containing trifluralin were not subject to any detectable exposure to the nitrosamine. Likewise, potable waters from treated areas and the principal US manufacturing site (10, 11) demonstrated no nitrosamine exposure.

Ross et al. (9) took air samples during the application of trifluralin and did not detect nitrosamines. However, the sampling system employed was not mobile and did not truly reflect the potential exposure of the applicator to the nitrosamine contaminant.

In order to evaluate exposure to the nitrosamine contaminant in the spray suspension, it was deemed necessary to sample the environment in the vicinity of the tractor (or truck) driver during the application of the product in

typical use situations. Exposure via inhalation was of particular interest since nitrosamines are known to exhibit high vapor pressures and readily volatilize from soil (12, 13).

Reported herein are the techniques used and the analytical results from a number of experiments conducted to measure the possible inhalation exposure of workers to NDPA resulting from the use of trifluralin. Operators were monitored while applying herbicide with several equipment configurations and in a number of typical geographic locations. Workers responsible only for the herbicide mixing and spray tank loading operations were monitored separately in two experiments. In one experiment, air samplings were taken during a second disking conducted 3 days after treatment. The air over this treated field was also monitored for NDPA and trifluralin during a 9-day period to estimate the potential exposure to workers who may enter a field after herbicide application.

### Experimental Section

Two sets of experiments were conducted. Set I consisted of nine experiments in which the breathing zone of the operators was monitored with battery-powdered personal air samplers while the herbicide was being applied. Set II consisted of seven experiments in which the air sampling rate more closely approximated the breathing rate of tractor driver. A summary of the general experimental conditions in the 16 experiments is presented in Table I. Applicator or grower equipment was used to apply the herbicide at the recommended rate for the crops and soil type. In some cases, application and incorporation of the herbicide were a simultaneous operation while in others they were carried out sequentially. In the latter case, both the spray applicator driver and the incorporation driver were monitored.

**Air Sampling Apparatus and Procedures. Set I.** In the first set of experiments, air samples were taken with portable air sampling pumps (Bendix Model BDX44) connected to activated charcoal tubes (No. 226-09, SKC, Inc.). The pumps were clipped to the belt of the worker, and the charcoal tubes were clipped to the front of the worker's shirt to collect air from his breathing zone.

Field collection efficiencies were determined in each of the experiments by placing 10  $\mu$ L of a hexane solution containing 0.022  $\mu$ g of NDPA and 0.20  $\mu$ g of trifluralin just inside each of four freshly opened charcoal tubes. The pumps were turned on before placing the solutions in the

Table I. Field Conditions for NDPA Air Monitoring Experiments

expt no.	date	location	current (or planned) crop	acreage treated	appl/incorp <sup>a</sup>
I-1	5/77	Flat Rock, IN	(soybeans)	40	separate
I-2	6/77	Horn Lake, MS	(soybeans)	40	simultaneous
I-3	6/77	Hernando, MS	(soybeans)	70	simultaneous
I-4	6/77	Fulton, KS	(soybeans)	70	separate
I-5	6/77	Breckenridge, MI	(dry beans)	40	simultaneous
I-6	6/77	Dixon, CA	sugar beets	45	simultaneous
I-7	6/77	Davis, CA	tomatoes	20	simultaneous
I-8	7/77	Cutler, CA	plums	30	simultaneous
I-9	7/77	Cutler, CA	nectarines	31	simultaneous
II-1	9/77	Huron, CA	(cotton)	70	simultaneous
II-2	9/77	Huron, CA	(cotton)	80	simultaneous
II-3	10/77	Queen Creek, AZ	pecan	45	simultaneous
II-4	10/77	Chandler Hts, AZ	grapefruit	30	simultaneous
II-5	10/77	Ferris, TX	(cotton)	80	simultaneous
II-6	10/77	Ferris, TX	(cotton)	65	simultaneous
II-7	10/77	Knightsstown, IN	(soybeans)	16	separate

<sup>a</sup> Indicates whether application and incorporation of the herbicide were accomplished in separate or simultaneous operations.

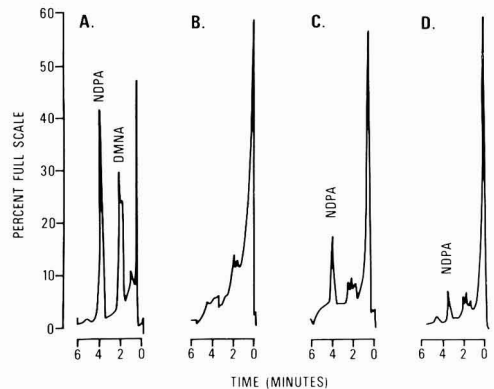
tubes so that all of the volatilized materials could be collected on the charcoal. These pumps and tubes were placed upwind from the treatment field along with two pumps and tubes which had not been spiked. These latter tubes served as blanks (controls) for each experiment.

**Set II.** The sampling of air in the vicinity of workers in the set II experiments was accomplished by pulling air through glass tubes packed with charcoal using an electric pump (Bendix Model 25004) powered by a gasoline generator. The tubes were 18 cm × 1.8-cm i.d. glass packed with an 8-g front section and a 2-g back section of charcoal separated with glass wool. The charcoal (PCB grade, 20–50 mesh, Calgon, Corp., Pittsburgh, PA) was baked 16 h at 200 °C, and portions were extracted and analyzed for thermal energy analyzer (TEA) responsive substances before use. The tubes were packed just before the initiation of each experiment and were wrapped in aluminum foil to exclude direct sunlight.

Eight tubes were packed for each experiment. Four of the tubes were mounted on the tractor approximately 0.5 m from the head of the operator and were connected to a single pump. Before placement in an inverted position, 0.5 µg of dipropylamine (DPA) in 0.1 mL of hexane was placed just inside the inlet of two of the tubes and air flow commenced immediately. This enabled the DPA to volatilize onto the charcoal to permit a check on potential artifact formation during the experiments. For sampling the air over a treated field (experiment II-7), two blank and two DPA-spiked tubes were mounted in an inverted position about 0.5 m above the surface of the soil, and the pump was operated between 8:00 a.m. and 8:00 p.m. if weather conditions permitted.

During all experiments, four other packed tubes were used at the control site, which was located upwind but adjacent to the experimental field. The tubes were mounted on a ring stand and connected to a Model 25004 pump via rubber tubing. One of the tubes was a blank, one was spiked with 0.5 µg of DPA, and the other two were fortified with NDPA (0.05 µg) and trifluralin (0.2 µg) to determine field collection efficiencies.

The driver of the application equipment in the set II experiments performed none of the mixing and loading operations. Exposure to the worker performing these tasks was evaluated in experiments II-3 and -4. Four charcoal tubes were attached to the shirt of this worker. The tubes were connected to another pump via a harness of rubber tubing which permitted him to carry out his required tasks.



**Figure 1.** GC-TEA chromatograms, small (600 mg) charcoal tubes: (A) direct standards, NDPA (0.054 µg/mL) and DMNA (0.038 µg/mL); (B) blank charcoal extract; (C) field recovery, experiment II-5, 105%; (D) air sample from breathing zone of operator, experiment II-5, response for 0.11 µg of NDPA on contents of single tube. All injection volumes, 50 µL. TEA attenuation, ×4.

This sampling was conducted during each fill operation (approximately every 1.5–2.0 h) with the same set of tubes. Thus, the results are the cumulative exposure for 1 day of mixing and loading.

**Analytical Methodology.** All samples collected in these experiments were analyzed for both NDPA and trifluralin. All NDPA measurements were made with a gas chromatography–thermal energy analyzer (GC-TEA) system using appropriate modifications of the methods of West and Day (11), and trifluralin determinations were carried out by electron capture gas chromatography methods similar to those of Tepe and Scroggs (14). Some representative GC-TEA chromatograms are presented in Figures 1 and 2.

### Results and Discussion

**Collection Efficiency.** The efficiency of activated charcoal as a collection medium for NDPA was determined in the laboratory before the field experiments. The collection was nearly quantitative using both the small pumps with the small tubes and the large pumps with the large tubes for 0.1–1.0 µg of NDPA. The efficiency for the collection of trifluralin vapor was also quantitative at the

Table II. Field Collection Efficiencies for NDPA and Trifluralin

expt no.	amt added, $\mu\text{g}$		air sampling time, h	av vol of air, $\text{m}^3$	% collection efficiency	
	NDPA	trif <sup>a</sup>			NDPA	trif <sup>a</sup>
I-1	0.022	0.20	5.5	0.55	91, 68 86, 86	65, 70 70, 100
I-2	0.022	0.20	7.5	0.68	91, 100 95, 91	49, 65 50, 55
I-3	0.022	0.20	6.0	0.58	105, 95 114, 105	75, 95 75, 85
I-4	0.022	0.20	5.0	0.50	109, 109 123, 118	<i>b</i>
I-5	0.022	0.20	7.8	0.75	68, 105 109, 105	95, 85 75, 95
I-6	0.022	0.20	7.8	0.77	127, 118 114, 118	115, 120 115, 115
I-7	0.022	0.20	8.0	0.77	109, 109 118, 114	95, 115 160, 115
I-8	0.022	0.20	7.0	0.69	105, 100 95, 86	70, 75 9, 10
I-9	0.022	0.20	8.0	0.78	95, 86 100, 91	85, 95 85, 85
II-1	0.05	0.20	6.5	5.23	88, 40	95, 85
II-2	0.05	0.20	7.3	5.69	68, 58	<i>b</i>
II-3	0.05	0.20	6.5	5.54	36, 72	90, 78
II-4	0.05	0.20	6.0	5.11	100, 72	<i>b</i>
II-5	0.05	0.20	3.5	2.52	64, 72	54, 55
II-6	0.05	0.20	3.0	2.16	86, 96	97, 89
II-7	0.05	0.20	4.0	2.83	98, 104	108, 81
II-7 (2nd)	0.05	0.20	3.0	2.30	100, 94	125, 85

<sup>a</sup> Trifluralin. <sup>b</sup> Interferences or contamination observed in these samples.

Table III. Results of Monitoring the Breathing Zones of Field Workers during the Application of Treflan Low-Volume Sampling Experiments

expt no.	Treflan rate, lb/acre	NDPA in Treflan, ppm	spray boom position	field worker	sampling time, h	av air vol, <sup>a</sup> $\text{m}^3$	obsd. concn in air, <sup>a</sup> $\mu\text{g}/\text{m}^3$	
							NDPA <sup>b</sup>	trif <sup>c</sup>
I-1	1.0	4.6	rear	applicator	1.5	0.14	ND	29.3
				incorporator	4.0	0.40	ND	1.1
I-2	1.0	3.8	rear	applicator	8.0	0.75	ND	9.8
I-3	0.5	3.8	belly	applicator	6.0	0.59	ND	4.3
I-4	1.0	3.0	rear	applicator	2.0	0.19	ND	62.7
				incorp 1	4.0	0.34	ND	2.3
				incorp 2	4.0	0.39	ND	5.0
I-5	0.5	4.6	front	applicator	7.75	0.76	0.016	22.7
I-6	0.75	3.4	belly	applicator	8.0	0.67	ND	13.5
I-7	0.75	3.3	rear	applicator	8.0	0.67	ND	10.5
I-8	2.0	2.0	front	applicator	7.0	0.70	ND	7.9
I-9	2.0	2.0	front	applicator	8.5	0.79	ND	11.9

<sup>a</sup> Average of two or four values. <sup>b</sup> ND = none detected at a test sensitivity of 0.005  $\mu\text{g}$  per adsorber tube. <sup>c</sup> Trifluralin.

1- $\mu\text{g}$  level and greater than 90% at the 20- and 100- $\mu\text{g}$  levels.

The laboratory findings were generally supported by the recoveries observed in the field, which are listed in Table II. In the nine set I experiments, the NDPA field recoveries ranged from 68% to 127% with an average of 102%. For trifluralin, the range was 49-120% (ignoring the anomalous values in experiments I-8 and I-7) with an average of 97%. The collection efficiencies using the larger equipment ranged from 36 to 104% for NDPA and from 54 to 125% for trifluralin. The averages were 78% and 87% for NDPA and trifluralin, respectively. The variations and losses observed in field are most likely due to experimental handling difficulties under field conditions rather than deficiencies in the trapping medium itself.

**Low-Volume Sampling.** The results of monitoring the breathing zones of the workers in the set I experiments are presented in Table III. In each of these nine trials, the herbicide was applied at the recommended rate for the specific crop and soil type in accordance with the farmer's

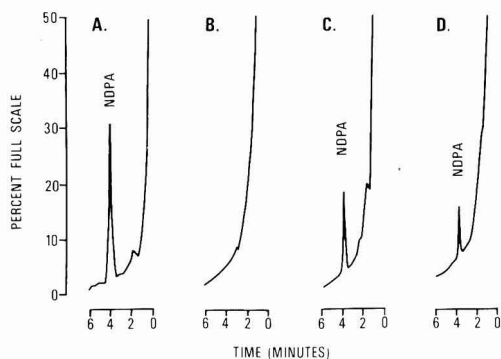


Figure 2. GC-TEA chromatograms, large charcoal (8 g) tubes: (A) direct standard NDPA, 0.025  $\mu\text{g}/\text{mL}$ ; (B) field control charcoal, experiment III-4; (C) field recovery, 0.05  $\mu\text{g}$  NDPA (72% efficiency); (D) air sample, breathing zone of tractor driver, response of 0.024  $\mu\text{g}$  of NDPA. All injection volumes, 50  $\mu\text{L}$ . TEA attenuation,  $\times 4$ .

Table IV. Results of Monitoring the Breathing Zones of Field Workers during the Application of Treflan High-Volume Sampling Experiments

expt no.	Treflan rate, lb/acre	NDPA in Treflan, ppm	worker monitored	sampling time, h	sampling rate, L/min	air vol, m <sup>3</sup>	amt collected, <sup>a</sup> $\mu\text{g}$		av concn in air, $\mu\text{g}/\text{m}^3$	
							NDPA <sup>b</sup>	trif <sup>c</sup>	NDPA	trif <sup>c</sup>
II-1	0.69	3.7	driver	7.1	12.9	5.44	0.020	185	0.0037	34.0
							0.025	203	0.0046	37.3
II-2	0.69	3.7	driver	7.3	12.6	5.54	0.019	130	0.0034	23.5
							0.032	164	0.0058	29.6
II-3	2.0	3.6	driver	7.1	13.3	5.65	ND	22	<0.001	3.9
							ND	18	<0.001	3.2
			mixer	1.1	12.0	0.78	ND	13	<0.01	16.7
							ND	6.5	<0.01	8.3
							ND	25	<0.01	32.0
							ND	30	<0.01	38.5
II-4	2.0	3.6	driver	6.9	13.2	5.42	0.037	117	0.0068	21.6
							0.028	87	0.0051	16.1
			mixer	1.0	10.9	0.63	0.008	13	0.013	20.6
							0.006	14	<0.009	22.2
							0.009	17	0.015	27.0
ND	18	<0.009	28.6							
II-5	1.3	6.4	driver	6.4	12.7	4.89	0.029	139	0.0060	28.4
							0.026	111	0.0054	22.7
II-6	1.3	3.5	driver	5.6	12.7	4.25	0.012	84	0.0028	19.8
							0.011	83	0.0026	19.5
II-7	1.0	4.3	driver (app + inc) <sup>d</sup>	4.8	12.0	3.42	ND	6.7	<0.001	2.0
							ND	5.7	<0.001	1.7
			driver (2nd disking) <sup>e</sup>	2.8	12.3	2.03	ND	0.24	<0.002	0.12
							ND	0.32	<0.002	0.16

<sup>a</sup> Values are corrected for field collection efficiencies. <sup>b</sup> ND = none detected at test sensitivity of 0.005  $\mu\text{g}$ . <sup>c</sup> Trifluralin. <sup>d</sup> Application and incorporation were separate operations; sampling was cumulative. <sup>e</sup> Second disking was carried out 3 days after application.

usual program. In experiment I-1, the product was sprayed onto the soil by a custom applicator with a boom mounted on the rear of a tanker truck. A co-worker then incorporated the herbicide by using a tractor and disk. In experiment I-4, the product was applied by a custom applicator and incorporation was carried out by the farmer and a co-worker using two separate tractor-disk configurations. The breathing zones of all three workers were monitored during their respective operations. In the remainder on the set I tests, application and incorporation were carried out in a simultaneous operation with the spray boom mounted in various positions on the tractor or on the front of the incorporation tool (to the rear with respect to the tractor driver).

No NDPA was detected in eight of the nine set I experiments. The single experiment (experiment I-5) showing a detectable amount of NDPA also showed a relatively high trifluralin value, although two other experiments exhibited higher trifluralin values without exhibiting detectable NDPA levels. Overall, the concentrations of chemicals collected from the air could not be correlated with any specific factor. There appeared to be no dependency on boom position, rate of application, duration of sampling, air and soil temperature, or climatic conditions.

At the conclusion of these nine studies, it was apparent that the techniques employed would have been adequate if the purpose of the tests had been to determine exposure to the herbicide itself but that they were not adequate for the measurement of a contaminant in trifluralin which was present at the 5 ppm level or less. The small, battery-powered pumps were not capable of pulling enough air through a trapping system in an 8-h day to permit a reliable estimation of the contaminant concentration in the air breathed by the applicators. The sampling rate of 1.5 L/min was also much less than the 13.4 L/min which Green (15) and Himes (16) estimated that a man inhales

while driving a tractor. The set II experiments were designed to improve the probability of detecting the contaminant.

**High-Volume Sampling.** A total of seven experiments was conducted with the larger monitoring equipment. The results are presented in Table IV. The sampling rates ranged from 12.0 to 13.3 L/min, which were near the 13.4 L/min suggested as typical inhalation rates for tractor drivers. The front and rear sections of the adsorber tubes were assayed for both NDPA and trifluralin, but the rear sections were all negative, indicating no overloading of the adsorbent. The amounts found in the front sections were corrected for field collection efficiencies to determine the actual quantities collected. The concentrations in the volume of air sampled were then calculated from the amounts collected and the volumes sampled.

The duplication of the analytical results in each experiment was adequate but there was little correlation between the amounts of NDPA observed and the amounts of trifluralin collected. This was probably due to the relative differences in the physical and chemical properties of these two chemicals and indicated that one could not serve as an internal standard for the other.

The fields used in experiments II-1, -2, -5, and -6 were bare and had been cultivated in anticipation of planting cotton the following spring. There was good agreement among the assay results in these four experiments. The NDPA concentration in the breathing zones of the tractor driver ranged from 0.0026 to 0.0060  $\mu\text{g}/\text{m}^3$  with an average of 0.0043  $\mu\text{g}/\text{m}^3$ . For trifluralin, the concentrations ranged from 19.5 to 37.3  $\mu\text{g}/\text{m}^3$  with an average of 26.9  $\mu\text{g}/\text{m}^3$  of air.

The agreement between experiments was not as good in the Arizona tests (experiments II-3 and -4). Experiment II-3 was conducted in a grove of 6-year-old pecan trees while II-4 was carried out in a mature grapefruit grove less than 5 mi from the pecan grove. The same application and

Table V. Analytical Results on Air Monitoring Samples Taken over Treflan-Treated Field for Experiment II-7

sampling period, DAT <sup>a</sup>	total air sampling time, min	air sampling rate, L/min	total vol of air sampled, m <sup>3</sup>	amt found in adsorber, µg		av % collection eff		amt collected µg		air concn, µg/m <sup>3</sup>	
				NDPA <sup>b</sup>	TR	NDPA	TR	NDPA	TR	NDPA	TR
1-2	1440	12.7	18.3	ND	0.95	46	54	<0.011	1.8	<0.0006	0.098
				ND	0.73			<0.011	1.4	<0.0006	0.077
5-7	1380	13.6	18.8	ND	1.2	63	68	<0.008	1.8	<0.0004	0.096
				ND	1.3			<0.008	1.9	<0.0004	0.101
8-9	1440	12.8	18.4	ND	0.31	97	65	<0.005	0.48	<0.0003	0.026
				ND	0.36			<0.005	0.55	<0.0003	0.030

<sup>a</sup> DAT = days after treatment. <sup>b</sup> ND = none detected at a test sensitivity of 0.005 µg of NDPA.

sampling equipment was used in both trials, and the weather conditions were nearly identical. The differences in the results of the two studies defy definitive explanation but are reflective of the difficulty of conducting quantitative studies in a nonlaboratory environment and indicate the need for conducting replicated tests when generating data of this type.

The individual (the mixer) who mixed the herbicide was monitored separately in the two Arizona tests (experiments II-3 and -4) to determine the extent to which this operation contributed to the total exposure during application of the herbicide. The data in Table IV suggest that exposure was higher during the mixing and loading phase, but, since these operations were of short duration relative to the time required for spraying, it only made a small contribution to the total potential exposure.

**Artifact Formation.** Dipropylamine (DPA) was added to tubes on the tractor and at the control site to check for possible artifact formation, i.e., formation of NDPA on the charcoal from its precursors. The possibility of artifact formation had been verified in the laboratory by passing NO<sub>x</sub> through charcoal tubes fortified with DPA and has also been reported by Rounbehler et al. (17). It was also known that the product used in these experiments contained small amounts (0.01–0.02%) of DPA, which presumably would be collected on the charcoal during sampling. It was not known whether there would be any nitrosating agents in the air being sampled. If such agents had been present, the DPA on the charcoal would likely have been nitrated to NDPA and the NDPA level in the DPA-fortified tubes would have been higher than the levels in the unfortified tubes. No such elevated levels were observed in the DPA-containing tubes.

**Extended Monitoring Study.** Experiment II-7 was established to permit the monitoring of air over a Treflan-treated field for an extended period of time to study potential exposure in a reentry situation. The exposure to the driver of the tractor which applied and incorporated the herbicide sequentially is given in Table IV along with the data from the other set II experiments. NDPA was not detected in the air sampling tubes and the trifluralin concentration was found to be 6.2 µg/m<sup>3</sup>. Only 1.8 h was required to apply the herbicide and 3.0 hours for incorporation. Sampling was cumulative during the two operations, and, since the concentration of the chemicals in the air are probably very low during incorporation, the low level of measured exposure was not unexpected. Three days after application, the field was disked again and the air was sampled in the breathing zone of the operator to determine whether nitrosamine and trifluralin in the soil were released by these operations. No nitrosamines were detected, and the concentration of trifluralin was only 0.14 µg/m<sup>3</sup>.

On the day after the field was treated with 1.0 lb/acre of Treflan (1 DAT), four charcoal tubes and a pump were

placed within the treated field. The results from these samplings are presented in Table V. The charcoal tubes were not replaced daily, and the results reflect air concentrations over 2- or 3-day periods. The treated field was disked a second time 3 DAT. One-half inch of rain fell 4 DAT, and no samplings were taken. The field collection efficiencies of NDPA in the 24-h samplings ranged from 46–97% while those for trifluralin were more consistent. No nitrosamines were detected in any of the charcoal adsorbers. The concentrations of trifluralin during DAT 1–2 was 0.088 µg/m<sup>3</sup> and was 0.099 µg/m<sup>3</sup> during the 5–7-DAT period. These values are not significantly different from the 0.14 µg/m<sup>3</sup> observed during the second disk on DAT 3 and are in the same range as that observed by Soderquist et al. (18) above a moist trifluralin-treated field in California. The concentration in the air dropped to 0.028 µg/m<sup>3</sup> during the 8–9 DAT period, probably due to depletion of the trifluralin at the soil surface (19).

#### Summary

The potential inhalation exposure to users of the soil-applied herbicide trifluralin and a nitrosamine contaminant has been determined in field experiments. Sampling air for 6–8 h with portable, battery-powered pumps at the rate of 1.5 L/min permitted the collection of adequate trifluralin for the determination of the concentration of this specific herbicide. However, these small pumps were not adequate for measuring air concentrations of the trace contaminant, NDPA, which was present in the herbicide formulation. Sufficient air was sampled at 13 L/min to permit detection of NDPA in five out of six experiments in which the product used contained from 2 to 6 ppm of the contaminant. The amounts of NDPA collected were about 2–7 times the limit of detection. If the product had contained less than 1 ppm NDPA, as does the trifluralin currently being produced in the US (20), the NDPA in the air would not likely have been detected by using the techniques employed in these studies. But even the more highly contaminated material was deemed to present no significant risk to potential users.

No NDPA was observed in the air above a single trifluralin-treated field for days following application of the product using sampling periods of 24 h. Shorter sampling periods would have been suitable for the determination of trifluralin concentration in the air during this period.

The results of these experiments are indicative of the difficulty of conducting precise quantitative experiments in the field. In spite of the extra precautions taken in these experiments to perform all operations as uniformly as possible and the preserve the integrity of samples, the results were highly variable. Collection efficiencies ranged from 9% to 160%, and the data obtained from nearly identical experiments were not always in agreement. This should be taken into account when using such data to make hazard evaluations.

Acknowledgments

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## Quantitative Analysis of Nitrate Ion in Ambient Aerosols by Fourier-Transform Infrared Spectroscopy

James S. Bogard,<sup>†</sup> Stanley A. Johnson,\* Romesh Kumar, and Paul T. Cunningham

Argonne National Laboratory, Chemical Engineering Division, 9700 S. Cass Avenue, Argonne, Illinois 60439

■ A sensitive, quantitative method has been developed for determining the amount of nitrate ion in atmospheric aerosol samples collected by impaction. This method consists of Fourier-transform infrared absorption spectrophotometry of the sample in a KBr matrix. The nitrate ion can be determined from the absorbance at 1384 and 2430  $\text{cm}^{-1}$ , the two absorption bands covering different ranges of the amount of nitrate in the sample. Using calibration standards prepared from nitrates of ammonium, sodium, potassium, calcium, and magnesium, we determined that the absorbance at 1384  $\text{cm}^{-1}$  is given by  $[(4.63 \pm 0.04) \times 10^{-2}](\mu\text{g of NO}_3^-)$  and the absorbance at 2430  $\text{cm}^{-1}$  is given by  $[(6.87 \pm 0.09) \times 10^{-4}](\mu\text{g of NO}_3^-)$ . With a workable infrared absorbance range of 0.002-1 absorbance units, 0.1-20  $\mu\text{g of NO}_3^-$  can be determined from the absorbance at 1384  $\text{cm}^{-1}$ , and 6-1500  $\mu\text{g of NO}_3^-$  can be determined from the absorbance at 2430  $\text{cm}^{-1}$ . Thus, for most practical work, the  $\text{NO}_3^-$  absorption band at 1384  $\text{cm}^{-1}$  is useful for  $<20 \mu\text{g}$  of nitrate, whereas the 2430- $\text{cm}^{-1}$  absorption band can be used for  $>20 \mu\text{g}$  of the ion. This technique was used with archived samples of atmospheric aerosol collected for an earlier study in the Los Angeles basin; the results showed excellent agreement between the nitrate ion amounts measured by the two absorption bands in the overlapping region.

Nitrate ion is often a major constituent of atmospheric

aerosols, especially in marine and coastal environments. Over Nagoya, a coastal city in Japan, the size distribution of the nitrate fraction of the aerosols has been shown to be bimodal, like that of the total aerosol populations (1), with ammonium nitrate being the dominant species in the submicrometer fraction, and sodium nitrate being dominant in the larger-size particles (2). Up to 30% of the total suspended particulate burden in the air over Los Angeles, CA, has been reported to be inorganic nitrate, principally ammonium nitrate (3). Examination of the infrared spectra of dust samples from arid inland sites, such as south-central New Mexico, also revealed the presence of nitrate ion (about 4% of the total sample was sodium nitrate), presumed to be carried aloft by turbulence at ground level (4). The nitrate ion in ambient aerosols results from natural sources such as sea-salt spray and from anthropogenic sources such as the emissions of nitrogen oxides from fossil-fuel combustion. In urban and industrialized areas, the anthropogenic contribution is believed to be the dominant source of nitrate in the atmosphere. When the nitrate is formed from precursor  $\text{NO}_x$  gases, it is referred to as secondary nitrate, and most of it is present in particles in the accumulation size range of less than  $\sim 3 \mu\text{m}$  in aerodynamic diameter. Thus, if one is interested in secondary nitrate (or sulfate), it is desirable and useful to separate the ambient aerosol into size fractions less than and greater than  $\sim 3 \mu\text{m}$ .

The nitrate ion in aerosol particles is unique when compared to other inorganic species present in ambient aerosols in that the most common nitrate species, ammo-

<sup>†</sup>Present address: Union Carbide Corp., Nuclear Division, P.O. Box Y, Building 9203, Mail Stop 1, Oak Ridge, TN 37830.



nitrate, is a volatile compound which is believed to rapidly establish equilibrium between the gas and the particle phases as the gaseous environment of the particles changes. This equilibrium is affected by the partial pressure of nitric acid and ammonia in the gas, as well as by other factors such as temperature and humidity. The formation of artifact nitrate in filter-sampling techniques, as well as the loss of nitrate from the collected sample as the gas is depleted in nitric acid or ammonia, have been documented (5). Thus, since the nitrate in the particle phase is affected by changes in the environmental conditions, it is desirable to collect aerosol samples with a relatively short time resolution of a few hours, rather than the 24 h of sampling conventionally used with high-volume air filtering techniques. In a typical 24-h period the ambient temperature and the relative humidity vary over a wide range, and the net collected sample may be more a reflection of the environmental conditions at the end of the 24-h period than of a sample integrated over that period.

Quantitative determination of the nitrate ion in aerosol samples is conventionally performed by wet chemical analyses involving extraction followed by a suitable analytical procedure, such as the 2,4-xylene method, use of a specific-ion electrode, etc. (6). These methods generally require a large sample, are time consuming, and involve considerable sample handling and processing. Because of the sample quantity requirements, these methods can not be used for samples collected over a period of only a few hours.

We have previously described (7) a dry procedure in which infrared spectroscopy is used for the analysis of ambient aerosol samples; this procedure substantially reduces sample handling compared to the wet chemical methods and is also applicable to relatively small quantities of the sample material, so that time- and size-resolved samples can be analyzed.

In the earlier paper we identified infrared absorption bands at 1768 and 840  $\text{cm}^{-1}$  as being due to bulk nitrate, and a band at 1384  $\text{cm}^{-1}$  as being due to what was referred to as surface nitrate. In subsequent work, an absorption band at 2430  $\text{cm}^{-1}$  was also identified as being due to the presence of the nitrate ion. In a study of the infrared spectrum of the matrix-isolated nitrate ion, Tsuboi and Hisatsune (8) determined that the absorption at 2430  $\text{cm}^{-1}$  results from a combination of the  $\nu_1$  (symmetric stretching) and  $\nu_3$  (degenerate stretching) modes, that the absorption at 1384  $\text{cm}^{-1}$  derives from the  $\nu_3$  mode, and that the absorption at 840  $\text{cm}^{-1}$  is due to the  $\nu_2$  (out-of-plane deformation) mode. The  $\nu_3$  band (at 1384  $\text{cm}^{-1}$ ) has been observed for a variety of nitrates prepared in KBr pellets, but it is not seen in Nujol or hexachlorobutadiene mulls. The  $\nu_3$  band is believed to result either from nitrate exchange with the halide ion in the KBr matrix or from the formation of a solid solution of the nitrate ion in the KBr when the pellet is pressed (8-11).

In this paper we describe the work conducted in our laboratory to quantify the nitrate ion in standard samples by use of infrared spectroscopy, with particular reference to the absorption bands at 2430, 1384, and 840  $\text{cm}^{-1}$ . We also discuss the application of infrared spectroscopy to the quantitative analysis of the nitrate ion in ambient samples collected in Riverside, CA, for a separate field study conducted for a different program.

#### Experimental Section

Standards were prepared from reagent-grade nitrates of ammonium, sodium, potassium, calcium, and magnesium, mixed with varying quantities of potassium bromide

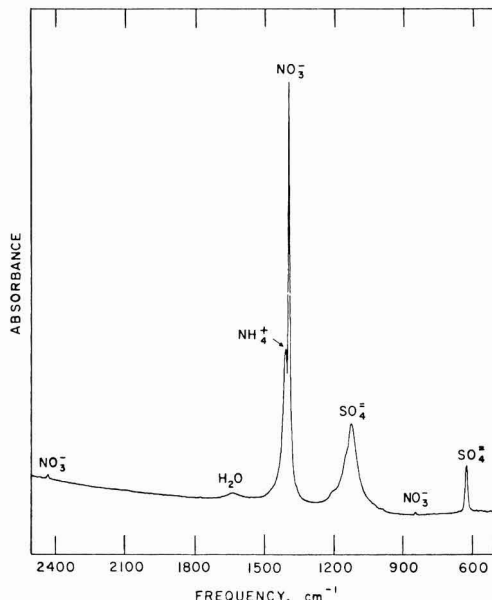


Figure 1. Infrared spectrum from a standard sample containing  $\text{NH}_4\text{NO}_3$  and  $(\text{NH}_4)_2\text{SO}_4$ .

to produce KBr pellets containing known amounts of dispersed nitrate ion. A subset of the ammonium nitrate standards also contained ammonium sulfate (a chemical species commonly present in ambient aerosols). A primary standard was prepared in each case by weighing the nitrate compound directly on a microanalytical balance and subsequently mixing it with a known amount of potassium bromide. The primary standards were then diluted with various amounts of additional KBr and pressed into 13-mm diameter pellets for infrared spectrometric analysis using standard procedures (12).

The infrared spectra of the standard samples were obtained by using a Digilab Model FTS-14 Fourier-transform spectrometer at 8- $\text{cm}^{-1}$  resolution and 20 scans per sample. The digitized spectra were recorded on magnetic tape for subsequent analysis. A computer program FTSEXP was developed in Fortran IV to analyze the infrared spectra for absorption frequencies, peak heights, and peak areas for the nitrate absorption bands at 2430, 1384, and 840  $\text{cm}^{-1}$ , as well as the absorption bands arising from other species commonly present in ambient aerosol samples.

The quantitative analysis was applied to a set of archived samples that had been collected earlier for another program. These samples had been collected with a modified Lundgren cascade impactor sampling air at 0.1  $\text{m}^3 \text{min}^{-1}$ . The modified impactor provided a time resolution of 3 h, and four separate fractions with size resolution of >10, 3-10, 1-3, and 0.3-1  $\mu\text{m}$  aerodynamic diameter particles. Only the size fractions collected on stage III (1-3  $\mu\text{m}$ ) and stage IV (0.3-1  $\mu\text{m}$ ) were analyzed, since these would contain most of the secondary nitrate. These samples had been collected during 3-week-long periods in the fall of 1974 and the winter of 1975.

#### Results and Discussion

The infrared spectrum from a standard sample containing ammonium nitrate and ammonium sulfate (the two species most commonly present in the fine-particle size range of atmospheric aerosols) is shown in Figure 1. The

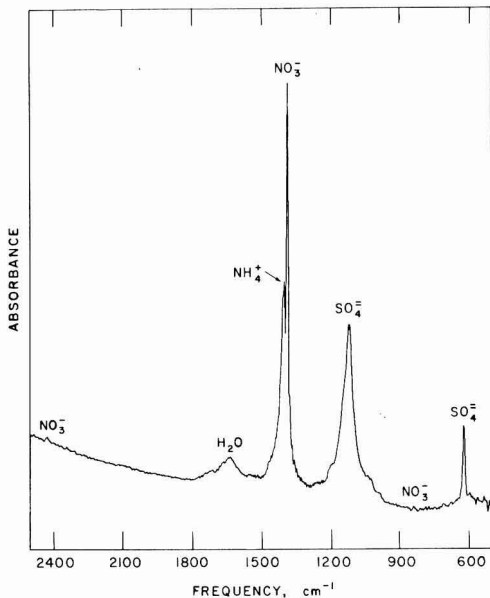


Figure 2. Infrared spectrum of the submicrometer size fraction of the ambient aerosol sample, I-LA3-IV-21.

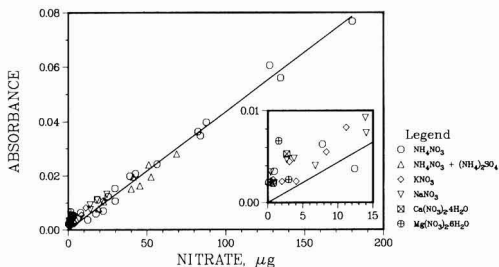


Figure 3. Infrared absorbance at 840  $\text{cm}^{-1}$  vs. the amount of nitrate ion in the standard sample.

nitrate absorption bands at 2430, 1384, and 840  $\text{cm}^{-1}$  are clearly evident. The ammonium absorption band at 1400  $\text{cm}^{-1}$  and the sulfate bands at 620 and 1110  $\text{cm}^{-1}$  are also present in the spectrum. Figure 2 shows the infrared spectrum obtained from a sample of the submicrometer-sized aerosol collected in Riverside, CA. As in the case of the spectrum from the laboratory standard, the nitrate bands at 840, 1384, and 2430  $\text{cm}^{-1}$ , and the sulfate bands at 620 and 1110  $\text{cm}^{-1}$  can be seen in the spectrum from the atmospheric sample.

A total of 67 standard samples were prepared, of which 35 contained ammonium nitrate, 12 contained sodium nitrate, and 11 were prepared with potassium nitrate, 5 with calcium nitrate, and 4 with magnesium nitrate. Of the 35 ammonium nitrate standards, 8 also contained varying amounts of ammonium sulfate.

Figures 3-5 show plots of the infrared absorbance (peak height) at 840, 1384, and 2430  $\text{cm}^{-1}$  vs. the amount of the nitrate ion present in the standard samples. As evident from these figures, the absorbance for each of the three bands was directly proportional to the amount of the nitrate ion present. It was determined that the peak height was a more reliable measure of the nitrate ion than the

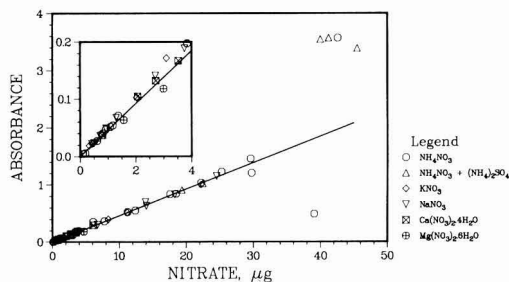


Figure 4. Infrared absorbance at 1384  $\text{cm}^{-1}$  vs. the amount of nitrate ion in the standard sample.

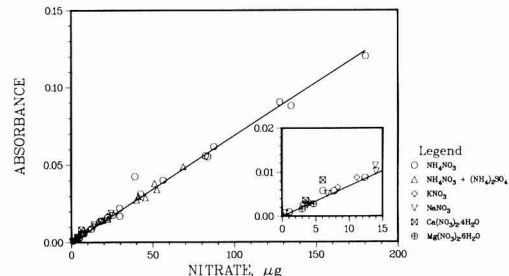


Figure 5. Infrared absorbance at 2430  $\text{cm}^{-1}$  vs. the amount of nitrate ion in the standard sample.

peak area. Regression analysis of the data led to the following expressions for absorbance (A):

$$A_{840} = [(4.36 \pm 0.07) \times 10^{-4}] (\mu\text{g of NO}_3^-) \quad (1)$$

$$A_{1384} = [(4.63 \pm 0.04) \times 10^{-2}] (\mu\text{g of NO}_3^-) \quad (\text{for NO}_3^- < 30 \mu\text{g}) \quad (2)$$

$$A_{2430} = [(6.87 \pm 0.09) \times 10^{-4}] (\mu\text{g of NO}_3^-) \quad (3)$$

The correlation coefficients for the above expressions are 0.993, 0.998, and 0.997, respectively. In each case, the correlation coefficient is greater than the corresponding  $R_{\text{test}}$  for a 99.99% confidence level. The solid lines in Figures 3-5 represent these linear regressions. Comparison of these three figures at low values of nitrate shows that, for the absorption band at 840  $\text{cm}^{-1}$ , there is more error than is the case for the other two bands. In Figure 4, only the data for samples containing less than 30  $\mu\text{g}$  of nitrates were used for the regression fit, since higher amounts of nitrate lead to absorbance values of  $>1.4$ , making the interpretation of the spectra unreliable for the 1384- $\text{cm}^{-1}$  absorption band. Data from samples containing more than 50  $\mu\text{g}$  of nitrate are not shown in Figure 4. Figure 5, which illustrates the absorbance at 2430  $\text{cm}^{-1}$  vs. the amount of nitrate, shows a very good linear correlation of the data. Finally, it may be noted from these three figures that the absorbance at each of the three nitrate bands is independent of the associated cation.

With a typical noise level of 0.002 absorbance units in the infrared spectra, and a minimum signal-to-noise ratio of 2, the limit of the detection of nitrate for the three bands is as follows: 2430  $\text{cm}^{-1}$ , 6  $\mu\text{g}$  of  $\text{NO}_3^-$ ; 1384  $\text{cm}^{-1}$ , 0.1  $\mu\text{g}$  of  $\text{NO}_3^-$ ; 840  $\text{cm}^{-1}$ , 9  $\mu\text{g}$  of  $\text{NO}_3^-$ . With an assumed maximum workable absorbance of 1 absorbance unit (equivalent to 90% absorption of the incident infrared light) for any of these bands, the largest amount of nitrate in the sample that can be analyzed from these bands is as follows:

2430  $\text{cm}^{-1}$ , 1500  $\mu\text{g}$  of  $\text{NO}_3^-$ ; 1384  $\text{cm}^{-1}$ , 22  $\mu\text{g}$  of  $\text{NO}_3^-$ ; 840  $\text{cm}^{-1}$ , 2300  $\mu\text{g}$  of  $\text{NO}_3^-$ . Thus, the absorption band at 1384  $\text{cm}^{-1}$  provides a sensitive indicator for nitrate ion present at low concentrations, down to submicrogram levels, whereas the absorption bands at 840 and 2430  $\text{cm}^{-1}$  can be used to determine milligram quantities of nitrate in the sample. Using the three bands, therefore, the infrared spectrometric technique can cover a nitrate concentration range of 4 orders of magnitude.

#### Effect of Sample Aging on the Absorbance at 1384 $\text{cm}^{-1}$

Hoidale and Blanco (4) reported that the absorbance at 1384  $\text{cm}^{-1}$  was not reproducible for synthetic dust samples and that this absorbance apparently changed as the sample aged. Although there was not enough information in their report to assess the reason for the nonreproducibility of their spectra, we have found that the absorbance in our pressed pellets of  $\text{KNO}_3$  and  $\text{NaNO}_3$  standards changed slowly with time and that the rate of this change was both time and concentration dependent. For the potassium nitrate standard

$$\Delta A = (4.88 \pm 0.87) \times 10^{-4} \text{ day}^{-1} \text{ ppm}^{-1} \quad (4)$$

and for sodium nitrate

$$\Delta A = (1.64 \pm 0.59) \times 10^{-4} \text{ day}^{-1} \text{ ppm}^{-1} \quad (5)$$

where  $\Delta A$  is the change in absorbance at 1384  $\text{cm}^{-1}$ , and ppm is the nitrate fraction in KBr in parts per million by weight. Data for the other nitrates used to prepare the standards indicate that their rate of change of absorbance at 1384  $\text{cm}^{-1}$  was of the same order as, or perhaps less than, the values given above.

#### Spectrometric Analysis of Nitrate in Riverside, CA, Samples

We had on hand several samples of the ambient aerosol collected in Riverside, CA, in the course of an earlier field study. These samples had been collected by using a modified Lundgren cascade impactor, as described in the Experimental Section. Since these samples were collected in a time- and size-classified manner, they generally contained only microgram quantities of the nitrate ion. However, the samples did contain widely varying amounts of the nitrate ion, and the absorbance at 1384 and 2430  $\text{cm}^{-1}$  could be used to compare the relative absorbances of the field samples with those of the laboratory standards. (In our work, the nitrate band at 840  $\text{cm}^{-1}$  is not used for analysis of field samples because of interference from other atmospheric species in the 840- $\text{cm}^{-1}$  region of the infrared spectrum.) Of the total set of 223 samples collected in Riverside, the 122 samples that could be used for this comparison are listed in the supplementary table. (See paragraph at end of text regarding supplementary material.) Not included in that table are samples for which either the absorbance at 2430  $\text{cm}^{-1}$  was very low or the absorbance at 1384  $\text{cm}^{-1}$  was greater than about 3 (well above the normal working range referred to earlier). Included in the supplementary table are the absorbances at 1384 and 2430  $\text{cm}^{-1}$ , as well as the amounts of nitrate ion computed from the two absorbances by using the regression correlations listed above. The sampling date, the sampling start time, the sample weight (of the specific size fraction), the amount of ammonium ion, and the weight percent of nitrate in the samples are also given in the table.

Figure 6 shows the nitrate values computed from the two absorption bands plotted against each other for all of the samples listed in the supplementary table. The solid line

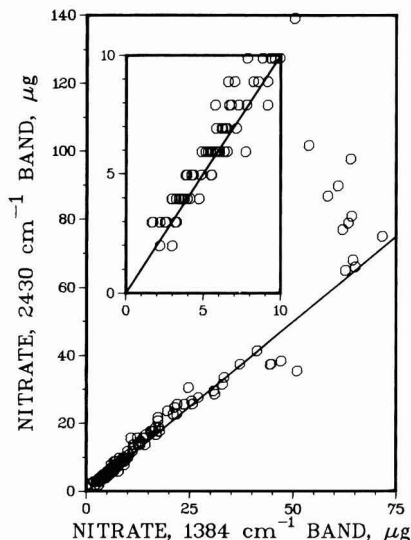


Figure 6. Nitrate in the samples from Riverside, CA, determined by the absorbances at the 1384- and 2430- $\text{cm}^{-1}$  bands.

in Figure 6 shows where the data should lie if the correspondence between the two absorption bands were exact. As is evident from Figure 6, there is good agreement between the nitrate values calculated from the absorbance at the 1384- and 2430- $\text{cm}^{-1}$  bands for samples containing less than about 40  $\mu\text{g}$  of the nitrate ion. For samples containing more nitrate, the correlation between the two bands breaks down, as may be expected from the results on the standard samples shown in Figures 4 and 5. However, even for samples containing between 5 and 30  $\mu\text{g}$  of nitrate, the range in which both bands should give similar values for the nitrate ion, the 2430- $\text{cm}^{-1}$  band gives a nitrate value about 10% higher than the nitrate value computed from the 1384- $\text{cm}^{-1}$  band. This is also evident from the last column of the supplementary table, which shows the relative deviation between the nitrate values calculated by the absorbance at 1384 and 2430  $\text{cm}^{-1}$ . A reexamination of the spectra of the standard samples did not reveal any significant bias between the two bands. The bias in the field samples probably results from interferences from other infrared-active species present in the ambient samples.

#### Conclusion

Analysis of synthetic samples prepared in the laboratory as well as samples obtained in the field shows that the mass of the nitrate ion in aerosol samples can be determined quantitatively by infrared spectroscopy. In these samples the absorbance at 1384  $\text{cm}^{-1}$  can be used effectively down to a nitrate content of about 0.1  $\mu\text{g}$ , whereas absorbance at 2430  $\text{cm}^{-1}$  can be used to measure milligram quantities of nitrate. By using Fourier-transform infrared spectroscopy on samples in KBr pellets, we have demonstrated that precise quantitative measurements of nitrate ion can be made in field samples containing variable amounts of nitrate. With this procedure, sample preparation and handling is considerably reduced over that for other analytical procedures. This method has special applicability in the examination of size- and time-resolved samples of the ambient aerosol, where only small amounts of sample material are generally available for analysis, and which may not be amenable to wet chemical analytical methods. Also

this procedure is generally faster than the conventional wet chemical processes.

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We are grateful to Drs. John Ferraro and David Green, both of Argonne National Laboratory, for the many useful discussions held with them and to Ms. Carol Steen, who initially conducted the laboratory work on the nitrate standards and assisted in the analysis of the field samples from Riverside, CA. We also appreciate the help of Oscar Hellrich of the California Statewide Air Pollution Research Laboratory for his assistance in collecting the aerosol samples in Riverside.

*Supplementary Material Available*

Table 1, listing sample absorbances at 1384 and 2430 cm<sup>-1</sup>, the amounts of nitrate ion computed from the two absorbances by using the regression correlations in the text, sampling dates, sampling starting times, sample weights, amounts of ammonium ion, and the weight percent of nitrate in the samples (3 pages), will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper or microfiche (105 × 148 mm, 24 × reduction, negatives) may be obtained from Business Operations, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, DC 20036. Full bibliographic citation (journal, title of article, author) and prepayment, check or money order

for \$3.00 for photocopy (\$4.50 foreign) or \$4.00 for microfiche (\$5.00 foreign), are required.

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## Multitechnique Screening of Chicago Municipal Sewage Sludge for Mutagenic Activity

Phillp K. Hopke,\* Michael J. Plewa,† James B. Johnston,† Danny Weaver,† Susanne G. Wood,† Richard A. Larson,† and Thomas Hlmesly‡

Institute for Environmental Studies and Department of Agronomy, University of Illinois, Urbana, Illinois 61801

■ A sample of anaerobically digested Chicago municipal sewage sludge has been examined for mutagenicity by using a variety of biological assays with different genetic end points. The sludge clearly contains components that induce mutagenic responses in all of the species employed. Acetone extracts from the equivalent of 155 μL of neat sludge induced a doubling in the number of revertant colonies of the Ames *Salmonella typhimurium* strain TA98 after activation with mammalian microsomes. In situ and laboratory studies indicate the induction of point mutations in the germ cells of *Zea mays*. Cytogenetic damage was demonstrated by the increased frequency of micronuclei observed in meiotic cells of *Tradescantia paludosa*.

*Introduction*

A major problem facing the United States is the disposal of the sludge resulting from the treatment of municipal sewage. There has been a substantial increase in the number and efficiency of sewage treatment plants in the past decade particularly in suburban and rural areas resulting in an increased amount of sludge requiring disposal. In addition, previously employed sludge disposal methods such as ocean dumping are soon to be severely limited or

stopped entirely. The incineration of sludge requires expensive facilities and may result in increased air pollution. An attractive alternative disposal method is the application of this organic matter to agricultural lands or its use in the reclamation of land stripped of its organic matter by surface mining.

There may, however, be problems associated with sludge disposal by land application. Analyses of sludge from the Calumet and Southwest treatment plants of the Metropolitan Sanitary District of Chicago showed that concentrations of several heavy metals were substantially enriched over typical soil compositions. Thus, in 1967, a large demonstration and research program was initiated to examine the feasibility of land application of digested sewage sludge from the Metropolitan Sanitary District of Chicago waste water treatment plants. A major objective was to examine compositional changes in soil, crops, and water arising from sludge-amended fields.

In the intervening period, there has been a great deal of study of the uptake and accumulation of heavy metals (most notably zinc and cadmium) in corn, the effects of these elements on soil bacteria, and the potential for transmission of heavy metals through a food chain that might result in impacts on the general public health if widespread use were made of sludge as a soil additive (1-6). It has been found that zinc and cadmium accumulate in corn grain and leaf tissues (5, 6). High levels of sludge treatment appear to inhibit the development of several inbred strains of corn but do not cause overt symptoms

\* Address correspondence to this author at the Institute for Environmental Studies, University of Illinois, Urbana, IL 61801.

† Institute for Environmental Studies.

‡ Department of Agronomy.

of metal toxicity (6). Long-term studies of food-chain and field productivity effects of sludge are in progress.

Additional contaminants that may be present in municipal sewage sludge are organic compounds from industrial processes or other anthropogenic activities. Of potential concern are compounds that are genetically active and may cause mutations, birth defects, or cancer. In a metropolitan area like Chicago there are major chemical, petrochemical, petroleum-refining, and other industries that utilize organic chemicals in large quantities. Other activities such as fossil-fuel combustion produce genotoxic compounds that may find their way into the sanitary sewer system. Therefore, there exists the possibility that there are genotoxic compounds present in the sewage sludge that may be released into the environment by leaching into surface water or groundwater or incorporated into the human food chain through the use of sewage sludge as a soil additive. In order to examine this question, a sample of Chicago sewage sludge from the Southwest treatment plant of the Chicago Metropolitan Sanitary District at Stickney, IL, was obtained from the storage tanks of the University of Illinois Agronomy Research Center at Elwood, IL, where it is stored before being applied to the fields. This sludge sample was a composite of the sludge received at Elwood during the period from November 1978 to July 1979. This sludge has been subjected to a multiorganism screening procedure to determine whether mutagenic compounds are present in sludge and sludge-amended soil.

#### Microbial Assay

**Methods and Materials.** The *Salmonella*/microsome reversion assay employing Ames tester strains TA98 and TA100 was conducted by using the top agar incorporation procedure described by Ames et al. (7), incorporating the recommendations of deSerres and Shelby (8). TA98 and TA100 are the most widely used strains because together they are the most sensitive and they respond to the widest range of chemical types. The overnight cultures had densities of approximately  $2 \times 10^9$  cells/mL, and the spontaneous reversion frequencies of each strain were within their acceptable range (8). The strains were periodically tested for their genetic markers as prescribed by Ames et al. (7). Positive controls for the S-9 activated samples were run by using benzo[*a*]pyrene (BaP). The slopes of the linear dose-response curves in revertants per gram of BaP averaged 221 and 344 for TA98 and TA100, respectively. The hepatic S-9 fraction was prepared as described by Ames et al. (7) from male Sprague-Dawley rats induced with Aroclor 1254. The purpose of adding S-9 to the assay is to simulate mammalian metabolism of test compounds and, in particular, to detect promutagens, compounds that become mutagenically active as a result of metabolism. There is a wide range of response of the Ames strains to a given quantity of mutagenic compound. As shown by Johnston and Hopke (9), the response per unit weight varies over 6 orders of magnitude so that a small response may be the result of a large quantity of a weak mutagen or a small quantity of a potent agent. Also, a weak response is not an indication that a sample is harmless. There are potent carcinogens such as the nitrosamines that show low activity in the Ames strains. This difference in sensitivity emphasizes the need for a multiorganism testing approach as used in this study. The lack of a quantitative relationship between the mutagenic activity in the Ames assay and carcinogenic potency in animal cancer bioassays is also widely recognized as indicated by the use of the Ames strains as the first tier of genetic toxicology tests recommended by the U.S. Envi-

ronmental Protection Agency (10). It recognizes the excellent qualitative response of the Ames assay to mutagens, and this screening is used to *qualitatively* separate chemicals needing further examination in other genetic assays. The Ames strains are relevant and useful in evaluating the possible presence of mutagenic activity in complex environmental mixtures, but it does not tell whether a sample is a threat to humans. That relationship requires identification of the active components and carcinogenicity testing.

**Sludge Fractionation.** Sixteen liters of sewage sludge was centrifuged at 12500 rpm in a Sorvall GSA rotor (maximum 25 400g) for 60 min. One liter of the supernatant liquid was filter sterilized by passing through a 0.45- $\mu$ m Millipore filter (fraction A1). Another 2 L of supernatant liquid was passed through a column of XAD-2 resin previously cleaned as recommended by Junk et al. (11). The column was eluted with 200 mL of methanol (fraction A2a) and then with 200 mL of diethyl ether (fraction A2b). Two milliliters of dimethyl sulfoxide ( $\text{Me}_2\text{SO}$ ) was added to each eluate. The eluates were reduced in volume on a rotovac until only the  $\text{Me}_2\text{SO}$  solution remained. In addition, 10 L of supernatant was concentrated 100-fold by vacuum distillation at 30 °C (fraction A3). Each of these samples was tested for mutagenicity in the TA98 and TA100 strains with and without S-9 activation except for fraction A3. Fraction A3 was highly contaminated with bacteria and could not be filter sterilized because of its high viscosity.

The 2.5-kg solid pellet was extracted 3 times with two volumes of acetone, and the extracts were pooled (fraction E1). The residue was extracted 3 times with one volume of *n*-hexane, and these extracts were pooled (fraction E2). Fifteen milliliters of  $\text{Me}_2\text{SO}$  was added to both the acetone and hexane extracts, and each extract was concentrated as before. It was necessary to lyophilize fraction E1 to remove the residual water sequestered from the solid by the acetone. These solutions were filter sterilized and assayed for mutagenicity as described above.

To determine the amount of mutagenic activity recovered by the acetone extraction, another 100 g of pellet obtained from a different subsample of sludge was extracted 3 times with 200 mL of acetone. The extracts were tested separately as fractions F1, F2, and F3. The weight of material dissolved in each fraction was measured by evaporation of 200- and 500- $\mu$ L aliquots to dryness in a desiccator. The residue remaining was weighed, and the concentration of acetone-soluble material in each fraction was calculated. Fifty milliliters of each fraction was dried over anhydrous sodium sulfate. Five milliliters of  $\text{Me}_2\text{SO}$  was added, and each fraction was concentrated as before.

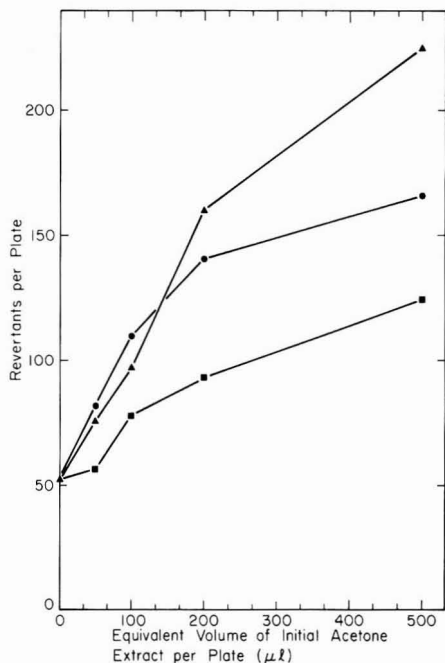
**Results.** The mutagenic activities of the aqueous supernatant liquids are shown in Table I. Fractions A1 and A2b did not show the presence of any direct-acting mutagens. Fraction A2a evoked equivocal response in strain TA98 with S-9 activation and in TA100 without activation. Therefore, no appreciable mutagenic activity was associated with the aqueous supernatant liquid.

The examination of the extracts of the sludge pellet are also presented in Table I. Direct acting mutagens were not detected in extracts E1 or E2 (data not shown). With the addition of the S-9 mix, these fractions became mutagenic. The equivalent of 0.6  $\mu$ L of E1 produced an approximate doubling in the number of revertant colonies per plate. The unusual dose-response behavior of extract E2 should be noted. The elevated but flat response of the assay to this fraction precluded estimation of a reliable doubling dose. This dose-response behavior illustrates the

**Table I. Mutagenicity of Pooled Extracts of Municipal Sewage Sludge Using Strains TA 98 and TA 100**

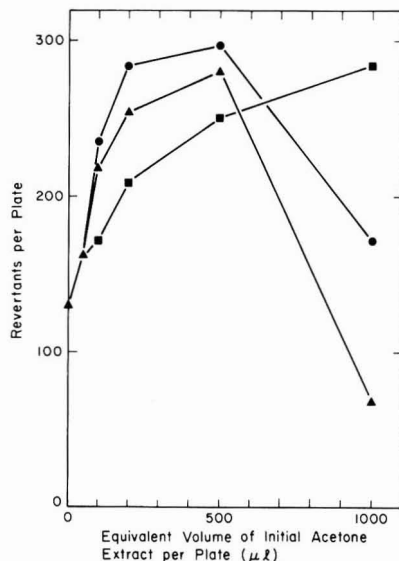
sample	sludge extracts					revertants per plate <sup>c</sup>			
	volume per plate, $\mu$ L	dilution factor	equiv vol per plate, $\mu$ L	concn factor (v/v)	equiv vol of neat sludge per plate, $\mu$ L	TA 98		TA 100	
						-S-9	+S-9	-S-9	+S-9
Me <sub>2</sub> SO E1	100						57 $\pm$ 23 <sup>a</sup>		
	10	0.02	0.2	325	65		89 $\pm$ 17		
	20	0.02	0.4		130		100 $\pm$ 15		
	30	0.02	0.6		195		131 $\pm$ 17		
	40	0.02	0.8		260		133 $\pm$ 19		
E2	50	0.02	1.0		325		136 $\pm$ 21		
	10	0.1	1.0	260	260		89 $\pm$ 24		
	20	0.1	2.0		520		103 $\pm$ 25		
	30	0.1	3.0		780		109 $\pm$ 21		
	50	0.1	5.0		1300		117 $\pm$ 29		
water A1	100	0.1	10.0		2600		100 $\pm$ 12		
	2000					60 $\pm$ 5 <sup>b</sup>	80 $\pm$ 6	155 $\pm$ 3	184 $\pm$ 8
	100		100	1.25	125	69 $\pm$ 7	86 $\pm$ 10	165 $\pm$ 10	192 $\pm$ 8
	300	1.0	300		375	63 $\pm$ 1	90 $\pm$ 2	167 $\pm$ 18	192 $\pm$ 4
	2000	1.0	2000		2500	67 $\pm$ 20	79 $\pm$ 6	161 $\pm$ 4	174 $\pm$ 2
Me <sub>2</sub> SO A2a	100					31 $\pm$ 1	70 $\pm$ 21	115 $\pm$ 7	130 $\pm$ 7
	50	0.1	5	125	625	37 $\pm$ 1	72 $\pm$ 11	131 $\pm$ 16	103 $\pm$ 10
	100	0.1	10		1250	29 $\pm$ 1	59 $\pm$ 13	143 $\pm$ 17	114 $\pm$ 4
	20	1.0	20		2500	35 $\pm$ 8	55 $\pm$ 9	146 $\pm$ 2	140 $\pm$ 17
	50	1.0	50		6250	39 $\pm$ 0	60 $\pm$ 23	140 $\pm$ 40	146 $\pm$ 2
A2b	100	1.0	100		12500	37 $\pm$ -	95 $\pm$ 45	173 $\pm$ 8	154 $\pm$ 6
	50	0.1	5	125	625	29 $\pm$ 2	44 $\pm$ 15	115 $\pm$ 9	108 $\pm$ 13
	100	0.1	10		1250	35 $\pm$ 1	50 $\pm$ 3	139 $\pm$ 24	125 $\pm$ 25
	20	1.0	20		2500	42 $\pm$ 5	55 $\pm$ 13	127 $\pm$ 18	135 $\pm$ 7
	50	1.0	50		6250	36 $\pm$ 6	nd	156 $\pm$ 6	153 $\pm$ 17
100	1.0	100		12500	41 $\pm$ 1	nd	146 $\pm$ 12	148 $\pm$ 17	

<sup>a</sup> Data are derived from triplicate platings. <sup>b</sup> Data are derived from duplicate platings. <sup>c</sup> Mean  $\pm$  standard deviation. nd = not determined.



**Figure 1.** Mutagenicity in strain TA 98 on an equivalent volume of acetone extract basis for the three sequential extractions of the sewage sludge pellet following activation with S-9: (▲) first extraction (F1); (●) second extraction (F2); (■) third extraction (F3).

difficulties of analyzing complex mixtures and indicates the need for further fractionation to resolve the active compounds. The equivalent amount of original sludge



**Figure 2.** Mutagenicity in strain TA 100 on an equivalent volume of acetone extract basis for the three sequential extractions of the sewage sludge pellet following activation with S-9: (▲) first extraction (F1); (●) second extraction (F2); (■) third extraction (F3).

required to double the number of TA98 colonies per plate is 155  $\mu$ L for fraction E1.

The successive extraction of mutagenic compound(s) by acetone from the sludge pellet is presented in Table II. The dose-response curves for the three fractions assayed with TA98 and TA100 are shown in Figures 1 and 2, respectively. The response of an organism to a pure muta-

Table II. Mutagenicity of Three Sequential Acetone Extractions of Sewage Sludge Pellet

sample	vol per plate, $\mu$ L	concn factor	equiv vol per plate, $\mu$ L	concn, mg/mL	mass per plate, mg	revertants per plate <sup>c</sup>	
						TA 98 + S-9	TA 100 + S-9
Me <sub>2</sub> SO	100					52 $\pm$ 6 <sup>a</sup>	130 $\pm$ 7 <sup>b</sup>
F1	50	1	50	2.1	0.1	76 $\pm$ 6	162 $\pm$ 12
	100	1	100	2.1	0.2	97 $\pm$ 9	218 $\pm$ 11
	20	10	200	2.1	0.4	160 $\pm$ 11	254 $\pm$ 1
	50	10	500	2.1	1.0	255 $\pm$ 28	280 $\pm$ 3
	100	10	1000	2.1	2.1	nd	68 $\pm$ 23
F2	50	1	50	7.3	0.4	83 $\pm$ 1	164 $\pm$ 4
	100	1	100	7.3	0.7	110 $\pm$ 20	235 $\pm$ 24
	20	10	200	7.3	1.5	144 $\pm$ 30	284 $\pm$ 1
	50	10	500	7.3	3.7	164 $\pm$ 7	297 $\pm$ 20
	100	10	1000	7.3	7.3	nd	172 $\pm$ 13
F3	50	1	50	23.9	1.2	57 $\pm$ 6	166 $\pm$ 18
	100	1	100	23.9	2.4	78 $\pm$ 9	171 $\pm$ 13
	20	10	200	23.9	4.8	93 $\pm$ 11	208 $\pm$ 14
	50	10	500	23.9	12.0	124 $\pm$ 13	253 $\pm$ 11
	100	10	1000	23.9	23.9	nd	287 $\pm$ 35

<sup>a</sup> Data are from triplicate platings. <sup>b</sup> Data are from duplicate platings. <sup>c</sup> nd indicates that a value was not determined.

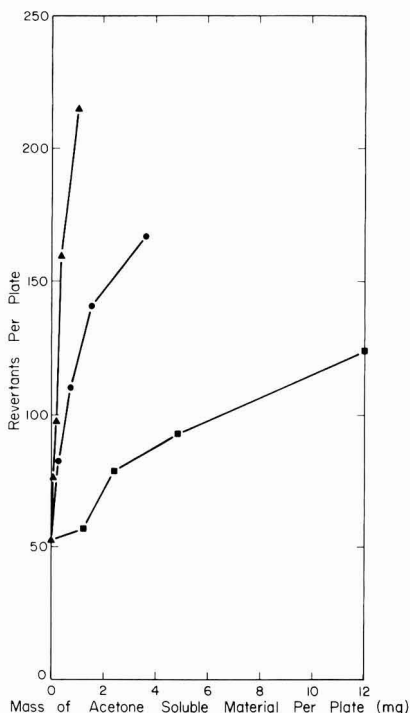


Figure 3. Mutagenic response in strain TA 98 against the mass of acetone-soluble material from the three sequential extractions of the sludge pellet following activation with S-9: (▲) first extraction (F1); (●) second extraction (F2); (■) third extraction (F3).

genic compound would follow a curve where the number of mutational events observed increases with increasing concentration to the point where on the average one lethal mutation per organism is occurring. From that point there will be a decline in response due to the accumulation of deleterious mutations leading to the killing of the test organism. In complex mixtures such as these extracts, there can also be direct toxicity to the organism superimposed on the mutagenic response curve leading to declining events with increasing concentration at a lower applied dose. As reflected by the initial slopes in Figures 1 and 2, the mutagenic activity recovered in fractions F1 and F2

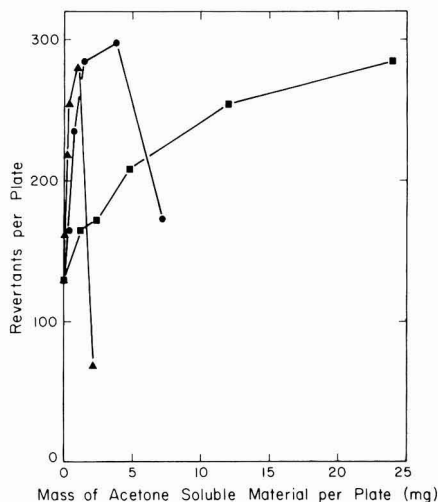


Figure 4. Mutagenic response in strain TA 100 against the mass of acetone-soluble material from the three sequential extractions of the sludge pellet following activation with S-9: (▲) first extraction (F1); (●) second extraction (F2); (■) third extraction (F3).

are roughly the same for both TA98 and TA100. The mutagenic activity present in F3 was less than in fractions F1 and F2. When assayed with TA100, fractions F1 and F2 are more toxic per volume of extract than fraction F3 since there are lower numbers of revertant colonies observed for the higher doses assayed. It, therefore, appears that the majority of the mutagenic activity was recovered in the first two extractions of the pellet. The third extraction did not increase the recovery of these mutagenic substances. However, the amount of the pellet dissolved by the acetone increased in each successive extraction as shown in Table II. Therefore, the amount of mutagenic activity per milligram of acetone-soluble material decreased with each extraction as shown in Figures 3 and 4 for TA98 and TA100, respectively. It is apparent that fraction F1 had the highest mutagenicity-to-mass ratio of the three fractions.

#### Maize wx Locus Assay

**Background.** The waxy (*wx*) locus is located on chromosome 9 of *Zea mays* at map position 9-59 (12). The

Table III. History of the NW900 Plots at the University of Illinois Agronomy Research Center

yr	treatment
1968	Plots received 61.06 Mton/ha sludge solids.
1969	Plots planted to kenaf, received 41.48 mton/ha sludge solids.
1970	0.5 gal/ha Eptam 6E was applied and disked into the soil. Alfalfa was seeded. 32 g of dalapon (Dowpon) in 1.5 gal of water/ha was applied to the sludge plots. Plots received 28.38 Mton/ha sludge solids.
1971	No sludge applied. Plots in alfalfa. Dowpon sprayed on grassy areas for grass control.
1972	Plots in alfalfa. Plots received 12.16 Mton/ha sludge solids.
1973	Plots in alfalfa. Plots received 20.77 Mton/ha sludge solids.
1974	No crop. Plots received 46.21 Mton/ha sludge solids.
1975	No sludge applied. Plots in alfalfa.
1976	No sludge applied. Plots in spinach.
1977	No sludge applied. Plots in spinach.
1978	No sludge applied. Plots in spinach.
1979	Plots 5, 13, 14, and 15 used in the maize <i>wx</i> locus assay.

Table IV. Summary of Data for Maize *wx* Reversion in the in situ Tests

expt no.	no. of mutant pollen grains	no. of viable pollen grains	% abortion	frequency of mutant pollen grains	$\phi$ statistic
<i>wx-C</i> Inbred M14					
control	37	1 267 963	19.4	$2.9 \times 10^{-5}$	
1/4 max sludge	17	1 052 855	36.5	$1.6 \times 10^{-5}$	-2.18, $p > 0.01$
1/2 max sludge	5	1 429 642	46.5	$3.5 \times 10^{-6}$	-5.49, $p > 0.001$
max sludge	6	1 299 568	49.9	$4.6 \times 10^{-6}$	-4.96, $p > 0.001$
<i>wx-90</i> Inbred M14					
control	2	1 266 242	27.9	$1.6 \times 10^{-6}$	
1/4 max sludge	2	1 268 930	26.6	$1.6 \times 10^{-6}$	-0.50, $p > 0.05$
1/2 max sludge	4	1 256 245	29.9	$3.2 \times 10^{-6}$	0.42, $p > 0.05$
max sludge	22	1 212 922	28.2	$1.8 \times 10^{-5}$	3.98, $p > 0.001$

*wx* locus controls the synthesis of the starch amylose. Pollen grains (microgametophytes) are functional haploids, and they express their genetic constitution rather than that of their parental sporophyte. A pollen grain that carries a dominant allele (*Wx*) can synthesize amylose as part of its starch component. Amylose when reacted with iodine turns a dark blue-black color (13), and *Wx* grains will therefore stain blue-black. A pollen grain that carries the recessive allele (*wx*) cannot synthesize amylose and will appear tan when reacted with iodine. Thus, the color of the pollen grain after staining with iodine gives a clear indication of its genotype. Thus, genetic reversion of *wx* to *Wx* can be quantitatively determined by counting the number of black stained pollen grains within the field of tan stained grains. In the forward mutation assay, *Wx* to *wx*, tan stained forward mutant grains are counted in a field of black stained pollen grains. In each case the frequency of mutant pollen grains is determined by counting individual mutant grains and estimating the number of viable pollen grains by counting the number present in 20 randomly selected 1-mm<sup>2</sup> areas and multiplying by the slide area. The use of the maize *wx* locus assay in situ and laboratory studies of mutagenesis have been reviewed by Plewa (14) and Plewa and Wagner (15).

It can be determined whether there are statistically significant increases in the frequencies of mutant pollen grains between the control and treatment groups by using the  $\phi$  statistic described by Katz (16). Katz has adapted the test specifically for the pollen grain assay (17). The test statistic,  $\phi$ , is defined by

$$\phi = \frac{n(M - 0.5) - N(m + 0.5)}{[nN(m + M)]^{1/2}}$$

where *m* is the observed number of mutant pollen grains in the control group, *M* is the observed number of mutant grains in a treatment group, *n* is the estimated number of

pollen grains analyzed in the control group, and *N* is the estimated number of pollen grains in the treatment group. A one-tailed test for a 0.05 level of significance would be obtained for  $\phi > 1.64$ .

**In Situ Studies. Materials and Methods.** An in situ study of the possible mutagenic effects of municipal sewage sludge was conducted between May and August 1979. Test plots were constructed on the NW900 plots at the University of Illinois Agronomy Research Center near Elwood, IL. A history of these plots covering the period 1968-1979 is presented in Table III. If in situ studies are to be valid, it is important to know the past history of such plots since prior application of mutagenic substances could seriously interfere with the planned studies. It is particularly important to know that the sample and control areas have the same history so that the controls properly reflect the base conditions of the study.

*Z. mays* kernels of inbred M14 homozygous for either the *wx-C* or the *wx-90* allele obtained from the maize nursery of M. Plewa were siblings and were inbred for over 12 generations to ensure a high level of isogeneity. One row of each allele type was planted in a control plot and in each of three treatment plots. The maximum treatment group received 17.8 cm of liquid sludge equivalent to 21.0 Mton/ha of dry material over the growing season. The other treatment groups received one-half and one-quarter of this amount, respectively. The control plot received adequate nutrients by the application of chemical fertilizer. No insecticides or herbicides were applied to these plots.

The plants grew until early anthesis when each tassel was individually labeled, harvested, and stored in 70% ethanol for subsequent analysis. Pollen grains were removed from the tassels and analyzed as described by Plewa (14). The frequency of revertant pollen grains was determined by dividing the total number of revertant grains by the total number of viable pollen grains. The percentage of clear, collapsed, aborted pollen grains was also



Table V. Forward Mutation at the Maize *wx* Locus Induced by Chicago Sewage Sludge

treatment	no. of mutants	no. of pollen grains analyzed	% pollen abortion	frequency of mutant pollen grains	$\phi$ statistic
control	34	788 000	13.3	$4.3 \times 10^{-5}$	
low (1/12) concn	7585	825 000	17.1	$9.2 \times 10^{-3}$	$p < 0.001$
medium (1/6) concn	5650	898 000	20.4	$6.4 \times 10^{-3}$	$p < 0.001$
high (1/3) concn	1776	836 000	19.9	$2.1 \times 10^{-3}$	$p < 0.001$

determined by estimating the number of aborted pollen grains and dividing by the sum of the viable plus aborted grains.

**Results.** The data for the induction of revertant pollen grains at the *wx-C* and *wx-90* alleles from *Z. mays* grown in the sludge test plots are presented in Table IV. For the *wx-C* allele, over  $5.1 \times 10^6$  pollen grains were analyzed. The frequencies of reverse mutation did not increase with the increased amount of sewage sludge added to the soil. However, a direct relationship was observed between the amount of applied sludge and the frequency of pollen abortions within the range of 19.4% for the control to 49.9% in the highest treatment group.

The relationship between the abortion frequency in plants homozygous for *wx-C* and the concentration of amended sludge indicated an increasing rate of gametophytic death. Thus, for this allele some agent in the sludge was toxic to the developing pollen grains. No increased frequency of revertants in the *wx-C* allele was seen and may be due in part to the observed toxicity.

A different situation was obtained for the *wx-90* reversion tests. For *wx-90* there was an increased frequency of revertants with increased sludge amendment for the half-maximum and maximum treatment plots. In the control plots, the frequency of revertants was  $1.6 \times 10^{-6}$ ; plants grown in the half-maximum sludge plots exhibited a reversion frequency that was twice that of the controls. There was a tenfold increase in the frequency of revertants for the highest treatment group. The percentage of pollen abortions was essentially constant among the control and treatment groups. The sludge was apparently not toxic to the developing pollen grains in this inbred line.

These data indicate that these two alleles express different sensitivities to constituents that are present in sludge. Although the molecular nature of the lesions in the *wx-C* and *wx-90* is not known, it has been suggested that *wx-C* is a base-pair substitution (18). A difference in the specific types of lesions may account for the differences in response to exposure to sludge.

**Forward Mutation Test in Early-Early Synthetic Maize. Materials and Methods.** Inbred Early-Early Synthetic *Z. mays* kernels were obtained from sibling crosses and are homozygous for the dominant *Wx* allele. Five plants were grown as a control group in individual 10-cm diameter plastic pots filled with a standard soil mixture and watered with deionized water. Standard potting soil consists of four parts loam, two parts peat moss, and one part sand. Once a week 50 mL of a 20:20:20 nitrogen/phosphorus/potash fertilizer solution was added to each pot. Three treatment groups of five plants each were prepared with differing amounts of sludge added to the initial soil mixture. For the highest treatment group, one part sludge was added to two parts of standard soil. These plants were watered with a 1/3 dilution of sludge in deionized water. For the next treatment group, one part sludge was added to 5 parts of soil. The plants were watered with a 1/6 dilution of sludge. In the lowest treatment group, 11 parts of soil were combined with one part of sludge and these plants were watered with a 1/12 sludge/deionized water solution. The treatment groups

were grown in a separate chamber from the control plants. The chambers were set for a 17-h photoperiod of 300  $\mu$ einstein/(m<sup>2</sup> s) with day and night temperatures of 25 and 20 °C, respectively. The plants in the treatment groups were watered with the appropriately diluted sludge until tassel emergence and then watered with deionized water only. At early anthesis the tassels were harvested, labeled, and stored in 70% ethanol for subsequent analysis. The pollen grains were then analyzed in the same manner as described above except that forward mutants (*Wx* to *wx*; black to tan pollen grains) were scored.

**Results.** The forward mutation test was conducted to detect a broader range of mutational events and to allow the administration of higher concentrations of sludge than were possible in the *in situ* assays. Inbred Early-Early Synthetic was chosen because its convenient growth characteristics permit its use in plant growth chambers where well-controlled conditions can be assured. The genetic end point of this assay is the forward mutation at the *wx* locus in pollen grains. The plants used in this test were homozygous for the dominant *Wx* allele. Mutation is to the recessive *wx* allele, and the presence of tan grains after treatment with iodine is the visual end point.

The results of the induction of forward mutation at the *wx* locus in Early-Early Synthetic maize are presented in Table V. The data clearly show that the administration of sludge increased the frequency of mutation by 2 orders of magnitude. The control frequency of mutant pollen grains of  $4.3 \times 10^{-5}$  is consistent with spontaneous frequencies observed in other studies with this inbred (15). The frequencies of mutant pollen grains decreased with increasing amounts of added sludge, indicating that even the lowest concentration of applied sludge is high enough to reach to toxic region of the mutational dose-response curve. The percentage of pollen abortions is higher at the higher sludge concentrations than the control group. The control frequency is 13.3% while it is 19.9% in the highest treatment group. There is, however, no dose dependence to the abortion data.

There is a clear indication that sludge induced forward mutation in the pollen grains with a substantial increase in frequency over the control-group value. The increased abortion rate indicated the presence of toxic as well as mutagenic agents.

#### *Tradescantia* Micronucleus Test

**Background.** The *Tradescantia paludosa* micronucleus test measures chromosome damage in tetrads following meiosis of the pollen grain mother cells (19, 20). A micronucleus may result from the induction of a multipolar nuclear division or by chromosome aberrations that result in acentric fragments. The fragment of broken chromosome can be observed as a separate micronucleus within the tetrad. Figure 5 illustrates both a normal tetrad with each of the four meiotic cells having a single nucleus and a tetrad where two cells contain a micronucleus. Inflorescences of *Tradescantia* from plants originally obtained from T. H. Ma (Western Illinois University, Macomb) were cut, leaving stems approximately 3–4 cm long. Typically 8–10 inflorescences were used per treatment

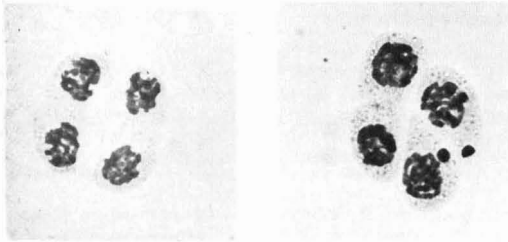


Figure 5. Photomicrograph of two tetrads of *Tradescantia* showing a normal tetrad (left) and one with micronuclei (right).

group. The cuttings were placed in test tubes containing various mixtures of sludge and Hoagland's solution (21). A negative control of Hoagland's solution and a positive control of 50 mM maleic hydrazide in Hoagland's solution were used for each experiment. The inflorescences were treated for 24 h with the test mixture and then placed into only Hoagland's solution for an additional 24 h. The solutions were aerated by bubbling water-saturated air through each tube. The temperature was maintained at 24 °C by using a water bath. After the treatment period, the inflorescences were removed from the treatment tubes and fixed in a solution of ethanol/glacial acetic acid (3:1, v/v) for 48 h. The samples were then stored in 70% ethanol for subsequent analysis.

The analysis procedure for scoring the micronuclei-containing tetrads has been described by Ma (20). The number of multiple micronuclei per tetrad was also recorded. The frequency of micronuclei induction was determined by dividing the total number of micronuclei observed by the number of tetrads analyzed. This ratio was multiplied by 100 to yield the number of micronuclei per 100 tetrads.

**Results.** The results of the micronucleus test are presented in Table VI. These experiments include the analysis of over 100 000 tetrads. The frequency of micronucleus induction for the negative controls ranged from 3.2 to 3.6 per 100 tetrads. The positive control frequencies ranged from 9.4 to 11.8 per 100 tetrads. The data demonstrate an increase in the frequency of micronuclei observed with increasing sludge concentration. As illustrated in Figure 6, dilutions above 1/4 induced a significant increase in the frequency of micronuclei. It should also be noted that the whole sludge, the 1/2 dilution, and the positive control induced an increased number of tetrads containing more than one micronucleus. Thus, sludge can induce cytogenetic damage including the possibility of multiple events in a single tetrad.

### Conclusions

The Chicago municipal sewage sludge sample clearly has components that induce a variety of mutagenic responses. Although it is not possible to compare the quantitative responses in the various test organisms employed, the sludge or sludge extracts did induce a response in all of the species employed. The supernatant liquid was not active in the Ames *Salmonella* assay, but both the acetone and hexane extracts of the pellet contained promutagens that could be activated by mammalian microsomes. Acetone was a more effective solvent than hexane in the extraction of the promutagens from the sludge pellet. The results indicate that a moderately potent agent can be extracted from the sludge since the material extracted from only 155  $\mu$ L of whole sludge was able to induce a doubling in the number of revertant colonies of TA98 following S-9 activation.

Table VI. Induction of Micronuclei in *Tradescantia* by Sewage Sludge

treatment	no. of tetrads analyzed	total no. of micronuclei	micro-nuclei per 100 tetrads	10 <sup>3</sup> . (frequency of multiple micro-nuclei)
Experiment 1				
control	9980	337	3.4	2.7
1/16 dilution	4654	160	3.7	3.2
1/8 dilution	4958	185	3.7	1.8
1/4 dilution	6471	234	3.6	2.2
1/2 dilution	5691	273	4.8	4.7
Experiment 2				
control	6673	236	3.5	2.8
50 mM maleic hydrazide	3176	358	11.3	6.0
whole sludge	2355	199	8.5	4.2
Experiment 3				
control	8056	294	3.6	3.6
50 mM maleic hydrazide	1906	226	11.8	4.7
1/4 dilution	5655	206	3.6	1.4
1/2 dilution	7011	405	5.8	4.0
whole sludge	10627	889	8.4	7.8
Experiment 4				
control	10452	336	3.2	0.9
50 mM maleic hydrazide	4517	425	9.4	9.1
1/4 dilution	8656	301	3.5	2.5
1/2 dilution	5955	290	4.9	2.9
whole sludge	2596	255	9.8	10.0

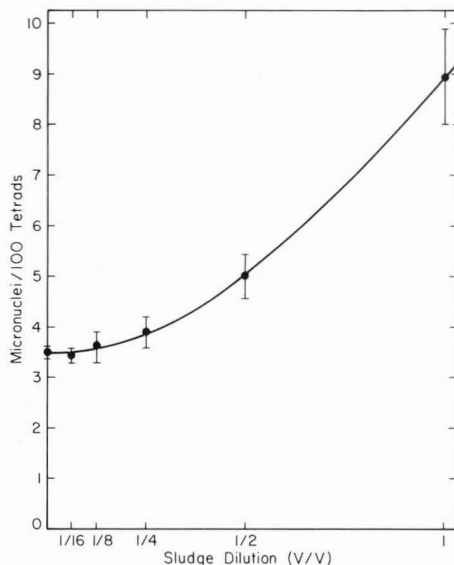


Figure 6. Induction of micronuclei in tetrads of *Tradescantia* as a function of sludge concentration. The data from the four experiments have been averaged, and the error bars represent one standard error of the mean.

The in situ tests using the maize *wx* locus assay demonstrate that mutagens are available to the plant when sludge is used as a soil amendment. Toxic as well as mutagenic responses were observed. The laboratory studies indicate that sludge can induce a substantial number of mutations at the *wx* locus in inbred Early-Early

Synthetic as well as reverse mutation at the *wx-90* locus observed in the field studies.

The micronucleus test in *Tradescantia* demonstrates that the sludge can cause cytogenetic damage such as chromosome aberrations in meiotic cells. Thus, there are components in the sludge that can interact with organisms in ways that can cause several different types of genetic changes. It is important to note that the microbial assays indicate that there were no direct-acting mutagens present in this sewage sludge sample. A mutagenic response appeared only upon activation with the S-9 microsomes. However, all of the plant genetic assays gave a positive response to direct treatment with the sludge. Although it may be that the components in the sludge are acting directly in these plants, it must be recognized that plants are also capable of activating promutagens (22). If this activation is occurring in the corn plants, then the plants grown on sludge-amended soil may represent a mechanism for the introduction of direct-acting mutagens into the environment. Since it is clear that the active agent can move through a corn plant to the germ cells to induce damage, the ability to be transported into the growing plants indicates the possibility of mobilization of these compounds in the environment. These studies do not provide any indication of mutagenicity in the kernels grown on sludge-amended soil or transfer of the mutagens from the sludge to groundwater or surface water. However, these results do suggest the need for further study of the possible adverse effects of land application of sludge from large industrialized cities.

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# Analysis of Fly Ash Produced from Combustion of Refuse-Derived Fuel and Coal Mixtures

David R. Taylor,\* Michael A. Tompkins,† Sarah E. Kirton, Thad Mauney, and David F. S. Natusch

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523

Phillip K. Hopke

Institute of Environmental Studies, University of Illinois, Urbana, Illinois 61801

■ Mixtures of coal and refuse-derived fuel (RDF) were burned and the fly ash was collected and analyzed for concentration trends with respect to RDF/coal ratio and particle size. RDF contributes more Cs, Mn, Sb, and Pb to the fly ash while coal contributes greater amounts of As, Br, Fe, Hf, Ni, Sc, V, and the rare earths. Smaller particles in the RDF fly ash had higher concentrations of As, Cd, Ga, K, Na, Sb, and the rare earths. RDF fly ash contains four distinct morphologies, exhibits a high specific surface area, and does not resemble fly ash derived from a conventional coal-fired power plant. The morphology of the ash helps explain the high solubility of many species in the RDF-rich fractions.

## Introduction

The use of municipal refuse as a fuel is currently receiving widespread attention. Factors such as rising costs, lack of available landfill sites, a growing interest in recycling, and ever increasing energy demands have made refuse an increasingly attractive alternative to coal as an energy source. Several authors (1, 2) have pointed out that the energy content of refuse-derived fuel (RDF) is considerably less than that of coal. In order to compensate for this deficiency, the use of mixtures of coal and RDF is now being explored. These mixtures combine the higher energy output of coal with the ready availability of urban waste.

The use of RDF constitutes an entirely new and not well-characterized source of environmental pollutants, notably potentially toxic trace metals. For example, both Cambell (3) and Law and Gordon (4) have discussed the sources of metals in emissions from municipal incinerators. These authors have mentioned printing inks as sources of lead and zinc; paints as sources of titanium, chromium, and lead; and plastic stabilizers as sources of tin and cadmium. If municipal solid waste (MSW) is used to form the RDF, the possibility of metal contamination is considerably greater (4, 5).

High metal concentrations have been reported in particles derived from refuse combustion. Rolsten (2) reported that lead emissions increased substantially when RDF was added to coal. Greenberg and co-workers (6) found elevated levels of Zn, Cd, Sb, and possibly Ag, In, and Sn when refuse was burned in two incinerators in Washington, D.C., and Alexandria, VA. Subsequent work by Greenberg et al. (7) showed that the emissions from these two incinerators and that of a third in Chicago did not differ appreciably in the concentrations of metals. All showed elevated levels of the above-mentioned metals. In view of

these results, further investigation of the RDF-coal system is warranted.

In this investigation, a comprehensive study has been made of fly ash derived from the combustion of mixtures ranging from pure coal to pure RDF. This study was undertaken to address the following objectives: (1) to determine the morphological and compositional characteristics of RDF/coal ash, (2) to determine the elemental composition of RDF/coal fly ash with respect to (i) the ratio of RDF to coal (ii) the size of the particles, (3) to determine the extent that individual elements present in the fly ash can be mobilized into solution as a result of an aqueous leaching process, and (4) to determine the factors that appear to be responsible for the partitioning of elements present in RDF/coal fly ash as a function of size and RDF content. It was felt that these factors would both define the physicochemical nature of RDF/coal fly ash and provide data for comparison with those already reported (8-20) for the fly ash derived from conventional coal-fired power plants. It has been established, for example, that fly ash derived from conventional coal combustion is generally spherical in nature and consists of several well-defined particle types (11, 18, 20). It has also been shown that many elements exhibit a trend of increasing concentration with decreasing particle size (8-20) although not all elements are consistent in their behavior. In addition, theories have been advanced that the outer surface of the particles contains substantially greater concentrations of many elements than does the fly ash bulk (11, 21) and that smaller particles are most likely to exhibit this phenomenon. As a result, toxic trace elements associated with the surface could potentially increase the health risk of inhaling small particles even further (22). Given these well-defined characteristics of coal fly ash, an investigation of RDF/coal fly ash mixtures permits comparisons in a number of areas.

In addition to characterizing the RDF/coal ash on the basis of morphology, composition, size, and RDF/coal ratio, the mobility of the elements in solution was also examined. Since much of the ash derived from RDF/coal combustion is destined for landfills, leaching of trace elements in the ash by rainfall, water runoff, or groundwater may play a significant role in the eventual environmental impact of RDF/coal combustion.

Finally, the study reported herein was designed to evaluate those factors which were responsible for any partitioning of trace elements with respect to either size or RDF content, since it is only through an understanding of that process that effective control procedures can be designed (8, 20).

## Experimental Section

**Materials.** All fly ash samples were collected from a small power plant located in Hagarstown, MD. The plant, located at the Maryland Corrections Institute, is used

\* Address correspondence to this author at the following address: Systems, Science and Software, P.O. Box 1620, La Jolla, CA 92038.

† Present address: Chromatrix, 560 Oakmead Parkway, Sunnyvale, CA 94086.

primarily to generate steam for heating and cooking purposes and is of the shaking grate stoker type. All mixtures were burned under similar operating conditions so that results would be directly comparable. The RDF burned in the study was obtained in pelletized form from the National Center for Resource Recovery, Inc., Washington, D.C., which had separated out all noncombustible material. The coal was of the Kentucky Swickley seam type. The RDF/coal mixture was burned in proportions of 1:0, 1:1, 1:2, and 0:1 RDF/coal by volume which corresponded to 0%, 35%, 52%, and 100% RDF by weight, respectively.

**Apparatus.** Samples were collected by using an inertial cascade impactor (Meteorology Research Institute, Altedina, CA) which had normal aerodynamic equivalent cutoff diameters at 50% efficiency of 30, 15, 6, 2.4, 1.5, 0.65, and 0.37  $\mu\text{m}$  for its seven stages. The combustion temperature was approximately 2230 °F (1220 °C), while the collection temperature was 400 °F (204 °C). Particles were scrapped off of the various stages into Teflon-lined glass bottles by using a Teflon scraper. Two collections were composited when the 1:0 RDF/coal mixture was burned, three for both the 1:1 and 1:2 mixtures, and six for the 0:1 mixture.

Particle morphologies were observed by using a Hitachi Model HHS-2R scanning electron microscope. The unit was equipped with a Kevex Model 5000A energy dispersive X-ray spectrometer (XES) which was utilized in individual particle analysis of the 2.4- $\mu\text{m}$  subsample.

Elemental analyses were conducted by using several techniques. Semiquantitative analysis of the 6- $\mu\text{m}$  size fraction was undertaken by using dc arc emission spectrometry (DCAES) in which the spectra were recorded photographically on a Baird-atomic 3-m grating spectrometer, Model 6x-1. Selected fly ash samples were analyzed by instrumental neutron activation analysis (INAA) utilizing the Illinois Advanced Reactor Facility having a neutron flux at the sample of approximately  $2 \times 10^{12}$  neutrons/(s/cm<sup>2</sup>). Finally, the size fractions 6–0.65  $\mu\text{m}$  were analyzed for 18 elements by using plasma emission spectrometry (PES). A Spectrometrics Spectroscan III equipped with a three-electrode dc plasma source and an Echelle monochromator was employed in these analyses. Anionic analyses were performed by using a Dionex Model 10 ion chromatograph (Dionex Corp., Sunnyvale, CA).

Surface area measurements were made through the use of the Quantasorb Sorption System (Quantachrome Corp., Glenvale, NY) using nitrogen as the adsorbate and helium as the carrier gas.

**Procedures.** To study particle morphologies and make individual particle X-ray studies, we mounted samples on double-sided cellophane tape and coated them with carbon. In those cases where X-ray information was not required, the samples were coated with gold by using a standard vapor deposition technique so as to minimize charging effects on the sample.

Because of a limited quantity of sample, the standard procedure for making surface area measurements by nitrogen adsorption had to be modified. Under the usual operating conditions, samples are outgassed at 300 °C to remove any adsorbed material before determining the surface area. Prolonged exposure to this temperature can result in loss of potentially volatile elements such as arsenic or cadmium. To prevent this, outgassing was carried out at room temperature to enable subsequent elemental analyses of the same samples. Comparison of surface area measurements made under both conditions indicated incomplete outgassing at room temperature as expected. However, the values obtained were proportional to those obtained at 300 °C when outgassing and adsorption were

Table I. Surface Areas (m<sup>2</sup>/g) of RDF/Coal Fly Ash for the Seven Size Fractions Collected by Using an MRI Stack Sampler

% RDF/coal	stage cutoff ( $\mu\text{m}$ ) 50% efficiency						
	30	15	6	2.4	1.5	0.65	0.37
0			4.96	5.73	8.38	10.2	10.1
50			7.26	9.02		9.90	
67				9.61	11.4		
100	2.7	5.5	15.3	17.9	20.8	23.0	30.0

carried out under identical conditions for all samples.

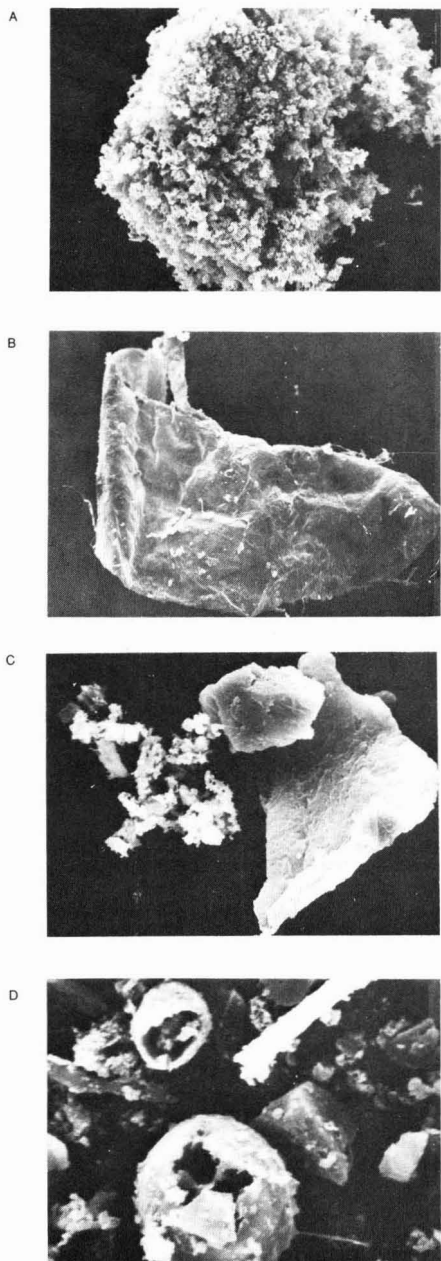
Samples analyzed by the DCAES were diluted with National SP-2 spectroscopic graphite using a Spex Mixer-mill. Indium (400  $\mu\text{g/g}$ ) was added as an internal standard. Samples were excited by a 28-A dc arc for 30 s. The spectra so obtained were analyzed with a manual densitometer. Those samples analyzed by PES were first digested in an acid mixture consisting of 3.5 mL of aqua regia, 2.5 mL of 48% hydrofluoric acid, and 0.5 mL of deionized water. The resulting digest was neutralized by using approximately 2 g of boric acid to remove the excess HF in the form of boron trifluoride (11). Specific analysis for arsenic was performed by generation of the hydride which was then determined by conventional flame atomic absorption spectrometry in a modification of the method described by Braman et al. (23).

Twenty-seven elements were detectable by INAA using both short and long irradiations. Following removal from the reactor, the samples were analyzed by using a Ge/Li detector in conjunction with a 4096-channel multichannel analyzer. The results were transferred to magnetic tape and analyzed by using the PIDAQ program (24). Analyses performed by INAA have a precision (based on counting statistics) of less than 10% for most elements. The accuracy appears to be comparable. Precisions of 1–2% are associated with the results obtained for As, Mn, and Na. It should be noted, however, that because of the small amounts of sample available, the sampling statistics are likely to be the limiting factor in determining the precision and the accuracy of the overall measurements. Thus, it is possible that the analyses are not totally representative of the overall sample.

In order to obtain information about the solubility characteristics of RDF/coal fly ash, the size fractions from 6 to 0.37  $\mu\text{m}$  were agitated by using a Heat Systems Model W 200R sonicator cell disruptor for 2 h with 15 mL of triply distilled deionized water. Sample masses varied from 0.0019 to 0.230 g (previous studies have established that water-soluble material can be quantitatively extracted under these conditions) (14). Following sonication the samples were filtered through a 0.45- $\mu\text{m}$  Millipore filter and analyzed by using plasma emission spectrometry and ion chromatography.

## Results

The fly ash derived from burning RDF/coal mixtures appears to contain four basic morphological types, regardless of either size or RDF/coal ratio. These types are shown in Figure 1 and include particles resembling "shredded sponge", "rolled paper", "paint chips", and spheres. Unlike fly ash derived from a conventional coal-fired power plant, the majority of the observed particles were not spherical, and there is little evidence of smooth solid spheres or of cenospheres or plerospheres (11, 18, 20). In contrast, most material appeared to be of the type shown in Figure 1A. Most of the spherical particles, as is shown in Figure 1D, were not solid and were significantly smaller than the other particles types.



**Figure 1.** Photomicrographs of RDF/coal fly ash particles: (A) "shredded sponge" type; (B) "rolled paper" type; (C) "paint chip" type; (D) spherical type.

The results of the surface area measurements are given in Table I. It should be reiterated that, although the relative values of the specific surface area are consistent within the sample set investigated, the absolute values may be higher than those indicated because these samples were incompletely outgassed as discussed above.

The elemental concentrations of the fly ash as a function of RDF/coal ratio are given in Table II. Results are from the 2.4- $\mu\text{m}$  size fraction or, in some cases, the 6- $\mu\text{m}$  size fraction. The elemental concentrations of the 100% RDF

**Table II.** Elemental Concentrations ( $\mu\text{g/g}$ ) of RDF/Coal Fly Ash for Different Percentages of RDF in the 2.4- $\mu\text{m}$  Cutoff Impactor Stage

element	vol % RDF			
	0	50	67	100
aluminum	84800	57900	101000	46400
antimony	60	160	350	17
arsenic	1560	710	480	1250
barium	850	580	950	1000
bromine	50	150	90	70
cadmium <sup>a</sup>	3	20	20	3
calcium	25000	44000	51000	21000
cerium	93	86	78	79
cesium	<0.8	5	7	10
chromium <sup>a</sup>	150	300	300	70
cobalt	77	51	40	100
copper <sup>a</sup>	100	60	50	100
dysprosium	18	11	8	11
europium	3	2	2	2
gallium	120	80	49	80
hafnium	11	9	7	4
iron	61000	37000	33000	35000
lanthanum	69	59	43	41
lead <sup>a</sup>	300	800	1000	500
lutetium	2	1	1	1
magnesium	4000	4550	6810	4060
manganese	380	560	740	190
molybdenum	<14	<19	<90	<20
neodymium	<19	<34	<28	35
nickel <sup>a</sup>	300	600	600	1000
phosphorus	3710	2340	3250	1770
potassium	12900	18000	16000	11600
rubidium	70	110	110	82
scandium	44	28	24	30
selenium	38	18	33	62
strontium	1220	1520	1240	1090
tantalum	1	4	1	3
thallium	1	2	1	2
thorium	23	18	16	19
uranium	14	12	<2.7	9
vanadium <sup>a</sup>	1500	500	300	800
ytterbium	6	3	2	4
zinc	<400	3470	14000	<560
zirconium	<50	890	430	250

<sup>a</sup> 6- $\mu\text{m}$  size fraction used for analysis.

fly ash as a function of size are presented in Table III. High blank levels limited the DCAES results to order of magnitude accuracy; as a consequence, most of the data reflect INAA results.

The 2.4- $\mu\text{m}$  size fraction was studied by using the X-ray spectrometry capability of the scanning electron microscope. A number of individual particles were analyzed and found to contain Al, Ca, Fe, K, and Si and, at much lower levels, Ti and Zn. The presence of As, Na, P, and S was indicated in some particles, but signal intensities were too weak for positive identification.

In the second part of this study, samples of RDF/coal fly ash were subjected to bulk leaching. A total of 22 species (Al, Ba, Be, B, Cd, Ca, Cl<sup>-</sup>, Cr, Cu, F<sup>-</sup>, Pb, Mg, Mn, Mo, Ni, NO<sub>3</sub><sup>-</sup>, P, K, Si, SO<sub>4</sub><sup>2-</sup>, Sr, and Na) were determined in the aqueous leachates. Results for those species demonstrating either clearly defined or limited trends are presented in Table IV.

### Discussion

The results of the surface area measurements established several points of interest. First, it is apparent that there is a clear dependence of specific surface area on aerodynamic size for these particles. Second, there appears to be a general trend of increasing specific surface area with increasing RDF-to-coal content. Considering the pre-

Table III. Elemental Concentrations ( $\mu\text{g/g}$ ) As a Function of Particle Size for Fly Ash Derived from RDF Combustion

element	stage cutoff ( $\mu\text{m}$ ) 50% efficiency						
	30	15	6	2.4	1.5	0.65	0.37
antimony	22	24	31	17	30	30	103
arsenic	321	565	915	1248	1435	1619	712
barium	<405	334	789	1000	880	988	252
bromine	546	150	57	66	95	140	85
cadmium <sup>a</sup>		<92	416	<167	<631		
calcium	<33000	<41000	20000	21000	17000	30000	<56000
cerium	17	16	72	79	75	76	32
cesium	<3	4	5	10	12	13	6
cobalt	24	32	79	10	59	90	81
dysprosium	<1	5	10	11	11	10	4
europium	<1	<1	2	2	2	2	2
gallium	32	22	69	80	114	173	165
hafnium	<4	<4	6	4	4	2	<3
iron	127000	119000	39000	45000	28000	28000	89000
lanthanum	19	17	47	41	47	48	21
lutetium	<1	<1	1	<1	1	2	<1
manganese	947	666	206	189	183	167	79
neodymium	<42	<41	<18	35	86	<22	<31
potassium	2500	3000	1000	11600	11500	11800	5400
rubidium	<41	<44	101	82	70	59	68
scandium	5	7	3	30	29	33	10
selenium	177	166	64	62	41	45	<6
sodium	1900	1470	2680	2930	3000	3350	1720
strontium	<161	<330	910	1090	640	1030	420
tantalum	<2	<4	2	3	1	3	<2
thorium	2	4	15	19	17	20	3
uranium	<3	<3	9	9	12	27	7
ytterbium	<2	4	4	4	3	4	<1
zinc	24300	1420	<410	<560	530	830	600
zirconium	<98	<75	250	250	<62	290	<51

<sup>a</sup> 6- $\mu\text{m}$  size fraction used for analysis.

dominance of particles of the type shown in Figure 1A, the large specific surface area of these fractions as compared to conventional coal fly ash is not surprising.

The samples were analyzed for 41 elements in all by using the different techniques previously described. Because of limited sample sizes, however, it was not possible to determine all elements in all samples. It should also be emphasized that the analytical techniques employed in this study have considerably different precisions and accuracies and are not equally reliable. Nonetheless, good agreement was obtained among the techniques employed for the elements As, Ba, K, and Sr. Agreement was not as good for the other elements for which other than one technique was used (Cd, Cu, Mn, Pb, Ni, Na) because of the high blank levels for the PES which permitted only an upper limit for the elemental concentrations to be calculated. The relative precisions and accuracies achieved, however, enabled trends to be observed and permitted comparison to the results of other workers.

In general, the actual concentrations of the various elements in RDF/coal fly ash were found to be within the ranges reported in earlier work (8-20) for coal fly ash. Comparison of our results for 100% RDF with those reported by Law and Gordon (4) for three municipal incinerators reveals, however, that considerable differences exist. For Sb, Br, and Cd our concentrations were considerably lower (more than 1 order of magnitude). For Co, Pb, Mg, Mn, and Na, concentrations were lower (less than 1 order of magnitude). The elements Al, Cr, and Cu had comparable results. The elements As, Ba, La, and Ni were all more concentrated in our pure RDF fraction. These results are not altogether surprising given the diversity in the sources and composition of RDF.

Of greater interest, however, are the observed variations of elemental concentration with RDF/coal ratio and with particle size. To better observe these two trends, repre-

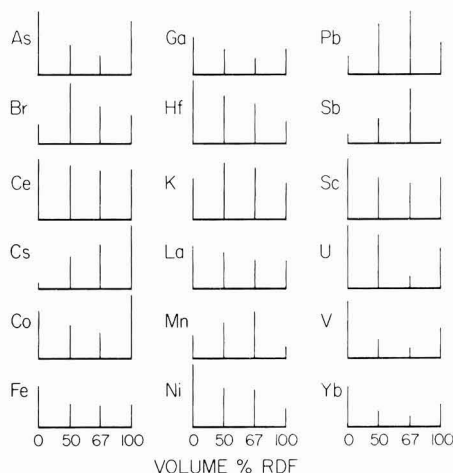


Figure 2. Concentration trends as a function of RDF/coal composition. Scales for different elements are not the same.

sentative histograms showing elemental analyses as a function of RDF/coal ratio are presented in Figure 2. Histograms showing elemental analyses of representative elements as a function of particle size for the RDF fraction are given in Figure 3. The histograms represent widely diverse concentrations and should be examined on an element-by-element basis for trends and are not otherwise comparable to each other.

As seen in Figure 2, only Cs shows a progressively increasing concentration as a higher percentage of RDF is burned. Three elements, Sb, Mn, and Pb, increase progressively but drop off in the pure RDF fraction. These

Table IV. Concentrations of Several Metallic Elements and Anions in Aqueous Leachates from RDF/Coal Fly Ash ( $\mu\text{g/g}$  of Fly Ash Leached)

size (50% eff) cutoff, $\mu\text{m}$	composition (by vol)			
	0% RDF/coal	50% RDF/coal	67% RDF/coal	100% RDF/coal
	Cadmium			
6	1.17	0.189	0.236	0.395
2.4	<7.20	13.9	13.0	13.4
1.5	12.8	24.8		53.0
0.65	15.6	100		252
0.37	167	120		527
	Chloride			
6	560	223	72.6	2310
2.4	<137	56.9	<792	6310
1.5	<356	<699		13000
0.65	28.7	<2710		33700
0.37	417	<1290		54900
	Copper			
6	0.926	0.274	0.684	<3.14
2.4	2.33	<5.50	<5.15	<5.35
1.5	<3.39	<6.56		<14.0
0.65	<4.14	5.26		76.2
0.37	27.3	228		292
	Lead			
6	<5.04	3.70	4.79	7.71
2.4	<1.04	15.5	6.10	12.0
1.5	18.1	22.1		283
0.65	13.9	1740		2420
0.37	60.5	7890		4720
	Nitrate			
6	60000	142000	199000	207000
2.4	1550	2160	1980	2620
1.5	1580	7690		21500
0.65	6090	10400		29800
0.37	5380	<19400		8890
	Potassium			
6	257	525	160	630
2.4	870	1200	835	2260
1.5	1460	2710		11100
0.65	1480	7950		24000
0.37	1280	15400		38000
	Manganese			
6	2.22	4.79	5.47	2.43
2.4	10.6	29.0	25.2	4.00
1.5	26.8	36.4		74.0
0.65	25.4	26.3		119.
0.37	57.6	30.0		36.8
	Sodium			
6	444	514	1050	1920
2.4	545	3340	3120	6700
1.5	584	7900		29200
0.65	295	18100		63600
0.37	<3280	32600		82400
	Sulfate			
6	43100	82500	80800	110000
2.4	10800	17900	17700	25400
1.5	11600	23800		40800
0.65	11900	56800		66200
0.37	8640	107500		75000

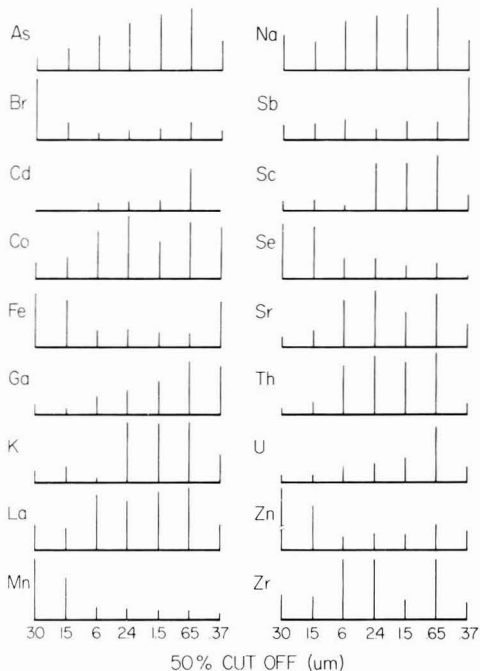
results correspond, at least in part, to studies of municipal incinerator emissions by other workers (2, 4, 6, 7) who also reported MSW to contain considerable Sb and Pb.

A much larger number of elements were found to be generally coal associated. These included As, Br, Fe, Hf, Ni, Sc, V, and the rare earths La, Lu, U, and Yb. Again, the pure RDF fraction is somewhat inconsistent with the overall trends or, in some cases, ranges reported in coal fly ash (10, 12-17). That so many elements were found to be more attributable to coal is not too surprising since few anthropogenic sources for hafnium, scandium, or the

rare earths exist. The higher levels of arsenic, iron, nickel, and vanadium in the coal suggests that the RDF had minimal amounts of these elements remaining following the separation procedure.

Trends in concentration as a function of particle size were generally poorly defined. There was, however, a general tendency for the elements As, Cd, Ga, K, Na, and Sb and the rare earths to increase in specific concentration with decreasing particle size, as seen in Figure 3. Large particles showed elevated Fe, Mn, and, surprisingly, the relatively volatile element Se. The preference of As, Ga,





**Figure 3.** Concentration trends as a function of particle size for 100% RDF sample. Scales for different elements are not the same.

K, Na, and Sb for small particles is to be expected since these elements are capable of being volatilized during combustion and then preferentially absorbed onto small particles (8, 11, 18–20). The behavior of Se in this regard is not understood.

Of possible greater concern than the composition of the ash itself is the availability of substances in the ash to the environment. Thus, it can be argued that toxic trace elements can exert an adverse environmental impact only if they can be transferred from solid material to solution. Since RDF generates 4–7 times more ash than the same weight of coal (1) and since much of this ash goes into landfills where leaching by rain or groundwater is possible, the solubility of species in RDF/coal fly ash is an important consideration.

From the data in Table IV, it is apparent that, for most species, the amount of soluble material increases with RDF/coal ratio of the original fuel. This trend can be seen quite clearly for Ca, Cu, K, Na, Pb,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$ . Most of the remaining elements show trends for some size fractions but not for all. Thus, it appears that B, Ba, Cd,  $\text{F}^-$ , Mo, Mn, and Si are often more readily leachable from RDF than from coal but not consistently. Nickel and phosphorus show a tendency to be more leachable from coal, but again the trends were not definitive. The fact that many of the major matrix elements exhibit increasing solubility with increasing RDF percentage suggests that the RDF/coal mixtures do not form insoluble aluminosilicate glasses as readily as does coal fly ash (11, 18, 20). The particle morphologies, Figure 1A–D, suggest this as well in that few of the particles showed the characteristic spherical appearance of fly ash and those that were spherical were unlike any of the particle types reported by Fisher et al. (18). In addition, the “spongelike” nature of the majority of the RDF particles with their associated large surface areas would be expected to facilitate leaching.

The second obvious solubility trend is toward increasing mobilization of species with decreasing particle size. This is apparent for Cd, Cr, Cu, K, Mn, Mo, Na, Ni, Pb, and  $\text{Cl}^-$  and may also occur for Ba, Be, P, and  $\text{F}^-$ . Such a trend may be due to the condensation of these species from the vapor phase in soluble form as mentioned earlier; it may result from the more efficient formation of soluble oxides (i.e., calcining) in small particles; or it may be due to greater accessibility of the element to the solvent in small particles. In the first case one would expect to see similar size dependences for both the bulk (Figure 3) and the soluble (Table IV) fly ash. In the case of K and Na, for which both bulk and solubility data are available, concentrations are observed to increase with decreasing particle size in both analyses. For these elements, the data are consistent with solubility trends as a function of particle size being a result of vapor deposition of volatile species. Conversely, Mn is more soluble in the small particles. One can tentatively conclude that, for this element at least, its increasing solubility with decreasing particle size is due either to the existence of different chemical compounds having greater bulk solubility in small particles or else to the insoluble matrix in these particles providing less protection from the solvent.

Further consideration of the data in Table IV provides some interesting insights into the fractional solubility of RDF/coal fly ash. As an initial general statement it can be said that matrix elements such as Al, Ba, Mg, P, Si, and Sr exhibit quite low solubility (10%) whereas minor and trace elements such as Be, Cd, K, Mn, and Na are fairly soluble (20–80%). Calcium is a notable exception to this rule insofar as it exhibits high solubility. There is a trend of increasing fractional solubility with decreasing particle size for several elements including Mn, K, Na, and Pb.

These studies provide considerable information about both the chemical characteristics and potential environmental impact of RDF/coal fly ash. Of probably greatest impact are the very high levels of chloride and sulfate (up to several percent) and the much greater solubility shown by RDF over that of coal fly ash. The high salt content in waters which have been leached could be toxic to both plant and animal life as well as requiring more cleanup downstream.

### Conclusions

In summary, the following conclusions were drawn from this study: (1) The concentration of most elements is similar in coal and RDF fly ash. (a) RDF is the main contributory source of Cs, Mn, Sb, and Pb to the fly ash. (b) Coal is the main contributory source of As, Br, Fe, Hf, Ni, Sc, V, and the rare earths to the fly ash. (2) Small particles tend to be higher in As, Cd, Ga, K, Na, Sb, and rare earths. (3) Fractional solubility of RDF/coal fly ash increases with increasing RDF content. (4) The increased fractional solubility of RDF/coal fly ash is attributed mainly to the spongelike nature and high surface area of RDF-derived particles. (5) Fractional solubility of trace and matrix species is significantly greater in small particles than in large particles.

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## Ambient Aerosol Sampling. History, Present Thinking, and a Proposed Inlet for Inhalable Particles

James B. Wedding

Aerosol Science Laboratory,<sup>†</sup> Colorado State University, Fort Collins, Colorado 80523

■ This paper will chronologically review the various approaches to ambient aerosol sampling and will present data describing the wind-tunnel performance of a prototype inhalable particles (IP) inlet developed at the Aerosol Science Laboratory based upon the  $D_{50} = 15 \mu\text{m}$  sampling strategy, prevalent during 1980. The inlet utilizes an aerodynamically sound housing and fluid flow design that efficiently transports the particles to the fractionating element. The inlet uses a unique omnidirectional/cyclone fractionator. Over the range of wind speeds from 0.5 to 24 km/h the 50% cut point was seen to be virtually invariant, 14.4-13.7  $\mu\text{m}$ . The slope of these curves was found to be quite steep. The present inlet is currently undergoing design improvements but represents a working device that can serve as a viable inlet system for IP sampling.

### Introduction

**History.** The effective sampling of aerosols in the ambient atmosphere has received considerable and increasing attention over the past 5 years. To obtain a representative measurement of the particulate mass present, one must draw a sample containing the particle size range of interest through an inlet device onto a suitable sampling substrate. To provide meaningful data, the inlet must allow all particles of interest to be collected with the same slope and shape of the collection-effectiveness curve (see ref 1 and Figure 1) independent of sampling conditions. These conditions include mean velocity (magnitude and three-

dimensional direction), turbulence scale and intensity, and extraneous airborne matter (rain, snow, insects, debris, etc.). Up until 1972, characterization of atmospheric particulate matter had been accomplished through use of the standard Hi-Vol samplers (2, 3) which measured total suspended particulate (TSP) and operated at a flow rate of 1.41 m<sup>3</sup>/min (50 cfm). (See Figure 2.) Even though the national ambient air quality standards for particulate matter are defined in terms of TSP (4), this approach did not supply acceptable information for a variety of reasons. Initially, the collection capability of the samplers has been found to be strongly a function of particle size, approach flow wind speed, and sampler orientation (see ref 1 and the next section). Additionally, characterization of the aerosol concentration becomes nearly impossible when the upper size limit is variable. Hi-Vol samples are not size segregated near the center of the bimodal mass distribution (3). These shortcomings prompted the U.S. Environmental Protection Agency in 1972 to examine conventional impactors as a means of fractionating the sample prior to collection. The drawback of particle bounce documented by Dzubay and Stevens (5) led to the adoption of the virtual impaction principle as an appropriate alternative. The single-stage version was first described by Hounam and Sherwood (6). This device produces two samples separated into what has been termed respirable vs. non-respirable particle sizes. Subsequent analysis of samples collected by these devices has revealed a different chemical constituency of the two size modes providing a reasonable basis for the need to size segregate samples. The small-particle mode is acidic—composed mostly of lead, bromine,

<sup>†</sup>Affiliated with the Research Institute of Colorado.

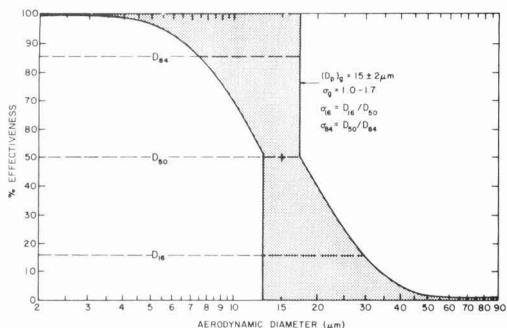


Figure 1. Effectiveness performance envelope for IP (9).

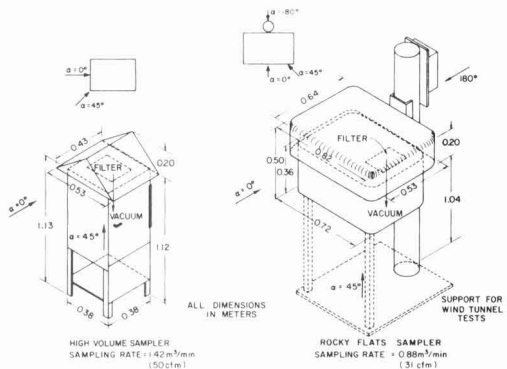


Figure 2. Standard ( $11\frac{1}{2} \times 14$ ) in.<sup>2</sup> Hi-Vol (4) and Rocky Flats (Rockwell International) sampler (36).

and a number of other elements in trace concentrations. The large-particle mode is generally basic—composed of a variety of minerals including quartz, limestone, calcite, mica, and clay and trace quantities of tire dust, pollen, and lead oxides. Thus, at the present time, there are two basic approaches to the sampling of atmospheric particulate matter: the Hi-Vol and the dichotomous samplers.

**Present Thinking.** Recent EPA emphasis is aimed at developing air quality standards based upon the collection of a specific size fraction—termed inhalable particulate (IP) matter. Miller et al. (9) define IP as particles having aerodynamic diameters of  $\leq 15 \mu\text{m}$ . Additionally, there exists a strong possibility that the IP standard may be based upon  $10 \mu\text{m}$ . The impetus for this thinking came from the International Standards Organization (ISO TC146, 1981), which proposed consideration of a standard based upon those particles depositing in the tracheo-bronchial and alveolar regions of the human respiratory tract—subsequently termed thoracic deposition or TP (thoracic particle) fraction. Inlets for IP must have well-defined large particle cut size characteristics necessitating the usage of a suitable fractionating device to remove unwanted aerosol from collection substrates. Figure 1 reveals the September 1980 strategy on performance for an acceptable inlet for IP based on the  $15\text{-}\mu\text{m}$  IP definition, but it is currently undergoing intense scrutiny. The effectiveness of an inlet is defined as the ratio of the mass collected on the sampler substrates to that collected by an isokinetic sampler, the latter providing the reference on cloud concentration approaching the inlet. The adoption of these  $D_{50}$  guidelines (aerodynamic diameter at an effectiveness of 50%) may undergo further changes as knowledge increases on the overall effects of various par-

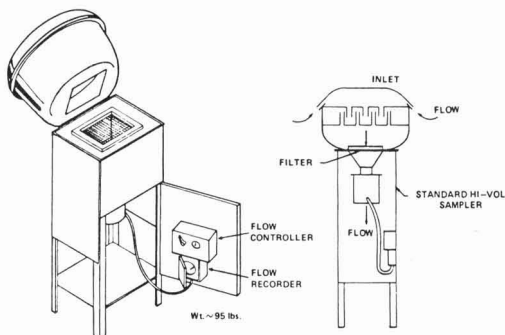


Figure 3. Size-selective Hi-Vol (10).

ticle sizes on public health and environment. Note that the ultimate shape of the fractionating curve has at this point been left quite flexible. However, one would desire an inlet with the curve shape and  $D_{50}$  independent of wind speed for consistent sampling. Additionally, the present dichotomous sampler operates at a flow rate of  $16.67 \text{ L/min}$  with both manual and automatic filter changing options available. The need for all samplers to have a size-segregating capability can be questioned, as well as a need for larger flow rates to enable collection of more mass. These thoughts have resulted in the continuing presence of the Hi-Vol approach. If one does not wish to fractionate the sample and more mass is desired to be collected in a shorter period of time, one alternative to the dichotomous sampler is the size-selective Hi-Vol system. (See Figure 3.) This unit, developed by McFarland et al. (10) under funding by the Environmental Monitoring Systems Laboratory (EMSL) of the U.S. Environmental Protection Agency, collects particles at a flow rate of  $1.13 \text{ m}^3/\text{min}$  (40 cfm), has a  $D_{50} = 15 \mu\text{m}$ , and utilizes the standard glass-fiber filter. The latter makes chemical analysis difficult or impossible, acting as a chemical reactor and causing so-called artifact formation. Thus, an intermediate flow rate sampler (4 cfm) utilizing a membrane filter seems advisable. If the standards are indeed set at  $D_{50} = 10 \mu\text{m}$ , this system will be obsolete.

This paper will chronologically review a great percentage of the various approaches to ambient aerosol sampling. Data have been collected on many of the devices in the Aerosol Science Laboratory and will be presented here. Also presented will be data on a  $D_{50} = 15 \mu\text{m}$  inlet for the dichotomous sampler designed and tested at the Aerosol Science Laboratory to meet the  $15\text{-}\mu\text{m}$  IP sampling criteria.

#### Inlet Designs for Ambient Aerosol Sampling

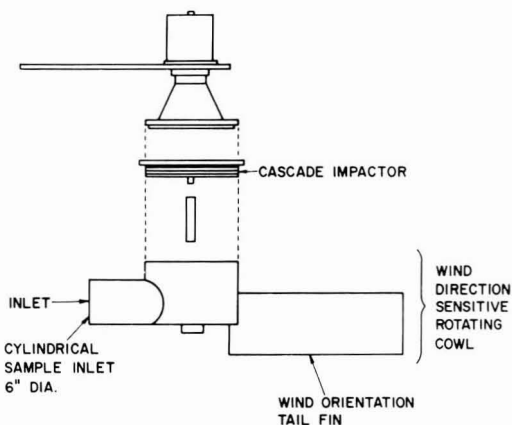
Until recently, there had been relatively little rigorous attention given to examining the basic fluid and aerosol mechanics associated with the challenging problem of collecting an unbiased sample of atmospheric particulate matter independent of the environmental conditions. Several investigators (11–26) have studied the basic problems associated with the sampling of particles for simple collector geometries. Davies (16) has developed a model for the sampling efficiency of tubes as a function of particle size, mean velocity, and sampling rates. Davies (27), Kaslow and Emrich (28), and Agarwal and Liu (29) have investigated sampling of aerosol under quiescent conditions. Agarwal (29, 30) solved the Navier–Stokes equation to obtain insight into the fluid flow pattern of cylindrically shaped inlets. Davies (31) and Davies and Subari (32) have investigated the sampling of these walled tubes in a crosswind. Zebel (33) applied a potential flow

**Table I. Comparative Performance Data for Ambient Aerosol Samplers/Inlets**

Sampler/Inlet	D <sub>50</sub> or D (efficiency, %)	Test Wind Speed km/hr	Figure	Literature Reference	Test Flow Rate
Standard Hi-Vol: 0°, 45° Sampler	12, 18	13.65		Wedding et al. (1)	1.42 $\frac{m^3}{min}$ (50 cfm)
Standard Hi-Vol: @ IRPM Sampler	16.5, 31, 730	2, 8, 24	2	McFarland (10)	
Rotating Wind and Impactor Sample	15 (-100%)	4.55	4	Wedding et al. (1) Sehmel (17)	0.566 $\frac{m^3}{min}$ (20 cfm)
Virtual Impactor Inlet	15(30.1), 20(16.9), 25(7.2) 15(6.3), 20(6.51), 25(2.9)	8.03 27.4	5	Dzubay (5)	Primary inlet 201 L/min (7.10 cfm) Secondary inlet 14 L/min (.49 cfm)
Rockwell International Sampler	0°: 24, 13.5, 13.5 45°: >35, 14.5, 14.5	5.49, 21.95, 43.89 5.49, 21.95, 43.89	2	Wedding et al. (36)	0.88 $\frac{m^3}{min}$ (31 cfm)
Southern Research Institute Inlet	5(39, 30, 20) 12(35, 12, 35)	9, 46, 68 9, 46, 68	6	Beid et al. (38)	
Beckman Inlet	15.5 13 10.5	2 8 24	9	McFarland (10)	16.67 $\frac{L}{min}$ (.59 cfm)
Sierra Inlet	11 22 15 9.5	0 5 15 40	9	Wedding et al. (37)	16.67 $\frac{L}{min}$ (.59 cfm)
Size Selective Hi-Vol. Sampler	13.4 14.4 12.5	2 8 24	3	Wedding (unpublished)	1.13 $\frac{m^3}{min}$ (40 cfm)

solution to determine fluid streamlines existing around a slit or hole in an infinite wall. May et al. (34) performed a field study on the capability of various sampling devices to collect windborne particles. Burton et al. (35) field tested a 566 L/min (20 cfm) Hi-Vol cascade impactor, further evaluated by Sehmel (17). Studies by Steen et al. (13-15) evaluated the performance of samplers used in Europe to sample ambient aerosols. Wedding et al. (1) studied the performance of the standard Hi-Vol sampler, followed by a broader study conducted by McFarland et al. (10). Also evaluated in the study by Wedding (1) was the rotating cowl and impactor system designed and utilized in field studies by Sehmel (see ref 17 and Figure 4) and an inlet employing a virtual impactor fractionator (see ref 5 and Figure 5). Wedding et al. (36) also evaluated a Hi-Vol sampler in use by Rockwell International at Rocky Flats, Co (see Figure 2).

Beginning with the study by Wedding et al. (1) which revealed the extreme biasing of the Hi-Vol performance, much-needed attention began to focus seriously on the inlet required for the successful introduction of atmospheric particulate into the dichotomous sampler. A prototype inlet conceptualized, fabricated (made of Plexiglas), and partially evaluated (see ref 1) under the same study during the summer of 1975 at the Aerosol Science Laboratory was intended to provide a means to collect particles independent of wind direction and environmental conditions. The device was performance tested by using an Andersen impactor on the outlet (see ref 1). No special shape of the fractionation curve or design rationale was specified for that device. The inlet was later recommended to EPA for adoption on their IP network. An ensuing rigorous analytical and experimental evaluation of that inlet was later performed by Wedding et al. (37), and its performance was found to be unsuitably dependent upon wind speed. A study just completed by Wedding (unpublished) on the size-selective Hi-Vol shown in Figure 3 indicates that the sampler tested is marginally unaccept-



**Figure 4. Rotating cowl and impactor (17, 1).**

able by the Figure 1 criteria. Unpublished data by McFarland indicate modifications made to the SSI have resulted in a D<sub>50</sub> of 14 μm at 2, 8, and 24 km/h. The only other inlet device found in the literature at this time was designed and tested by Bird et al. (38). (See Figure 6.)

The results of all of the above referenced work confirm the difficulty that one encounters in designing an inlet/sampler system to operate independently of sampling conditions. Table I summarizes the results of the work, with literature references given for convenience and figures accompanying for elucidation of design and principle of operation.

*Proposed Inlet for IP*

**Design Rationale.** The design rationale is based upon the need for an ambient aerosol sampling inlet capable of collecting all particles of interest with the same D<sub>50</sub>, slope

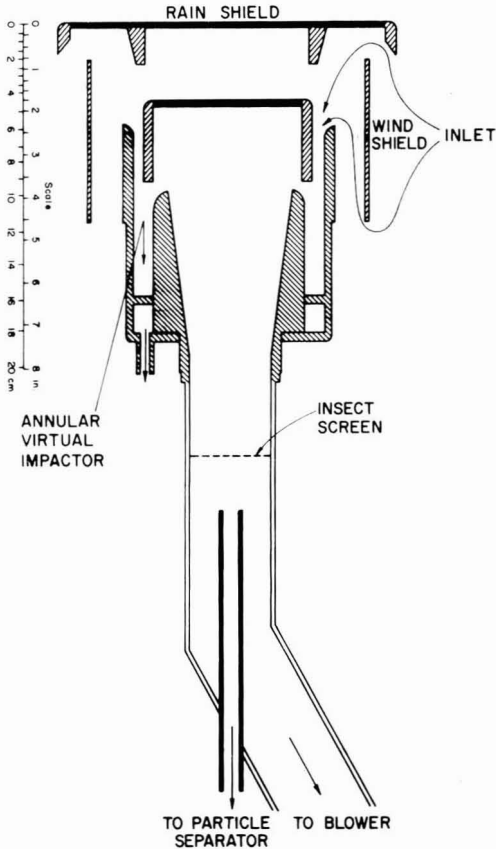


Figure 5. ERC virtual impactor (5).

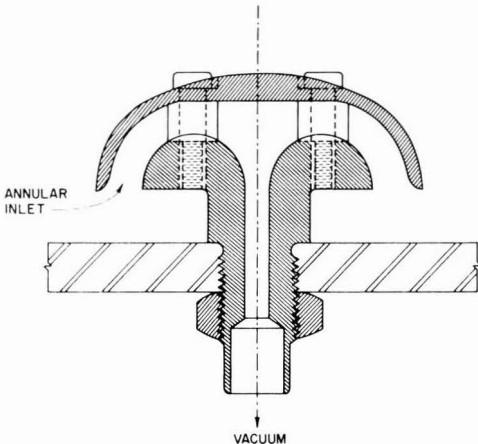


Figure 6. Southern Research Institute inlet (38).

and shape of the collection-effectiveness curve vs. aerodynamic diameter independent of the sampling conditions. An inlet for IP must at this time meet the criteria as illustrated in Figure 1, which means that the inlet sampling-effectiveness curves must lie within the shaded region. At this point in time Figure 1 represents only a proposed guideline for IP inlets. The resulting effectiveness curve of an inlet system is the product of the frac-

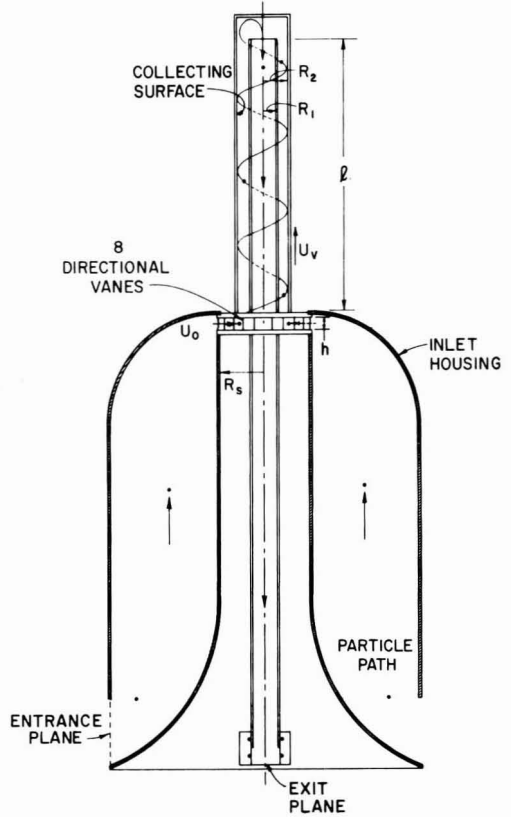


Figure 7. Wedding IP inlet, section view, not to scale.

tionating device efficiency used to establish the desired  $D_{50}$  and the efficiency of the inlet geometry which transports the aerosol to the fractionator and protects the system from environmental factors. As it is not practical or necessary to achieve isokinetic sampling in the field, the inlet must only effectively transport to the fractionating device the particle sizes of interest with consistent or predictable losses independent of fluid mechanics (wind speed, three-dimensional direction, turbulence intensity, and scale) and environmental conditions (precipitation, airborne debris, insects, etc.). Thus, separated flow regions within the device must be avoided as these areas will cause varying deposition loss as a function of fluid energy. The inlet geometry must serve to self-limit the number of entering fluid streamlines commensurate with the approach flow velocity so as to collect a particle phase sample with mass and size range of interest independent of ambient conditions.

The choice of the fractionation device is practically limited to a conventional impactor, a virtual impactor, or a cyclone. The conventional impactor suffers from particle bounce problems which may be reduced for a time with an appropriate coating or an angled collection surface to alter the bounce trajectory but will always require unpredictable periodic maintenance. The virtual impactor may be a candidate, but to date no workable prototypes have emerged. The inlet shown in Figure 5 performed poorly (41). The cyclone, if designed to be omnidirectional, would appear to be the best candidate as the slope of the fractionation curve is comparable to that for an impactor. It possesses a large surface area for deposition, and it has

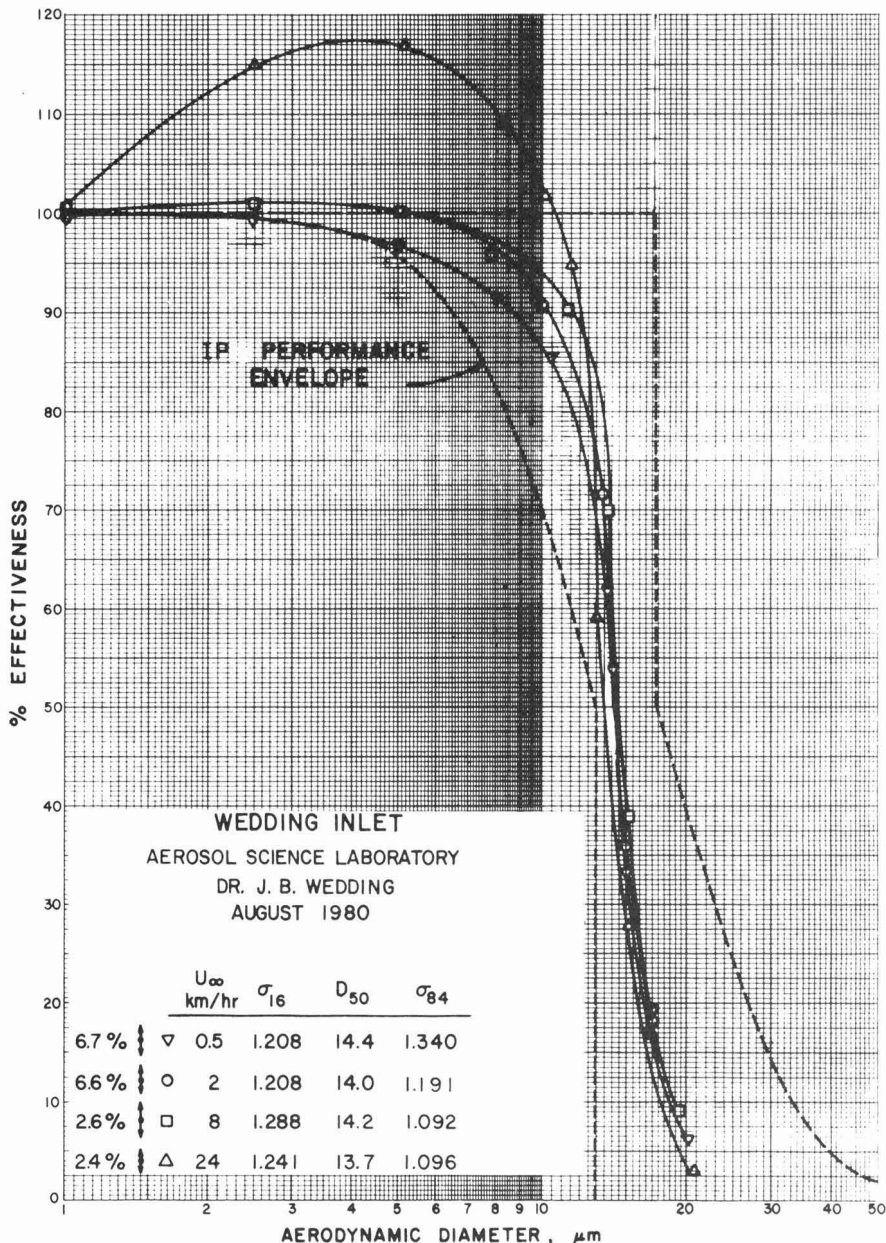


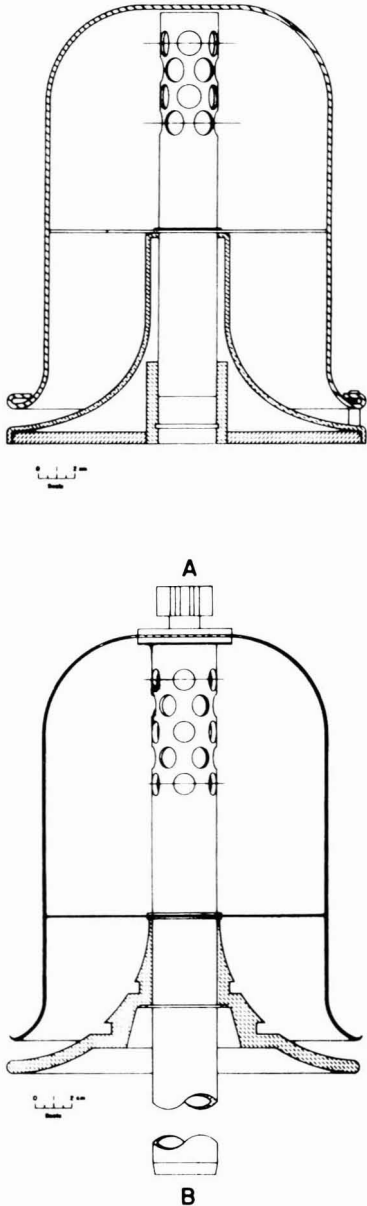
Figure 8. Effectiveness curve for the Wedding IP inlet.

considerably less susceptibility, if any, to particle bounce. Note that no force of sufficient magnitude exists to cause reentrainment or bounce from the surface of a properly designed cyclone unless that particle is elastic enough to add energy to the particle phase during the particle-wall collision. A particle of this nature would not represent those commonly found in the atmosphere. It is for these reasons that the cyclone approach was adopted for this proposed IPM inlet.

**Design of the Cyclone Fractionator.** As shown in Figure 7, this cyclone is unique. It is omnidirectional, allowing the aerosol entry from any angle of approach. An

angular impetus is imparted to the particle motion via the eight evenly spaced entrance vanes. The body of the cyclone is cylindrical in cross section.

As the particle enters the cyclone (see Figure 7), it follows the circular path defined by the vanes and accelerates toward the outer radius of the cyclone defined by  $R_2$ . The particle arrives at  $R_2$  with velocity  $U_0$  where it begins its upward ascension at velocity  $U_w$ . If the particle is not removed, it will travel the distance  $l$ , negotiate the turn at  $R_1$ , and travel downward to the exit plane of the inlet. Particles that are removed will deposit on the inside collector surface as shown in Figure 8.



**Figure 9.** Inlets for the dichotomous virtual impactor: (A) Sierra 244E and (B) Beckman (1, 10).

The present design allows a potential collection area of over 200 cm<sup>2</sup> and an additional volume for storage of collected particulate matter exceeding 500 cm<sup>3</sup>. This unit should be capable of operating in the field maintenance-free for a considerable period of time.

**Design of the Fractionator Housing.** Figure 7 shows the bell-shaped housing and lower radius similar in concept to the inlet developed at the Aerosol Science Laboratory in the summer of 1975 (see ref 1 and 11) and later sold commercially by Sierra and Beckman (Figure 9). This design is a modification of these units following the theoretical predictions from the model presented by Wedding et al. (37). This approach was adopted after other tech-

niques failed to satisfy performance criteria or would prove susceptible to environmental factors. Additionally, the approach has a wealth of data available on its performance as well as a predictable model.

#### Experimental Measurements

The proposed IP inlet operating at 16.67 L/min is shown in Figure 7 and was tested in the closed-loop Aerosol Science Laboratory wind tunnel at Colorado State University (shown in Figure 10). The tunnel has a cross-sectional dimensional of 1.22-m square at the test section. The longitudinal component of turbulence intensity at the test location was found by hot-wire anemometer measurements to be 4%. Similarly, the longitudinal macroscale was ~20 cm, and the vertical macroscale was <2 cm. The tests utilized monodisperse aerosols with nominal aerodynamic diameters of 7–20 μm generated by a vibrating orifice atomizer operating in an inverted manner. Particles employed in the study were made from an oleic acid-ethanol mixture tagged with uranine. The aerosol was sized both by calculation and microscopically. The spread factor, or ratio of measured to aerodynamic diameter, of oleic acid for this size range on oil-phobic (coated with 3M fluorocarbon) glass slides has been found on the average to be 1.39. Measurements of doublets utilizing a Casella impactor in the system have been found not to exceed 4% at the test section. Aerosol from the atomizer was injected through a 15.24-cm diameter pipe containing a Kr-85 charge neutralizer. The pipe diverged into the annular region between two cones. Six pipes spaced around the annular region led the aerosol into the tunnel. This injection system produced a particle concentration profile across the test section which was found to be independent of wind speed over the range of 0.5–40 km/h. Variation of the concentration across the width of the inlet never exceeded 12.2%.

The sampling inlet was tested at wind speeds of 0.5, 2, 8 and 24 km/h, as measured upstream of the test section with a calibrated hot-wire anemometer (Andersen air velocity meter). The anemometer was calibrated by using a precision pitot tube and micromanometer. To determine the inlet effectiveness, the aerosol concentration was measured before and after each test using a sampling manifold 0.90-m wide with six isokinetic sampling nozzles spaced at equal intervals (~15 cm) in the same horizontal plane and at the same location in the test section as the inlet opening. Each nozzle led to a 47-mm Gelman AE glass-fiber filter. The inlet was mounted on a vertical tube approximately 1 m long sealed to a millipore filter holder on the bottom. The sampling effectiveness of the inlet was determined by comparing the quantity of aerosol passed by the inlet and deposited on the filter to that collected by the isokinetic sampling system with appropriate corrections for differences in sampling volume and pressure drops as monitored in the lines. Collection substrates were washed in 50 mL of pure ethanol and then diluted 1:1 with distilled, deionized water which served as a buffer to stabilize fluorescence. A 4-mL aliquot of each sample solution was measured for uranine content with an Aminco fluorometer.

#### Results and Discussion

Results of the wind-tunnel tests on the sampling effectiveness of the Wedding inlet are shown in Figure 8. Each plotted point represents the averaged value of at least eight data points taken on different days. Note the error bars on the data. Tests are quickly and reproducibly performed for speeds of 5–24 (and greater) km/h. For the 0.5 and 2 km/h tests there is insufficient fluid energy to adequately

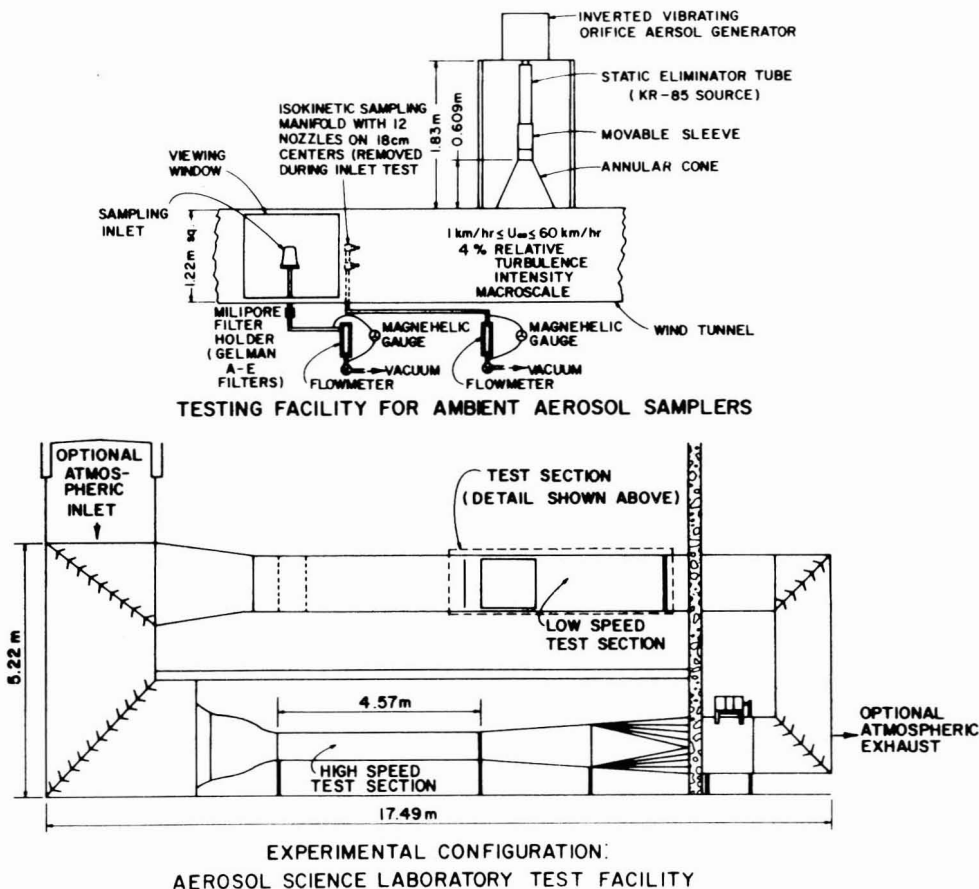


Figure 10. Aerosol Science Laboratory test facility, Colorado State University.

mix the injected aerosol—thus the greater error potential must be noted. Figure 8 shows the results of the inlet shown in Figure 7. All curves generated at the various wind speeds are essentially parallel curves from the  $D_{50}$  point and larger. The  $D_{50}$  values at 0.5, 2, 8, and 24 km/h are 14.4, 14.0, 14.2, and 13.7  $\mu\text{m}$ , respectively. Though not mathematically rigorous, and noting that these curves are not truly log-normal, the values of  $\sigma_{84}$  and  $\sigma_{16}$  are presented instead of using the  $\sigma_g$  notation. The enrichment condition seen in the performance curves at the smaller particle sizes has been shown by computer analysis not to present any problem in collection of consistent, accurate data. The enrichment condition arises from the subsokinetic operation of the inlet and the sufficient inertia of the 5- $\mu\text{m}$  particles to penetrate the nonentering fluid streamlines of the inlet opening. There is undoubtedly some enrichment of larger particles, but these are removed by a combination of the inlet housing and the cyclone fractionator. The computer analysis utilizes an ambient mass distribution curve (42) and performs a point-by-point analysis employing the inlet-effectiveness curve to determine the mass sampled by the inlet. There is insufficient mass represented at this range to bias the results in any way. Detailed results of the technique and analysis procedure are to appear in *Atmospheric Environment* in 1982.

Independent tests on solid particle bounce by Dr. John at the Air and Industrial Hygiene Laboratory indicated the following: "The inlet as shown in Figure 7 exhibits

negligible solid particle bounce" (39).

Additional studies are needed to test the instrument for effectiveness with mean velocities at different angles with respect to the horizontal plane, at different levels of turbulence scale and intensity, and under conditions of simulated rainfall in air moving at 24 km/h and higher.

#### Conclusions and Comments

(1) An acceptable IP inlet for the  $D_{50} = 15 \mu\text{m}$  criterion has been designed, fabricated, and performance tested. It is believed to present a complete, viable candidate for use on the trial EPA IP network. Note that small  $\sigma_{16}$  values are important to ensure wind-speed independency. A new completely revised fractionator and inlet housing concept is presently being designed and tested specifically to eliminate the enrichment condition exhibited in Figure 8 and to improve the performance characteristics of the cyclone fractionator.

(2) The technology to date represented by this particular IP device does not purport to be the ultimate answer. As health effects and other environmental factors and national/scientific needs dictate changes in monitoring strategies (i.e.,  $D_{50}$ , flow rates), other inlet systems will need to be developed, specifically to comply with the suspected advent of the  $D_{50} = 10 \mu\text{m}$  IP or TP approach. Technology will undoubtedly lag somewhat behind the needs of science.

(3) It is strongly urged that research in this area be continued so that, in the intervening 5 years proceeding



the next review of the Clean Air Act, good aerometry can be collected utilizing reliable, accurate instrumentation. With the true mass concentration of the size fraction of aerosols that appear at present to be most potentially deleterious to public health, a good basis can be provided for setting meaningful air quality standards.

#### Acknowledgments

The invaluable assistance in the design and laboratory testing of this device performed by Michael Weigand must be duly noted and is greatly appreciated.

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# Effects of Complexation by Cl, SO<sub>4</sub>, and S<sub>2</sub>O<sub>3</sub> on Adsorption Behavior of Cd on Oxide Surfaces

Mark M. Benjamin\*

Department of Civil Engineering, University of Washington, Seattle, Washington 98195

James O. Leckie

Department of Civil Engineering, Stanford University, Stanford, California 94305

■ Adsorption of metal ions on oxide surfaces mediates the transport of these ions in natural aquatic systems as well as in many waste treatment operations. Often the metals exist in the bulk aqueous phase as complexes with inorganic or organic ligands. The effects of complexation by Cl, SO<sub>4</sub>, and S<sub>2</sub>O<sub>3</sub> on adsorption of Cd onto four different oxide solids have been studied. Increasing concentration of the ligand increases Cd adsorption in some cases and decreases it in others. All of the results are consistent with a model in which chloro and sulfato complexes are assumed to adsorb with the metal closer to the surface than the ligand, and thiosulfato complexes adsorb with the ligand closer than the metal.

Many metals exhibit toxic effects at total concentrations approached and occasionally exceeded in natural aquatic systems. Because of this, it is important to understand speciation of metals in these systems and factors which affect their transport. Numerous investigators have concluded that adsorption onto suspended and bottom sediments is an important process in controlling dissolved metal concentrations (1-4) and metal availability to biota (5, 6). Adsorption is also important in soil-water interactions and in water and wastewater treatment operations.

Previous studies of trace metal adsorption phenomena can be divided into two groups. While one group has emphasized the use of naturally occurring solids and solutions in order to closely simulate real environmental systems, a second group has emphasized systems which are less realistic but better defined. Conclusions from the first type of experiment are of necessity more empirical but also more directly applicable than the second. As the chemistry of complex natural aquatic systems and the chemistry of adsorption phenomena become better understood, the gap between the two groups narrows.

Among the important advances in "synthetic" adsorption experiments in recent years has been an increased awareness of the importance of complexing ligands on metal ion adsorption (7-9). Both inorganic and organic complexing ligands are present in all natural aquatic systems and may have a dramatic effect on metal ion behavior and on the surface properties of potential adsorbents.

Interactions between metal ions and complexing ligands in the presence of an adsorbent surface may be divided into three groups based on the origin and the strength of the interaction: (1) Metal-ligand complexes may form in solution and adsorb only weakly or not at all. In this case, formation of soluble complexes may be considered to compete with reactions forming "surface complexes", and adsorption is decreased compared to the ligand-free system. (2) The species may interact indirectly at the surface, by altering the surface electrical properties. For instance, if the ligand is an anion, it may adsorb and make the Coulombic interaction between the solid and a cationic metal ion more favorable, even if the metal adsorbs at a

site distant from the ligand. (3) The metal-ligand complex may adsorb strongly, thereby enhancing removal of metal, ligand, or both from solution compared to the case where either one is present alone.

If one treats the surface as analogous to a complexing ligand, adsorption of a metal-ligand complex may be considered analogous to formation of a mixed-ligand complex. Such species are entirely reasonable and are to be expected. In fact, the distinction between "free" and "complexed" metal ions is somewhat artificial anyway, since in the absence of other ligands metals are typically present in aqueous solution as aquo complexes.

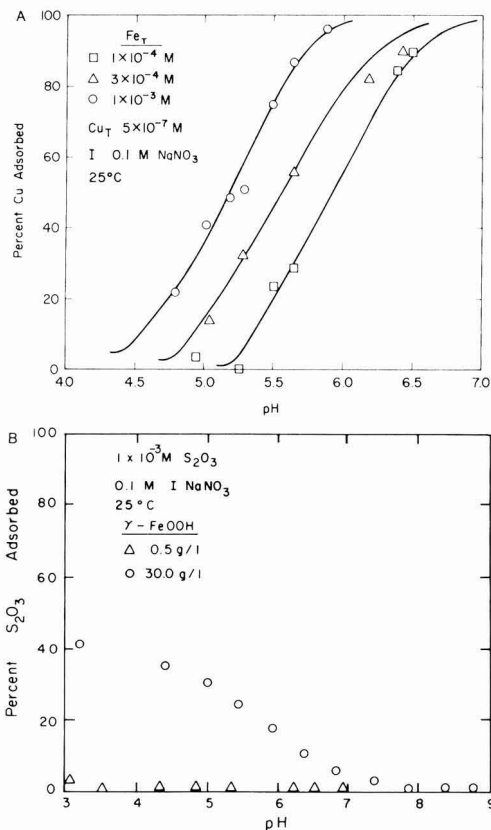
Examples of each of these types of interactions have been reported or can be inferred from the recent literature. For instance, nonsorbing Hg-Cl complexes have been reported by MacNaughton and James (8) and Avotins (10). Davis and Leckie (11) have described complexes of Ag and Cu with S<sub>2</sub>O<sub>3</sub> and some organic ligands in which metal adsorption increases as ligand is added to the system. While strictly indirect electrical interactions between the surface, the metal, and the ligand have not been reported, there is no question that adsorption of ions changes surface electrical properties such as the point of zero charge (PZC), the isoelectric point (IEP), and the surface electrical potential, and these changes are expected to affect the Coulombic attraction between the surface and adsorbate ions.

In a previous paper (12) a generalized model for metal ion adsorption in the presence of complexing ligands was developed which considers all of the potential interactions noted above. In this paper we review characteristic adsorption behavior of metals and ligands and present experimental results for metal adsorption in complexing systems. In the final section the model is used to make inferences about the structure and the orientation of adsorbed metal-ligand complexes in several model systems.

## Adsorption Patterns for Cations, Anions, and Complexes

**Dependence on Solution pH.** Recent models of adsorption phenomena (13, 14) have emphasized the similarities between adsorption of ions at oxide interfaces and complexation reactions. In particular, adsorption behavior of cationic metal ions (Me<sup>m+</sup>) is similar to metal ion hydrolysis and is characterized by a steep "pH-adsorption edge" (15). The adsorption edge is a narrow pH region, often about 2 pH units wide, in which partitioning of the metal changes with increasing pH from nearly all in the solution phase to nearly all adsorbed, provided sufficient adsorption sites and/or adsorbent area are available. The reaction is generally accompanied by release of protons to solution, either by ion exchange at the surface or by hydrolysis occurring simultaneously with adsorption (16, 17).

Adsorption of anions at oxide surfaces is in many ways a "mirror image" of cation adsorption. For anions, the pH-adsorption edge goes from nearly complete removal

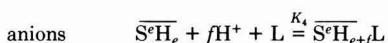
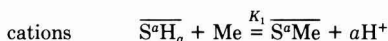


**Figure 1.** Effects of adsorbent concentration on pH-adsorption edges of cations and anions: (A) Cu on  $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}(\text{am})$ ; (B)  $\text{S}_2\text{O}_3$  on  $\gamma\text{-FeOOH}$ .

from solution at low pH to no removal at higher pH, and protons are consumed when the anions adsorb (18, 19). An analogous solution phase reaction is protonation of bases.

**Effects of Adsorbent Concentration.** For both cations and anions, increasing the adsorbent concentration increases the tendency to adsorb, just as increasing ligand concentration increases metal ion complexation (Figure 1, A and B).

This observation can be explained by model adsorption reactions such as the following:



where  $\overline{\text{S}^{\circ}\text{H}_a}$  and  $\overline{\text{S}^{\circ}\text{H}_e}$  are surface sites, Me is an adsorbable cation, and L is an adsorbable anion. The subscripts have been chosen to correspond with those in ref 12. Charge assignment has been omitted for simplicity. Other model equations might be written to include the hydrolysis of metal ions, adsorption and interaction with other adsorbates including bulk electrolyte ions, etc. However, the above reactions include all of the interactions that are essential to this discussion.

The equilibrium expressions for these reactions are

$$K_1 = \frac{(\overline{\text{S}^{\circ}\text{Me}})(\text{H}^+)^a \text{EDL}_a}{(\overline{\text{S}^{\circ}\text{H}_a})(\text{Me})} \quad (1)$$

$$K_4 = \frac{(\overline{\text{S}^{\circ}\text{H}_{e+f}\text{L}})\text{EDL}_e}{(\overline{\text{S}^{\circ}\text{H}_e})(\text{H}^+)^f(\text{L})} \quad (2)$$

where parentheses indicate activity of a species and EDL is a term accounting for the effect of the nonzero electrical potential in the double layer. Its magnitude is not well-known and is estimated differently by different workers. Assuming activity coefficients in the bulk solution and at the surface are constant and abbreviating  $\overline{\text{S}^{\circ}\text{Me}}$  and  $\overline{\text{S}^{\circ}\text{H}_{e+f}\text{L}}$  as SMe and SL, respectively, one can rewrite the equilibrium expressions in logarithmic form:

$$\log \frac{[\text{SMe}]}{[\text{Me}]} = \log K_1 + (a)(\text{pH}) - \log \text{EDL}_a + \log [\overline{\text{S}^{\circ}\text{H}_a}] \quad (3)$$

$$\log \frac{[\text{SL}]}{[\text{L}]} = \log K_4 - (f)(\text{pH}) - \log \text{EDL}_e + \log [\overline{\text{S}^{\circ}\text{H}_e}] \quad (4)$$

where brackets indicate concentration.  $[\overline{\text{SMe}}]/[\text{Me}]$  and  $[\overline{\text{SL}}]/[\text{L}]$  are measures of the partitioning of adsorbate between the surface and the solution.

The value of the EDL term is primarily a function of the concentration of major electrolyte ions and pH (14). Thus, for a system in which bulk ionic composition is fixed

$$\log \frac{[\overline{\text{SMe}}]}{[\text{Me}]} = \log K_1 + F_1(\text{pH}) + \log [\overline{\text{S}^{\circ}\text{H}_a}] \quad (5)$$

$$\log \frac{[\overline{\text{SL}}]}{[\text{L}]} = \log K_4 + F_4(\text{pH}) + \log [\overline{\text{S}^{\circ}\text{H}_e}] \quad (6)$$

where  $F_1(\text{pH}) = (a)(\text{pH}) - \log \text{EDL}_a$  and  $F_4(\text{pH}) = (f)(\text{pH}) - \log \text{EDL}_e$ .  $F_1$  and  $F_4$  are functions of pH only. Equations 5 and 6 indicate that for any given adsorbent/adsorbate pair the pH region of the adsorption edge depends on the adsorbent concentration ( $[\overline{\text{S}^{\circ}\text{H}_a}]$  or  $[\overline{\text{S}^{\circ}\text{H}_e}]$ ). This point has not been sufficiently appreciated previously. For instance, if in a given system 50% adsorption ( $\log [\overline{\text{SL}}]/[\text{L}] = 0$ ) occurs at a given pH, by using  $10^2$  or  $10^{-2}$  as much adsorbent one can adjust fractional anion adsorption at this pH to approximately 99% or 1%, respectively. The exact fractional adsorption may be somewhat less than 99% or greater than 1% in these systems because of changes in the value of the EDL term. However, the general conclusion that the pH region of the adsorption edge can be adjusted by varying the concentration of surface groups is valid in any system. This point is illustrated by Figures 1, A and B. For instance, Figure 1B shows adsorption of  $\text{S}_2\text{O}_3$  onto  $\gamma\text{-FeOOH}$ , a solid with isoelectric point (IEP) at pH 2. (X-ray analysis indicated no peaks other than those characteristic of  $\gamma\text{-FeOOH}$  for this solid. Nevertheless its PZC was at  $\text{pH} \sim 7.0$ , indicating the presence of some impurity. The most likely cause of the discrepancy between the IEP and the PZC is inclusion of oxyanions of sulfur when the solid is prepared by oxidation of iron sulfide). In a suspension of 0.5 g/L  $\gamma\text{-FeOOH}$ , no  $\text{S}_2\text{O}_3$  adsorbs in the pH range 3–9, suggesting that the driving force for  $\text{S}_2\text{O}_3$  adsorption is unable to overcome the Coulombic repulsion between the ion and the surface. However, when the solid concentration increases to 30 g/L, a significant fraction of the total  $\text{S}_2\text{O}_3$  in solution adsorbs up to pH 6.0, even though the surface carries a significant negative charge under these conditions. Thus, the fact that adsorption of a component approaches zero near the IEP of the solid for a given set of conditions does not justify the conclusion that adsorption is dominated by electrostatic interactions. This point cannot be stressed too

strongly. Correlation of the pH-adsorption edge with the pH of the PZC, the IEP, or the pK for a hydrolysis reaction results from choice of adsorbent and adsorbate concentrations and does not necessarily imply a fundamental relationship.

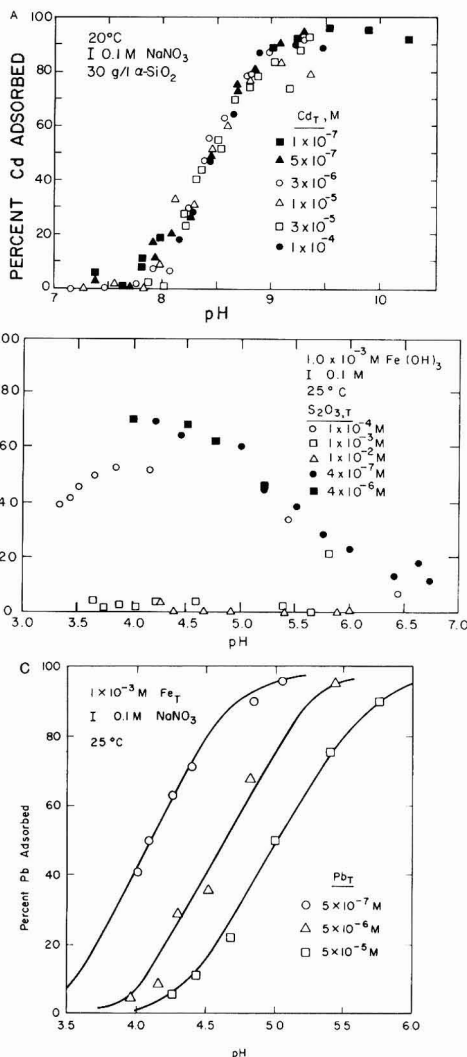
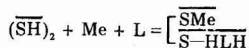
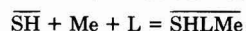
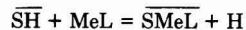
**Dependence on Adsorption Density.** One convenient format for presenting adsorption data is a plot of fractional adsorption (mass of A adsorbed/total mass of A in system) vs. pH. This format emphasizes the importance of pH in driving the adsorption reaction. As adsorption density increases, fractional adsorption may change in several different ways. At low surface coverage, fractional adsorption is expected to be independent of adsorption density. That is, for a given concentration of adsorbent, increasing the total adsorbate in the system increases the soluble and adsorbed concentrations proportionately so the fraction adsorbed remains constant. This is true as long as the surface is far from saturated, i.e., site availability is not a limiting factor, and the EDL term is approximately constant at fixed pH. Adsorption of Cd onto  $\alpha$ -SiO<sub>2</sub> is representative of such systems (Figure 2a).

When availability of surface sites is a limiting factor, adsorption density approaches a maximum value and the adsorbate may not be removed from solution under conditions which otherwise favor strong partitioning to the surface. Such behavior has been reported for adsorption of sulfate, selenate, and glutamic acid on amorphous iron oxyhydroxide (Fe<sub>2</sub>O<sub>3</sub>·H<sub>2</sub>O(am)) by Davis and Leckie (11), and an example showing adsorption of S<sub>2</sub>O<sub>3</sub> on Fe<sub>2</sub>O<sub>3</sub>·H<sub>2</sub>O(am) is shown in Figure 2B.

If an ion is strongly adsorbed, it may significantly affect surface charge and potential. In this case, increasing total adsorbable solute in a system while holding adsorbent concentration constant may change the slope of the pH-adsorption edge or shift the edge to a more acidic (for anions) or more alkaline (for cations) pH region. This situation has been reported by Anderson and co-workers (20), who studied adsorption of arsenate on Al<sub>2</sub>O<sub>3</sub>(am), and by Pierce and Moore for adsorption of arsenite on amorphous iron hydroxide (21).

In some cases, the pH-adsorption edge for metals shifts to higher pH with increasing adsorption density even though surface sites are apparently available in excess and the electrical properties of the surface are approximately constant. This phenomenon has been attributed to non-uniformity of surface sites and seems to be more characteristic of trace metal adsorption than ligand adsorption (17) (Figure 2C).

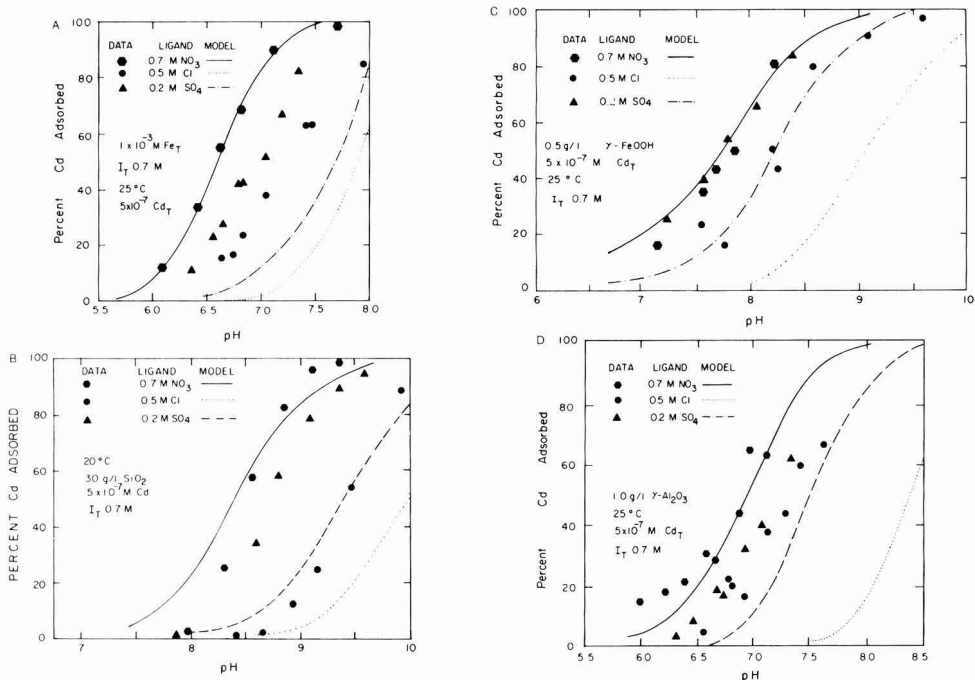
**Adsorption of Metal-Ligand Complexes.** The formation of surface-metal-ligand complexes may occur by sequential bonding of the ions or by adsorption of the complex. Thermodynamically, these mechanisms are equivalent and equilibrium adsorption data provide no information by which to distinguish between them. In addition, complexes may adsorb in any of several different surface configurations or orientations. Discussion about which orientation is most likely is presented later. Throughout this paper the phrase "adsorption of the metal-ligand complex" is meant to include any series of reactions which leads to a surface species in which a metal and a ligand are simultaneously bonded to the surface site and to each other. Examples of such reactions are as follows:



**Figure 2.** Effects of adsorbate concentration on pH-adsorption edges: (A) Cd on  $\alpha$ -SiO<sub>2</sub>; (B) S<sub>2</sub>O<sub>3</sub> on Fe<sub>2</sub>O<sub>3</sub>·H<sub>2</sub>O(am); (C) Pb on Fe<sub>2</sub>O<sub>3</sub>·H<sub>2</sub>O(am).

As noted earlier, typical pH-adsorption edges for cations and anions are mirror images of one another. It is reasonable that complexes may in some cases have pH-adsorption edges similar to those of cations, and in others similar to those of anions. We define a "metallike complex" as one for which the tendency to adsorb increases dramatically as pH increases, as is the case for most cations. Similarly, "ligandlike complexes" are those for which the tendency to adsorb decreases with increasing pH.

If metallike complexes are formed in a system, the pH-adsorption edge for a metal is approximately parallel to that in the ligand-free system. If ligandlike complexes are formed, the slope of the pH-adsorption edge for metal progressively decreases and may change sign (+ to -) as ligand is added. Overall metal adsorption patterns expected for these systems have been discussed in detail in a previous paper (12). In the following sections we describe effects of complexation by several ligands on Cd adsorption



**Figure 3.** Effects of Cl and  $\text{SO}_4$  on Cd adsorption onto various solids: (A)  $\text{Fe}_2\text{O}_3\cdot\text{H}_2\text{O}(\text{am})$ ; (B)  $\alpha\text{-SiO}_2$ ; (C)  $\gamma\text{-FeOOH}$ ; (D)  $\gamma\text{-Al}_2\text{O}_3$ . Lines labeled "Model" are predictions based on the assumption that complexes do not adsorb.

**Table I.** Summary of Surface Properties of  $\text{Fe}_2\text{O}_3\cdot\text{H}_2\text{O}(\text{am})$ ,  $\gamma\text{-FeOOH}$ ,  $\alpha\text{-SiO}_2$ , and  $\gamma\text{-Al}_2\text{O}_3$

adsorbent	PZC	IEP in metal-free systems	specific surface area, $\text{m}^2/\text{g}$	surface sites/ $\text{nm}^2$	ref
$\text{Fe}_2\text{O}_3\cdot\text{H}_2\text{O}(\text{am})$	7.9	7.9	600 <sup>a</sup>	9.8	14
$\alpha\text{-SiO}_2$	~2.5	~2.5	3.3	3-6	23-25
$\gamma\text{-Al}_2\text{O}_3$	8.9	8.9	125	8	26, 27
$\gamma\text{-FeOOH}$	~7.0	2.0	22	10	23

<sup>a</sup> Equivalent to 500  $\text{m}^2/\text{g}$  if solid stoichiometry is  $\text{Fe}(\text{OH})_3$ .

and compare the results with the expected trends for metallike and ligandlike complexes.

### Experimental Section

Batch experiments were performed at 20 °C under a nitrogen atmosphere.  $\text{Fe}_2\text{O}_3\cdot\text{H}_2\text{O}(\text{am})$  was precipitated in situ and aged 4 h at pH 7.0 before addition of the adsorbates. The  $\alpha\text{-SiO}_2$  was purified according to the method of MacNaughton (22). The  $\gamma\text{-FeOOH}$  and  $\gamma\text{-Al}_2\text{O}_3$  were used in adsorption experiments without pretreatment.

Surface properties of these solids are summarized in Table I.

In a typical experiment, the adsorbent was dispersed in a solution containing the ligands and sufficient  $\text{NaNO}_3$  was added to adjust the solution to the desired ionic strength. An appropriate concentration of Cd, including cadmium-109 tracer, was added, and pH was adjusted by incremental additions of 0.1 M NaOH. After each addition of NaOH a 15-mL aliquot of suspension was transferred to a nitrogen-purged centrifuge tube. The tubes were placed on a roller until the slurries had equilibrated. Preliminary kinetic experiments indicated that an equilibration period of 2-4 h is sufficient for this purpose. The pH was then measured in each tube, the slurries were centrifuged, and a sample of the clear supernatant was withdrawn and analyzed for cadmium-109. The amount of Cd adsorbed was determined by comparison of the activity of the tracer remaining in solution to that of the slurry.

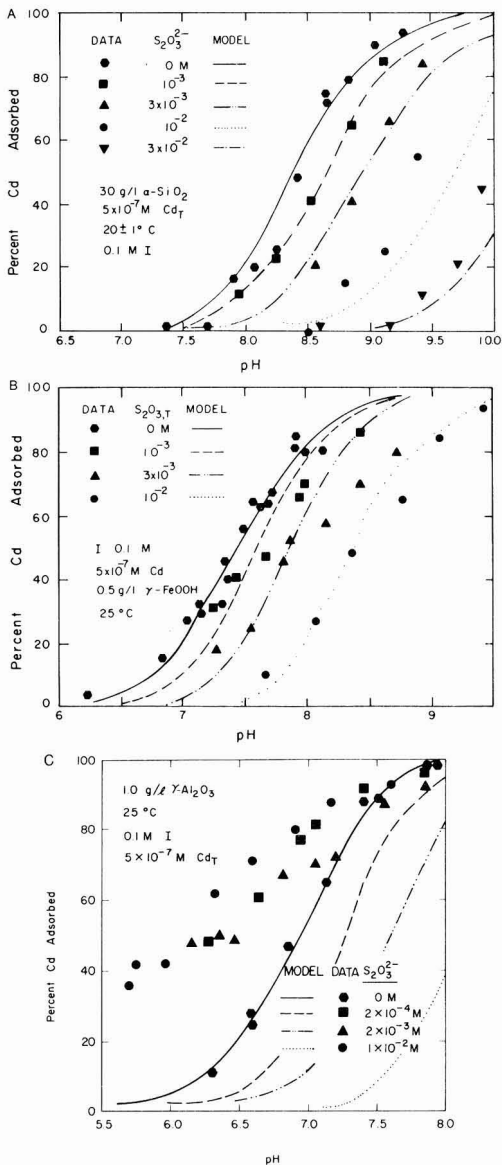
### Results and Discussion

**Ligandlike and Metallike Cadmium Complexes.** The effects of  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{S}_2\text{O}_3^{2-}$  on cadmium adsorption on four different solids are shown in Figures 3-5. The

**Table II.** Speciation of Dissolved Cadmium in Systems Containing Various Ligands

ligand	concn, M	% total Cd activity as <sup>a</sup>					av charge per Cd ion
		$\text{Cd}^{2+}$	$\text{CdL}_1$	$\text{CdL}_2$	$\text{CdL}_3$	$\text{CdL}_4$	
$\text{SO}_4^{2-}$	0.2	4	49	47	0	0	-0.86
$\text{Cl}^-$	0.5	1	29	50	17	3	+0.08
$\text{S}_2\text{O}_3^{2-}$	$2 \times 10^{-4}$	63	36	1	0	0	+1.24
	$2 \times 10^{-3}$	11	76	13	0	0	-0.04
	$1 \times 10^{-2}$	2	57	41	0	0	-0.78

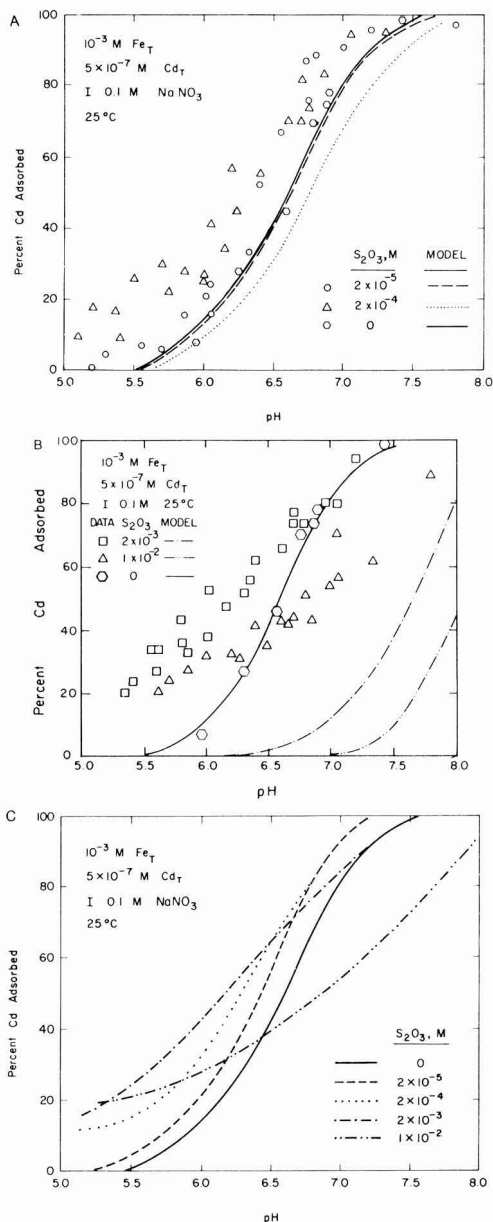
<sup>a</sup> Hydroxo complexes, which are unimportant at pH < 9, are excluded. Activity coefficients calculated from the Debye-Hückel equation. Stability constants were taken from ref 28 and 29.



**Figure 4.** Effects of  $S_2O_3$  on Cd adsorption onto various solids: (A)  $\alpha$ - $SiO_2$ ; (B)  $\gamma$ - $FeOOH$ ; (C)  $\gamma$ - $Al_2O_3$ . Lines labeled "Model" are predictions based on the assumption that complexes do not adsorb.

speciation of Cd in solution in these systems is summarized in Table II. In all systems containing  $Cl^-$  or  $SO_4^{2-}$  the pH-adsorption edge for Cd is approximately parallel to that for the ligand-free system. Adding either of these ligands decreases metal adsorption, except in the  $\gamma$ - $FeOOH/Cd/SO_4$  system in which the ligand ( $SO_4$ ) has almost no effect.

The Cd adsorption behavior in the systems containing only a noncomplexing ligand ( $NO_3^-$ ) has been modeled by using a site-binding adsorption model developed by Davis et al. (14). Equilibrium constants were determined for the reaction between Cd and the surface such that the model and the experimental data were in close agreement. Then the effects of  $Cl^-$  and  $SO_4^{2-}$  on Cd adsorption were modeled,



**Figure 5.** Effects of  $S_2O_3$  on Cd adsorption onto  $Fe_2O_3 \cdot H_2O(am)$ . Part C is a summary of the data in parts A and B, and the lines in part C represent smooth curves through the experimental data in parts A and B. Lines labeled "model" are predictions based on the assumption that complexes do not adsorb.

assuming that they affect metal adsorption only by complexation reactions in solution, i.e., they compete with the surface for the Cd. The modeling results are presented in Figures 3A-3D. In all cases the predicted effect of the ligands is much greater than that observed experimentally.

Enhanced adsorption compared to the model predictions may be due to metallike adsorption of complexes or to changes in surface potential resulting from sorption of the anionic ligands. Benjamin and Bloom (30) have suggested that changes in surface potential do not affect Cd sorption

Table III. Computation of Fractional Adsorption of Cd(S<sub>2</sub>O<sub>3</sub>)<sub>x</sub> Complexes on γ-Al<sub>2</sub>O<sub>3</sub><sup>a,b</sup>

total S <sub>2</sub> O <sub>3</sub> in system	2.0 × 10 <sup>-4</sup>	2.0 × 10 <sup>-3</sup>	1.0 × 10 <sup>-2</sup>
(1) S <sub>2</sub> O <sub>3</sub> adsorbed, %	36	7	1
(2) dissolved S <sub>2</sub> O <sub>3</sub>	1.3 × 10 <sup>-4</sup>	1.9 × 10 <sup>-3</sup>	1.0 × 10 <sup>-2</sup>
(3) Cd adsorbed, %	36	42	42
(4) dissolved total Cd	3.2 × 10 <sup>-7</sup>	2.9 × 10 <sup>-7</sup>	2.9 × 10 <sup>-7</sup>
(5) dissolved complexed Cd	8.6 × 10 <sup>-8</sup>	2.5 × 10 <sup>-7</sup>	2.8 × 10 <sup>-7</sup>
(6) adsorbed complexed Cd	1.8 × 10 <sup>-7</sup>	2.1 × 10 <sup>-7</sup>	2.1 × 10 <sup>-7</sup>
(7) adsorption of complexed Cd, %	68	46	43

<sup>a</sup> All calculations are for systems containing 5 × 10<sup>-7</sup> M total Cd, pH 6.0. All concentration values are in mol/L. <sup>b</sup> Values in rows 1 and 3 are from Figures 6 and 4B, respectively. Values in row 5 are computed by knowing (S<sub>2</sub>O<sub>3</sub><sup>2-</sup>) activity and Cd-S<sub>2</sub>O<sub>3</sub> stability constants. Values in row 6 are based on the assumption that all adsorbed Cd at pH 6 is complexed. Values in row 7 equal (row 6)/(row 5 + row 6).

significantly in systems similar to those reported here based on the absence of significant change in Cd adsorption when several strongly sorbing anions are added to the system. Also, partitioning of Cu and Zn between surface and solution phases is essentially independent of chloride concentration on these surfaces (19). Changes in the surface electrical potential should affect Cu, Zn, and Cd adsorption approximately equally. The accumulated evidence indicates that changes in Cd adsorption behavior when chloride or sulfate is added to the system cannot be accounted for by changes in coulombic interactions between the surface and free metal, and hence must be due to adsorption of Cd complexes.

Increasing the ligand concentration in solution increases the activity of complexed metal relative to free dissolved metal. If complexed metal species adsorb more strongly than free metal ions, a shift in solution conditions favoring formation of the complex (i.e., increasing ligand concentration) should lead to an overall increase in metal adsorption. Alternatively, if the complex adsorbs less strongly than the free metal, shifting the equilibrium to favor complexation will decrease overall metal adsorption. In most cases investigated, adding Cl<sup>-</sup> or SO<sub>4</sub><sup>2-</sup> to solution decreases Cd adsorption. Therefore, chloro and sulfato complexes of cadmium must adsorb less strongly than uncomplexed cadmium ions in these systems. Since addition of sulfate does not affect the Cd/γ-FeOOH adsorption edge, free cadmium and Cd(SO<sub>4</sub>)<sub>2</sub> complexes apparently bind with approximately equal strength on γ-FeOOH.

Conceptually, it is entirely plausible that complexes may adsorb in a metallike fashion with binding strength greater than the corresponding free metal. Results presented by Theis and Richter (9), Davis (31), and Siegel (32) suggest that this may be the case for some organic complexes of nickel and copper. There is no evidence that chloro or sulfato complexes adsorb in a ligandlike manner on any of the solids studied, but the low-pH region where such behavior would be most obvious was not investigated.

Contrary to the other ligands studied, the effect of thiosulfate on cadmium adsorption is in all cases consistent with that predicted for ligandlike adsorption of the complex. The fractional adsorption of free S<sub>2</sub>O<sub>3</sub><sup>2-</sup> onto α-SiO<sub>2</sub> and γ-FeOOH is negligible under the experimental conditions investigated (Figures 1B and 6). Extrapolating this result to ligandlike Cd-S<sub>2</sub>O<sub>3</sub> complexes, one may expect that fractional adsorption of free Cd may be significant on these solids but that of Cd(S<sub>2</sub>O<sub>3</sub>)<sub>x</sub> species would not. Experimental results for systems containing S<sub>2</sub>O<sub>3</sub><sup>2-</sup> are consistent with this prediction (Figure 4, A and B). On each adsorbent, for several different concentrations of S<sub>2</sub>O<sub>3</sub><sup>2-</sup>, dissolved ligands compete with the surface for Cd ions and there is no indication that these complexes adsorb at all.

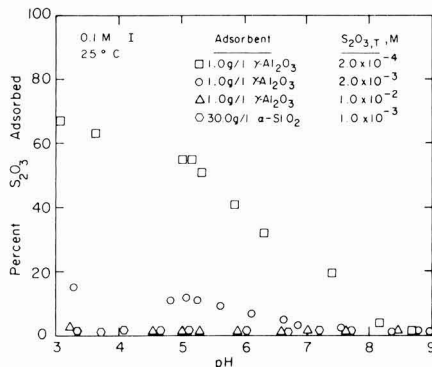


Figure 6. pH-adsorption edges for S<sub>2</sub>O<sub>3</sub> on γ-Al<sub>2</sub>O<sub>3</sub> and α-SiO<sub>2</sub>.

On γ-Al<sub>2</sub>O<sub>3</sub>, significant amounts of free S<sub>2</sub>O<sub>3</sub><sup>2-</sup> adsorb at pH < 8 in the systems studied (Figure 6). As a result one may expect a ligandlike complex to adsorb also, thereby enhancing removal of metal from acidic solutions. This prediction has been experimentally verified, and adsorption of Cd onto γ-Al<sub>2</sub>O<sub>3</sub> is dramatically enhanced at pH < 8 by the presence of S<sub>2</sub>O<sub>3</sub><sup>2-</sup> (Figure 4C).

The γ-Al<sub>2</sub>O<sub>3</sub>/Cd/S<sub>2</sub>O<sub>3</sub> system is complicated by the facts that (1) adsorption of the free ligand is approaching a condition of surface saturation for the range of S<sub>2</sub>O<sub>3</sub> concentrations studied and (2) the pH-adsorption edges for free S<sub>2</sub>O<sub>3</sub> and free Cd overlap. Therefore, fractional adsorption of the free ligand and the ligandlike complex decreases significantly in the same pH region where fractional adsorption of the free metal increases significantly. The combined effects of these two factors may help explain why there is an increase in Cd adsorption when S<sub>2</sub>O<sub>3</sub><sup>2-</sup> concentration increases from 0 to 2 × 10<sup>-4</sup> M but Cd adsorption increases only slightly or decreases when S<sub>2</sub>O<sub>3</sub><sup>2-</sup> concentration is increased further.

Despite these complications, an estimate of the bonding strength of Cd(S<sub>2</sub>O<sub>3</sub>)<sub>x</sub> complexes relative to that of free S<sub>2</sub>O<sub>3</sub><sup>2-</sup> can be made. If the complexes adsorb exactly as strongly as free S<sub>2</sub>O<sub>3</sub><sup>2-</sup>, fractional adsorption of the complexes should be the same as fractional adsorption of free S<sub>2</sub>O<sub>3</sub> at any pH. Fractional adsorption of the complex is defined as (adsorbed complex)/(adsorbed complex + dissolved complex). In the Cd/γ-Al<sub>2</sub>O<sub>3</sub> systems studied adsorption of free Cd is negligible at pH 6.0. Thus, when S<sub>2</sub>O<sub>3</sub> is added to solution, any Cd adsorption at pH 6 can be attributed to adsorption of complexes. While adsorption of S<sub>2</sub>O<sub>3</sub> would increase electrostatic attraction of the surface for all cations, this factor should have a negligible effect on Cd adsorption due to the swamping concentration of Na in the system. Making the approximation (adsorbed complex) = (total Cd adsorbed), and knowing the stability

Table IV. Characteristics of CdL<sub>x</sub> Sorption on Various Adsorbents

adsorbent	ligand		Cl <sup>-</sup>		SO <sub>4</sub> <sup>2-</sup>		S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	
	type <sup>a</sup>	strength <sup>b</sup>	type	strength	type	strength	type	strength
Fe <sub>2</sub> O <sub>3</sub> ·H <sub>2</sub> O(am)	M	<Cd	M	<Cd	L	>S <sub>2</sub> O <sub>3</sub>		
α-SiO <sub>2</sub>	M	<Cd	M	<Cd	L(?) <sup>c</sup>	d		
α-Al <sub>2</sub> O <sub>3</sub>	M	<Cd	M	<Cd	L	>S <sub>2</sub> O		
γ-FeOOH	M	<Cd	M	≈Cd	L(?) <sup>c</sup>	d		

<sup>a</sup> M = free metallike; L = free ligandlike. <sup>b</sup> "<Cd" means complex sorbs, but less strongly than uncomplexed Cd. <sup>c</sup> Adsorption of complex was not observed, but failure of complex to adsorb under experimental conditions is consistent with ligandlike behavior. <sup>d</sup> Cannot be determined since neither the free ligand nor the complex adsorbs to a significant extent under experimental conditions.

constants for forming Cd-S<sub>2</sub>O<sub>3</sub> complexes in solution, we calculate the fractional adsorption of the complex to be greater than the fractional adsorption of the free ligand at all three ligand concentrations studied (Table III). This indicates that, on the average, Cd(S<sub>2</sub>O<sub>3</sub>)<sub>x</sub> complexes adsorb more strongly than free S<sub>2</sub>O<sub>3</sub>.

When Fe<sub>2</sub>O<sub>3</sub>·H<sub>2</sub>O(am) is the adsorbent, it is possible to distinguish a low-pH region where adsorption of a ligandlike complex dominates from a higher-pH region where free-metal adsorption dominates (Figure 5A-C). In the low-pH region (pH ≤ 5.7), the effect of increasing S<sub>2</sub>O<sub>3</sub> concentration is to increase Cd adsorption, while at pH > 6.5 increasing S<sub>2</sub>O<sub>3</sub> decreases Cd adsorption. Plots of fractional adsorption vs. pH become progressively less steep as S<sub>2</sub>O<sub>3</sub> is added to the system. These trends are all consistent with formation of ligandlike complexes (12). Calculations similar to those in Table III indicate that fractional adsorption of Cd(S<sub>2</sub>O<sub>3</sub>)<sub>x</sub> complexes is once again greater than that of free ligand, so the complexes adsorb more strongly on Fe<sub>2</sub>O<sub>3</sub>·H<sub>2</sub>O(am) than does S<sub>2</sub>O<sub>3</sub>. In an analogous system where Ag<sup>+</sup> was the metal adsorbate, Davis and Leckie (11) found that stoichiometric amounts of Ag and S<sub>2</sub>O<sub>3</sub> were removed from solution at low pH under conditions where free Ag<sup>+</sup> did not adsorb, showing unambiguously that Ag-S<sub>2</sub>O<sub>3</sub> complexes adsorb in a ligandlike fashion.

Adsorption in the range 5.7 < pH < 6.3 is especially interesting because cadmium adsorption first increases and then decreases as ligand is added to the system. This behavior is consistent with ligandlike adsorption on a nonhomogeneous surface (one comprising several distinct types of adsorption sites, each with different binding strength for the adsorbate) (12). There is strong independent evidence that Fe<sub>2</sub>O<sub>3</sub>·H<sub>2</sub>O(am) has multiple site types for binding many metal ions, including cadmium (17).

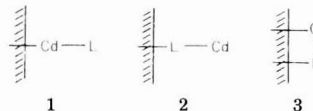
Strong adsorption of ligandlike complexes may in some cases lead to complete removal of the metal from solution at low pH. However, in the Cd/S<sub>2</sub>O<sub>3</sub> systems adsorption of the complexes on γ-Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>·H<sub>2</sub>O(am) is apparently site limited at low pH. That is, competition between complexes and free S<sub>2</sub>O<sub>3</sub><sup>2-</sup> for binding sites limits the number of complexes which can adsorb. Adsorption of the free ligand is clearly site limited under these conditions. In such a case 100% metal removal is not expected, even at low pH. Metal adsorption does increase to near 100% in analogous systems containing silver instead of cadmium, and in which free-ligand adsorption is not site limited (11).

The effects of SO<sub>4</sub>, Cl, and S<sub>2</sub>O<sub>3</sub> on Cd adsorption on all four adsorbents are summarized in Table IV.

**Stereochemistry of Adsorbed Complexes.** A tentative conclusion that can be drawn from these results is that adsorption behavior of a complex is apparently independent of the adsorbent. That is, it appears that CdCl<sub>x</sub> and Cd(SO<sub>4</sub>)<sub>x</sub> complexes always adsorb in metallike fashion

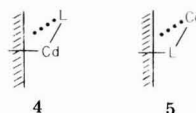
and Cd(S<sub>2</sub>O<sub>3</sub>)<sub>x</sub> complexes always adsorb in ligandlike fashion. The different types of complex adsorption behavior may be attributable to different orientations of the complexes at the surface, which may in turn be partially explained by coordination chemistry.

There are at least three possible conformations for adsorbed complexes:



If net molecular charge were the dominant factor controlling adsorption of the complex, one could explain the adsorptive behavior of a metal simply from its speciation in solution. For instance, one would then expect CdCl<sup>+</sup> to be a metallike and CdCl<sub>3</sub><sup>-</sup> to be a ligandlike adsorbate. Table II shows dissolved speciation of cadmium in the systems studied. Some complexes, e.g., Cd(S<sub>2</sub>O<sub>3</sub>)<sub>x</sub>, adsorb analogously to anions even when the net charge on the dominant dissolved species is zero (CdS<sub>2</sub>O<sub>3</sub><sup>0</sup>) and the average charge on all Cd species is positive. It is likely, therefore, that specific adsorption of these complexes via direct surface-to-ligand bonds controls adsorptive behavior, rather than electrostatic factors. This makes configuration 1 an improbable orientation for ligandlike complexes. Similarly, CdCl<sub>x</sub> and Cd(SO<sub>4</sub>)<sub>x</sub> exhibit metallike adsorption when the dominant dissolved species are uncharged or anionic. For these complexes, configuration 2 is highly improbable.

Complexes having orientation 3, by virtue of having two surface-to-complex bonds (i.e., forming a bidentate surface complex) may adsorb more strongly than either free metal or free ligand. Of course intermediate structures such as the following may also exist:



Structures such as 3 or 5 may explain the extra specific adsorption energy of Cd(S<sub>2</sub>O<sub>3</sub>)<sub>x</sub> relative to free S<sub>2</sub>O<sub>3</sub><sup>2-</sup>. Since CdCl<sub>x</sub> and Cd(SO<sub>4</sub>)<sub>x</sub> complexes generally adsorb less strongly than free Cd, there is no evidence that these complexes are multidentate with the surface.

The preferred conformation of an adsorbed molecule is related to the bond strengths of the constituent groups, i.e., the stronger bond will form preferentially. The specific adsorption energy of most transition metals, including Cd, is greater than that of the ligands investigated in this study. Therefore, in the absence of other factors, complexes would bind to the surface via the metal ion. However, if complexation decreases the driving force for forming a metal-surface bond much more than that for forming



a ligand-surface bond, the adsorbed complex may orient with the ligand facing the surface.

Thiosulfate ion can be thought of as a sulfate ion and a sulfide ion joined by a double bond:



When  $\text{S}_2\text{O}_3$  adsorbs to an oxide, the most likely orientation is with the oxygen atoms bonding to surface metal ions, based on the similarity between sulfate adsorption and thiosulfate adsorption. However, "soft" metal ions such as  $\text{Cd}^{2+}$  generally bond to the sulfide end of the ligand, since sulfide is classified as a "soft" base, or soft ligand (34). Thus, complexation of the metal may have a relatively minor effect on the surface binding part of the  $\text{S}_2\text{O}_3^{2-}$  ion. Apparently, formation of the complex sufficiently destabilizes the Cd-surface bond that the free energy change accompanying adsorption is most negative if the  $\text{S}_2\text{O}_3$  group, rather than the Cd, faces the surface.

Elliott and Huang (35) report data for Cu adsorption onto  $\gamma\text{-Al}_2\text{O}_3$  in the presence of NTA that are generally consistent with the ligandlike complex behavior. They concluded that the Cu-NTA complex adsorbs with the Cu nearer the surface than the N, and the three carboxylic terminal oxygen atoms hydrogen-bonded to protonated surface sites. They considered only Coulombic interactions between the surface and the complex, and hence their conclusion may be questioned since chemical interactions other than electrostatic probably dominate the bonding. However, their proposed orientation of the adsorbed complex is consistent with the discussion presented here, if the carboxyl-surface interactions dominate when the complex adsorbs.

Similarly, Theis and Richter (9) investigated Ni adsorption on  $\alpha\text{-FeOOH}$  in the presence of several ligands. Their results suggest that  $\text{Ni}(\text{CN})_x$  species are ligandlike, that Ni-glycine complexes are metallike, and that Ni complexes with citrate and NTA adsorb weakly or not at all. They suggest that the complexes bind to the surface through the carbon (Ni-CN) and nitrogen (Ni-Gly) atoms, respectively. With sufficient information about the structural and coordination chemistry of other complexes, it may be possible to predict a priori which orientation will be preferred at an oxide-aqueous solution interface, and whether complexation will lead to metallike or ligandlike adsorption behavior.

### Summary

Complexed metal ions can adsorb to oxide surfaces with either the metal or the ligand bonding directly to the surface. Overall metal adsorption in these systems is a function of the speciation in solution, the concentration and the surface characteristics of the solid, and solution pH. The effect of a given ligand does not vary much from one adsorbent to the next. If the metal end of the complex is surface bound, a plot of fractional adsorption vs. pH is approximately parallel to that for the ligand-free system and is usually shifted to higher pH. If the ligand end of the complex is surfacebound, as ligand concentration increases metal adsorption increases in one pH range and decreases in a higher pH range. These are the extreme situations, and intermediate cases are possible and expected.

Adsorption of chloro and sulfato complexes of cadmium is analogous to that of free metal, but adsorption of thio-sulfato complexes is more like that of free ligand. The differences among the complexes may be due to differences in the stereochemical arrangement at the surface. Spe-

cifically, it is proposed that  $\text{CdCl}_2$  and  $\text{Cd}(\text{SO}_4)_x$  complexes bond with metal closer to the surface, while  $\text{Cd}(\text{S}_2\text{O}_3)_x$  complexes generally bond with the ligand closer to the surface. The different orientations of various complexes can be explained by consideration of structural factors and coordination chemistry.

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## Selective Passage of Hydrophilic Nitrogenous Organic Materials through Macroreticular Resins

Nell M. Ram\* and J. Carrell Morris

Harvard University, Division of Applied Sciences, Cambridge, Massachusetts 02138

■ Prefiltration of natural water samples through XAD-8 and Tenax GC macroreticular resins removed, selectively, hydrophobic carbonaceous organic materials without significantly effecting hydrophilic nitrogenous organic substances. Hydrophobic carbonaceous adsorbates competitively decrease adsorption of hydrophilic materials. This phenomenon permits high recoveries of organic nitrogen while simultaneously removing humic material.

### Introduction

Natural and polluted waters contain a numerous variety of natural and synthetic compounds that seriously interfere with the isolation, identification, and determination of individual nitrogenous organic compounds. Humic substances, in particular, comprise a large percentage of the dissolved organic carbon in natural waters while contributing minimally to the total organic nitrogen content (1). Humic substances have hydrophobic characteristics (2), while the bulk of organic nitrogen is associated with hydrophilic substances (2, 3). Since macroreticular resins of intermediate and high polarity are known to adsorb selectively a broad range of hydrophobic organic compounds (3-10), it was hypothesized that humic and other carbonaceous organic materials could be removed by filtration through such macroreticular resins without significant reduction in most nitrogenous constituents, with the exception of heterocyclic aromatic substances.

Several studies have been conducted on the adsorption of humic substances onto XAD macroreticular resins (Rohm and Haas, Co., Philadelphia, PA). Although Oulman (11) reported that XAD-4 had poor capacity for humic substances, Cheng (12), Blunk (13), Stuermer and Harvey (2), and Weber and Wilson (14) observed strong adsorption of humus onto macroreticular resins of varying polarity. Cheng (12) found that adsorption of humic acid by XAD resins was generally favored at neutral conditions (pH 6-7). Blunk (13) found that 97-99% of humic material, as assayed at 450 nm, was adsorbed from untreated river water onto XAD-7. Weber and Wilson (14) reported adsorption of fulvic acid onto XAD-2 at pH 1, and Stuermer and Harvey (2) reported adsorption efficiencies greater than 90% for humic substances in seawater acidified to pH 2 onto XAD-2. Junk et al. (6) observed an increase in the adsorption of organic compounds onto XAD-2 by adding 5 mL of hydrochloric acid per liter

(equal to 0.056 M or pH of about 1.3) of standard water sample tested. Oliver (15) and Christman et al. (16) acidified water samples to pH 2.0 and pH 2.2, respectively, to adsorb humic material in these samples onto XAD resins.

Cheng (12) found that humic substances at pH 5 were more strongly adsorbed onto XAD-1, -2, -4, -7, and -12 than onto XAD-8. Leenheer and Huffman (3) reported that XAD-8 was more effective in adsorbing fulvic acid than were XAD-2 and 4. They also reported the adsorptive capacity of XAD to vary from 5 to 20 mg of organic carbon per gram of resin for different hydrophobic organic compounds.

In addition to the XAD series, other macroreticular resins have been developed for selective adsorption of organic compounds from water. Tenax GC (Applied Sciences Laboratory, Inc., State Collete, PA) has been used to concentrate organic compounds from air (17) and has been suggested as a useful direct accumulator for organic compounds from water in a manner similar to XAD resins (5). Novotny et al. (18) proposed that Tenax be used as an adsorbent for a wide range of both polar and nonpolar compounds. Webb (5) found significantly better recoveries of phenol (72%), camphor (83%), and  $\alpha$ -terpineol (87%) on a 13-cm Tenax column in comparison with a comparable XAD column. Twenty organic compounds were recovered with 80% efficiency on the Tenax resin.

The objective of this work was to demonstrate the ability of a mixed resin bed, consisting of equal-volume combinations of XAD-8 and Tenax-GC macroreticular resins, to remove, selectively, hydrophobic carbonaceous organic materials without significantly adsorbing hydrophilic nitrogenous substances. Such a method might be used, for example, as a pretreatment step in the analysis of N-organic hydrophilic substances by first selectively adsorbing potentially interfering hydrophobic materials from solution. The inability of N-organic substances to be adsorbed onto the macroreticular resin combination was examined by (a) measuring total organic nitrogen recovery of field samples taken from various water sources, after elution through the resin combination, and (b) analysis of breakthrough curves of several model nitrogenous organic compounds eluted individually through the resins. The measurement of organic-N recovery values provided data on the inability of the resin combination to adsorb complex mixtures of nitrogenous organic compounds typically present in natural waters and coexposed to hydrophobic carbonaceous substances. The determination of breakthrough curves for several model organic compounds illustrated the varying adsorptive capacities of the resin

\* Address correspondence to this author at the following address: University of Massachusetts, Department of Civil Engineering, Amherst, MA 01003.

combination for the model nitrogenous materials tested, humic acid, and carbonaceous substances examined in previous studies (3, 6).

Most of the N-organic model compounds chosen for the study have been identified previously in surface waters (19-23). Such N-organic heterocycles are additionally important because of their ability to form falsely positive tests for free chlorine (24) or because some are potential precursors to haloform formation (19, 25). Their behavior with respect to adsorption on macroreticular resins is, therefore, of particular interest. The model N-organic compounds chosen for this study are not necessarily representative of the many individual hydrophilic nitrogenous organic compounds present in any one given water supply since this composition will vary with sample location. However, most of the model compounds chosen are either widespread throughout animal and plant tissues, being constituents of nucleic acids or coenzymes, or are present in human urine or chlorinated sewage and are therefore likely to be found in natural or polluted waters.

#### Materials and Methods

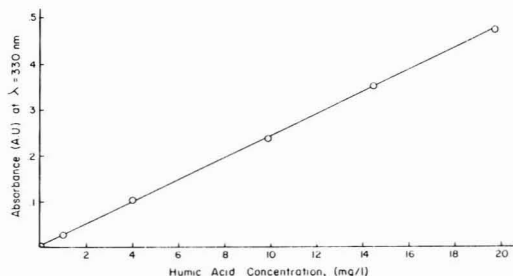
XAD macroreticular resins, of about 10 g per batch, were thoroughly purified by sequential solvent extractions with methanol, acetonitrile, and diethyl ether in a Soxhlet extractor for 8 h per solvent. The purified resins were stored in glass-stoppered bottles under methanol to maintain their purity. Tenax-GC was purified with methanol and acetonitrile extractions.

The purified resins were added as methanol slurries into 1-cm i.d. glass columns and were used as mixed resin beds. These beds consisted of equal-volume combinations of XAD-8 and Tenax-GC macroreticular resins and were prepared by sequential addition of each resin to a depth of about 6 cm (1.5 g of dry resin each). Glass-wool plugs were inserted near the stopcock, between the two resin beds, and above the final resin layer.

**Elution and Regeneration Procedures.** Methanol was drained to the top of the uppermost resin bed and then flushed with approximately 200 mL of distilled water. Distilled water was then drained to the top of the resin bed before passage of a sample. A flow rate of about 10 mL/min was maintained by application of 1-psi pressure supplied from a regulated, filtered air line. The first 20 mL of eluted sample was discarded because this was the dead volume of residual distilled water in the column. The remaining eluted sample was collected for analysis. The resin was regenerated after elution of each liter of sample. Regeneration was achieved by sequential equilibration with 50 mL of  $10^{-2}$  M NaOH,  $10^{-2}$  M HCl, and methanol followed by rinsing with 300 mL of distilled water.

**Breakthrough Determination.** The ability of macroreticular resin combination to adsorb selected carbonaceous substances or nitrogenous organic compounds was investigated by passage of known concentrations of reference compounds or natural water samples through the combination of resin beds, at pH 2.0 and 7. Breakthrough curves for individual test compounds were determined by measuring their concentrations in the column effluents after passage of increasing volumes of sample through the resins. The filtered aliquots were then analyzed spectrophotometrically. UV absorbance was converted into concentration values from least-squares-fit equations determined from absorbance measurements of reference compounds at several concentrations (relative standard deviation ranged from 1.2% to 5.1%).

Adsorption of  $\text{NH}_3\text{N}$  and Kjeldahl N, of natural waters, onto the macroreticular resins was also examined.  $\text{NH}_3\text{N}$  was determined by using a scaled-down indophenol me-



**Figure 1.** Standard curve for humic acid concentration in aqueous solution at pH 2 vs. absorbance at 330 nm. Least-squares fit through origin: humic acid concentration (mg/L) = 41.9(absorbance) (A.U.).

thod of Strickland and Parsons (26). Total Kjeldahl was measured by ammonia determination after decomposition of the organically bound nitrogen to ammonia by acid digestion. Samples were acidified to pH 2 with  $\text{H}_3\text{PO}_4$  before elution through the resin.

Adsorption of commercially available humic acid on the combination of XAD-8 and Tenax resins at acidic and basic pH values was investigated. The humic acid was dissolved in 1 L of 0.03 M NaOH. Acidic humic acid solution was prepared by titration of about 980 mL of the basic humic acid solution to pH 2 with concentrated  $\text{H}_3\text{PO}_4$  followed by dilution to 1 L with ammonia-free water. Humic acid concentration was determined spectrophotometrically at 330 nm (Figure 1).

The total organic carbon (TOC) content of several natural water samples was determined before and after filtration to evaluate the efficiency of the resins in adsorbing carbonaceous organic materials. Twenty-milliliter samples were collected, acidified with 1 drop of 1 M HCl, and then shipped, on ice, to the central laboratory of the US Geological Survey, Water Resources Division, in Dorrville, GA. There they were analyzed for total organic carbon content by using an O.I. Inc. TOC instrument. The lower limit of detection for this analysis is about 0.2 mg of carbon/L  $\pm 3\%$ .

#### Results and Discussion

**Recovery of  $\text{NH}_3\text{N}$  and Organic N.** The inability of macroreticular resins to remove hydrophilic N-organic materials was demonstrated by measuring organic-nitrogen recovery after elution of field samples, collected from various water sources, through the combination of XAD-8 and Tenax GC macroreticular resins. Table I summarizes the percent recoveries of Kjeldahl N,  $\text{NH}_3\text{N}$ , and organic N in several natural waters after elution through the resin combination. Recovery values were calculated according to the following equation:

$$\% \text{ recovery} = \frac{\text{effluent concentration of test compound}}{\text{influent concentration of test compound}} \times 100 \quad (1)$$

The mean concentration values and standard deviations (shown in parentheses) in the unfiltered samples (excluding the second sampling of Middleton Pond) were as follows: 1.6 mg/L Kjeldahl N (0.9 mg/L), 0.7 mg/L  $\text{NH}_3\text{N}$  (0.5 mg/L), and 1.4 mg/L organic N (0.7 mg/L). Organic nitrogen comprised 65-99% of the total Kjeldahl N of the water samples (mean = 88%; standard deviation = 12%). An unusually high organic-N content was observed in the second sampling of Middleton Pond (Kjeldahl N = 22.0 mg/L;  $\text{NH}_3\text{N}$  = 0.3 mg/L). This was attributed to extracellular release of organic N by an intense blue-green algal bloom that was occurring at the time of sampling.

Table I. Recovery Values for NH<sub>3</sub> N, Kjeldahl N, and Organic N After Elution through a Combination of XAD-8 and Tenax-GC Macroreticular Resins<sup>a</sup>

water source	vol eluted	% recovery		
		NH <sub>3</sub> N	Kjeldahl N	organic N
Middleton Pond, Danvers, MA (sampling 1)	first 100 mL	100	71	67
	100-1000 mL	100	86	83.3
Middleton Pond, Danvers, MA (sampling 2)	1-L filtrate	100	98	98
Bethesda, OH, surface water	first 100 mL	100	83	80
	100-1000 mL	100	83	80
Concord River, Billerica, MA	1-L filtrate	70	79	83
	filtrate from laboratory-grown culture, of <i>Oscillatoria tenuis</i>	first 100 mL	100	39
filtrate from laboratory-grown culture, of <i>Anabaena flos aquae</i>	100-1000 mL	100	72	71
	1-L filtrate	100	74	73

<sup>a</sup> An equal-volume combination of XAD-8 and Tenax GC macroreticular resins (1.5 g each) was used. Samples were adjusted to pH 2.0 before elution.

Samples were eluted at pH 2 since improved color removal was observed at this acid pH value. The mean percentage recoveries for Kjeldahl N, NH<sub>3</sub>N, and organic N, after elution of 1 L of sample through the resins, were 81% (10%), 95% (11%), and 81% (11%), respectively. Values in parentheses are standard deviations. These data indicate that the majority of ammonia N and organic nitrogen contained in such samples is not adsorbed onto the resin combination.

A poorer recovery was sometimes observed for the first 100 mL of eluant from each liter of sample filtered through the resins. This indicated that the resins had a small adsorptive capacity for the nitrogenous material resulting in a rapid breakthrough and high recovery of this material in the total filtered sample. A very high recovery value was observed for the second sampling of Middleton Pond, taken during the occurrence of a blue-green algal bloom. This was attributable to the higher concentrations of nitrogenous compounds resulting in a very rapid breakthrough.

Recovery data for samples eluted through the resin combination at pH 7 were 93% (12%), 94% (4%), and 90% (18%) for Kjeldahl N, NH<sub>3</sub> N and organic N, respectively. Values in parentheses are standard deviations. Statistical tests (Student's *t* test and *f* test) indicated that the observed differences in recoveries between pH 2 and pH 7 were not statistically significant.

**Recovery of Individual Test Compounds.** Breakthrough curves for individual test compounds at pH 2.0, after passage of increasing sample volume through a combination of XAD-8 and Tenax-GC resins, are shown in Figure 2. The ratio of the effluent concentration to the influent concentration ( $C_e/C_i$ ) is plotted against the volume of water eluted through the macroreticular resin. A  $C_e/C_i$  value of 1.0 represents 100% recovery of the test compound or no adsorption of the substance onto the resin. Recovery values of greater than 90% were observed for three of the seven nitrogenous organic compounds tested after elution of less than 100 mL of sample. Six of the seven tested compounds displayed a 90% recovery after elution of about 300 mL of sample. Indole, however, was strongly adsorbed onto the resin and was therefore poorly recovered in the column effluent. Humic acid was also strongly adsorbed onto the resin combination. A  $C_e/C_i$  value of only 0.3 was observed after elution of 400 mL of solution containing 13.5 mg/L humic acid through the resin combination. These data demonstrate that the XAD-8 and Tenax-GC resin combination selectively adsorbs humic material without adsorbing most of the N-organic substances tested. This is further supported by

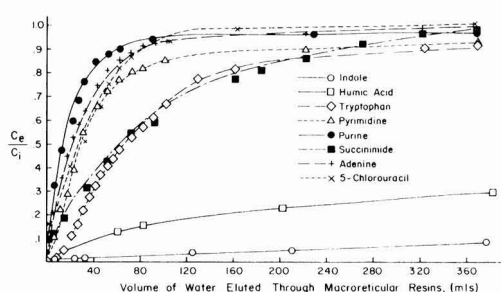


Figure 2. Breakthrough curves for several nitrogenous compounds after separate elution at pH 2 through an XAD-8 and Tenax GC macroreticular resin combination (1.5 g of dry resin each). Compound concentration = 10 mg/L except for humic acid = 13 mg/L.

Table II. Adsorptive Capacity of XAD-8/Tenax GC Resin Combination for Several Individually Tested Nitrogenous Organic Compounds

compd	adsorptive capacity of resin combination <sup>a</sup>		fractional difference <sup>b</sup>
	pH 2	pH 7	
adenine	0.16	0.19	-0.19
5-chlorouracil	0.19	0.16	0.16
purine	0.12	0.10	0.17
pyrimidine	0.23	0.16	0.30
succinimide	1.75	0.60	0.65
tryptophan	0.48	0.16	0.30
uracil	0.08		
tyrosine	0.34	0.33	0.03

<sup>a</sup> mg of compd/g of dry resin. <sup>b</sup> Fractional difference = (value at pH 2 - value at pH 7)/value at pH 2.

the previously discussed finding that the resin combination is unable to absorb the majority of organic nitrogen contained in water supply samples.

A useful parameter in evaluating the extent of adsorption of different compounds on the macroreticular resins is adsorptive capacity, which is the mass of material adsorbed at a predetermined breakthrough value per weight of resin. Adsorptive capacities defined at  $C_e/C_i = 0.8$  can be calculated from the equation

$$\text{adsorptive capacity (mg of compound/g of resin)} = \frac{\text{influent concn} \times \text{liters filtered to reach 80\% recovery}}{\text{g of resin used}} \quad (2)$$

Table III. Percentage of Total Organic Carbon (TOC) Adsorbed onto a Combination of Tenax-GC and XAD-8 Macroreticular Resins<sup>a</sup>

sample	pH adjustment of sample before filtration	TOC before filtration, mg/L	TOC after filtration, mg/L	TOC adsorbed onto resin, <sup>b</sup> mg/L	% TOC adsorbed adsorbed onto resin <sup>c</sup>
Concord River, Billerica, MA (7/4/78)	acidified to pH 2 with HCl	51	34	17	33
Merrimack River, Lawrence, MA (6/14/78)	pH unadjusted	8.1	4.8	3.3	41
Middleton Pond, Danvers, MA (6/21/78)	pH unadjusted	16	11	5.0	31

<sup>a</sup> 3 g of total resin; resin generated after filtration of 1 L of sample by sequential equilibration with 50 mL of 10<sup>-2</sup> M NaOH, 10<sup>-2</sup> HCl, and methanol followed by rinsing with 300 mL of distilled water. <sup>b</sup> TOC adsorbed onto resin (mg/L) = (TOC before filtration) - (TOC after filtration). <sup>c</sup> % TOC adsorbed onto resin = 100(TOC adsorbed onto resin)/(TOC before filtration).

These values are shown in Table II. Quantities of compounds exceeding the adsorptive capacity of the resin for them break through into the column effluent. The adsorptive capacities of the resins for the N-organic compounds (with the exception of indole) eluted at pH 2 ranged from only 0.08 to 1.75 mg per gram of resin as compared to the greater adsorption (5-25 mg of carbon per gram of resin) of nonnitrogenous compounds reported in the literature (Junk et al. (6); Leenheer and Huffman (3)). The adsorptive capacity of the XAD-8/Tenax-GC resin combination for the hydrophilic nitrogenous organic materials tested, then, was 5-60 times less than that reported in the literature (Junk et al., (6-8)) for hydrophobic carbonaceous materials.

All but one of the nitrogenous compounds tested (adenine) displayed somewhat stronger adsorption onto the resin at pH 2 than at pH 7. However, the adsorptive capacities of the resin combination for the tested N-organic compounds at pH 7 were still 40-50 times less than that reported in the literature for hydrophobic carbonaceous materials.

Although the adsorptive capacities of the resins for the N-organic compounds eluted in distilled water were small, they were, theoretically, large enough to effect a considerable portion of the organic nitrogen content in the field samples. The high organic-nitrogen recoveries of field samples presented in Table I, then, indicated competition between the hydrophobic and hydrophilic materials for adsorption sites on the resins. Individual nitrogenous organic compounds were most likely present in these samples at the low levels at which corresponding test compounds had been adsorbed onto the resins. The high concentration of more strongly adsorbing carbonaceous materials in these samples, however, apparently prevented these nitrogenous materials from being adsorbed onto the macroreticular resins. The presence of hydrophobic carbonaceous adsorbates, then, appears to competitively decrease adsorption of hydrophilic materials. This phenomenon permits high recoveries of organic nitrogen while simultaneously removing humic material.

**Removal of Total Organic Carbon.** Adsorption of organic carbon onto macroreticular resins was examined by TOC determination before and after filtration of three water supply samples through the XAD-8 and Tenax-GC resin combination. Table III shows the amounts of TOC adsorbed onto the resin combination. The resins removed an average of 35% TOC from the field samples. Since organic nitrogen comprises as much as 30% of the TOC in natural water, the low percentage of TOC removal was partially attributable to passage of hydrophilic nitrogenous

organic substances through the macroreticular resins. Higher composition percentages of organic nitrogen would result in poorer TOC recovery values.

### Conclusions

Filtration of water samples through a combination of macroreticular resins XAD-8 and Tenax GC was examined as a method of selectively removing hydrophobic carbonaceous materials, such as humic acid, from aqueous solution. The resin combination did not adsorb the majority of ammonia N and organic N contained in water supply samples, nor did it strongly adsorb several individually tested nitrogenous organic compounds. Alternatively, humic acid was strongly adsorbed onto the resin combination as well as about 35% of the TOC in several field samples. The adsorptive capacities of the resins for the N-organic compounds eluted at pH 2 were 15 to 60 times less than for nonnitrogenous compounds reported in the literature.

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## Fingerprinting Inorganic Arsenic and Organoarsenic Compounds in in Situ Oil Shale Retort and Process Waters Using a Liquid Chromatograph Coupled with an Atomic Absorption Spectrometer as a Detector<sup>†</sup>

Richard H. Fish\*

Energy and Environment Division, Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720

Frederick E. Brinckman and Kenneth L. Jewett

Chemical and Biodegradation Processes Group, Center for Materials Science, National Bureau of Standards, Washington, D.C. 20234

■ Inorganic arsenic and organoarsenic compounds were speciated in seven oil shale retort and process waters, including samples from simulated, true, and modified in situ processes, by using a high-performance liquid chromatograph automatically coupled to a graphite furnace atomic absorption detector. The molecular forms of arsenic at ppm levels ( $\mu\text{g mL}^{-1}$ ) in these waters are identified for the first time and shown to include arsenate, methylarsonic acid, and phenylarsonic acid. An arsenic-specific fingerprint chromatogram of each retort or process water studied has significant implications regarding those arsenical species found and those marginally detected, such as dimethylarsinic acid and the suspected carcinogen arsenite. The method demonstrated suggests future means for quantifying environmental impacts of bioactive organometal species involved in oil shale retorting technology.

### Introduction

It is now highly important for our nation to scrutinize all fossil fuel alternatives and develop those that appear promising both commercially and environmentally.

<sup>†</sup>The work was partially presented at the following meetings: 3rd Annual Oil Shale Conversion Symposium, Jan 15-17, 1980, Denver, CO; 179th National Meeting of the American Chemical Society, March 23-28, 1980, Houston, TX, Abstract Fuel 28; 13th Annual Oil Shale Symposium, April 16-18, 1980, Golden, CO, Proceedings P 385; 2nd Symposium on Environmental Analytical Chemistry, June 18-20, 1980, Provo, UT, Abstract IIIK; 180th National Meeting of the American Chemical Society, Aug 24-29, 1980, Las Vegas, NV, Abstract Geoc 20; and DOE/NBS Workshop on Environmental Speciation and Monitoring Needs for Trace Metal-Containing Substances From Energy-Related Processes, May 18-20, 1981, National Bureau of Standards, Gaithersburg, MD.

Among several possibilities, one that emerges as extremely viable is the recovery of shale oil from our substantial domestic deposits of oil shale (1).

Shale oil is recovered from oil shale kerogen by a controlled pyrolysis at 500 °C using surface and in situ technologies. These produce, along with the shale oil, considerable amounts of process waters which originate from mineral dehydration, combustion, groundwater seepage, and steam and moisture in the input gas. Since the waters are in intimate contact with raw and partially retorted shale and shale oils, they constitute a leachate of these products (2).

Several possible environmental problems are recognized in the formation and disposal of these retort process products. Firstly, the shale oils and retort waters contain a host of trace organic compounds (2, 3) as well as a large array of trace metals and metalloids that are potentially toxic in certain forms to aquatic biota and man (4-6). Secondly, in order to evaluate the latter contaminants for their environmental impacts, the key inorganic and organometallic forms associated with these toxic metals or metalloids (e.g., arsenic, cadmium, mercury, selenium, etc.) must ultimately be identified and their molecular features characterized or speciated (7).

Recent advances, since the introduction (8) of a high-performance liquid chromatograph (HPLC) automatically coupled to a graphite furnace atomic absorption spectrometer as a detector (GFAA), permit element-specific characterization of environmentally important trace inorganic and organometallic compounds. These advances provide an effective tool that allows direct separation and identification of these types of compounds in oil shale process products (8-14). In this paper, we report the successful use of two HPLC-GFAA units (10), in our re-

Table I. Water Types, Sources, and Retort Operating Conditions for Samples Used in Arsenic Speciation Study

retort or process water	retort/process	shale source	retorting atmosphere	retorting temp, °C
Simulated in situ Retorts				
L-2 retort water	LLL 6000-kg/modified in situ	Anvil Points, CO	air/stream	887
150-ton retort water (run 13)	LETC 150-ton/modified in situ	Anvil Points, CO	air	816
Field in situ Retorts				
Omega-9 retort water	LETC site 9/true in situ	Rock Springs, WY	air	a
Geokinetics retort water	retort 16/true in situ	Book Cliffs, UT	air	a
Occidental retort water	retort 6/modified in situ	Logan Wash, CO	air/stream	a
Occidental boiler blowdown	retort 6/modified in situ	Logan Wash, CO	air/stream	a
Occidental heater-treater water	retort 6/modified in situ	Logan Wash, CO	air/stream	a

<sup>a</sup> Field retorting temperatures are not accurately known because of corrosion problems with thermocouples. However, mineral analyses of spent shales from the Geokinetics and Occidental processes suggest that temperatures may locally reach 1000 °C.

spective laboratories, to separate and identify inorganic and organic arsenic compounds occurring in oil shale retort and process waters representing current experimental technology.

Arsenic was selected for the present investigations because of its widely acknowledged toxicity in groundwaters (15) and because previous work indicates (3) that total arsenic concentrations in oil shale process waters range from 5 to 15 µg mL<sup>-1</sup> (ppm) (4).

#### Experimental Section

**Instrumentation.** Two Perkin-Elmer graphite furnace atomic absorption spectrometers, Models 4000 and 460, were used as arsenic-specific detectors for high-performance liquid chromatographs (Altex Model 100A), in the respective laboratories. Additionally, each setup had an Altex 153 ultraviolet detector, which was used at 254 nm to monitor the organic matrix and to measure solvent fronts (*t<sub>0</sub>*). Experimental parameters for coupling the HPLC to the GFAA detector, and optimization of arsenic speciation, have been previously described (8-11).

**Standards and Oil Shale Retort and Process Water Samples.** Inorganic arsenic and organoarsenic compounds were purchased from commercial sources and used as obtained. Distilled deionized water (18 MΩ cm) was produced by a Millipore Corp. Model Milli-Q apparatus and used to prepare all standards and HPLC mobile phases.

Dr. J. Fruchter, Pacific Battelle Northwest Institute, Richland, WA, kindly supplied preserved (at 4 °C) Occidental retort and process water samples along with collection histories. Dr. D. Farrier, Laramie Energy Technology Center, WY, supplied preserved (at 4 °C) Omega-9 retort water. The samples of the other three retort waters were received from personnel at Laramie Energy Technology Center (150-ton retort water), from Lawrence Livermore Laboratory (L-2), and from Geokinetics, Inc., and were not preserved at 4 °C until they reached our laboratories. All samples were maintained at reduced temperature throughout their storage in order to minimize post-collection chemical alterations or volatilization and possible biodegradation by microorganisms (16). Dr. G. J. Olson, National Bureau of Standards, kindly surface plated 0.2 mL of each retort water or process water sample on modified IP medium (low nutrient) at pH 7 or at pH 9.7 plus 5 g L<sup>-1</sup> NaCl. No growth of aerobic heterotrophic microorganisms was evident after 1 week; consequently, we regarded chemical decomposition as the main possibility of sample degradation.

Seven important in situ oil shale retort and process water samples were examined, including three waters from Occidental's Logan Wash modified in situ process (17) (retort, boiler blowdown, and heater-treater waters); Geokinetic's

horizontal, true in situ retort water (18); Laramie Energy Technology Center's Rock Springs site 9 true in situ experiment Omega-9 retort water (19); and two large-scale simulated, modified in situ retort waters: one run, L-2 Lawrence Livermore Laboratory's 6000-kg retort (20), and one from Laramie Energy Technology Center's 150-ton retort (21). These materials were warmed to room temperature, filtered (0.45 µm, Millipore), appropriately diluted with deionized water, and directly injected (100-250 µL) into the HPLC-GFAA systems. A summary of the retort and process water sample sources and their respective process features is presented in Table I.

**Chromatographic Procedures.** Several available (11) gradient compositions were used for the HPLC speciation of arsenicals in the basic (pH ~9.2) retort and process waters, a very effective combination being that of a commercial anion-exchange column (Dionex) with an eluent composition recommended by Woolson and Aharonson (14). This method used a step gradient starting 10 min after injection from 100% water-methanol (80:20 v/v) to 100% 0.02 M (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> in water-methanol (85:15 v/v) at 5% min<sup>-1</sup>, with a flow rate of 1.2 mL min<sup>-1</sup>. The HPLC eluent was automatically sampled from a specially designed (8) flow-through Teflon cup for periodic graphite furnace atomic absorption detection at 193.7 nm for arsenic.

Each chromatogram consisted of a series of histogrammic peaks which, in combination, represented an individual eluting chromatographic peak. We then summed the individual histograms comprising each arsenical species peak over the range of *t<sub>R</sub>* ± σ (Table II) to determine total chromatographic peak areas (9, 10).

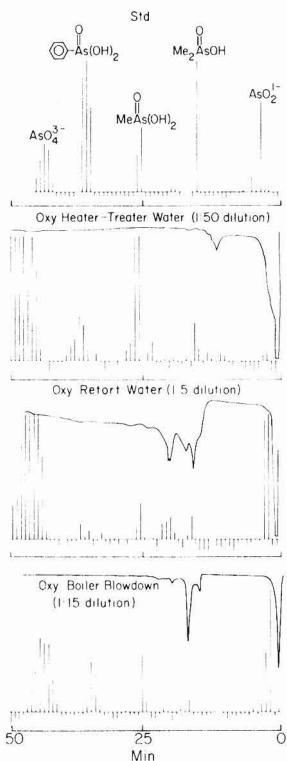
#### Results and Discussion

**Peak Identification.** Figures 1 and 2 compare the arsenic-specific GFAA chromatograms obtained for five of the seven retort or process waters described. Conventional chromatograms, taken with an ultraviolet (254 nm) detector in series with the GFAA detector, are shown superimposed (solid traces) on the arsenic-selective outputs; these clearly reveal the intensity and complexity of the organic matrix, and the analytical limitations of nonselective detectors. Each time that we ran a sample, we also ran five authentic arsenic standards (as 10 ng of As in each peak) combined into one solution. These included sodium arsenite, dimethylarsinic acid, methylarsonic acid, phenylarsonic acid, and sodium arsenate. We regarded each GFAA chromatographic peak as "positively" identified (Table II) if its retention volume matched that of the mean value of the calibration peak for each As species within two standard deviations of RSD < 5% *t<sub>R</sub>*' (8, 9, 14). "Tentative" assignments were given to those peaks outlying 2σ, although spiking the field samples with authentic

**Table II. Tentative Identification of Inorganic Arsenic and Organoarsenic Compounds by HPLC-GFAA in Various Oil Shale**

sample	$t_R \pm \sigma,^a$ min					
	NaAsO <sub>2</sub>	(CH <sub>3</sub> ) <sub>2</sub> -As(O)(OH)	CH <sub>3</sub> As(O)(OH) <sub>2</sub>	PhAs(O)(OH) <sub>2</sub>	Na <sub>3</sub> AsO <sub>4</sub>	unknown
calibration solutions <sup>b</sup>	2.1 ± 0.4	16.3 ± 1.8	25.4 ± 0.4	35.7 ± 0.4	44.8 ± 1.1	—
simulated in situ retorts <sup>c</sup>						
L-2 retort water	—	—	25.2 (+)	35.6 (+)	42.9 (+)	1.0
150-ton retort water	—	—	23.8 (±)	—	43.9 (+)	0.5
field in situ retorts <sup>c</sup>						
Omega-9 retort water	—	—	25.2 (+)	34.9 (+)	43.7 (+)	1.4
Geokinetics retort water	—	—	26.0 (+)	33.3 (±)	44.5 (+)	20.4
Occidental heater-treater water <sup>c</sup>	—	—	25.1 (+)	36.4 (+)	46.8 (+)	1.0
Occidental boiler blowdown water	—	—	24.9 (+)	34.6 (±)	44.2 (+)	14.6
Occidental retort water	—	—	24.6 (+)	35.9 (+)	44.8 (+)	0.8
						0.5
						15.0

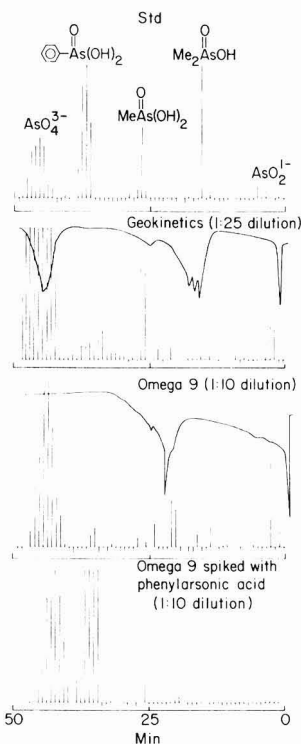
<sup>a</sup> A dash (—) signifies that the species was not detected. A (±) signifies that the species was tentatively identified. The numerical values are the retention times at which the species or unknown peaks were detected. <sup>b</sup> Mean ± standard deviation of five or more scattered runs. <sup>c</sup> Positive identification (+) fell within ±2σ (2–5% RSD) for calibration runs taken in sequence with unknown runs.



**Figure 1.** Element-specific chromatograms of arsenic species obtained by HPLC-GFAA (bottom of each sample set) and associated UV detector chromatograms (continuous trace shown at top of each set, inverted) are compared against authentic arsenic standards for three water samples taken at different stages of the Occidental modified in situ process, retort 6, Logan Wash, CO. The chromatogram of the aqueous calibration solution shown at top identifies each of the five arsenicals present at a concentration of 10 ng mL<sup>-1</sup> (as As).

arsenic compounds (see below) yielded the same (increased) single chromatographic peak for both positively and tentatively identified species.

Moreover, our spiking results confirmed that peak en-



**Figure 2.** Arsenic fingerprints and corresponding UV chromatograms are compared, as in Figure 1, against authentic arsenicals for two retort water samples derived from Geokinetics and Omega-9 true in situ processes.

hancement occurred for only those arsenic compounds spiked, without affecting the peak area of other arsenicals in the matrix. This result is in contrast to other workers (14) who observed a methanol-dependent change in retention time for arsenate when dissolving the sample in methanol. This methanolic arsenate derivative could have interfered with phenylarsonic acid, since it had a similar retention time.



Table III. Estimation of Inorganic and Organic Arsenic Compounds Separated and Detected by HPLC-GFAA Analyses

retort or process water	compd <sup>a</sup>	concn, <sup>b</sup> μg mL <sup>-1</sup> (ppm)
Occidental retort water	unknown organoarsenic compound	
	arsenite	(0.13)
	methylarsonic acid	0.16 (0.10)
	phenylarsonic acid	0.003 (0.02)
Occidental heater-treater process water	unknown organoarsenic compound	
	methylarsonic acid	< 2.0
	phenylarsonic acid	< 0.42
	arsenate	~10
Occidental boiler blowdown process water	unknown organoarsenic compound	
	methylarsonic acid	0.58
	phenylarsonic acid	0.15
	arsenate	0.63
LETC 150-ton retort water	unknown organoarsenic compound	
	methylarsonic acid	< 1.5
	arsenate	< 3.0
LLL L-2 retort water	unknown organoarsenic compound	
	methylarsonic acid	0.63
	unknown inorganic or organoarsenic compound	
	phenylarsonic acid	0.31
Geokinetic retort water	unknown organoarsenic compound	
	methylarsonic acid	< 2.0
	phenylarsonic acid	< 0.38
	arsenate	> 10
LETC Omega-9 retort water	unknown organoarsenic compound	
	methylarsonic acid	< 0.18
	phenylarsonic acid	< 0.02
	arsenate	< 1.6

<sup>a</sup> Determination of identified compounds by retention times with known authentic compounds, Table II. <sup>b</sup> Each standard 10 ng as As. Area under each peak estimated by method of summing peak heights digitized with an integrator (9-11) and comparison with calibration solutions in deionized water or method of additions (22) with spikes in sample solutions (in parentheses).

**Quantitation of Identified Arsenic Species.** The representative figures clearly demonstrate that each retort or process water has a distinctive "fingerprint" and that substantial but variable quantities of arsenate, methylarsonic acid, and phenylarsonic acid are present, while arsenite and dimethylarsinic acid are probably absent or, at best, marginally detected. Estimated detection limits and sensitivities for each arsenic species were found to vary, mainly a consequence of the alkaline organic matrix and the fixed GFAA atomization program (9, 14). Consequently, we compared each sample chromatogram against that of a standard solution of authentic arsenicals in distilled water. Reliable retention times discussed above were obtained this way, as were approximate concentrations of major arsenic species in retort or process waters.

In order to more fully assess matrix effects on  $t_R$  and concentrations of minor components, we also ran authentic arsenicals as spikes in several retort waters. For example, as shown in Figure 3 in Occidental retort water (diluted 1:10), HPLC-GFAA system detection limits at 95% confidence levels (22), using standard additions of 0, 2.5, 5, 10, or 15 ng of analyte, were as follows (ng mL<sup>-1</sup> (as As)): arsenite, 8.2; dimethylarsinic acid, 20.4; methylarsonic acid, 20.1; phenylarsonic acid, 7.4; and arsenate, 5.2, respectively. The arsenical concentrations in the Occidental retort water were estimated to be as follows (μg mL<sup>-1</sup>): arsenite, 0.13 ± 0.08; dimethylarsinic acid, 0.049 ± 0.20; methylarsonic acid, 0.096 ± 0.20; phenylarsonic acid, 0.018 ± 0.074; and arsenate, 0.32 ± 0.05. Clearly from these results and Figure 1 this was a worst-case analysis, although AsO<sub>4</sub><sup>3-</sup>, and AsO<sub>2</sub><sup>-</sup> appeared to give reasonable error limits. For the remaining samples more favorable error limits and concentrations prevailed, as illustrated in Figures 1 and 2 and summarized

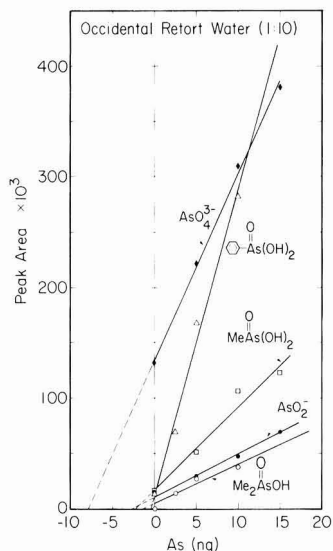


Figure 3. Plots of chromatographic peak areas vs. standard additions of individual arsenicals to diluted (1:10) Occidental retort water showing relative concentrations.

in Table III. The neutral arsenical(s) eluting just before arsenite undoubtedly interfered with estimations of the latter, but chromatograms obtained with both NBS and LBL instruments suggest that we presently place an upper limit on its presence in the seven sample waters at <0.1

$\pm 0.06$  ppm; for dimethylarsinic acid, we tentatively place an upper limit of  $<0.05 \pm 0.20$  ppm.

**Comparisons between the Retort and Process Waters.** Tables II and III correlate the identified arsenic species and their estimated concentrations with the corresponding retort or process waters. Arsenate is by far the major (0.6–10 ppm) arsenical component identified in all of the samples studied, but the variable concentrations of the other species suggest quantitative diagnostics for monitoring widely different production sites. It is interesting to note that Occidental's retort and process waters (Figure 1) all contain methylarsonic acid, phenylarsonic acid, arsenate, and one or several neutral or weakly ionized arsenicals, possibly in the molecular  $R_3As$  or  $R_3AsO$  classes. Generally, neutral or weakly ionized molecules elute with the solvent front (at  $t_0$  min) or with only slight retention (at  $t_R$  min) in well-behaved ion-exchange columns where  $k' \sim 1/\mu$ ;  $k' = (t_R - t_0)/t_0$  and  $\mu =$  ionic strength (24).

The two true in situ retort waters, Geokinetic and Omega-9, also display (Figure 2) early peaks and contain methyl- and phenylarsonic acids, arsenate, and another unknown ionic arsenic species eluting at 20.4 min. Important in a different way, both simulated in situ process waters, 150-ton and L-2, were distinguished by a significant diagnostic feature involving absence of detectable ( $<0.002$  ppm) phenylarsonic acid in the 150-ton sample whereas L-2 water contains  $>0.3$  ppm of this species. Beyond this, both 150-ton and L-2 samples contained methylarsonic acid, arsenate, and the neutral component which suggested their similarity to Omega-9. These distinguishable fingerprints may reflect different operating parameters used in the controlled pyrolysis reaction possible with the 150-ton and L-2 facilities. The similarities last noted may well indicate that basic chemical phenomena are the same in certain laboratory and field retorts and imply that HPLC-GFAA fingerprinting may serve as a monitoring tool for correlating such operations.

**Biogeochemical or Process Origins of Organoarsenicals.** The origin of these observed organoarsenic compounds, at this time, is not understood. Kerogen, generally regarded as a biogeochemical creation, largely from lipid fractions of ancient algae (2), forms the ubiquitous oil source matrix in shales. Thus, it is conceivable that these methyl- and phenylarsonic acids occur naturally following original biosynthesis or bioaccumulation (6, 23) and subsequent mineralization in oil shale and are released with little decomposition upon pyrolysis, ending up as leachates in the process water after intimate contact with the shale oil. Ample evidence is available for both terrestrial and marine biomethylation of inorganic arsenic(V) by modern microorganisms (6, 25) and marine algae (6, 23) to produce both dimethylarsinate and methylarsonate species; no analogous biophenylation is reported as far as we know. The negligible amounts of dimethylarsinate or arsenite in our sample waters may result from oxidative loss of the latter in aged sample (26) or from oxidative pyrolysis of both species in aerobic retorts (5, 26), selective rates of formation during original biogenesis, or an alternative purely abiotic synthesis forming methyl- or phenylarsenic bonds in the hot reaction zone of the retort. This last pathway seems quite reasonable for the methylarsonic acid observed, since it parallels the long-known Meyer reaction (27) between alkyl halides and arsenite salts. In boiling aqueous solution both alkylarsonic and dialkylarsinic acids can form, but arylarsonic acids are not similarly obtained (28), thereby suggesting that the phenylarsonic acid observed may arise from other sources. Finally, we cannot rule out formation of these organo-

arsenic compounds after the retort or process water reaches at the exit of the retort. For example, biomethylated arsenicals could be introduced with boiler feedwater (Occidental boiler blowdown) or by groundwater seepage (29) into in situ retorts (Omega-9 and Geokinetic retort waters) and converted to the observed arsenic acids under conditions of high temperatures and pH.

### Conclusions

The significant environmental implications of our study are that potentially toxic inorganic arsenic and organoarsenic compounds in varied mixtures at appreciable concentrations are either released or synthesized during oil shale retorting processes representing present-day technology. The methods applied by us presage similar efforts with other toxic elements. The possibility of their bioaccumulation in soils, water, and edible biota at appreciable distances from the retorting site via disposal of retort leachate waters containing bioactive forms may represent potential health hazards for humans as well as a threat to aquatic species. Suggested biobleaching of petroliferous shales (30, 31) as an energy-conserving alternative to pyrolysis must now be regarded with new concerns for re-release or biotransformation of arsenicals entrapped in kerogen, and this should guide research on other metals as well (25). A more immediate consequence of low-level exposure of workers in these future retort process plants to such inorganic and organoarsenic compounds will require monitoring, since there is not presently a complete understanding of in vivo mechanisms of arsenic and other heavy-metal toxicity (6).

We believe this to be the first positive molecular characterization of any trace inorganic or organometallic substances in such fossil fuel recovery products. Since the HPLC-GFAA technique is shown to be broadly applicable to a wide variety of elements in many molecular classes, with great freedom from usual matrix interferences (8–14), we envision similar utility for speciating other toxic metal-containing molecules in oil shale products. Among these prospects, mercury, selenium, and lead are important because of their known biotransformations (25) and presence in kerogen pyrolysates (5, 30, 31). Since the HPLC-GFAA method permits use of a large variety of nonionic separation columns (8–13), we are also examining the shale oils as well as oil shale kerogens with the aim of establishing the molecular form of hydrophobic or macromolecular organoarsenicals not readily partitioned into retort waters. It is hoped that current qualitative survey work of this type can later offer quantitative bases for optimizing retort process parameters while minimizing impacts of speciated metal toxicants.

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# Extractable Organic Matter in Municipal Wastewaters. 1. Petroleum Hydrocarbons: Temporal Variations and Mass Emission Rates to the Ocean<sup>†</sup>

Robert P. Eganhouse\* and Isaac R. Kaplan

Department of Earth and Space Sciences, and Institute of Geophysics and Planetary Physics, University of California at Los Angeles, Los Angeles, California 90024

■ Samples of final effluent were collected from the major municipal wastewater dischargers in southern California during 1979 and analyzed for total, aliphatic, and aromatic hydrocarbons. Mean total hydrocarbon contents of those effluents having received mainly primary treatment ranged from 6.1 to 16.3 mg/L, whereas sludge concentrations were approximately 340 mg/L. The vast majority of these hydrocarbons are associated with particulate matter; however, their composition was virtually identical for all effluents. The temporal variations of wastewater total hydrocarbon concentrations (~13-37%) appear to be independent of sampling frequency. From these data, southern California's treatment plants are estimated to discharge more than  $17.4 \times 10^3$  metric tons of hydrocarbons/yr or 4.9 g/capita day to coastal waters. This is approximately double the input rate due to surface runoff in this region. Moreover, it represents nearly 6% of the worldwide input of wastewater-borne petroleum to the ocean. Problems associated with global input assessments are discussed, and a correlative means of estimating wastewater hydrocarbon concentrations is presented.

## Introduction

Information on the composition and variability of organic substances in municipal wastes and their input rates to the ocean is extremely limited. Although there have been isolated studies of sewage constituents of environmental concern (1-6), and certain compound classes (7-10), no comprehensive work has appeared in the literature. Nevertheless, substantial descriptive and statistical data bases are urgently needed for the following reasons: (1) to determine the potential chemical threats, if any, posed by the systematic, chronic discharge of wastes to the environment and (2) to assess the role that municipal wastes play in the overall carbon budget of the coastal zone. In this and succeeding papers, we provide new data for use in addressing these problem areas.

This report presents background information on the study site, southern California, along with results of hydrocarbon analyses of effluents from the major wastewater dischargers in the area. A 1975 NAS study of petroleum hydrocarbon (PHC) inputs to the marine environment (11) stated that municipal wastes contribute roughly  $3.0 \times 10^5$  metric tons of PHC to the sea per annum. This corresponds to approximately 5% of the total yearly global input from all sources. Although highly rated by the NAS panel, the confidence of this estimate is in some doubt because of the paucity of reliable data. Therefore, major objectives of the present work are to generate new data on the PHC content of municipal wastewaters and to examine possible predictive tools for use in global inventories. The research presented here is part of a large study aimed

at characterizing the terrestrial sources of organic matter to the southern California Bight and constructing a reasonable budget for this coastal system.

**Study Area.** The southern California Bight is a body of water contiguous with the North American continent extending from Pt. Conception, CA, in the north to Cabo Colnett, Baja California, in the south (Figure 1). It is roughly bounded on the west by the edge of the continental slope at a water depth of approximately 3000 m (12). As such, the Bight encompasses an area of roughly 100 000 km<sup>2</sup>. Owing to the intense human activity in the adjoining urban complex stretching from Los Angeles to San Diego, the possibility of adverse environmental effects has repeatedly been noted (12-15). Localized accumulations of numerous toxic substances have been found in the vicinity of sewage discharge sites (12, 16-18), and it is generally thought that domestic/industrial wastes are among the most serious threats to the ecology of the Bight.

The majority of southern California's municipal wastewaters (~86%) receive only primary treatment (19) and are introduced directly to the ocean via submarine outfall systems at a water depth of approximately 60 m. The rationale for this disposal plan, details of which can be found elsewhere (20), rests upon the effective dispersion of a buoyant wastewater plume by currents at subthermocline depths. In 1979, the year of this study, four of southern California's five major treatment plants contributed more than 98% of the total regional waste flow,  $3.84 \times 10^9$  L/day (21). The locations of these four plants are shown in Figure 1, and a list of their treatment procedures, influent properties, and some general effluent characteristics is given in Table I.

Because of its relatively high industrial component and large flow rates, the Joint Water Pollution Control Plant (JWPCP—Los Angeles County Sanitation Districts) has historically discharged the greatest quantities of oil and grease (Table II). Therefore, this facility was targeted for a detailed study of total extractable organic and hydrocarbon contents of its effluent. The other plants studied (cf. Table I) are as follows: (1) Hyperion treatment plant (City of Los Angeles) which discharges two effluents: HYP-7mi (sludge + secondary effluent) through the 7-mi outfall into the head of the Santa Monica Canyon, and HYP-5mi (primary + secondary effluent) through the 5-mi outfall into Santa Monica Bay, (2) Orange County plants (OCSD—Orange County Sanitation Districts), and (3) Point Loma plant (CSD—City of San Diego). Details of the outfall systems and effluent monitoring data tabulations can be found elsewhere (12, 19, 21-25).

**Sampling.** During 1979, a series of flow-proportioned 24-h composite samples were collected by personnel at each of four treatment plants (Table I). In the case of JWPCP, HYP-5mi, OCSD, and CSD effluents, duplicate (3-L) samples were obtained by either automatic sampling devices or manual methods. These samples were mechanically homogenized and placed in calibrated, organic-free glass bottles sealed with Teflon-lined lids. One of the two samples was adjusted immediately to pH 1 with CHCl<sub>3</sub>-extracted 6 N HCl and preserved with 200 mL of hexane.

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\*Address correspondence to this author at the following address: Department of Earth and Space Sciences, University of California at Los Angeles, Los Angeles, CA 90024.

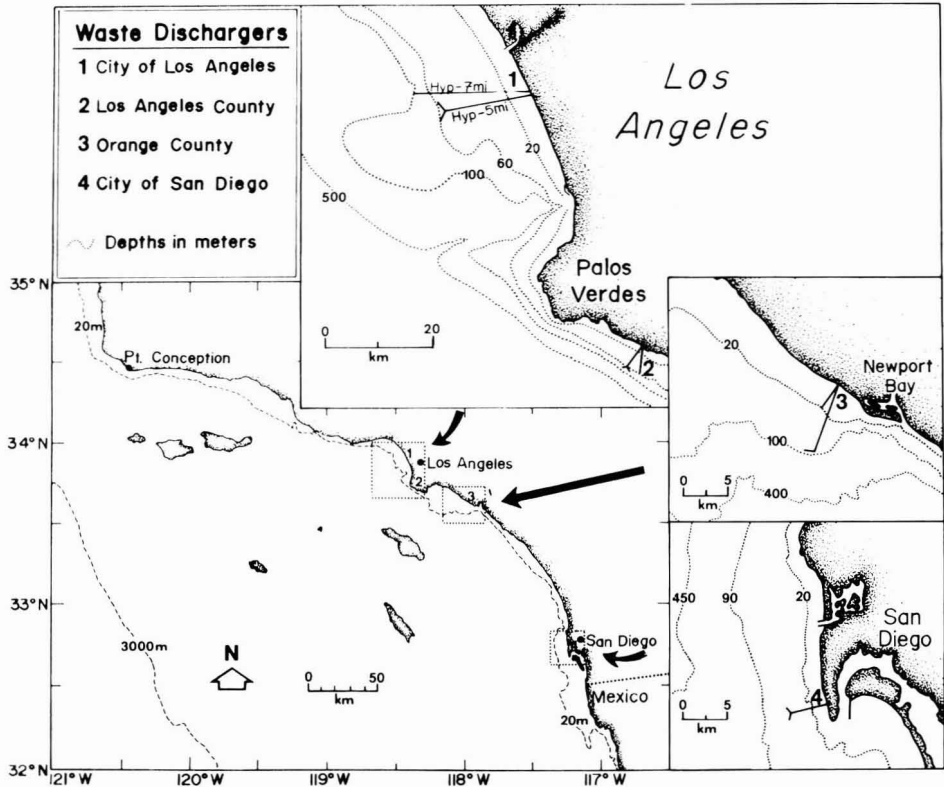


Figure 1. Southern California Bight. Insets depict the locations of the major municipal wastewater outfall systems in southern California.

Table I. Description of the Major Southern California Wastewater Dischargers and Average Concentrations of Some Important Constituents in 1979<sup>a</sup>

discharger	agency/municipality	industrial/ domestic influent <sup>b</sup>	popula- tion served, mil- lions	nature of effluent treatment	total effluent flow, ML/day	total sus- pended solids, mg/L	oil and grease, mg/L
Joint Water Pollution Control Plants (JWPCP)	Los Angeles County Sanitation Districts	18/82	3.65	primary, digested sludge centrate	1390	195	39.9
Hyperion plant	City of Los Angeles, Bureau of Sanitation	15/85	3.10				
HYP-5 mi				primary, secondary	1336	75	19.0
HYP-7 mi				digested sludge, secondary	18	7060	400
Orange County plants (OCS D)	Orange County Sanitation Districts	25/75	1.70	primary, secondary	712	140	26.0
Point Loma plant (CSD)	City of San Diego	7/93	1.35	primary	484	143	36.7

<sup>a</sup> Data taken from ref 19 and 21. <sup>b</sup> Given as percentages of the total plant inflow.

Table II. Mass Emission Rates (metric ton/yr) of Oil and Grease for Major Municipal Wastewater Dischargers in Southern California from 1971 to 1979<sup>a</sup>

yr	JWPCP	HYP-5mi	HYP-7mi	OCS D	CSD	total	JWPCP, % total
1971	38 000	6550	6330	ND <sup>b</sup>	4600		
1972	36 500	9210	4040	7450	3440	60 640	60.2
1973	29 300	8380	6130	8430	4980	57 220	51.2
1974	26 300	8470	5860	8210	5900	54 740	48.0
1975	28 900	9530	5760	8230	4000	56 420	51.2
1976	30 600	9950	3860	10300	4100	58 810	52.0
1977	21 300	8380	3700	10100	5340	48 820	43.6
1978	21 900	8940	3270	7800	6800	48 710	45.0
1979	20 200	9270	2450	6760	6490	45 170	44.7

<sup>a</sup> Data obtained from routine effluent monitoring data (12, 19, 21-25). <sup>b</sup> Not determined.

This procedure was intended to terminate biological activity, minimize evaporative losses, and initiate extraction. Both bottles were then refrigerated on location. Sample pickup never exceeded 3 h from the time of collection/preservation. Sampling of the HYP-7mi (sludge) effluent was performed in a similar fashion; however, only 600–900-mL volumes were necessary because of the high suspended-solids and “oil-and-grease” contents (cf. Table I).

HYP-5mi, HYP-7mi, OCS D, and CSD effluents were each collected at approximately the same time on a quarterly basis. The JWPCP effluent was sampled more frequently. In this study, 24-h composites were taken at daily (8 consecutive days), weekly (6 consecutive weeks), and monthly (12 consecutive months) intervals.

**Methodology.** Upon return to the laboratory, 2 L of the untreated sample was filtered by using precombusted Whatman GF/A glass-fiber filters and a specially designed all-glass filtration system. The filtrates were then preserved with 200 mL of hexane and 6 N HCl as before. Only 500-mL samples of HYP-7mi (sludge) filtrate were generated in this way. If not extracted immediately, unfiltered and filtered samples were stored at 10 °C until a later time. Particulates from the remaining undisturbed sample were stored frozen for subsequent elemental/isotopic analyses.

Liquid/liquid extractions were performed in separatory funnels using the 200-mL hexane preservative solution followed by  $\text{CHCl}_3$  (100 mL/L sample, 3 times).  $\text{CHCl}_3$ -extracted NaCl was added to the mixtures to help break emulsions. Furthermore, all extractions were preceded by rinsing the sample bottle to recover lipid materials possibly adhering to the glass walls. For the HYP-7mi (sludge) effluent, the hexane was followed by six  $\text{CHCl}_3$  extractions (150 mL of  $\text{CHCl}_3$ /500–750-mL sample). In most cases, an emulsion layer remained after the last extraction. This was broken by centrifugation (2000 rpm), and the  $\text{CHCl}_3$  layer was combined with the extracts. Subsequent steps included concentration by rotary evaporation, water and sulfur removal, esterification, and thin-layer chromatographic separation of the esterified extractables into five organic fractions, one of which contained the total hydrocarbons (THC). In some cases, the THC fraction was further chromatographed to isolate aliphatic (Al) and aromatic (Ar) hydrocarbon subfractions. Technical details are given elsewhere (26).

Data presented here include gravimetric results for the total extractable organic (TEO), THC, Al, and Ar fractions. These measurements are based upon triplicate weighings of solution residues using a Mettler ME 22 electromicrobalance. Replicate determinations showed the precision to be (coefficient of variation)  $\pm 5\%$  or less. Molecular analysis of the hydrocarbon and nonhydrocarbon components will be discussed separately.

As a check on the extraction efficiency, exhaustive extractions were performed on two samples: JWPCP (3/14/79, unfiltered) and HYP-7mi (10/15/79, unfiltered); gravimetric measurements were made on each sequential extract. The results indicated that 95% of the TEO and 97–99% of the THC were recovered by the methods used in this study. Gravimetric yields of blanks treated by the same procedure were below detection limits.

## Results and Discussion

**General Findings.** Concentrations of total extractable organics (TEO), total hydrocarbons (THC), and aliphatic (Al) and aromatic (Ar) hydrocarbons measured in the five effluents are listed in Table III. Also given are values for oil and grease determined by treatment-plant personnel on unfiltered grab samples taken the same day (27). In nearly all cases, the values of TEO exceed those for oil and

grease. This is probably the result of differences in the extraction solvents (Freon is used for oil-and-grease determinations) and variations in technique.

Unfiltered samples of HYP-7mi (sludge) effluent have 10–20 times the TEO and THC contents of other effluents, the hierarchy thereafter being JWPCP > CSD > OCS D > HYP-5mi. These differences most likely reflect variations in the nature of influent composition and degree of treatment. Filtered samples of HYP-7mi effluent contain roughly 2–3 times the TEO and 4–5 times the THC content of the other effluents. Because the filters used here do not completely retain colloidal particulate matter (mean particle retention size  $\approx 0.9 \mu\text{m}$ ; ref 28), elevated levels of extractable substances in HYP-7mi filtrates probably reflect an enrichment in the mass of fine colloids. The other effluent filtrates have fairly similar TEO and THC concentrations despite varying total concentrations in unfiltered samples. This suggests that the aqueous phase of these effluents may have attained a common practical limit for the “accommodation” of organics. The surprisingly high percentage of TEO found in filtrates of the JWPCP, HYP-5mi, OCS D, and CSD effluents (21.5–52.1%) is due to the presence of water-soluble polar materials such as fatty acids, alcohols, sterols, and phenols (9). With the exception of the HYP-5mi wastewater, hydrocarbons were associated to a large extent (75.1–97.6%) with filterable particulate matter, a characteristic noted previously by others (29). The high percentage of hydrocarbons in the HYP-5mi filtrate is probably related to the low overall THC content of this effluent.

Aliphatic hydrocarbons represented slightly greater than half the total hydrocarbons in both unfiltered ( $54.2 \pm 2.2\%$ ) and filtered ( $53.0 \pm 2.2\%$ ) samples of all effluents. The fact that Al and Ar subfractions did not exhibit fractionation between the unfiltered and filtered samples may mean that equilibrium has not been established in these aqueous mixtures. Typically, Ar/Al ratios are greater in filtrates owing to the higher aqueous solubilities of aromatic hydrocarbons (26). A possible explanation is that fine colloids capable of passing through the filter and having the same composition as the bulk sewage may dominate the dissolved constituents of the filtrates. Thus, any fractionation associated with the solution process would be masked. Another remarkable finding was the similarity in the hydrocarbon compositions of different effluents. This suggests that wastewater treatment plants of southern California are probably receiving hydrocarbon mixtures from similar sources, each plant differing only in the amounts that they treat and ultimately discharge.

The total hydrocarbon concentrations found here (6.1–16.3 mg/L; 341 mg/L of sludge) are comparable to those previously reported (6, 29, 30). Because so few data are available, it is difficult to establish whether the observed variations are due to regional differences in hydrocarbon usage, disposal and treatment removal efficiencies, or simply nonrepresentative sampling. The possibility of temporal variation in the composition of sewage requires that the optimal sampling methodology and frequency be established. In recognition of this fact, we attempted to examine the temporal variation of TEO and THC concentrations by sampling the JWPCP effluent over different time intervals.

As Figure 2 illustrates, oil-and-grease levels measured daily at the JWPCP can change dramatically. This is partly due to the fact that the analyses are performed on grab, not composite, samples and are therefore subject to considerable fluctuation. Our measurements for TEO and THC contents on daily, weekly, and monthly intervals

Table III. Concentrations (mg/L) of Oil and Grease, Total Extractable Organics, Total Hydrocarbons, and Aliphatic and Aromatic Hydrocarbons in Southern California Wastewater Effluents in 1979<sup>d</sup>

sampling date	sample type <sup>b</sup>	oil and grease	total extractable organics		total hydrocarbons <sup>c</sup>	
			unfiltered	filtered	unfiltered	filtered
JWPCP						
1/15/79	1, 4	36.0	59.8	28.0	10.6	2.18
2/15/79	1	33.0	75.0	20.0	14.2	1.78
3/7/79	2, 3	50.9	71.0	26.9	13.4	
3/8/79	3	72.6	83.5	31.8	22.6	
3/9/79	3	58.6	79.6	29.0	22.0	
3/10/79	3	39.3	64.7	26.6	13.0	
3/11/79	3	39.0	66.1	24.7	15.8	
3/12/79	3	49.3	79.0	26.1	16.2	
3/13/79	3	56.3	79.7	25.1	18.5	
3/14/79	2, 3	31.3	71.2	27.2	14.3 (8.0/6.3)	2.36 (1.18/1.18)
3/21/79	2	50.0	85.7	22.6	20.2	
3/28/79	2	47.0	62.7	24.8	13.6	
4/4/79	2	45.3	71.5	22.6	16.6	1.53
4/17/79	1, 4	48.3	71.9	<i>d</i>	17.3	<i>d</i>
5/15/79	1	29.7	67.5	21.1	13.0	1.29
6/15/79	1	42.0	77.9	25.8	15.6	2.13
7/16/79	1, 4	33.7	79.8	23.5	15.9	2.18
8/15/79	1	38.5	83.6	29.0	20.9	3.29
9/13/79	1	33.0	69.0	22.3	18.2	1.61
10/15/79	1, 4	31.0	65.6	23.6	16.1	2.19
11/15/79	1	40.6	<i>d</i>	<i>d</i>	<i>d</i>	<i>d</i>
12/13/79	1	34.0	75.0	<i>d</i>	14.0	<i>d</i>
$\bar{x} \pm s$		42.7 ± 10.8	73.3 ± 7.4	25.3 ± 3.0	16.3 ± 3.2	2.05 ± 0.56
HYP-5mi						
1/15/79	4	13.0	47.3	17.2	5.1 (2.9/2.2)	1.92
4/18/79	4	20.0	48.8	23.4	6.9	3.04 (1.71/1.33)
7/16/79	4	22.0	43.8	22.8	5.7	2.90
10/16/79	4	17.0	46.2	21.4	6.5	3.10
$\bar{x} \pm s$		18.0 ± 3.9	46.5 ± 2.1	21.2 ± 2.8	6.1 ± 0.8	2.74 ± 0.55
HYP-7mi						
1/15/79	4	456	1088	81.0	397 (211/186)	17.6 (9.4/8.2)
4/18/79	4	425	994	64.5	374	13.2
7/16/79	4	355	796	50.3	297	9.4
10/15/79	4	476	717	41.5	297 (164/133)	7.1 (3.8/3.3)
$\bar{x} \pm s$		428 ± 53	899 ± 172	59.3 ± 17.3	341 ± 52	11.8 ± 4.6
OCSDe						
1/15/79	4	31.6	40.3	19.3	5.7 (3.0/2.7)	1.23 (0.63/0.60)
4/12/79	4	24.0	63.2	20.2	10.9	1.63
7/16/79	4	22.9	47.3	23.0	7.0	1.73
10/16/79	4	24.9	50.1	32.9	7.8	1.73
$\bar{x} \pm s$		25.8 ± 3.9	52.2 ± 9.6	23.8 ± 6.2	7.8 ± 2.2	1.53 ± 0.26
CSD						
1/16/79	4	67.4	56.3	12.1	11.8	1.22
4/17/79	4	32.1	58.9	21.1	8.2 (4.2/4.0)	1.78 (0.94/0.84)
7/17/79	4	27.0	65.3	23.3	10.4	2.21
10/16/79	4	41.2	69.1	22.2	18.7	2.66
$\bar{x} \pm s$		41.9 ± 18.0	62.4 ± 5.8	19.7 ± 5.1	12.3 ± 4.5	1.97 ± 0.61

<sup>a</sup> Data for oil-and-grease concentrations obtained from monthly and annual reports of the sanitation districts. <sup>b</sup> Sample type: 1, monthly; 2, weekly, 3, daily; 4, quarterly. <sup>c</sup> Aliphatic/aromatic concentrations are given in parentheses after the THC values. <sup>d</sup> Sample lost. <sup>e</sup> Data for oil-and-grease concentrations are quarterly means.

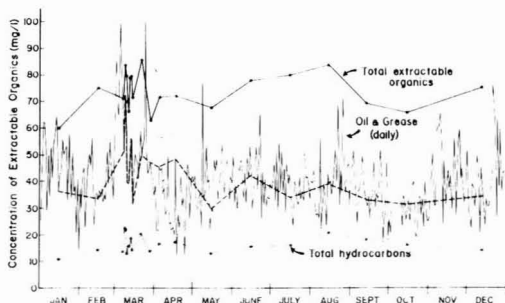
(Table IV) show virtually the same levels of variation regardless of sampling frequency. The differences between the daily means and those of the weekly and monthly samples, however, indicate that consecutive daily sampling, although more exact if done year-round, may be nonrepresentative when performed over short intervals of time. Compositing of samples on a weekly or monthly basis might better satisfy both the statistical requirements and the practical (i.e., economic, time) limitations of monitoring. However, the preservation of samples for other than hydrocarbon analyses over these periods is questionable in view of the lability of certain nonhydrocarbon lipid constituents.

**Mass Emission Rates.** One of the main goals of this project was to compute mass emission rates (MERs) of

wastewater-borne hydrocarbons to the coastal waters of southern California. Although these estimates are based upon relatively few measurements, they represent the most reliable data against which other inputs can be evaluated at this time. Values for the MERs of total suspended solids, oil and grease, TEO and THC given in Table V were calculated according to the formula

$$\text{mass emission rate (metric tons/yr (mta))} = 10^9 \sum_{i=1}^n \bar{F}_i t_i \bar{c}_i \quad (1)$$

where  $\bar{F}_i$  = mean flow for time interval  $i$  (L/day),  $t_i$  = number of days in time interval  $i$ ,  $\bar{c}_i$  = mean analytical concentration of parameter during time interval  $i$  (mg/L),



**Figure 2.** Variations in the total extractable organic, oil-and-grease, and total hydrocarbon contents of the JWPCP final effluent during 1979. Dashed line indicates oil-and-grease values for samples taken by plant personnel contemporaneous with samples analyzed in this study.

**Table IV.** Variations in the Concentration of Total Extractable Organics and Total Hydrocarbons in JWPCP Final Effluent As a Function of Sampling Frequency<sup>a</sup>

	daily	weekly	monthly
total extractable organics			
unfiltered	74.4 ± 7.0	72.4 ± 8.3	72.3 ± 6.8
filtered	27.2 ± 2.3	24.8 ± 2.2	24.5 ± 3.2
total hydrocarbons			
unfiltered	17.0 ± 3.7	15.6 ± 2.8	15.5 ± 2.8
filtered			2.05 ± 0.56

<sup>a</sup> All results given as means ± standard error (mg/L) for 24-h composite samples.

and  $n$  = maximum number of time intervals per year (JWPCP = 12; HYP-5mi, HYP-7mi, OCS, CSD = 4).

For the JWPCP estimate, mean values of 74.4 mg/L (TEO) and 16.3 mg/L (THC) were used to approximate the lost November sample. Gross estimates of aliphatic and aromatic hydrocarbon MERs were calculated by using MER values for the THC and applying data obtained from the few individual chromatographic separations that were performed (Table III).

From the present results (Table V), it appears that the JWPCP contributes nearly one-half (45.4%) of the petroleum hydrocarbons discharged by all wastewater treatment plants in southern California. This is very close to its relative input rate of oil and grease (Table II). The remaining hydrocarbon input is more or less evenly divided among the other outfall systems. The dominance of the JWPCP must be due to the relatively higher hydrocarbon burden of the effluent because flow and total suspended solids (MERs) represent only 35% and 39%, respectively, of the total. By comparison, the HYP-7mi sludge effluent, which represents a mere 0.5% of the total yearly flow, contributes 21%, 6.2%, and 13.1% of the combined suspended solids, oil-and-grease, and THC inputs, respec-

tively, a reflection of its high (lipid-rich) solids content.

On the basis of a limited number of hydrocarbon analyses of wastewater effluents from treatment plants in Rhode Island, Farrington and Quinn (30) estimated the total coastal US input of PHC to the ocean at between 28 000 and 140 000 metric tons/yr (mta). Subsequently, Storrs (31) and Van Vleet and Quinn (32) calculated annual US mass emission rates of approximately 200 000 and 46 500 metric tons, respectively. These latter estimates are based upon a US coastal population of 68 million and unit inputs of 8 and 2 g/(capita day). When computed on a daily per capita (cap) basis (cf. Tables I and V) southern California effluents discharge 3.3–6.0 g/(cap day) with a mean value of 4.86 g/(cap day). If this mean value is representative of similar discharges nationwide, and assuming a coastal population of 68 million persons, the US input should total roughly 120 600 mta. This estimated MER falls within the range proposed by Farrington and Quinn (30) and represents a remarkable 40% of the NAS-computed global input from municipal wastewaters (11). The combined MER of sewage-borne PHC to southern California waters ( $17.4 \times 10^3$  mta) comprises 5.8% of the global wastewater input (11). These results seem to indicate either that southern California treatment plants discharge especially large quantities of petroleum hydrocarbons in their wastes or that the NAS global estimate is low.

The other major route by which surface waters are delivered to the ocean is runoff. In southern California, rivers and streams discharge only one-third the volume of water to the Bight as do wastewater treatment plants (3), and recent calculations for all of southern California (26) place the surface runoff mass emission rates of TEO and THC at approximately  $17.9 \times 10^3$  and  $9.69 \times 10^3$  mta, respectively. Thus, municipal wastes contribute 5.1 and 1.8 times as much TEO and THC to the ocean as runoff. The discrepancy between these ratios arises from differences in the lipid compositions of wastewater and runoff water. The extractable organic matter of sewage contains 22% THC, whereas data for urban storm runoff indicates that hydrocarbons comprise about 51% of the extractable material (26). It should be noted that relative to wastewaters, surface runoff is subject to greater temporal and spatial variations in the composition and total concentration of extractable organics.

In considering potential environmental impacts to the marine ecosystem, it is also vital to recognize the contrast in their modes of delivery. Municipal wastes are effectively discharged from four point sources in southern California on a more or less continuous basis at subthermocline depths. Surface runoff, on the other hand, is generated by intermittent, and oftentimes dramatic, storm events which superimpose chronic dry weather flows. These highly seasonal discharges emanate from more than 150 rivers, streams, and drainage channels terminating in surface waters of the ocean. Differences such as these

**Table V.** Mass Emission Rates (metric ton/yr) of Wastewater Constituents from Major Dischargers in Southern California in 1979<sup>a</sup>

	JWPCP	HYP-5mi	HYP-7mi	OCS	CSD	total
total suspended solids	99 080	39 050	51 800	36 560 <sup>b</sup>	25 540	252 040
oil and grease	18 890 (14.2)	8 760 (10.2)	2 830 (10.2)	6 720 <sup>b</sup> (10.8)	8 160 (16.6)	45 360
total extractable organics	37 360 (28.0)	22 630 (25.2)	5 950 (25.2)	13 860 (22.2)	10 980 (22.3)	90 680
total hydrocarbons	7 990 (6.00)	2 950 (4.60)	2 260 (4.60)	2 040 (3.29)	2 160 (4.38)	17 400
aliphatics	4 470	1 680	1 230	1 070	1 110	9 560
aromatics	3 520	1 270	1 030	970	1 050	7 840

<sup>a</sup> Total suspended solids and oil-and-grease calculations based upon data from Table III; per capita mass emission rates (g/cap day) are given in parentheses. <sup>b</sup> Calculations based upon quarterly averages.



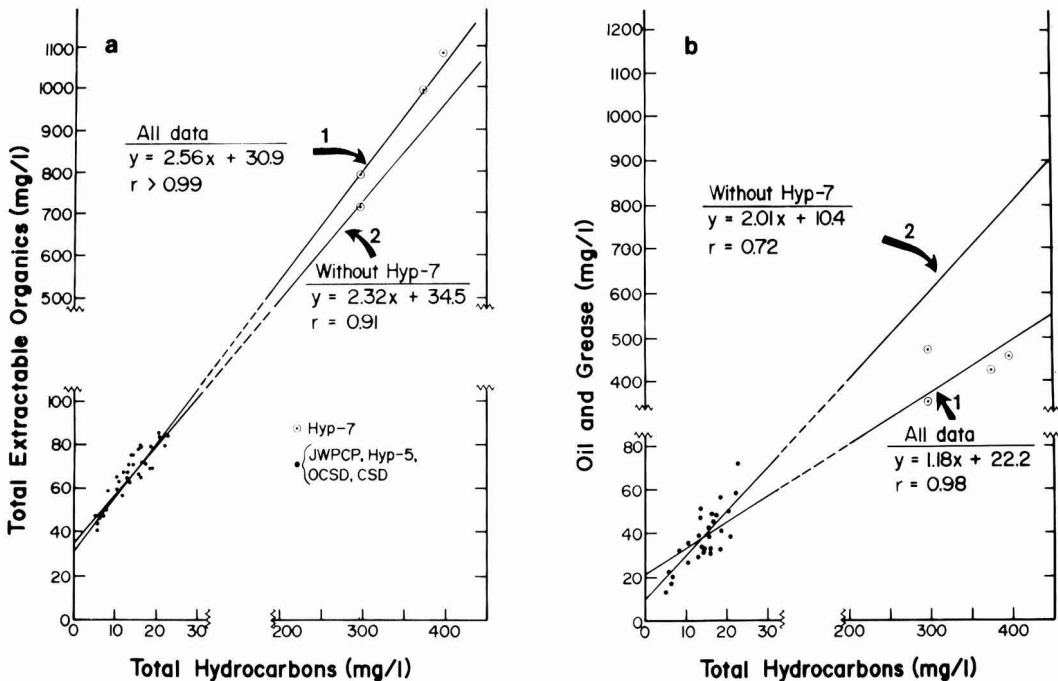


Figure 3. Correlation of total extractable organic, total hydrocarbon, and oil-and-grease measurements for southern California municipal wastes, 1979.

undoubtedly affect the transport and ultimate fate of terrigenous organic matter from these sources.

**Estimating the Hydrocarbon Content of Wastewaters.** From the viewpoint of input assessment, periodic measurements of total hydrocarbon concentrations in municipal wastewaters would seem desirable. However, the legal requirements for such monitoring do not presently exist, nor are they likely to in the near future. Hence, the impetus to develop a simple, indirect, and universally applicable method for estimating PHC burdens in wastewaters is obvious. Past assessments have relied on largely unsupported assumptions of the THC content of oil and grease. With refinement, this approach might be attractive because oil-and-grease levels are commonly monitored in treatment facilities worldwide. Therefore, we investigated the possibility of correlating our TEO and THC measurements with oil-and-grease data obtained by treatment-plant personnel.

Casual inspection of contemporaneous data for the JWPCP effluent in Figure 2 suggests that correlations among THC, TEO, and oil-and-grease concentrations exist. To be valid, however, a correlation used for estimation on a regional scale must be applicable for a number of effluents. Thus, we analyzed the data for all wastewaters together. Figure 3 illustrates the analytical curves obtained by linear regression under two different conditions, that is, with and without the HYP-7mi sludge data.

The correlation between TEO and THC data for all five effluents (Figure 3a, curve 1) is exceptionally good, indicating that, with respect to hydrocarbon content, the composition of the extractable organics is very consistent among these wastewaters. We also explored the possibility of excluding the sludge data from the regression analysis. Practically speaking, there is some justification for doing so because undiluted sludge is usually disposed by pyrolysis, landfilling, offshore dumping, or as a soil conditioner,

not by continuous discharge through relatively shallow water outfalls. Thus, most effluents discharged directly to the ocean will have received a combination of primary and/or secondary treatment and should have characteristics similar to those of the JWPCP, HYP-5mi, OCSD, and CSD wastewaters. When the regression analyses are performed on all but the sludge data, the correlation of TEO with THC remains very good ( $r = 0.91$ ), and the slope and intercept are similar (cf. Figure 3a, curve 2) to those obtained for the analysis using the complete data set. Thus, exclusion of the sludge data does not present a serious statistical problem for the correlation of TEO and THC measurements.

When the correlation of THC with oil and grease is considered, however, a different situation arises. Because oil-and-grease measurements were performed by plant personnel on entirely different (grab) samples than those used for the THC determinations, there is considerable sampling-related error associated with plot of THC vs. oil and grease (Figure 3b, curve 1). In addition, the analytic curve does not appear to fit the non-sludge effluents very well. This may be due to the fact that the HYP-7mi sludge, a highly concentrated effluent, is analyzed for oil and grease by a modification of the standard method which may not have the same extraction efficiency as that used for the other effluents (32).

If the linear equation for the THC vs. oil and grease correlation for all of the data (curve 1) is used in conjunction with annual mean values of oil-and-grease concentration and flow (Table I) to calculate a combined hydrocarbon MER for the dischargers, a value of 11 290 mta is obtained. This is in very poor agreement with that shown in Table V (17 610 mta). MER values for individual dischargers are even more deviant. In fact, because the y intercept of the line (curve 1), 22.3 mg/L exceeds the mean annual concentration of oil and grease in HYP-5mi

effluent, a negative MER is calculated when this equation is used.

Performing the regression analysis in the absence of the sludge data produces somewhat less satisfying statistical results (i.e., the  $r$  value is lower); however, the ability to accurately estimate THC mass emission rates is greatly improved. The final expression obtained by linear regression of the THC and oil-and-grease data (without HYP-7mi data; curve 2) is

$$y = 2.01x + 10.4 \quad (r = 0.72) \quad (2)$$

where  $y$  = concentration of oil and grease (mg/L) and,  $x$  = concentration of total hydrocarbons (mg/L). Using the average values of oil-and-grease concentrations and flow given in Table I, we calculated the following MERs with this formula (mta): JWPCP, 8443; HYP-5mi, 2014; HYP-7mi, 1600; OCSC, 2465; CSD, 2475; total, 16997.

By comparison with the data given in Table V, the predicted individual MERs show adequate agreement, whereas the grand total agrees quite well. This crude test simply demonstrates the self-consistency of the method. More data for other effluents may provide a means of evaluating whether the correlation found here is generally applicable and/or subject to changes with time. Such a tool will obviously be of value in estimating the wastewater input of petroleum hydrocarbons because of its simplicity, and applicability to existing monitoring data.

### Conclusions

The results of our analyses of municipal wastewaters in southern California have shown that large quantities of petroleum hydrocarbons (17 400 mta) are currently being discharged to the ocean in this area of the world. Indeed, it appears that calculated global PHC inputs due to sewage may have been underestimated in the past. The environmental significance of these findings is clouded, at best. This is because (1) the nature and quantities of specific organic compounds in wastewaters are largely unknown and (2) the fate of complex mixtures of natural and anthropogenic organic substances in the ocean are only poorly understood. We intend to address the detailed molecular composition of sewage in subsequent writings; however, the environmental fate of organic wastes will remain an important and difficult subject for future investigations.

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## NOTES

## Trace Element Content of Northern Ontario Peat

Walter A. Gloschenko\* and John A. Capoblanco†

■ Peat samples were collected at 0-20- and 20-40-cm depths from several peatland ecosystems located in northern Ontario, Canada. Analysis was made for the trace metals Zn, Pb, Cu, Cr, Cd, and Hg. Concentration values in general were in the low ppm range and did not significantly differ in terms of peatland type or depth except for Pb. This element was significantly higher in surface peats in bogs and fens. Concentrations of metals in peats found in the study were equivalent to those in US coals, suggesting caution during combustion in terms of potential atmospheric input of metals.

The combustion of peat as a source of energy occurs in several northern countries, mainly the USSR, Ireland, and Finland (1). Such power plants are up to 600-MW capacity, similar to that of large coal-burning facilities (2). Interest in the use of peat for energy production either by direct combustion or by gasification is increasing in North America, especially in the states of Minnesota and North Carolina, where extensive peat deposits occur (3). However, most peat areas are located in Canada, with  $170 \times 10^6$  ha of peat reserves, and the state of Alaska, with an estimated  $30 \times 10^6$  ha (1). Much of these reserves are located remote from population centers and may only serve as local energy sources.

Peat can contain relatively high trace element concentrations, and caution has been suggested in using such as an energy source (2, 4). However, few published data are available for metals in North American peats except for the Okefenokee Swamp in Georgia (5). Peat is a precursor to coal, and coal combustion can emit large amounts of trace metals mainly associated with fly ash (6-10). The purpose of this study is to determine the trace metal content of peat.

## Sampling and Analysis

The peat samples collected in this study were obtained from the Kinoje Lake area located in northern Ontario, Canada, at  $51^{\circ}34'N$ ,  $80^{\circ}48'W$ . This area lies in the Hudson Bay Lowland, a vast peatland complex of  $30 \times 10^6$  ha, or approximately 18% of Canada's estimated peatland acreage (1). Three major peatland ecosystem types occur in the region: bogs, fens, and swamps. Bogs are ombrotrophic; i.e., the amount of peat accumulation that has occurred leads to no mineral soil water exposure, and all chemical substances entering are derived solely from atmospheric precipitation. Fens and swamps are minerotrophic and in contact with mineral soil water; the main difference between these two ecosystem types is that

\* Address correspondence to this author at the following address: Ecological Impact Section, Aquatic Ecology Division, National Water Research Institute, P.O. Box 5050, Burlington, Ontario, Canada L7R 4A6.

† Department of Analytical Inorganic Chemistry, University of Geneva, Switzerland.

Table I. Results of Metal Analysis of Peat Samples

element	av concn, ppm	range	SD	no. of samples
Zn	31	5-87	17	69
Pb	16	3-31	7	67
Cu	7	2-20	5	69
Cr	3	0.3-9	2	69
Cd	1	0.1-7	1	68
Hg	0.06	0.01-0.11	0.03	12

Table II. Depth Distribution of Metals in Peat with Respect to Ecosystem Type

peatland type	depth, cm	n	element concn $\pm$ SD, mg kg <sup>-1</sup>				
			Pb	Cu	Cr	Cd	Zn
bog	0-20	11	18 $\pm$ 7	4 $\pm$ 2	3 $\pm$ 1	2 $\pm$ 1	35 $\pm$ 20
	20-40	8	7 $\pm$ 6	3 $\pm$ 1	2 $\pm$ 1	1 $\pm$ 1	21 $\pm$ 20
fen	0-20	11	21 $\pm$ 7	7 $\pm$ 5	3 $\pm$ 1	1 $\pm$ 1	38 $\pm$ 17
	20-40	12	8 $\pm$ 7	6 $\pm$ 4	4 $\pm$ 2	1 $\pm$ 1	20 $\pm$ 15
swamp	0-20	4	15 $\pm$ 4	7 $\pm$ 2	4 $\pm$ 4	1 $\pm$ 0	30 $\pm$ 16
	20-40	4	12 $\pm$ 5	9 $\pm$ 3	4 $\pm$ 3	4 $\pm$ 3	32 $\pm$ 27

swamps are wooded, while fens are dominated by sedges with limited grasses, reeds, shrubs, and trees.

The area of this study is very sparsely populated, and utilization of such peat does not appear feasible at the present time because of economic, technical, and environmental problems (11). However, such limitations may be overcome at a later time when other energy sources become limited.

During the summer of 1976, the area was visited by helicopter and peat samples collected from 23 sites; samples were split into living mosses, peat from 0-20- and 20-40-cm depth. Peat accumulation rates in the area have been estimated at 0.5-0.65 mm yr<sup>-1</sup> (11). Thus, these depths correspond approximately to a minimum age of 0-300 and 300-600 yr, respectively.

Samples were collected by hand using a shovel and were handled with plastic gloves to prevent contamination. They were kept under refrigeration at 4 °C until returning to the laboratory where they were kept frozen until analysis. They were then thawed, oven-dried at 90 °C for 48 h, and ground to 250  $\mu$ m in a Wiley grinding mill. The samples were then wet-ashed with HNO<sub>3</sub>/HClO<sub>4</sub>, and the elements Zn, Pb, Cu, Cr, and Cd run by atomic absorption (AA) (12). Mercury (Hg) was run by flameless AA on a limited number of samples.

## Results

Results of trace element analyses of peat are presented in Table I, based on all peats analyzed without regard to depth sampled. In general, all results were in the low ppm range with Zn showing the highest mean concentration. Standard deviation values were high, but typical of such environmental samples. Copies of the total numerical data are available from the authors.

Table III. Comparison of Data with Previous Studies of Peats and Coals<sup>a</sup>

element	this study	Okeefenokee Swamp peats (5)	coal (14)		
			Illinois	Appalachian	Western
Zn	31	14	250	25	7
Pb	16	13	32	6	3
Cu	6	25	14	18	10
Cr	3	21	18	20	9
Cd	1		2	0.2	0.2
Hg	0.06	0.4	0.2	0.2	0.09

<sup>a</sup> All results in ppm dry weight basis.

The data were further analyzed in terms of peatland ecosystem type—bog, fen, or swamp—and depth of sample in Table II. Such results were subjected to both a parametric two-way ANOVA statistical test and a Kruskal-Wallis nonparametric ANOVA test. No significant difference was found between bogs, fens, and swamps for either the 0–20- or 20–40-cm depth for the elements analyzed. Also for a given ecosystem type, no significant difference was found in element concentration between 0–20 and 40–20 cm for Cu, Cr, Cd, or Zn based upon both a Student's *t* test of the data and a nonparametric Mann-Whitney test. However, Pb was significantly higher at the 0–20-cm depth in bogs ( $p < 0.05$ ) and fens ( $p < 0.001$ ) while in swamps no significant difference occurred based upon the Mann-Whitney test. Concentrations of Zn were higher in surface peats in bogs and fens, but this was not a significant difference.

#### Discussion

Fossil fuel combustion is of concern in terms of metal input to the atmosphere. In fact, studies of metals in bogs have been used to assess patterns of atmospheric deposition of metals (13). Of particular interest is the preferential release of such metals included in the study as Hg, Cd, Pb, and Zn (6–10). Results of this study are compared with other North American peats (5) and coal (14) in Table III. Compared to Okeefenokee Swamp peats (5), this study found somewhat higher concentrations of Zn, while Cu, Cr, and Hg were lower. As for comparisons with coal

(14), Illinois coals were higher in certain metals, especially Zn, Pb, and Cd, than other US coals. Peat samples were of the same order of magnitude as Appalachian and Western coals in Zn and Hg, lower in Cu, Cr, and Cd, but higher in Pb (except for Illinois coals). These results would suggest that use of peat as a source of fossil fuel for combustion would present the same concerns as coal in terms of trace metal emissions to the environment.

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