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ENVIRONMENTAL SCIENCE & TECHNOLOGY

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ESTHAG 13(5) 497-626 (1979)
ISSN 0013-936X

ES&T

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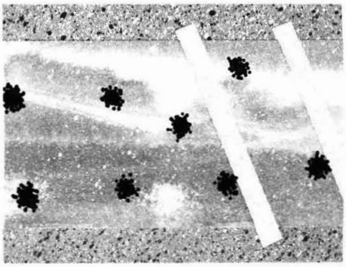

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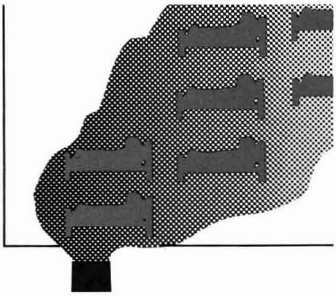

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Published monthly by the American Chemical Society from 20th and Northampton Sts., Easton, Pa. 18042. Executive Offices: Editorial Headquarters, 1155 16th N.W., Washington, D.C. 20036. Advertising office: 25 Sylvan Road South, Westport, Conn. 06880. Second-class postage paid at Washington, D.C., and at additional mailing offices.

SUBSCRIPTION PRICES 1979: Members, 1 year $16.00; 3 years $40.00. Nonmember personal, 1 year $24.00; 3 years $60.00. Institutions, 1 year $64.00. Foreign postage, $6.00 per year. Air freight rates per year available on request. Single copies: current issues, $5.00. Rates for back issues and volumes are available from Special Issues Sales Department, 1155 16th St., N.W., Washington, D.C. 20036. Claims for missing numbers will not be allowed if loss was due to failure of notice of change of address to be received in the time specified: if claim is dated (a) North America: more than 90 days beyond issue date, (b) all other foreign: more than one year beyond issue date; or if the reason given is "missing from files." Hard copy claims are handled at the ACS Columbus address.

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Credits: 506, Columbus (Ohio) Citizen Journal; 507, 509, 511, *ES&T*'s Julian Josephson; 515, Marcia Fine (4th photo), United Press International (5th photo); 530, Frank E. Gunnel

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Published by the
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1155 16th Street, N.W.
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For author's guide and editorial policy, see January 1979 issue, page 51, or write Katherine I. Biggs, Manuscript Reviewing Office *ES&T*. A sample copyright transfer form, which may be copied, appears on page 110 of the January 1979 issue.

Interference at EPA

The laws we in Congress intend are not always the laws we get.

In 1970 the Senate Committee on Government Operations held a hearing on President Nixon's reorganization plan to create a separate environmental agency. I testified in defense of the plan, which closely resembled legislation I introduced that same year.

"Removing environmental regulatory authority from promotional agencies . . . is the primary importance of the President's reorganization plan," I testified. "At the same time, concentrating environmental protection programs in one independent agency should give our environmental quality efforts a measure of stability and coordination they have never known."

Now, the well-meaning but misguided assault on the Environmental Protection Agency by the President's inflation fighters has called into question both the independence of the agency and the regulatory stability it has offered.

The White House has promoted its war on inflation by direct contact, memoranda, phone calls, letters, and one-man economic reviews.

There have been conflicting stories as to their success. But there can be little doubt that when high-level White House advisers appear at a meeting where regulations are being drafted—and they have appeared at such meetings—bureaucrats will not mistake their intent.

The recent change in the EPA standard for ozone brings into question just how independent the process really is.

The Clean Air Act directs the Administrator to set ambient air quality standards to protect "public health and welfare." Nowhere does the law say that economic factors should be considered. In fact, economic factors were consciously *excluded* by the Congress after long and agonizing consideration.

Twelve separate times after the close of the public comment period on the proposed revision to the ozone standard, however, White House economists contacted EPA staff responsible for developing the regulations.

EPA Administrator Douglas Costle did raise the ozone standard. It is not as high as White House economists wanted, but it is difficult to imagine that their views were not felt.

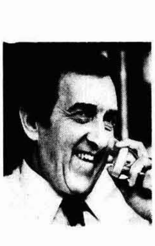
I am not naive enough to believe that any regulation can be developed in a vacuum, without political pressure. Indeed, the President should have influence over his agencies and what they produce. On the other hand, there are ample avenues for a President to put his mark on the output of a regulatory agency without his executive staff flirting with possibly illegal pressure tactics.

There ought to be more respect for process. Influential White House economists have been given access to regulatory decisionmakers at critical times in the process. No notes or minutes are available. Divergent views are excluded. The public is not allowed to know what transpired.

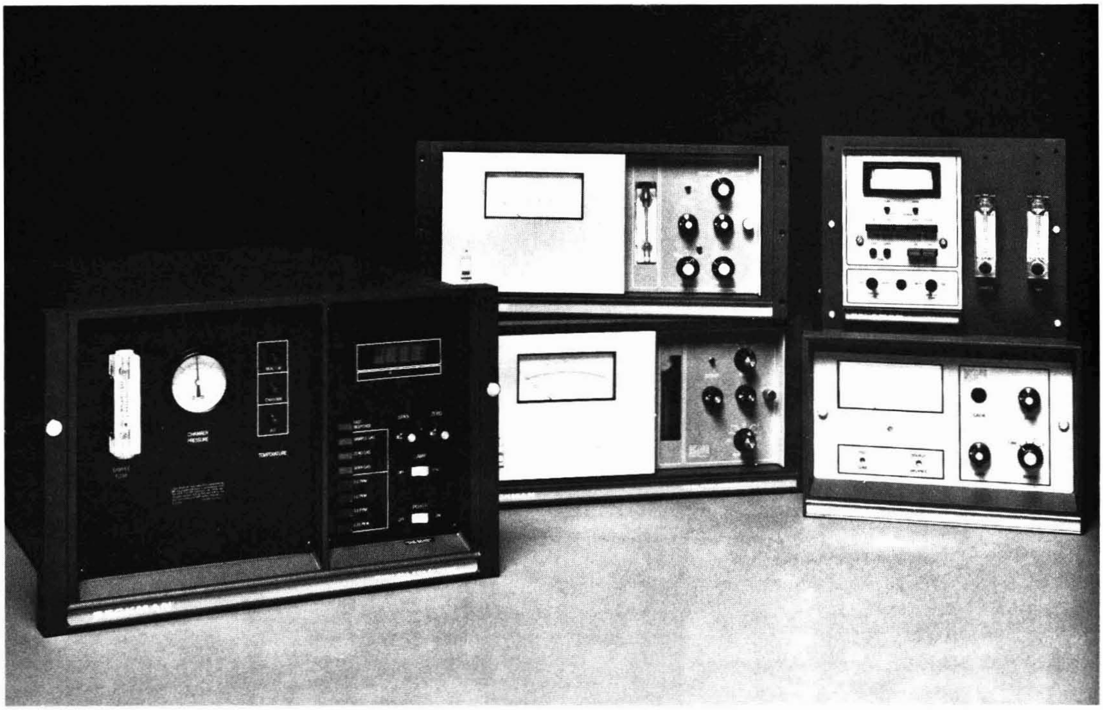
If voluntary restraints or guidelines for administrative intervention are not included in the Administration's regulatory reform proposals, an alternative might be to make EPA a truly independent agency—similar to the Federal Trade Commission.

Maybe then, ten years after we first discussed the creation of an Environmental Protection Agency, we might get what we had asked for.

Edmund S. Muskie



Senator Edmund S. Muskie (*D, Me.*) *is Chairman of the Subcommittee on Environmental Pollution. He was instrumental in setting up the EPA, and in the drafting and passage of the Clean Air and Clean Water Acts.*



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ES&T LETTERS

The cover runners

Dear Sir: To my husband's and my surprise, we are the runners on the December 1978 cover of *ES&T*.

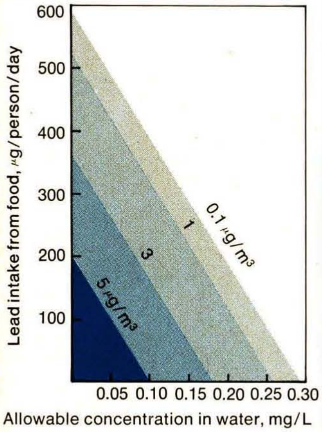
Amber & Anthony Reynoso
Ione, Calif. 95640

Man's lead burden

Dear Sir: I was pleased to read the aspects of integrated exposure assessment monitoring (*ES&T*, January 1979, p 34). In order to set standards for drinking water contaminants, the total exposure from air, food and water should be taken into consideration. A simplified approach for arriving at lead limits in drinking water is presented in Figure 1. Such limits are variable, as it should be, depending on lead intake from food and air. In making the computations (applicable to adults only), the following assumptions have been made:

Maximum no-observed-adverse-health-effect:	60 μg/d
Daily inspiration volume:	20 mg^3
Daily intake of water:	2 L
Lead absorption from food:	10%
Lead absorption from water:	10%
Lead absorption from air:	40%

FIGURE 1



It can be seen that in urban areas (for example air lead 1 μg/m^3), and with a daily lead intake from food of 430 μg (WHO's maximum tolerable daily intake), the allowable concentration of lead in drinking water should not exceed 0.05 mg/L. However, if for the same concentration of air lead, the daily lead intake from food is 300 μg only, then the allowable concentration of lead in drinking water could be increased to 0.11 mg/L. Such computation demonstrates that the WHO standard of 0.1 mg/L for lead in drinking water and the U.S. standard of 0.05 mg/L are in fact not conflicting, each one being appropriate under different exposure conditions.

Another example: in highly urbanized areas (3 μ/m^3), at an average intake of lead from food of 300 μg/day, the level of lead in drinking water should not exceed 0.03 mg/L. If the intake from food is 400 instead of 300 μg/day then the "safe" limit of 60 μg/day has already been exceeded and no lead should be allowed in the drinking water.

Such graphs could be constructed for a variety of contaminants provided certain metabolic and toxicological factors are known. They would serve to make "allocations" for the various routes of exposure as well as adopt standards that are appropriate to specific situations.

Hend Galal-Gorchev
1206 Geneva, Switzerland

Pesticides

Dear Sir: In the December 1978 issue of *ES&T* there is a letter on pesticides. The authors make a mathematically and grammatically meaningless statement . . . "the mirex (and other OC) levels in Lake Ontario Caspian Tern eggs are 4 to 6 times lower than in Herring Gull eggs . . .". Perhaps they mean " . . . are one fourth to one sixth of that in Herring Gull eggs . . . ".

I notice an increasing trend in North American literature for confusion with this type of usage (as well as between, for example, "eight times higher than" and the synonymous "nine times"). I hope that *ES&T* will prevent such future errors by careful editing and set an example for other publications.

Kenneth A. Hooton
Tempe, Ariz. 85283

January editorial

Dear Sir: I have been reading your January 1979 issue, and as usual (see letter, *ES&T*, May 1974, p 392) enjoyed it, as I do every issue. However, I would like to express in word, humble as my opinion is, that your Guest Editor, Dr. James P. Lodge, really touched on something that would and could, if accepted, turn the tide of history in this old world from its present deplorable state.

Authorities everywhere, searching for some solution to their many problems, are disregarding the "Whole Man."

In the eyes of the world science is esteemed, but on its own it has not proved wholly successful. Christianity, presenting only the spiritual side, is beyond man's natural understanding; but when the two are brought together—Science and Theology—as so wonderfully explained by Dr. Lodge, and the "Whole Man" in his entirety is considered, regardless of the sphere, a successful solution must be the result. We are body, we are intellect and we are spirit, and should be considered as such.

I appreciate your journal as a "Leader" and I am grateful for this article and trust that your publication, which reaches even Rhodesia still, will help us toward peace to humanity.

Rosaleen Kerr
Salisbury, Rhodesia

Corrections

- April 1979, p 416. The date of the Consent Decree is incorrectly reported. The correct date is June 7, 1976.
- April 1979, p 421. There is a mispelled word in the color type material. The correct wording is: An automated software program *completely* identified the presence or absence of the organic priority pollutants and quantifies them within minutes.

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CIRCLE 14: FOR MORE INFOR

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INTERNATIONAL

In its annual report on the Great Lakes water quality, the International Joint Commission stresses the "critical problem" posed by toxic substances and reiterates the need for effective controls. The report urges a cooperative effort between the U.S. and Canada to develop a program to inventory the 2800 toxic compounds found in the lakes, and evaluate their health risks.

To monitor water quality in Finland, Philips (The Netherlands) will help by setting up an automatic monitoring network. Initially, monitoring is to be done in the Kymi River catchment area in southeastern Finland, which comprises 36 500 km^2, of which about 20% is lakes. The aim is to ascertain both causes and effects of water pollution, so that urban and industrial growth can be attuned to water quality needs. To this end, Philips was contracted by the Finnish firm Nokia O/Y. A portion of the funding for this project comes from a World Bank Loan.

WASHINGTON

A recent report for the EPA claims that the benefits of air pollution control are $41 million annually, at a minimum. The study, "Methods Development for Assessing Air Pollution Control Benefits," was a three-year effort of the Universities of Wyoming, Southern California and New Mexico. Although the EPA cautions that direct comparisons may be misleading, total 1978 expenditures for air pollution control tallied $12.2 billion. Allan Carlin, EPA senior operations research analyst, says that the study uses innovative methodology and "represents the current state-of-the-art." A portion of this study shows that a 30% improvement in air quality in Los Angeles may be valued at $650–950 million annually in real estate values.

EPA announced an accelerated program to force the clean up of old dumpsites containing hazardous wastes. Among the actions taken will be the establishment of methods for investigating and preparing legal action on inactive sites, the drafting of legislation for a national fund for correcting these sites, and an update and expansion of the inventory of waste sites developed last fall.

EPA's Blum

Under a seldom used power, EPA took "emergency suspension" action on the herbicide 2,4,5-T. At a press conference, deputy administrator Barbara Blum explained that the action, taken to halt the spring spraying of the herbicide, was made on "the basis of new information indicating its potential link to human miscarriages." The miscarriages occurred in the Alsea area of Oregon. The suspension will now permit EPA full review of the herbicide's impact on human health as well as the benefits realized with continued use. Also placed on emergency suspension was the herbicide silvex; both 2,4,5-T and silvex are unintentionally contaminated by the dioxin TCDD. Dow Chemical Co. and 10 other producers promptly filed suit in federal court to block EPA's action.

The Commerce Dept. reports a 2% increase in pollution abatement and control spending in 1977, when real spending reached $24.5 billion. As a percentage of the Gross National Product, real spending on abatement and control was 1.8% in 1977. According to the report, regulation and monitoring spending increased 10%, while research and development spending rose 2% during the period 1972–1977.

An A.D. Little study for the EPA finds that the cost of completing TSCA Section 5 pre-manufacturing notification forms will run between $2500–41 000 per individual substance; the cost will vary with the size of the firm and the availability of data. The study claims that reporting compliance costs of $1000/chemical would have prevented the introduction of about 50% of the chemicals currently introduced to commerce; at $40 000/chemical, about 90% of the chemicals would not have been introduced. Another costly matter is cleanup of the 1200 improperly managed hazardous waste disposal sites in the U.S. According to a study by Fred C. Hart Associates for the EPA, the cost could reach $22 billion.

The Interagency Review Group on nuclear waste management submitted its final report to President Carter. A principal finding of the report is the public's concern that government programs be "more deliberate, better conceived and better managed than in the past." The report identifies many of the institutional issues that need to be addressed in assuring better nuclear waste management.

STATES

Construction is to begin next month on Denver, Colo.'s, pilot plant for conversion of sewage to potable water. The plant is designed to treat up to 1 million gal/day of municipal sewage, but none of the treated water will flow into the city's water system. If the health studies are negative, potable water from sewage may flow into Denver homes by the mid-1990's. Total cost of the project is about $21.6 million, of which EPA is paying $7.0 million. In another study, Colorado State University scientists report that fertilizing farmlands with sludge posed little or no problem. Beef steers fed varying amounts of sludge were found to retain undetectable or very low levels of heavy metals in their muscle.

Three Arkansas chemical manufacturers have banded together in a joint SO_2 emissions control program to recycle gas now burned off during manufacturing operations. The cooperative plan, approved by the Arkansas Pollution Control and Ecology Commission, involves Arkansas Chemicals, Great Lakes Chemical Corp., and Velsicol Chemical Corp., and will cost $2.6 million. The three plants together emit 17.2 tons of sulfur dioxide daily; their combined control facility located at the Great Lakes Chemical manufacturing site and scheduled for completion by August 1, will reduce daily SO_2 emissions to 1.44 tons.

California will be allowed to use its own regulations for assembly-line testing of 1979 model-year passenger cars, and trucks rather than the less strict federal pollution control regulations. The U.S. EPA granted the state a waiver to permit enforcement of its own regulations. Among California's regulations is one which states that "No more than 1% of the vehicles in an engine family can have emissions which exceed the applicable standards by 2.33 times the standard deviation of the test results." Ford Motor Co. supported, but GM objected to California's waiver request, the U.S. EPA stated.

Ohio EPA director McAvoy

Ohio has issued the largest number of air compliance orders when compared with all other states in EPA's Region V, James F. McAvoy, director of Ohio's EPA, says. The Ohio EPA, to date, has negotiated compliance orders with 39 air polluting sources, and additional orders are being processed, McAvoy says. On the hazardous waste front, the Ohio EPA contracted with Battelle Memorial Institute to survey the state's industrial waste generators to ascertain the type, quantity and distribution of wastes generated; Battelle was also to recommend a hazardous waste management program for Ohio. Battelle found that 80 millions tons/year of industrial wastes are generated in the state, of which 5–8 million tons may be classified as hazardous.

Illinois has the dubious distinction of being the first state to have its coastal zone funding terminated by the National Oceanic and Atmospheric Administration because it failed to adopt required legislation. In another first, Portland, Ore., became the first city to receive a grant under the joint EPA/Dept. of Transportation program designed to help urban areas in their transportation-related air pollution control efforts. Portland received $129 050.

Sarasota, Fla., is building the world's largest reverse osmosis potable water purification plant, a 4.5 million gallon/day (mgd) plant. The plant will reduce total dissolved solids in Sarasota's well water from 1744 to 90 ppm. The purified water will then be reblended with well water to produce 12 mgd of water having a total dissolved solids content of less than 500 ppm, WHO's drinking water standard.

The crippling of a nuclear power plant near Middletown, Pa., was initially thought to result from a combination of mechanical and human errors. While meltdown of the reactor core was thought unlikely, though never discounted, an explosion, the result of a trapped hydrogen bubble, was a possibility that engineers tried to avert. Reportedly, a malfunctioning valve at the Three Mile Island plant, operated by Metropolitan Edison Co., led to the series of reactions that caused an overheating of the reactor core. Attempts to cool down the core were thwarted by the presence of the trapped hydrogen bubble. Monitoring of the air and water around the plant was, at first, sporadic, but a systematic monitoring system was soon instituted. Evacuation of the surrounding rural communities was never carried out.

MONITORING

Many state and regional EPA labs are not equipped to do the analyses required by regulations, according to Christopher Timm of EPA Region V. Speaking at a breakfast session hosted by Centcom, Ltd., at last month's Pittsburgh Conference, Timm said that an EPA survey found that only eight of the 10 regions and, perhaps more shocking, eight of the 50 states had the equipment and manpower needed to perform the myriad analyses specified in regulations. Timm, director of the Surveillance and Analysis Division of the EPA Central Regional Laboratory, this month assumes a new position with the World Health Organization in Geneva, Switzerland.

TECHNOLOGY

One way of improving water quality can entail ultrafiltration. Here, water passes through a dense membrane, along with some lower-molecular weight compounds. High-molecular weight compounds are retained. The system's driving force is pressure. Thus, energy is saved, because only the pumps require electric power. One firm marketing ultrafiltration is A/S De Danske Sukkerfabrikker (Nakskov, Denmark). Its largest unit has a 1900-m^2 membrane area, and is in continuous operation. Membranes are easily changed, and can work in a full pH range, up to 80 °C.

Flue gas cleaning by electron beams will be studied by a subsidiary of Research-Cottrell, Inc., under contract with the U.S. DOE. The beams would convert SO_x and NO_x into particulate matter which is then removed. The aim is to develop a competitive system for simultaneous SO_x/NO_x control.

A baghouse is the answer to tapping and charging emissions at Atlantic Steel Co.'s downtown Atlanta (Ga.) Electric Arc Melt Shop. The baghouse uses a pulse-jet cleaning method, and was designed by The Cadre Corp. (Atlanta). It has a microprocessor-based control logic to monitor air cleaning requirements, and to protect against potentially damaging upset conditions. Bags can be cleaned while the system is on- or off-line. The system will filter 300 000 acfm of fume-laden air, with a cleaning efficiency of 99+%.

Catalytic converter checkout

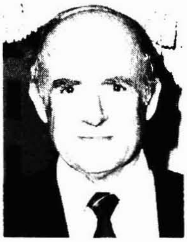
How is that catalytic converter working? You can have the answer in 20 min, or less, thanks to a new computer system developed by General Motors (GM). Previously, to get this information, many time-critical tasks were needed, as well as the sending of magnetic tapes generated to other data processing facilities, and return of test data by mail. All of that time-consuming procedure is now cut out. Data on carbon monoxide (CO), CO_2, hydrocarbons (HC), NO_x, and oxygen are gathered when exhaust gases enter the converter, and when they leave it.

An additional 50-y buildup of chlorofluorocarbons and carbon dioxide (CO_2) in the atmosphere could have permanent, deleterious effects upon the earth's weather, Hanwant Singh of SRI International warned. He said that these substances could deplete the ozone layer, cause excessive warming, and inhibit the air's ability to clean out pollution.

The first large-scale use of ozone for drinking water, in the U.S., will be at Newport, R.I. It will use the Emerzone™ Ozonation system developed by Emery Industries, Inc. (Cincinnati, Ohio). The drinking water plant will use two systems which can make a total of 350 lb/d of ozone, and which would process a peak capacity of 8 mgd (average flow, 5 mgd). Ozone will reduce chlorine use, and therefore, production of potentially hazardous chlorinated organic compounds. Emery is the world's largest producer/consumer of ozone.

INDUSTRY

"Small business can be really hurt, and new products cut back" because of provisions of TSCA that relate to PMN, Etcyl Blair, vice president, health and environmental sciences for The Dow Chemical Co., warned. PMN stands for premanufacturing notification, and involves a complicated form which an A. D. Little study (see Washington Currents, p 505) says can cost a firm $2500–41 000 to fill out for each new product planned to be introduced. And if the EPA declares a PMN invalid, "it's back to square one," Blair complained. He also said that if, because of a PMN, confidentiality is compromised, a competitor can produce a compound without need for a research/development investment. Blair also observed that many foreign firms are not burdened by such rules, so U.S. firms could be at a great disadvantage.



Etcyl Blair of Dow

"The most environmentally sound zinc refinery in the world" has been built at Clarksville, Tenn., by Jersey Miniere Zinc Co., a part of the Gulf & Western Natural Resources Group., and of Union Minière (Belgium). For instance, particulate matter will be controlled with 99.9% efficiency, by fabric filtration. Where possible, collected matter will be recycled. Less than 300 ppm of SO_2 (EPA limit, 650 ppm) will escape. Moreover, most of the 992 000 gpd of water will be cleaned, recycled, and reused, so that "water from the Cumberland River is cleaner than when it was removed."

Standards for solar collector thermal performance have been developed by the Solar Energy Industries Association (SEIA, Washington, D.C.). They are based on the ASHRAE 93.77 standard, but technical data are in terms that the consumer, for example, could understand. SEIA's aim was to make the standards not only comprehensible, but meaningful, fair, and non-manipulable. Association spokesmen expressed the feeling that the aim was achieved after 18 months of hard work. Meanwhile, Booz Allen & Hamilton Inc. assessed business risks of photovoltaics. For more information, write to them at 4330 East-West Highway, Bethesda, Md. 20014.

U.S. environmental regulations could strangle foreign trade and choke innovation, Bernard Broecker of Hoechst AG (West Germany), speaking for the European Chemical Industry Manufacturers Association (CEFIC), warned. These regulations could set up non-tariff barriers to trade, he said. Broecker also complained that EPA's "refusal to keep technical information confidential" is a "deep invasion of European chemical firms' rights of ownership." He also charged that PMN rules under TSCA, of which he was complaining, "are vague and unclear."

The largest flue gas desulfurization system contract ever awarded was granted by the TVA to Envirotech/Chemico Air Pollution Control. It will serve the 1400-MW Paradise Steam Plant at Drakesboro, Ky. The contract's value is $105 million, but Chemico president Robert Blinckmann said that the design should save TVA at least $40 million in energy costs over the remaining life of the steam plant. He noted that the design eliminates the need to reheat exhaust gas with supplemental energy, thanks to an innovative heat exchange process. The system will use limestone with a multiple-train venturi/absorber.

The focus on costs and benefits

With rapidly rising pollution control costs, one may expect many pointed questions as to what all this money is buying. Numerical answers will be wanted

The debate continues; it just won't die down! The issue is—and has been for a long time—should costs and benefits of pollution abatement be analyzed and quantified, and, if so, how? Senator Edmund Muskie (D, Me.) said no, people want a cleaner environment. Congress passed laws, and that is sufficient to get on with the setting of standards, and implementation of regulations. Lester Lave, head of the economics department of Carnegie-Mellon University, said yes, because just for air alone, for instance, costs run to about $20 billion/y, and are rising rapidly. "When that kind of money is being shelled out, questions about the worthiness of the standards are irrepressible," he observed.

This great cost/benefit debate was once again sharply brought into focus at the fourth annual conference of the Environmental Industry Council (EIC). Held at Washington, D.C., at the beginning of March, the conference drew approximately 200 people who heard Lave further remark that these multibillion-dollar costs lead to a "natural desire to see if the regulations make sense, and whether there isn't a cheaper way of achieving environmental improvement objectives."

"You tell us"

Are the massive amounts of dollars spent on pollution control working? Where are they working, or not working? Are some programs now antiquated? Should new research and development (R&D) funds be allotted, or existing R&D funds redirected? "Congress needs answers to these questions, and will look to the expertise of people such as EIC members to get the needed answers," Rep. Toby Moffett (D, Conn.) said. "And you can tell us whether control technology should be emphasized more than health effects should."

Congressman Moffett observed, "You can't quantify benefits of better breathing or health." But he added, "What about the quantifiable benefits that pollution control could bring in the form of reduced crop losses, work losses, tourism losses, and the like? There should be some effort to lay the value of these social benefits on the table, perhaps by considering them as a type of insurance."

Rep. Moffett also suggested that EIC members could help get first-hand information to their elected representatives by inviting their Congressperson or Senator to inspect the company's plant or facility, talk face-to-face with qualified experts, and see projects with which the company is involved.

Deadlines vs. goals

A way to improve cost-effectiveness of pollution abatement, as suggested by J. J. Combes, coordinator, environmental control for W. R. Grace & Co., is to convince Congress to replace performance deadlines with performance goals. Industry, municipalities, and the EPA should then be required to proceed toward those goals "with all reasonable speed."

Combes observed that adhering to deadlines "is frequently impossible, and does not strike the true cost-benefit balance." He acknowledged that in some cases, industry might stall. But he countered that "many EPA and state technical people come from industry," and that "it shouldn't take them long to detect stalling, and stimulate positive action."

Another extremely important thing industry must do, Combes said, is to communicate with environmentalists on all major problems, and to exchange information, ideas, viewpoints, and opinions. He explained how his own company did so, with respect to mining and coal projects in the western U.S. Combes told how Grace realized that with regard to developing a Colorado surface mining site, for example, some environmentalists' objections were quite valid, and were accommodated; and environmentalists withdrew objections that they realized were invalid. And Combes is in an excellent position to handle such communication, for he is active in an environmental group—specifically, the Audubon Society.

Rep. Moffett
"Congress needs answers"

Made more jobs

Pollution controls constitute about 2–2.5% of the gross national product (GNP), according to Gus Speth, member of the Council on Environmental Quality (CEQ). Federally mandated pollution controls, he said, constitute about 1% of the GNP. He estimated that some $48 billion were spent in the U.S. last year on all environmental efforts—about $215 per capita—and that business/industry expended about $7 billion of this total.

"There has been no significant effect of regulations on plant closings," Speth stated. Citing environmental laws, he gave a figure of 118 plants that closed between 1971 and 1978, affecting about 22 000 people, or about 0.02% of the labor force. "Many of those plants would have closed anyhow," he said.

Speth also estimated that if pollution control laws cost 22 000 jobs, they have created far more than the 680 000 estimated by the National Academy of Sciences in 1974. He expressed the belief that pollution control could cut unemployment by 0.2–0.4% over the next eight years, while increasing the inflation rate by, perhaps, 0.1–0.2 percentage points.

GNP percentages

J. William Haun, vice president of General Mills Corp., might take some issue with the CEQ's Speth. He reminded the conference that 3% of the GNP, at which he "pegged" pollution control outlays, works out to $60 billion/y, based on a GNP of $2 trillion. But costs, Haun observed, come to more than dollars paid out. He said that there is an uncounted cost of elimination of entrepreneurial risk, and the "spread of those costs over faceless bureaucrats," which, he felt, adds up to a large economic detriment to society.

Addressing entrepreneurial risks, John Robinson, director of environmental affairs at the U.S. Chamber of Commerce, forecast that regulatory reporting requirements alone "could put the little guy out of business." He charged that the impact of regulations changed the U.S. from the world's largest exporter of zinc in 1970, to the largest importer this year, and that the phasedown of lead in gasoline could add 500 000 bbl of oil to import needs by next year. Water pollution control regulations alone, he said, would cost metal finishers $25 million which, he warned, could put 20% of them out of work. Even the cost of corn seed could go up 35% because of environmental controls, Robinson predicted.

Robinson acknowledged that environmental controls will be part of the cost of doing business. He said that decisions must, therefore, be made as to what can and cannot be afforded, and that public willingness to pay the costs of these controls must be ascertained. But this willingness can be ascertained if the public has reliable cost-benefit data by which to judge, Robinson said.

Needed: quantification

Senator Gary Hart (D, Colo.) noted that pollution control costs "will often exceed estimates," but stated that there will be an unquantifiable payback in social benefits. He called for reducing costs by shifting from stressing regulations to emphasizing economic incentives for control, and disincentives in proportion to environmental damage done, for polluters. Sen. Hart also said that it is "very proper" to challenge legislators and legislation to make sure that cleanup benefits exceed costs, but noted that members of Congress, among others, require much more data concerning economic benefits of pollution control.

With regard to trying to quantify economic benefits, Carnegie-Mellon's Lester Lave provided air quality—especially SO_2 control—estimates, as an example. Cost figures, derived from a study in which he was involved, were put at about $13 billion/y. Benefits to society were assessed at $23 billion/y, which Lave said was "ultraconservative," because it did not take into account prevention of excess deaths caused by air pollution.

Carnegie-Mellon's Lave
"irrepressible questions"

But these figures, he noted, are educated estimates. That is why he asked the conference how one evaluates benefit statistics, such as the extent to which mortality or morbidity are proportional to air pollution. For instance, if airborne SO_2 concentration were 50 ppm, and a healthy, athletic 18-year-old boy were not affected, reduction of the SO_2 might not be considered as conferring a benefit in this case. On the other hand, for a 70-year-old emphysema patient, SO_2 reduction could offer a benefit of, say, alleviated suffering and lower medical bills which, in turn, translate into less Medicare costs.

What it boils down to, perhaps, is that serious, highly accelerated efforts should be made to get believable dollar estimates as to what social, and other benefits will be obtained from expending funds on environmental controls. Moreover, some idea of how those benefits may accrue to individual industries and companies, as well as to the nation, is needed. For, as Richard Hoard, EIC president, and a vice president of Ecodyne Corp., put it, the focus is on economics. Putting credible cost/benefit figures on the table will be the key to the success of environmental regulations and controls, and achievement of satisfactory cleanup, without breaking the country's financial back. JJ

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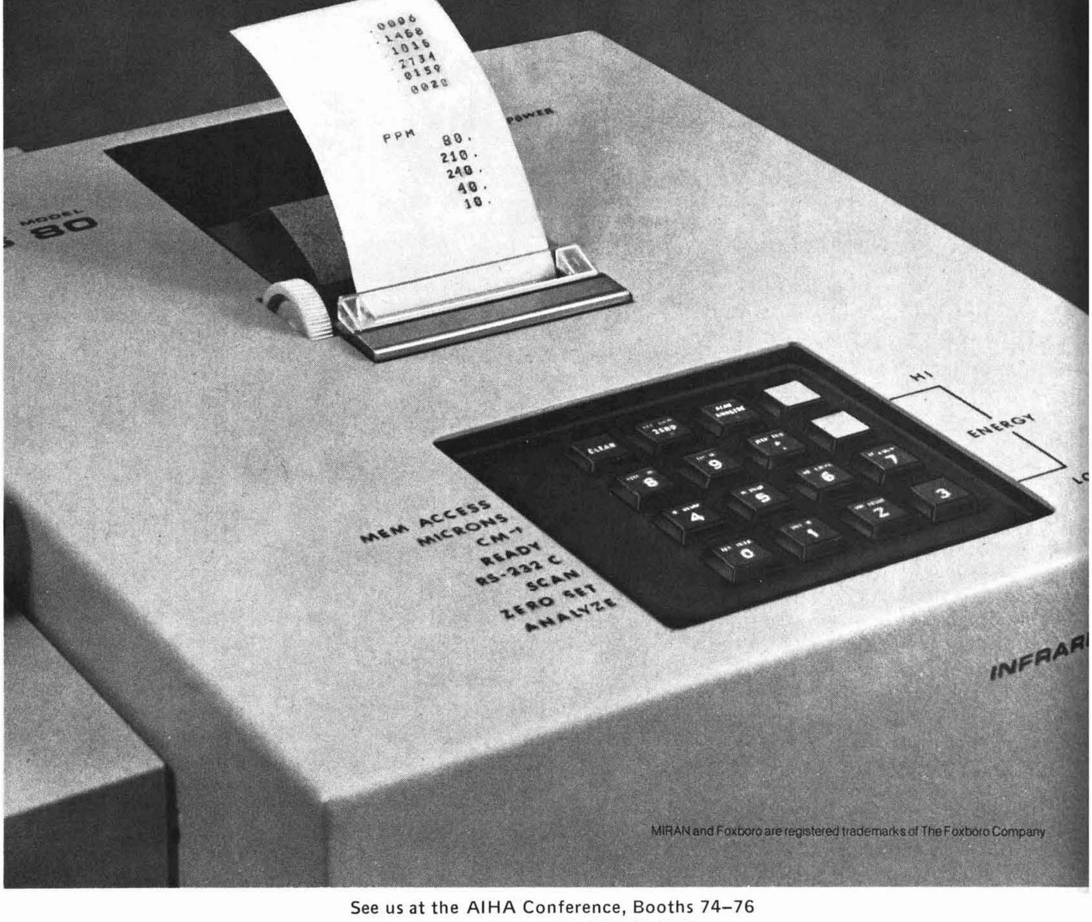

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Putting water cleanup back on track

A WPCF conference heard that emphases on mission, better money management, and renewed attention to operation and maintenance are needed

In the last analysis, the measure of the payoff of the nation's vast water cleanup program will be the success or failure to achieve the desired quality of receiving waters. That is what Martin Lang, president of the Water Pollution Control Federation (WPCF), told the opening session of WPCF's Government Affairs Seminar, held at Washington, D.C., in March.

Forget about plots

Lang warned that preoccupation with form, rather than the mission of protecting and enhancing water quality, has diverted a great national effort into "squalid squabbling," in which progress is measured by a "body count of fines and injunctions," rather than the response of receiving waters. He characterized this program as a *national*, rather than a federal mission, since the operation and maintenance of treatment plants will, in perpetuity, be financed by local funding.

WPCF president Lang
"mission, not form"

What obscured the water quality mission? Lang answered that question by saying that there is "fragmentation and poor communication among all members of the 'daisy chain'—cities, states, EPA, consultants, operators, industry, Congressional committees, and many other federal agencies also elbowing in."

Land decried the EPA hierarchy and its regions, and individual states "which cannot make decisions under the driving urgency of recurrent deadlines to allocate funds. The track record of obligation of funds is under close and searching scrutiny, but the track record of the response of the waters is not."

In addition, Lang strongly urged a return to "water quality-based decisions on the degree of treatment required." He also cited a House committee's critical overview of advanced waste treatment (AWT); the shift of priorities to toxics; the relaxation of required treatment for some coastal cities under the 1977 Amendments; and the EPA's own consultant's negative report on industrial cost recovery as "portents of a return to rational thinking.

"Let's forget recriminations, plots, territoriality, and 'turf'," Lang counseled. "Let's rather see that dollar expenditures are orderly and rational, because financial resources are limited. Let's also realize that all environmental decisions are, essentially, trade-offs."

Eyes on the dollar

Orderly, rational dollar expenditures for water cleanup are very much within the interest of the U.S. General Accounting Office (GAO), Comptroller-General Elmer Staats, GAO chief, explained. He told how, for instance, GAO criticized EPA for financing some AWT facilities in Maryland and Virginia, without sufficient water quality data or planning, or "reasonable" assurances that AWT would significantly upgrade water quality.

Staats also expressed GAO's view that in some cases even secondary treatment might not be needed, because it would improve receiving water quality "only marginally." If some rivers can absorb wastewaters with lower levels of treatment, without undue threats to health or the environment, this less costly alternative should be considered, he urged.

Staats gave, as an example, a planned $163-million upgrading of two municipal wastewater treatment (wwt) facilities, from primary to secondary wwt, in the St. Louis, Mo., area. The reason was that the law requires such upgrading, regardless of how much water quality may be improved. The purpose of the upgrading is to enhance oxygen levels, and to reduce suspended solids (SS) in receiving waters—in this case, the Mississippi River. Staats said that GAO found that in this instance, there was no oxygen problem, and that secondary wwt would have no significant effect on SS concentrations.

Comptroller-General Staats
some criticisms

Among other complaints, Staats listed the lack of comprehensive planning. Also, he remined the seminar that much of the money spent on wwt facilities might go for little or naught, because of nonpoint pollution problems that bedevil the water cleanup effort and have not been addressed to a very great extent.

The O&M connection

Even if a wwt plant, theoretically, can be a material aid to water quality improvement, and is planned, designed, and built properly, it still won't do its intended job, if unqualified persons are charged with the tasks of operation and maintenance (O&M). The matter of O&M has not been sufficiently addressed, William Hill of Floyd G. Browne & Associates, Ltd. (Marion, Ohio), speaking for the WPCF, told a seminar session. Worse, such EPA dollars as were to be dedicated to training personnel for O&M have declined, and O&M has been accorded no real priority, Hill complained. He warned that if EPA does not set an example, others will not concern themselves with this important matter.

To combat this serious problem, the WPCF will release a White Paper this year, Hill said. It will be aimed at many aspects of O&M. For example, it will call for proper training of wwt facility owners, be they municipal or private, as well as training/certification of managers and operators. This training should be updated, perhaps yearly, in many cases, Hill said. Users' rates, he suggested, should be set "realistically" to support O & M.

Regulators and designers should also become thoroughly familiar with O&M problems in the field, so that regulatory realism and more effective planning/design may be ensured. Moreover, Hill said, the plant, when operational, must be regarded as a utility, as is a gas or electric plant. Industrial users must be compelled to adhere to pretreatment regulations, and equipment suppliers should have properly qualified people on site to aid in training, startup, and initial operations.

These recommendations, and many others, will address owners, managers, operators, regulators, industrial waste dischargers, equipment suppliers, and designers, as well as contractors. They should, if implemented, go a long way to giving real muscle to O&M, without which the best-planned water cleanup program possible to launch would break down. But the general feeling is that the importance of O&M needs is, at last, receiving its long-awaited recognition. JJ

FBC: coming of age for industry

FBC—that's fluidized-bed combustion. It allows a choice of fuels, and will be making a grand entrance in Ohio

Soon, fluidized-bed combustion (FBC) will be used in industrial-sized boilers in the 50 000-500 000-lb/h of steam range. This development grows out of a joint agreement between Babcock Contractors, Inc. (Pittsburgh, Pa.) and Riley Stoker Corp. (Worcester, Mass.) to manufacture and market these types of boiler facilities. Spokesmen for the companies say that these systems have been demonstrated, and will carry full-performance guarantees for new boiler installations.

Use of abundant resources

The FBC system works at atmospheric pressure. It was tested and operated extensively in Britain, on high-sulfur coal and other fuels. The development was done by Britain's National Coal Board; then Babcock Contractors—the engineering/construction arm of Babcock & Wilcox Ltd., Britain, not related to the U.S. firm with the same name—financed the demonstration of a 45 000-lb/h plant. This plant has operated successfully at Renfrew, Scotland, since mid-1975.

Looking into the future, J. J. Farrell, president of Riley Stoker (a subsidiary of the Riley Co.), and Ronald Dean, president of Babcock Contractors, said that their companies provide an immediate and economical means to "use this country's abundant resources of high-sulfur coal, without addition of costly stack scrubbers." They added, "This agreement gives Riley access to proven, environmentally acceptable combustion technology superior to any currently available in the U.S. It gives Babcock access to Riley's national marketing organization, and expertise in design and manufacture of boilers for American industrial and utility customers."

A dance with limestone

In Ohio, high-sulfur coal is an abundant resource. That may be one reason why the Governor's Coal Use Committee selected the Babcock FBC system for several state institutional and industrial plants at which this coal will be burned. One such boiler, which generates 60 000 lb/h of steam, and is located at the Central Ohio Psychiatric Hospital (Columbus), will be retrofitted to this FBC technology, and will start up later this year.

The atmospheric-pressure FBC process lifts a bed of inert particles, generally consisting of a properly selected limestone, into a "dancing" motion, by means of injecting an airstream under the bed. The bed temperature is raised to 800-1000 °F by oil burners; then fuel is introduced, and ignites upon contact with the hot inert particles. Final combustion temperatures are 1500-1650 °F.

Heat is efficiently transferred to a water tube immersed in the bed. About 90% of the fuel's sulfur is trapped, according to the companies. They say that even 4-5% S coal, such as that found in Ohio, can be used in this system.

Among advantages listed for the process is low NO_x emission that meets present air standards, thanks to the low combustion temperature. Metallic salt emission, and fouling by volatile alkali metals, are also sharply reduced. Moreover, because bed temperature is below that of ash fusion, hard, abrasive clinkers are not formed.

There may also be useful by-products. These consist of ash, calcium oxide, and calcium sulfate. These materials might find use as agricul-

Setting regulations: a question of propriety

White House intervention in the rulemaking process—after close of the public comment period—may not be illegal, but may be improper

The environmentalists' domain, once an impregnable fortress built on a foundation of scientific evidence, is now being invaded by economic theory. Commanding the presidential ear in these inflationary times, his economic advisers are counseling cost-effectiveness in the setting of environmental regulations, and cost/benefit analyses as the means to achieve it.

Some claim that the inflation fighters' forays are succeeding, but to the detriment of all past environmental/health achievements. However, through congressional oversight and judicial review, environmentalists are attempting to thwart the forward thrust of the economists.

A recent skirmish took place before Senator Edmund Muskie's Subcommittee on Environmental Pollution. The Maine Democrat held oversight hearings to hear testimony on the "merit, legality and political ramifications" of White House intervention in environmental rulemaking procedures.

These interventions, endemic to the Executive Branch, are not peculiar to the Carter administration. During the Nixon years, for example, environmental regulations were made the scapegoat for rampant unemployment. To check this, the Nixon administration instituted the so-called Quality of Life Review designed to stifle environmental rules.

Though not exactly equating the Carter economists' thrusts to the Quality of Life Review, environmentalists, nevertheless, sense the shades of Nixon's tactic stalking the halls of such recent institutions as the Regulatory Analysis Review Group (RARG), headed by the President's Council of Economic Advisers (CEA); the Regulatory Council, headed by EPA administrator Douglas Costle; and several regulatory reform bills placed in the congressional hopper this legislative session.

In the end, the Carter economic analyses, like the Nixon reviews, tend to delay the regulatory decisionmaking process. Much of the input for analysis is collected off-the-record, thereby denying full public debate and a complete record for subsequent judicial review. And regulatory decisionmaking tends to shift downward from top policy officers to their subordinates.

Carter was elected as a professed environmentalist who also pledged regulatory reform and relief to burdened businesses. Then he was stampeded by galloping inflation. He is now faced with maintaining his environmentalist image, encouraging regulatory reform and fighting inflation. These may be mutually exclusive goals.

Nevertheless, in the pursuit of these goals, he may be sending his economists signals whose messages are being misread. This is vividly illustrated in the on-again, off-again EPA/TVA air cleanup settlement discussed later.

An economic veto

Muskie, the architect of the Clean Air and Clean Water Acts, as well as a founding father of the EPA, has a vested interest in seeing that these legislative programs are carried out as Congress intended. However, what he is seeing of late is economic considerations intruding in the setting of ambient air quality standards. Here the Clean Air Act explicitly states that the standards are to be based on scientific and medical evidence of health effects, not economic considerations.

In a cogent but emotional speech ladened with words such as "chilling" and "choking," which he delivered at the University of Michigan in February, Muskie stated that the major threat to the environment today "is a new mood of anti-regulators who claim it is too costly and burdensome to protect people from the hazards of pollution." These anti-regulators are Carter's inflation-fighting economists.

Muskie, who professes to encourage cost-effective programs, nevertheless sees the new regulatory reviews as "economic veto[s] of environmental, health and safety regulations." He points out that all too frequently, the "investment costs of . . . projects are emphasized, while the damage of environmental degradation is discounted," and benefits from environmental improvement are underestimated or ignored.

What Muskie appears to object to is the incursion of White House economists into terrain clearly demarcated by the Constitution or legislation as congressional or administrative territory. "Congress," he said, "determined that public health required certain levels of environmental control . . . Congress gave the program administrator flexibility as to method of achievement . . . These laws do not need to be second-guessed by bureaucratic economists."

In fact, Muskie, who feels that EPA administrator Costle made the "wrong decision" in relaxing the national air quality standard for ozone (formerly photochemical oxidants) by 50% last January, still maintains that the administrator has a "discretionary prerogative" under the Clean Air Act to change the standard.

Muskie also objects to regulatory reviews which occur after EPA completes its own economic analysis of the regulation, and after the close of the public comment period. As a matter of fact, there is strong belief among environmentalists that Costle's decision on ozone was strongly influenced by the President's economic advisers, who intervened after the close of the public comment period.

Costle vehemently denies that his decision on ozone was influenced by anything more than public comments and a review of the scientific record. However, he acknowledges receiving strong pressure to relax the standard from Alfred Kahn, chairman of the Council on Wage and Price Stability (COWPS), Charles Schultze, chairman of CEA, and Frank Press, the President's chief science adviser.

Yet, the EPA, which originally proposed to relax the ozone standard from 0.8 ppm to 0.10 ppm, settled on 0.12 ppm. Industry had clamored for a relaxation to 0.16–0.20 ppm and took its case to the White House economists, citing the inflationary impact of the standard. Whether the economic advisers influenced Costle's decision or not, the EPA, for the first time, weakened a national ambient air quality standard based on substantially little new medical evidence.

Costle goes to bat

The ozone revision is not the only time White House economists have meddled in the standard-setting process. Their intervention in OSHA's cotton dust standard prompted the threatened resignation of both Labor secretary Ray Marshall and OSHA administrator Eula Bingham.

In early February, Schultze and Kahn sent a memo to Costle suggesting alternative approaches to EPA's best available technology (BAT) control program for toxic effluents under the Clean Water Act. Disregarding or not knowing that the deadlines for the promulgation of BAT effluent guidelines for 21 primary industries were mandated by statute and by a court decree, the White House advisers made suggestions that were inappropriate and would have delayed the issuance of guidelines.

This memo, in the guise of inflation fighting and increased government efficiency, brought to the surface the simmering discontent of some senior EPA officials. These officials viewed the economists' intervention as a hindrance to the implementation of congressionally mandated antipollution laws. Threats of resignation surfaced again. To these threats, President Carter's press secretary Jody Powell replied: "gladly accepted."

The memo also elicited a strong nine-page rebuttal from Costle written the Friday before the Senate oversight hearings. Costle wrote to Kahn and Schultze: "While I respect your views, in this instance I think your specific suggestions are inappropriate. I feel bound to administer the BAT program in accordance with the principles that the Congress has established for its conduct. Any new ground rules for this program . . . would be counterproductive, contrary to the intent of Congress, and not in the public interest."

According to Karl Braithwaite, staff director of the Senate Subcommittee on Environmental Pollution, this is the only time Costle has rebutted White House intervention. In fact, as appointed head of the Regulatory Council, Costle has consistently been an apologist for the administration's regulatory reform efforts.

In this instance, however, Costle, successfully forestalled any further delay in setting BAT control regulations. Moreover, as Costle pointed out in his rebuttal, while the economists were counseling delay for further economic analyses, the President, in his first environmental message, had directed EPA "to give its highest priority" to developing these standards.

It would appear from this episode that Carter's economic emissaries sometimes work at cross purposes to the President's environmental commitment. Carter reiterated this commitment and his intention not to interfere with the development of environmental laws at a news conference on February 27, the second day of Muskie's hearings. Carter declared that he had "a statutory responsibility and right" to interfere but thought that "it would be a very rare occasion when I would want to do so."

Shifting authority

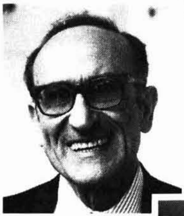
Another point of distress to the environmental lobby and to many senators on the environmental pollution subcommittee was articulated by John Quarles, former EPA deputy administrator, who testified before the subcommittee. The concern is that the economic reviews, the work of second- and third-level bureaucrats, may be used to influence executive agency administrators, or the courts. These reviews are seldom brought to the President's attention.

According to Braithwaite, only one RARG review, that for the cotton dust standard, ever reached Carter's desk, where it was overturned. The revised ozone standard never reached Carter, although Braithwaite says there is a possibility that EPA's new source performance standard for fossil fuel-fired electric generating plants may go

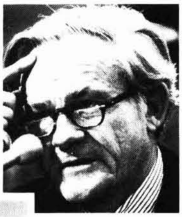
Congress hears environmentalists' charge of White House interference

Sen. Muskie (D, Me.)

Rep. Eckhardt (D, Tex.)



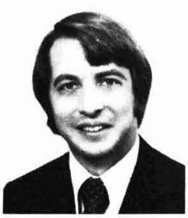
COWPS chairman Kahn



CEA chairman Schultze

COWPS director Bosworth

EDF attorney Rauch



NRDC attorney Ayres

to the President for review.

A case that reached the President's attention was the near scuttling of a landmark $1 billion, out-of-court settlement of a two-year legal battle between the EPA and the nation's largest utility, TVA. After months of contorted negotiations, TVA agreed to measures that would clean up emissions from 10 of its 12 plants, and bring them into compliance with the state implementation plans of Ala., Tenn. and Ky.

Months after TVA began to comply, Barry Bosworth, COWPS staff director, in an attempt to change the settlement conditions, sent identical letters to TVA chairman S. David Freeman and TVA director Richard M. Freeman. The letters said that the purchase of low-sulfur eastern coal and the use of scrubbers, two provisions of the settlement agreement, would have serious inflationary impact. The letters were ignored.

However, a second letter written on Jan. 10, 1979, to an E. G. Chaves whose company, the Consolidated Aluminum Co. (St Louis, Mo.), buys electricity from TVA, was widely circulated. Eventually it reached the bench of Judge Thomas Wiseman of the U.S. District Court in Nashville, Tenn., which has judicial review of the settlement.

In his letter to Chaves, Bosworth concluded that the settlement would "impose an unnecessary cost burden on the residential and industrial users of electric power in the Tennessee Valley." Shortly after the circulation of this letter, Judge Wiseman refused to approve the settlement until an inflationary impact statement is drafted and filed with the court. Wiseman claimed to be uninfluenced by Bosworth's letter. Nonetheless, what may be mere felicitous coincidence is seen by environmentalists as wanton and irresponsible intervention.

In repudiation of Bosworth's action, and to clarify any confusion Wiseman may have had about the administration's position, a March 9 letter was sent to Wiseman from Associate Attorney General Michael Egan. Egan's letter stated that the settlement "is in the public interest and consistent with the President's policies." The settlement has not yet been approved by Wiseman.

The Muskie hearings

In his opening salvo, Muskie cited "grave concerns" about the new economic analyses. First that "the process has the appearance of being slanted against environmental regulations," since five out of seven major RARG reviews deal with environmental and health regulations; and second that the "process builds a new bureaucracy which further encumbers and circumvents the regular process."

In even stronger language, Richard Ayres, an attorney with the Natural Resources Defense Council (NRDC), described the White House economists as "a roving commission" that participates "as decisionmakers in the writing and even enforcement of the regulations." Ayres further contended that the economists' discussions with administrators after the close of comment period are ex parte (one-sided) contacts, illegal under the Administrative Procedures Act of 1946. This act governs the conduct of executive agency administrators and the regulatory process itself.

> ***"Congress determined that public health required certain levels of environmental control . . . These laws do not need to be second-guessed by bureaucratic economists."***
>
> Sen. Edmund Muskie

The legality of ex parte communications is a cloudy issue. However, the Environmental Defense Fund (EDF) called on the Muskie subcommittee to direct the EPA to document these off-the-record discussions, and make transcripts available to the public for comment. Since the ex parte discussions are occurring at the behest of White House officials, however, EDF's suggestion would merely extend the public comment period at the whim of the executive office.

Ex parte contacts

EDF attorney Robert Rauch charged that the "White House officials may serve as 'conduits' for ex parte communications which have been provided them by private industry or other members of the public," and which bear the imprimatur of the President, with or without his knowledge.

Because the regulatory analysis group (RARG) is aided by the Council on Wage and Price Stability staff for its reviews, and COWPS has no more than 17 economists, the analyses, by necessity, must rely heavily on supplied information. The environmental lobby claims that COWPS seeks input only from industry, and thus becomes a conduit for industry views.

The environmental lawyers cited several instances of White House intervention after the close of the comment period. These included attempts to relax: the strip-mining regulations developed under the Surface Mining Control and Reclamation Act of 1977 before their promulgation on March 13; the setting of prevention of significant deterioration regulations under the Clean Air Act, which resulted in the restriction of the number of sources subject to full review; the setting of the national ambient air quality standard for lead under the air act, which resulted in an extension of the averaging time required to meet compliance; and the revision of the national air quality standard for ozone.

In his testimony before the environmental pollution subcommittee, Costle admitted to having received excessive pressure from the President's economic advisers on occasion, but he insisted that the ultimate decisionmaking powers always rested with him. He defended their right, as presidential emissaries, to question and comment on EPA rulemaking, even after the close of the public comment period. But he stressed that all off-the-record contacts were limited to issues in the public record.

Muskie, however, pointed out that because no transcripts of these "ad hoc" contacts are available for public scrutiny or comment, the intercessions, if not illegal, "give the appearance of impropriety."

President's emissaries testify

Muskie was merely warming up with Costle. With Kahn and Schultze, he really became animated, even impassioned. While the economists reassured the subcommittee of the administration's commitment to environmental improvement, they also stressed that environmental goals must be made cost effective to assure that the nation's economic welfare and its limited resources are preserved.

When Schultze said that "The Administration's concern for efficiency in the regulatory process is . . . not a narrow-minded attempt to trade off dollars for human health," Muskie countered with a recitation of the increasing severity of summer air pollution episodes, and a comment that "autopsy reports . . . may not list pollution as a cause of death."

By intervening in the regulatory process, the economists claimed to be carrying out Carter's mandate to improve the management of the federal government and fight inflation. When questioned by several committee members on their legal authority to intervene after the close of the comment period, they cited no specific authorities, pleading that they were economists not lawyers.

An independent agency

And here, inconclusively, the matter rests. The issues of whether, when and under what conditions presidential subordinates may influence agency rulemaking procedures remain unresolved. Clearly, these issues will be resolved by the courts, or through the power of the purse to confine the economic agencies to their statutory authority.

Another solution would be to insulate EPA from political entanglements by constituting it as an independent agency. Muskie is now mulling over the possibility of introducing such legislation, but he considers it a drastic measure not to be taken lightly. And according to his press secretary Robert Rose, Muskie is not yet certain that the problem "is soluble by one-stroke legislation." Muskie did state during Kahn's testimony that even though the EPA was established as an Executive Branch agency, it was Congress' intent that it be independent of political pressures.

Although the troublesome issues were not resolved during the oversight hearings, they were exposed to public scrutiny. From this scrutiny may come the establishment of clear-cut rules governing contacts between the President's economists and his environmental regulators, without resorting to the courts or to new laws.

Regulatory reform

The problems aired at the Muskie hearings ostensibly emanated from the need to fight the inflationary impact of the increasing number of regulations—about 7000 rules—being written each year. Carter made regulatory reform a cornerstone of his presidential campaign, and he has pursued it vigorously during his short term in office. To date, his efforts have produced the RARG, the Regulatory Council, and Executive Order 12044 "Improving Government Regulations," which has evolved into the administration's "Regulation Reform Act of 1979," S.755, recently submitted to Congress.

Among the bill's provisions, are those requiring

- cost/benefit analyses of alternative methods of achieving stated objectives before the issuance of regulations
- the setting of strict deadlines on regulatory proceedings to cut delays
- the earmarking of $20 million to fund participation in rulemaking proceedings by groups who otherwise would not be able to afford to participate
- a plan to further reduce paperwork
- "sunset" legislation that would require congressional review of every federal program every two years.

This bill would also update the 33-year-old Administration Procedures Act by placing independent agencies such as the Federal Communications Commission under many of the rules governing executive branch agencies (such as the EPA), thus bringing them more directly under presidential influence. And the proposed bill would revitalize the somnolent Administration Conference, which now has only advisory powers, into an agency that would oversee the $20 million public-participation fund, and select and monitor the performance of administrative judges, who now run the regulatory proceedings of independent agencies.

> ***"The Administration's concern for efficiency in the regulatory process is . . . not a narrow-minded attempt to trade off dollars for human health."***
>
> CEA chairman Charles Schultze

There are several other regulatory reform bills floating about the Senate. Senator John Culver (D, Iowa) has introduced his "Regulatory Flexibility Act," S.299. Senator Lloyd Bentsen (D, Tex.) has introduced four reform bills, S.51, S.52, S.53 and S.54 which, among other things, would require a regulatory budget for each regulatory agency, and modify the rulemaking procedures of independent agencies. And Senator Abraham Ribicoff (D, Conn.) has introduced S.262 which would improve the management practices of agencies, the efficiency of administrative proceedings, and metamorphose the Administrative Conference into a superagency charged with supervising the performance of all regulatory agencies.

The proposed reform bills attempt to streamline the rulemaking process. They are not designed, however, to eliminate the problems brought to light by the Muskie hearings and, according to environmental groups, may gut further progress of ongoing environmental programs. None are totally satisfactory to the Maine Senator.

Muskie's press secretary Rose says that the Senator sees no readily apparent legislative vehicle to solve the problem of eliminating the "shadow" rulemaking process that appears to have developed. Certainly the calls for regulatory analysis encourage rather than eliminate the formation of a "separate bureaucratic layer that deals superficially with issues" and, at times, subverts the intent of the laws.

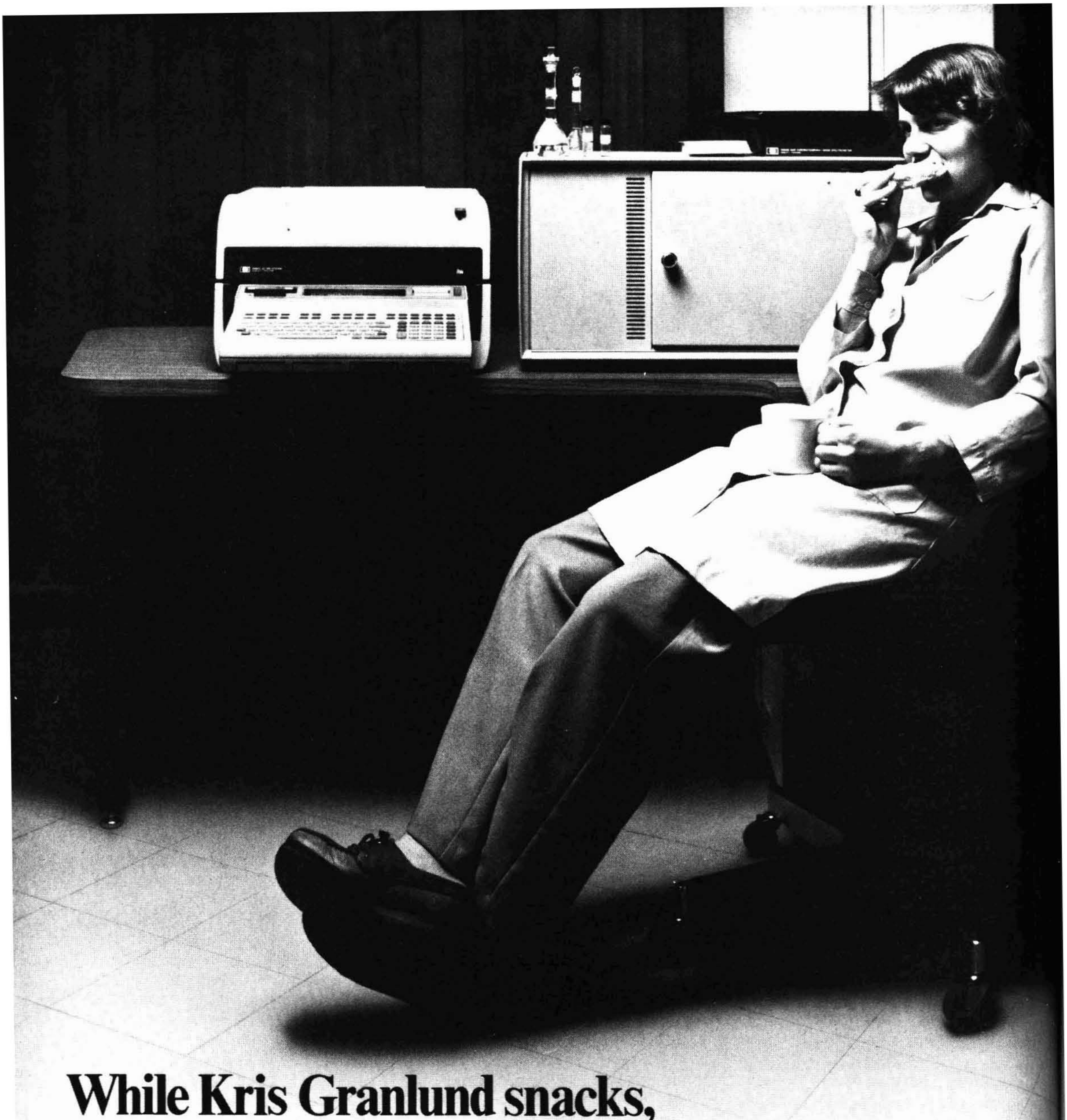
The legal questions await judicial clarification. However, the issues will be aired again in Congress. Representative Bob Eckhardt (D, Tex.) held hearings in April before his subcommittee on Oversight and Investigation which focused on the TVA/EPA settlement. He plans to hold additional hearings which will concentrate on the source of the authority of Presidential economic advisers to intervene in the regulatory process.

An Eckhardt subcommittee staffer mentions several ways that these off-the-record interventions can be checked. These range from oversight hearings, to legislation forbidding such ex parte contacts, to moving the regulatory review function from CEA/COWPS to another forum such as the Regulatory Council, which is comprised of all executive branch agency heads, to making EPA an independent agency.

A clear signal

Oversight hearings may be all that are necessary. The Muskie hearings appear to have been a clear signal to the administration that EPA must remain independent, if not by statute then by an understanding of congressional intent. "Clearly Carter's February 27th statement on noninterference and the administration's reaffirmation of the TVA settlement are indications that Muskie's signal got picked up," Braithwaite says.

It is hoped that the Senate oversight hearings will accomplish some other things as well: an improvement in the quality of work of the White House economists, and elimination of "one-man potshots," such as Bosworth's TVA shenanigans. Should the outcome of these oversight hearings be the development of ground rules that lay out the procedural steps to be followed by a regulatory agency and the White House staff in the course of rulemaking, then the hearings could be, in Judge Learned Hand's lyrical phrase, "[an] exhilarating opportunity of anticipating a doctrine which may be in the womb of time, but whose birth is distant." LRE



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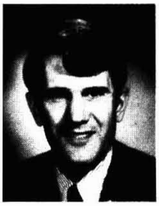
CIRCLE 6 ON READER SERVICE CARD

Air Quality Commission



Michael R. Deland
ERT, Concord, MA

Largely unnoticed amidst the swirl of controversy generated by the Clean Air Act Amendments of 1977 was the establishment under the Act of the National Commission on Air Quality. Congress was mindful that while the general strategies of the Act were formulated during more than a decade of discussion and debate, the consequences of implementing those strategies were largely unknown and needed to be carefully scrutinized. The National Commission on Air Quality was created to meet that need.

Sweeping mandate

The Act carefully defines the mandate of the Commission to study and report to Congress on a limited number of specified issues including:

- the available alternatives to meeting the public health and welfare and other goals of the Act
- the feasibility and consequences of meeting (or not meeting) certain requirements
- pollutants not presently regulated which may pose a threat to public health and welfare.

In addition, in seeming anticipation of the current controversy over EPA's Prevention of Significant Deterioration (PSD) regulations, Congress gave special emphasis to the study of the implementation of those provisions. The study issues address many of the underlying premises of the Act, giving the Commission a broad, comprehensive charter. A key to framing the scope of the Commission's mandate is the directive that it analyze the "economic, technology and environmental consequences of achieving or *not achieving* (emphasis added) the purposes of the Act."

This overview responsibility contrasts with EPA's role. In meeting its primary mission to establish and enforce, within extremely tight deadlines, environmental protection measures, EPA is constrained to give only cursory consideration to the "consequences" of its actions. Further, in several specific instances the agency is prohibited from evaluating economic factors and must establish requirements independent of their costs.

The Commission's charge to study "consequences," or the long-term picture, particularly when compared with EPA's more focused perspective and purpose, creates enormous potential for the Commission. It is the sole statutory mechanism by which the broad implications of the Act, including the intricate interrelationships between economics, technical feasibility, and public health and welfare are to be examined with detachment and impartiality.

The Commission is specifically authorized to contract with "non-governmental agencies" and to "hold public hearings, forums, and workshops," thereby providing an opportunity to bolster its own technical expertise and to obtain input from various interest groups.

Potential as yet unrealized

The Commission got off to a slow and controversial start. It is composed of two Senators and two Congressmen representing key Congressional committees, and nine members of the public appointed by the President, no more than one-third of whom "may have any interest in any business or activity regulated under (the) Act." The public members were not finalized until June 26, 1978, well after the March 1, 1978 due-date for the Commission's initial report to Congress on the motor vehicle aspects.

This early delay means that the Commission is likely to miss, by at least one year, the August 7, 1980 deadline for submission of its final report. In addition, the business community argued that only one of the President's original appointees could be classified as representing business or industrial interests and that therefore a balanced, impartial analysis was foreclosed.

The Commission conducted initial hearings in January 1979 followed by a second set in April. Its work plan is now being circulated for public comment and a majority of the 45-person staff has been named and is in the process of moving into permanent Washington, D.C. headquarters.

The staff has emphasized its efforts to try and counter the Commission's initial pro-environmentalist image and is actively soliciting and considering input from all constituencies. Various trade and business organizations, as well as environmental groups, are planning to participate in the public forums and to submit information to assist the Commission in its deliberations.

Congress authorized an $11 million budget and entrusted the Commission with a crucial fact-finding mission—to examine the consequences of the Clean Air Act Amendments and report in a timely enough fashion to permit meaningful mid-course corrections. The concept of the Commission makes sense. It remains to be seen whether its report, like so many others, will be merely "filed" or will lead to constructive changes.

While the Commission is in its formative stages, those who are concerned with the consequences of how air pollution is controlled in a growing industrial society, can, by thoughtfully contributing, shape the ultimate result and help ensure that the Commission's substantial potential is fulfilled.

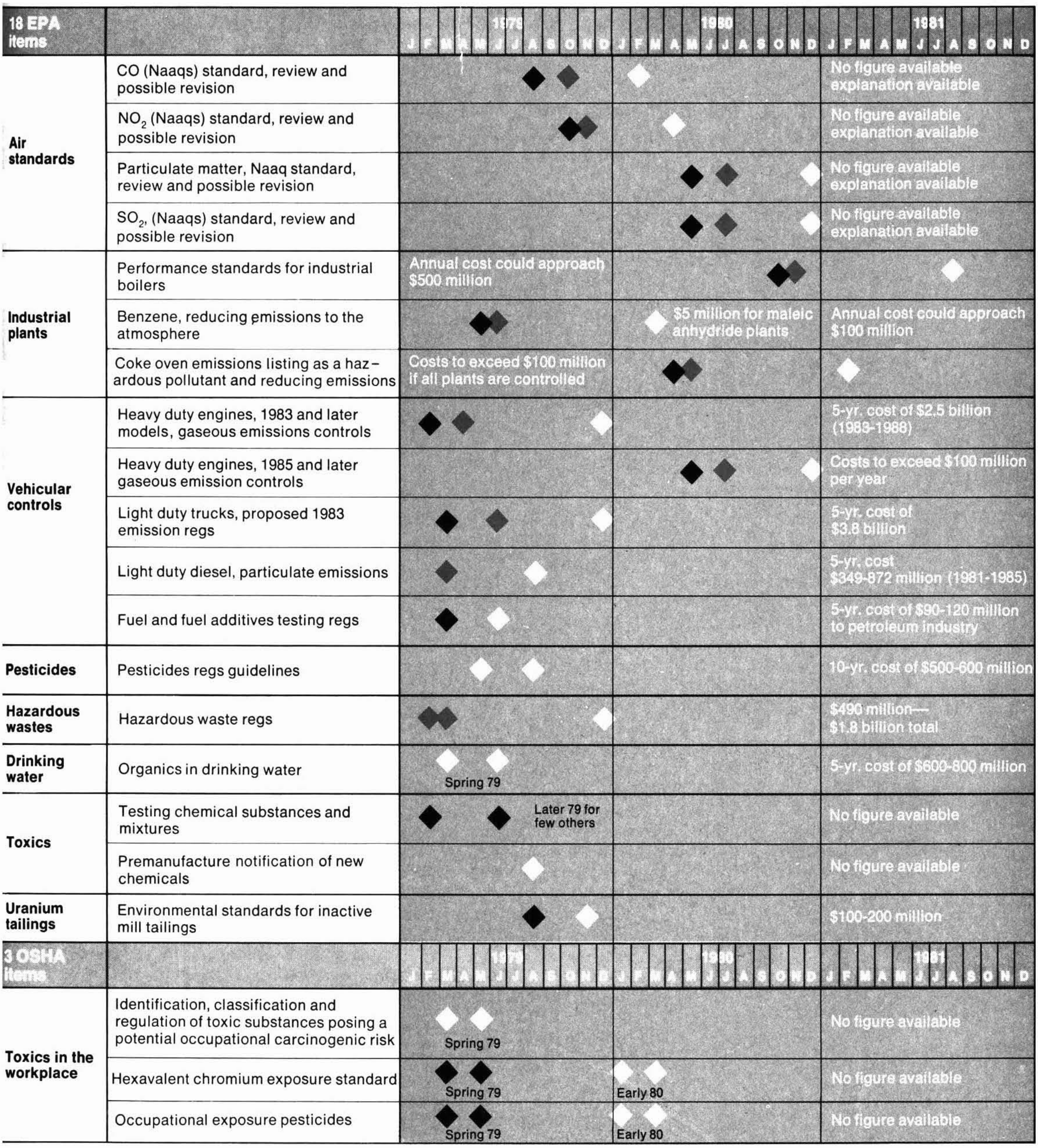
Regulatory calendar

Last year, President Carter established the Regulatory Council charged with:

- publishing twice a year a calendar of major governmental regulations
- monitoring the economic effects of governmental regulations on private industry.

The first calendar of the Regulatory Council is spelled out in the *Federal Register* of Wednesday, Feb. 28, 1979 (Volume 44, No. 41, Part IV). The myriad details in the *Federal Register* cover more than 100 pages for all regulations costing more than $100 million each and include 18 EPA items (excluding noise) and 3 OSHA items. Here then are the dates and economic effects of:

◆ Notice of proposed rulemaking
◈ Public hearing
◇ Final rule

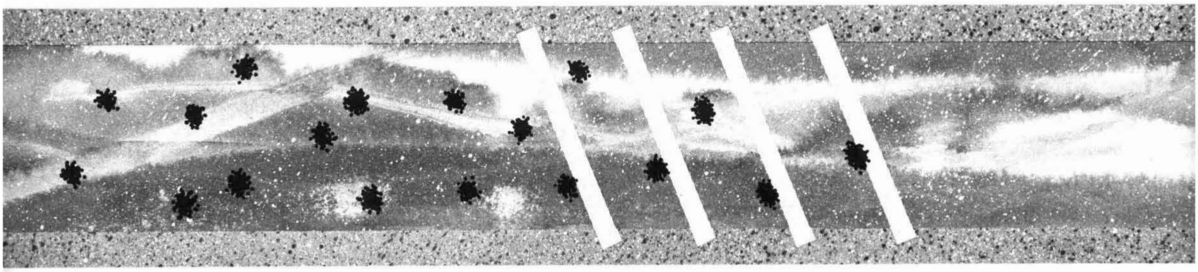


18 EPA items		1979 J F M A M J J A S O N D	1980 J F M A M J J A S O N D	1981 J F M A M J J A S O N D
Air standards	CO (Naaqs) standard, review and possible revision	◆ ◈	◇	No figure available explanation available
	NO_2 (Naaqs) standard, review and possible revision	◆◈	◇	No figure available explanation available
	Particulate matter, Naaq standard, review and possible revision		◆ ◈ ◇	No figure available explanation available
	SO_2, (Naaqs) standard, review and possible revision		◆ ◈ ◇	No figure available explanation available
Industrial plants	Performance standards for industrial boilers	Annual cost could approach $500 million	◆◈	◇
	Benzene, reducing emissions to the atmosphere	◆◈	◇ $5 million for maleic anhydride plants	Annual cost could approach $100 million
	Coke oven emissions listing as a hazardous pollutant and reducing emissions	Costs to exceed $100 million if all plants are controlled	◆◈	◇
Vehicular controls	Heavy duty engines, 1983 and later models, gaseous emissions controls	◆ ◈ ◇		5-yr. cost of $2.5 billion (1983-1988)
	Heavy duty engines, 1985 and later gaseous emission controls		◆ ◈ ◇	Costs to exceed $100 million per year
	Light duty trucks, proposed 1983 emission regs	◆ ◈ ◇		5-yr. cost of $3.8 billion
	Light duty diesel, particulate emissions	◈ ◇		5-yr. cost $349-872 million (1981-1985)
	Fuel and fuel additives testing regs	◆ ◇		5-yr. cost of $90-120 million to petroleum industry
Pesticides	Pesticides regs guidelines	◇ ◇		10-yr. cost of $500-600 million
Hazardous wastes	Hazardous waste regs	◈◈ ◇		$490 million—$1.8 billion total
Drinking water	Organics in drinking water	◇ ◇ Spring 79		5-yr. cost of $600-800 million
Toxics	Testing chemical substances and mixtures	◆ ◆ Later 79 for few others		No figure available
	Premanufacture notification of new chemicals	◇		No figure available
Uranium tailings	Environmental standards for inactive mill tailings	◆ ◇		$100-200 million
3 OSHA items		1979 J F M A M J J A S O N D	1980 J F M A M J J A S O N D	1981 J F M A M J J A S O N D
Toxics in the workplace	Identification, classification and regulation of toxic substances posing a potential occupational carcinogenic risk	◇ ◇ Spring 79		No figure available
	Hexavalent chromium exposure standard	◆ ◆ Spring 79	◇ ◇ Early 80	No figure available
	Occupational exposure pesticides	◆ ◆ Spring 79	◇ ◇ Early 80	No figure available

ES&T
FEATURES

Radionuclide removal from water

How to take out these materials, especially radium, in order to comply with applicable regulations, is explained



Louis J. Kosarek
El Paso Environmental Systems
El Paso, Tex. 79997

Naturally-occurring radionuclides within the aqueous environment present a formidable health hazard with respect to human exposure, and the possible consequential development of radiation-induced bone cancer, non-specific malignant neoplasms, and lung cancer. The etiology of these associated diseases is based upon the effects of ionizing radiation upon the cellular components of a person.

Materials emitting ionizing radiation usually cause cellular aberrations primarily when ingested or inhaled. This radiation is categorized as follows: alpha particles, beta particles and gamma emissions. An alpha particle is most detrimental, because of its high energy levels; it consists of two protons and two neutrons, and has a divalent positive charge. A beta particle is composed of a mass and a single charge equal to that of an electron. A gamma photon is a form of electromagnetic radiation of short wavelength.

What is in nature

Naturally-occurring radionuclides consist of unstable isotopes (isotopes are elements with the same number of protons but a variable number of neutrons) of which the major portion is primarily composed of potassium-40, rubidium-87, thorium-232 plus its decay series, uranium-235 plus its decay series, and uranium-238 plus its decay series. Potassium-40 is associated with non-radioactive potassium, and is a beta emitter with a maximum particle energy of 1.32 million electron volts (MeV). Rubidium-87 is a natural isotope which is a beta emitter, and it releases a particle with a peak energy of 0.274 MeV.

By contrast, cumulatively, the thorium-232/uranium-235/uranium-238 isotopes with their decay series contain over 36 unstable nuclides, which emit alpha, beta, and gamma radiation. Their energy levels range 0.05–9.0 MeV. Hence, the most detrimental naturally-occurring radionuclides in significant quantities are those within the decay series of thorium-232, uranium-235, and uranium-238.

The elements thorium-232, uranium-235, and uranium-238, and their associated decay series are found in significant amounts within deep water well supplies, private wells in the general vicinity of uranium deposits, certain public water supplies that use well water as a source, and all industrial uranium facilities, including mines and mills. The method used to measure the levels of various radioactive isotopes, both quantitatively and qualitatively, is the assessment of the amount of nuclear transformations per second, or a portion of a Curie (3.7×10^{10} disintegrations per second) within a given volume. A picocurie, which is the appropriate range of radioactivity with regard to human ingestion, is one trillionth (10^{-12}) of a Curie. The applicable unit of measurement for aqueous ingestion of ionizing radiation is a picocurie per liter (pCi/L).

Regulation of radium

To protect the general populace from excessive radiation exposure, legal limitations were placed upon industry and water suppliers, in order to control and minimize the ingestion of

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increased levels of nuclides from groundwater, surface water, and public water supplies. The pertinent federal and state radiological potable-water quality limitations which were imposed are listed in Table 1. The regulations specifically define the maximum allowable amount of gross alpha and gross beta radiation, but designate a radiological regulation for only one element—radium.

The basis of regulating only one element is well founded, because it minimizes confusion, and regulates one of the most critical radionuclides. There are various unstable isotopes of radium, but each radium isotope decays into a relatively short-lived daughter isotope which emits detrimental high-energy alpha particles. This situation is complicated, because a prominent daughter nuclide of radium is the gas radon. This gas changes the contamination problem related to solids to a contamination problem associated with air pollution.

The maximum tolerance level for radium in potable water systems was specified at the level of 3.0 pCi/L in the 1962 U.S. Public Health Service drinking water standards. This standard was subsequently increased to 5.0 pCi/L by the Regulations on Radionuclides issued by the Environmental Protection Agency (EPA), as part of the Interim Primary Drinking Water Regulations which were concurrent with the Safe Drinking Water Act.

To have aqueous systems comply with these regulations, technology aimed at the control of radionuclide contamination, and focusing on radium removal, have been established. These levels of technology are: Best Available Technology (BAT), Best Practicable Technology (BPT), and the newly implemented Best Conventional Pollutant Control Technology (BCT). These levels of technology vary in economics, state-of-the-art reliability, and field experience; nevertheless, as the levels of radium contamination increase, the sophistication of control technology must increase accordingly. Hence, a high level radium contamination problem may require the use of BAT, as opposed to BPT. However, BAT, which could employ reverse osmosis, may have a more economically attractive removal efficiency than would BPT, which uses the barium chloride method of removing radium.

The types of water treatment methodology which have been applied to alleviate aqueous radium contamination problems are directly related to the source of pollution, the mode of final water use, and the endogenous level of this nuclide. The presently available types of dissolved radium removal technology in the industrial sector consists of selective membrane mineral extraction (SMME), reverse osmosis (RO), barium sulfate coprecipitation, and both inorganic and macroreticular cationic resin ion exchange. The existing types of radium removal technology utilized in nonindustrial or municipal facilities are zeolite ion exchange, RO, manganese-impregnated acrylic fibers, and lime-soda softening. The modes of municipal water treatment which have a low radium removal efficiency are aeration with subsequent settling, greensand filters, and sand filtration (Table 2).

Membrane extraction

SMME is a proprietary system which combines the use of membrane components to remove the radium and other nuclides physically. It also involves a chemical removal process which does not use heavy metals such as barium, nor does it employ alternative sulfate precipitation methods. This system can receive waters containing up to 1500 pCi/L of radium, and produce an aqueous stream containing less than 5.0 pCi/L of radium, plus a slurry containing the removed nuclides and associated precious metals.

SMME consists of a filtration pre-

TABLE 1

Federal and state potable water quality regulations[a]

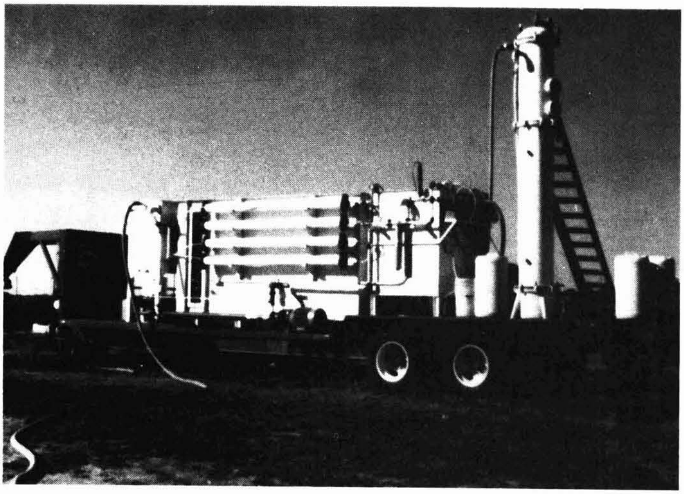
	U.S. Public Health Service 1962	EPA primary regulations 1976	Colorado[c] 1978
Combined radium, 226 228	3.0	5.0	5.0
Gross alpha	—	15	15
Gross beta	1000	4 millirem/y	50
Uranium	—[b]	—[b]	5 mg/L
Thorium	—[b]	—[b]	60

[a] In units of pCi/L unless specified. [b] 1/10 of applicable limit for an alpha or beta emitter. [c] Wyoming and Texas adopted Federal Regulations directly.

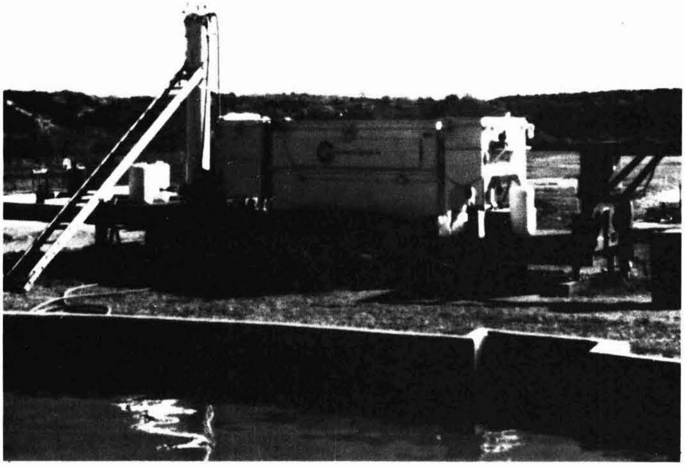
TABLE 2

Radium removal technology

Type	Municipal use	Industrial use	Efficiency of removal	Separation mechanism	Maximum allowable dissolved radium in feed to retain standard 5 pCi/L
Selective membrane mineral extraction	—	X	99.7%	Physical, chemical	1500 pCi/L
Reverse osmosis	X	X	99.4%	Physical	750 pCi/L
Barium sulfate coprecipitation	—	X	Varies with the amount of barium used	Co-precipitation	300 pCi/L
Ion exchange	X	X	95.0%	Cationic exchange	100 pCi/L
Manganese-impregnated acrylic fibers	Prototype	—	96.0%	Adsorption	125 pCi/L
Lime-soda softening	X	X	85.0%	Precipitation	35 pCi/L
Aeration	X	—	18.0%	Adsorption	5 pCi/L
Greensand filtration	X	—	50%	Adsorption	10 pCi/L
Sand filtration	X	X	Varies with the amount of suspended solids	Physical removal of suspended material	—



Radium remover. *A complete 5-gpm selective membrane extractor*



By the water. *The radium extractor at work*

treatment sector, chemical control of critical feedwater parameters, physical removal of radium via an appropriate membrane, chemical removal of radium from the effluent brine, and radium sludge-handling equipment. The generated slurry can be dewatered, and becomes a regulated solid waste discharge.

The SMME process removes radium, and partially reduces salinity. It is applicable to the aqueous streams of industrial uranium, and associated mining and milling facilities. Because of recovered resources, process users can enjoy a payback.

Reverse osmosis

RO is a physical membrane separation technique by which an applied pressure greater than the solution's inherent osmotic pressure is applied upon a semi-permeable membrane. Results are:

- a purified or permeate stream containing 2–8% of the total dissolved solids
- a brine which retains the bulk of the dissolved solids, and is an effluent by-product.

Various spiral-wound RO membranes, which are either commercially available or made to prescribed specifications, have produced permeate streams containing less than 5.0 pCi/L under field conditions. Feed levels of radium range 30–750 pCi/L.

These data were collected in Colorado, the Grant's mineral belt of New Mexico, southeastern Texas, and Central Wyoming. Collectively, the units were operated with a water recovery in the range of 85–93%. In addition to radium removal, ionizing radiation exclusive of that of radium and uranium is removed by reverse osmosis with 85–96% reduction of alpha radiation, and 95–99% elimination of beta radiation. RO purification will result in the reduction of radium and total dissolved solids, and is applicable to the industrial mining and municipal sectors.

Barium sulfate coprecipitation

The addition of barium salts to streams containing radium results in the coprecipitation of barium sulfate with radium sulfate. The coprecipitation process is based upon the irreversible adsorption of radium sulfate on barium sulfate. The radium removal efficiency with the use of barium is maximized at approximately 97.6%, which allows a maximum feed level of radium at approximately 300 pCi/L.

The efficiency of this process is subject to fluctuations in the stream's chemical and physical characteristics, such as salinity, the level of sulfates, endogenous organics, temperature, and flow rate. The efficiency is also directly related to the quantity of barium used. The forms of barium used are, in order of effectiveness, barium chloride, barium carbonate, and barium sulfate. Limestone and lime have been used together with barium to achieve radium removal.

The use of barium chloride will remove radium in proportion to the amount of barium used, but will not significantly alter the salinity of the water. The method of barium-radium sulfate coprecipitation has been used in the mining industry but has not been reported as being utilized in public or municipal water supplies. A principal reason for this may be the risk factor of a maximum allowable level of 1.0 mg/L for barium residual in potable water supplies.

Ion exchange

Inorganic ion-exchange materials such as Decalso, clinoptilolite, and baryte, as well as organic macroreticular strong and weak cationic exchange resins, have been used to remove radium from aqueous streams. Decalso (synthetic zeolite) has demonstrated a 95% radium removal efficiency in lime-neutralized water. The radium is easily eluted from the Decalso by means of ammonium ions.

Clinoptilolite (natural zeolite) retains a radium removal efficiency below 15% in acid water, and is efficiently eluted with ammonium salts. Baryte has shown a 99+% removal efficiency for radium in lime-neutralized water, but only 30% removal efficiency for radium in acidic waters; radium elution with ammonia is difficult. The removal efficiency of macroreticular ion-exchange resins (commonly termed sodium zeolite softener) averages 95%. The resin exchanges either sodium or acid for radium, and is easily eluted with acid or salt solutions.

Given an average removal efficiency of 95%, the maximum allowable quantity of radium in the feed water is 100 pCi/L, if an effluent containing 5.0 pCi/L is to be produced. The efficiency of radium removal via any type of ion-exchange material is subject to variations attributable to the extent of prefiltration, pH, inherent water hardness, and the type and quantity of cationic salinity. Ion exchange will reduce the level of radium contamination and water hardness, but will increase the salinity of the water produced. Ion exchange has been used extensively to remove radium from municipal streams, but to only a limited extent at industrial mining facilities.

Acrylic fibers

A method of radium removal which is presently being tested is the use of manganese-impregnated acrylic fibers to produce potable water from domestic well supplies. The reported performance of these fibers is such that well water containing over 110 pCi/L of radium-226 can be treated to meet the 5.0 pCi/L potable water regulation. The removal efficiency of dual fibers is about 96.0%, but data concerning the duration of operation, elution efficiency, and economics have not yet been fully reported.

Lime-soda softening

Lime-soda softening is a conventional water treatment process which combines the use of a pH in excess of 9.2 with a carbonated solution to precipitate calcium carbonate and magnesium hydroxide. The removal of radium via lime-soda softening varies with pH, but averages approximately 85%. With this removal efficiency, this treatment process can receive a stream containing 35 pCi/L of radium and produce a purified stream containing <5.0 pCi/L.

Lime-soda softening is used functionally to remove water hardness at municipal facilities, but its prime function is not radium removal. The industrial mining sector also utilizes lime-soda softening, but again its aim is not radium removal. Lime-soda softening will remove radium and water hardness, but will increase the salinity of the water processed.

Aeration

This standard municipal water treatment process is used to oxidize ferrous iron to ferric iron, and subsequently remove this undesirable constituent in settling ponds. The removal of radium by aeration and settling is said to be based upon adsorption on the precipitated ferric hydroxide, and while the suspended solids are separated in a settling pond.

The removal efficiency of this method averages 18%; therefore, it is an unsuitable radium removal technology. Aeration has been used in the industrial mining sector to decrease the volume of contaminated water, but this technique has resulted in these detrimental effects:

- a salinity in excess of discharge limitations
- air pollution caused by the emission of radon gas
- environmental contamination by effluent mists.

Filtration methods

Iron removal technology by greensand filtration uses manganese zeolite which is the medium that oxidizes iron and filters the suspended precipitate. The oxidizing capacity of greensand is exhausted by the transformation of ferrous iron to ferric iron, and is regenerated by the continuous or intermittent use of potassium permanganate. The radium removal efficiency of greensand filtration is approximately 50%, and is related to manganese removal. The basis of radium removal is believed to be adsorption of radium on the higher oxides of iron and manganese, as in manganese-impregnated fibers.

The water treatment technology of sand filtration accomplishes the removal of suspended solids from a given stream. Prefiltration is usually required for the SMME system, reverse osmosis, ion exchange, and barium sulfate coprecipitation, though seldom for the lime-soda softening process. Various streams contain both suspended and dissolved radium in equilibrium; thus, if the suspended radium is not removed prior to treatment, then, upon removal of the dissolved radium, a new equilibrium is established, by which the suspended radium dissociates, and becomes dissolved radium. Under these conditions, removal efficiency is greatly hampered. Field data consistently indicate that if a stream has a turbidity greater than 10.0 NTU, approximately 20% of the radium is suspended, and 80% is dissolved.

Possible analytical interferences

The various abatement technologies which facilitate the removal of radium have been developed within various water treatment sectors, and tested because of increased concern with the presence of naturally-occurring radionuclides. The analytical methodologies used to measure the various radium isotopes are well established. However, they may require further evaluation, because of interferences caused by water treatment chemicals that are used to optimize radium removal systems.

Various water treatment chemicals, including flocculants, chelating agents, surfactants, scale inhibitors, and polyelectrolytes may interfere with present analytical procedures, because of chemical interactions. But Controls for Environmental Pollution, Inc. (Santa Fe, N. Mex.) has developed a three-way safety check and quality control system to verify both precision and accuracy in detecting the presence of a radium problem, and determining the efficiency of a radium removal process.

The costs related to the aforementioned radium removal technologies vary, and must be estimated from the site characteristics of salinity, water hardness, pH, endogenous radium levels, sludge disposal capacity, and available land area for water impoundment. Along with these variable site parameters, the radium removal technology employed must render the water usable or dischargeable. Hence, the presence of other constituents such as salinity, additional nuclides or heavy metals, which preclude water use or discharge, must also be considered in the economics of the best overall treatment technology. Thus, the utilization of one technology to remove radium and other polluting compounds concurrently would seem to have strong economic merit.

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Coordinated by JJ

Analyzing environmental health hazards

The ideal level of hazards present will usually incorporate some degree of risk to health

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The recognition of scarcity is the starting point of all economic analysis involving health. For some time it has been recognized that good health can be produced by such scarce inputs as clean air, clean water, preventive medical care, and a good diet. Given this starting point, economic analysis seeks to determine what environmental factors cause existing health-hazard levels, whether these levels are optimal or excessive, and what courses of action can be taken to alter them. The range of answers to these questions has been enormous.

This article will summarize the wide array of economic arguments extant. The summary is presented in two sections. In the first section, the analysis assumes that individuals face the environment with given attitudes or values that allow a *social* evaluation of alternative levels of hazards.

Within a given policy framework, a wide variety of hazards can be analyzed, but the notion of autonomous individual valuations must be accepted to do so. It is this very notion which is challenged in the second category of analyses.

Individualistic approach

In the analysis of environmental hazards, the scarce resource is the environment—air, water, and land. Being scarce, an environment can have a number of alternative uses, and depending upon how the environment is used, different levels of environmental insults can result.

In identifying an optimal level of environmental hazard, it is first important to identify whose valuations are to be included in the overall social evaluation. The relevant value judgment used in the individualistic approach is that *every person's valuations are to be included.* This means incorporating both producers' and consumers' values. In effect, no group has any guaranteed prior claim or "property rights" to use the environment or keep the environment as it wishes.

A second value judgment associated with this approach is that each person is the best judge of his or her own interests. For better or worse, the value each one places on clean air or clean water is the value to be used in determining the optimum level of hazard.

In the context of this approach, a widely used definition of the optimal level of environmental hazard is that level which maximizes the net value of the environment to all users of the environment. This value statement is frequently buttressed in principle by the notion that, in moving from one level of environmental hazard to another, any existing user who is made worse off in the process should at least be compensated for his loss.

This notion of optimality can be demonstrated by an example. In this example there are two groups who compete for the use of the environment. One group—the polluters—can send varying levels of a pollutant into the environment such that various degrees of impurity can result. Let us measure these on a hypothetical scale, zero to ten. At ten the environment is totally polluted, and at zero it is totally free of impurities. We now inquire into the value to the two groups—polluters and victims—of the varying degrees of impurity.

The value of any degree of environmental purity to the polluters can be viewed in terms of the costs incurred in order to reach that level; these costs may be considered as the additional abatement costs that the polluter must incur to reach each successive level of purity. The analysis is thus presented in terms of the incremental or marginal costs of going from one level of impurity to another. In our example we assume marginal abatement costs (MAC) rise with the degree of purity (Figure 1). At very low levels of pollution, it becomes very costly to reduce the hazard more.

An alternative interpretation of abatement costs arises with the recognition that polluters are sometimes producers whose abatement costs can be passed on to consumers of their products in the form of higher prices. With such an approach, abatement costs are really incurred both by consumers whose welfare is reduced because of higher product prices, and by producers whose profit levels may be

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reduced. We adhere to the first view in this paper for expositional simplicity.

The second participating group in our analysis is the "victim" whose health is potentially or actually impaired.as a result of the hazard. The usual analysis assumes that the "victim" has a stable value which he or she places on alternative levels of environmental hazards. In fact, for such a proposition to hold, that individual should know the level of pollution or hazard and the influence of this level on his/her health. In addition, the individual should be able to evaluate what these alternative health levels are worth to him/her.

Given that the "victim" knows the implications of these hazards for his/her health, the value placed on alternative levels of the hazard can now be hypothesized. If each successively higher level of environmental impurity can be associated with a proportionately higher risk of illness, then one assumption might be that as we move from one level of environmental hazard to a higher one, the value of the additional risk of illness increases (see Figure 1, MHC curve).

The optimal level

We are now in a position to identify an optimum level of environmental hazard defined in terms of the individualistic values set out above. At a very high level, say 10, an additional unit of environmental purity is very valuable to the victims—it is worth $100 to go from level 10 to 9 (for this would equal the marginal costs avoided). The marginal abatement cost of moving from 10 to 9 is only $2.50. The net value of environmental purity to all participants—victims and polluters—would be increased by moving from 10 to 9.

As long as the marginal health cost is greater than the marginal abatement cost (MHC > MAC), the level of pollution is higher than optimal, for the marginal costs imposed on victims exceeds the marginal costs of abating the level of the hazard. The same reasoning in reverse holds for very low levels of the hazard.

As one moves from zero, the total net value (sum of the marginal net values) is increasing up to the point where MAC = MHC. In our example, this occurs at a level of hazard designated by level 2. In moving from level 3 to 2, marginal abatement costs incurred are $20; marginal health costs in moving from levels 1 to 2 are $20. Going beyond level 2 or stopping before reaching it does not capture all the gains in net value to be made. There is an optimal level of environmental hazard, and it is greater than the pollution-free level.

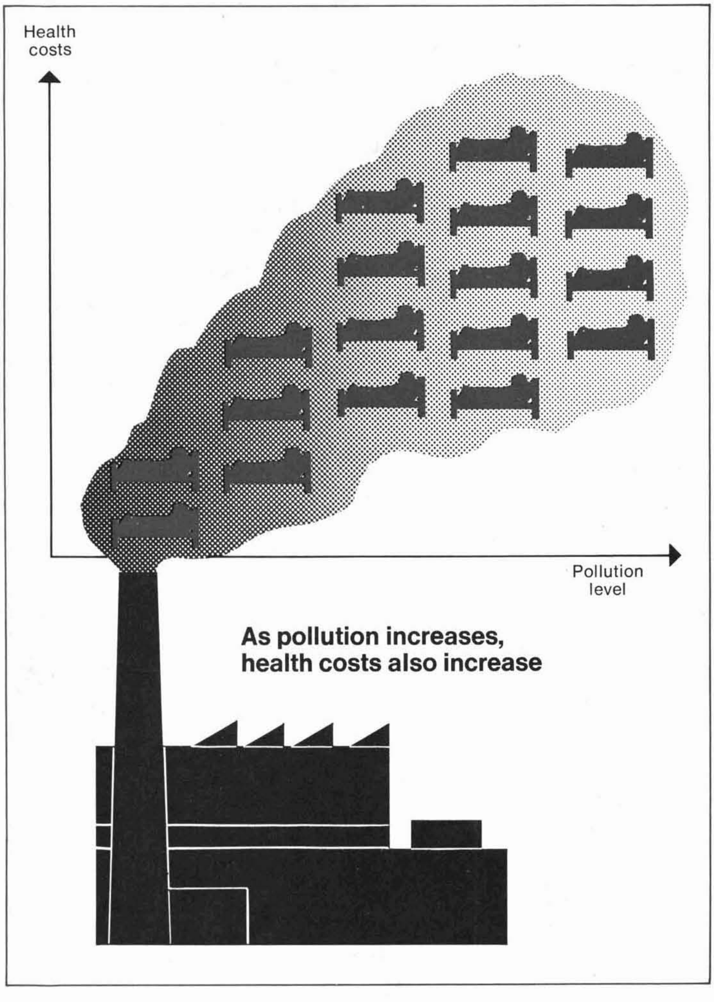
Reaching the optimal level

Having defined an optimal level of environmental hazard, one can go further to inquire how to get there. This problem is important when the costs incurred in reaching the optimal level are high; these costs of negotiating or regulating a change in the hazard level are called transaction costs.

High transaction costs mean that it is unlikely for the level of hazard to be moved from an excessively high level, say 10, to a more appropriate level, by negotiation. In the case of hazards such as air pollution, this is frequently the case: the costs to victims of identifying polluters and negotiating a more acceptable level are very high. Further, the victims cannot easily adjust the level of the hazard they face by moving away.

In those cases where consumers cannot afford to undertake transactions to buy rights to a cleaner environment, legislative action might bring about a more optimal level of environmental purity by assigning "victims" the rights to a cleaner environment. This is, in fact, what regulation of environmental hazard levels sets out to achieve. It must be remembered, however, that the promulgated standards create non-negotiable rights to levels of environmental purity, and if the standards are not set at optimal levels, the levels may prove lower than "victims" and polluters would have chosen voluntarily.

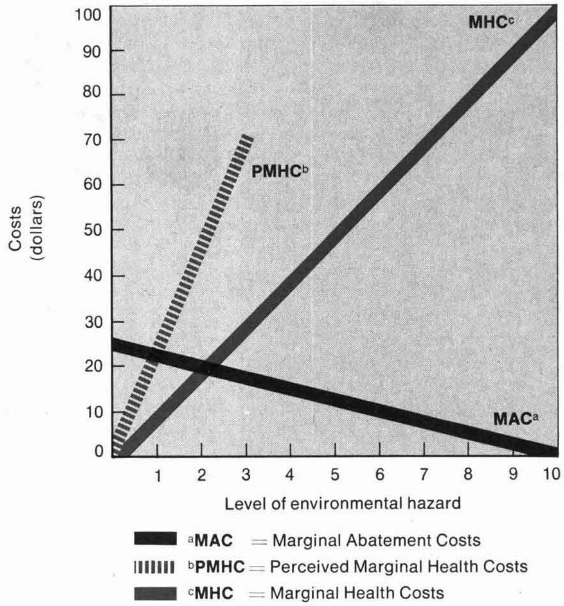
Along with the standards must go some effective policy instruments for obtaining them. There have been a number of policies suggested that might lower pollution hazards to the desired level. These include taxation of effluents, and selling "rights" to pollute (up to the standard level). The



As pollution increases, health costs also increase

FIGURE 1

Relationships between victims' health costs, polluters' abatement costs, and the level of environmental hazard



latter policy can ensure that rights are issued to emit only the allowable level of hazards.

Avoidance of hazards

There are a number of instances in which "victim" avoidance of a hazard is a more likely occurrence because avoidance costs on the part of the victims are lower. Among these instances are hazards of the workplace, where both employee and employer can undertake hazard reduction; the potential hazards of unsafe products, where both producer and consumer can take action to reduce hazards from product use; and automobile accidents, where drivers can drive defensively, and reduce the degree of highway unsafeness.

In the case of employment health hazards, the optimal hazard level is defined by weighing the health costs as perceived by the workers against the accident or illness avoidance costs incurred both by workers and employers. If further reductions by applying more hazard-reducing resources lower health costs by more than the costs of the extra resources used, then these abatement costs should be incurred. However, there is some level beyond which it will prove excessively costly to move to a lower level.

Recognizing that an optimal level does exist, we are faced with a problem of how to get there. As in the pollution case, rights can be assigned to the workplace environment. At one extreme, the employee can be fully liable for all illness and accidents. At the other extreme, the employer can be made liable, in which case he must compensate the employee for any damages incurred as a result of the hazard. In between lie plans such as liability with established fault and no fault. In the latter case, compensation out of a fund is paid to the victim even if he/she is at fault.

With zero transaction costs for employee and employer bargaining, the optimal level of hazard will occur either under full-employee or employer liability. In the case of employee liability, workers will only accept a wage which amounts to what they could earn in a riskless occupation plus a premium to cover expected health costs and avoidance costs—costs which would not be incurred in the riskless occupation. If health costs could be reduced by more than the worker's extra avoidance costs, workers would benefit from undertaking such reductions.

At the same time, employers would incur avoidance costs which reduce health costs by more than these avoidance costs because this would lower the risk premium, and thus the wage they paid. Similar reasoning holds for employer liability, except that employees will not incur hazard-reducing costs which can be passed off to employers who must, after all, fully compensate the workers for health costs. With zero transaction costs, employers can profitably "bribe" employees to undertake such avoidance whenever additional health costs exceed worker avoidance costs.

When transaction costs are not zero, and with employer liability, it may prove costly for employers to "bribe" workers to bring their avoidance costs to an efficient level. Since workers will be able to obtain compensation for *all* health costs they incur, there is little incentive for them to expend their own resources to avoid hazards for which they will be compensated. In this case, the liability rule creates a disincentive for workers to use hazard-avoiding resources in an efficient manner.

A similar problem occurs with hazards caused by dangerous products, some of whose costs might be avoided by consumer negligence. Liability rules similar to those of the workplace can be implemented: producers can be made fully liable for all health costs incurred by use of their product; consumers can be made fully liable; or liability with fault and no fault schemes can be devised.

Because of the high transaction costs which involve producers "bribing" consumers to use the product cautiously, strict producer liability will not encourage the system to take advantage of economies which might be obtained from consumer-hazard avoidance. Some degree of consumer responsibility for the hazard level is necessary to take advantage of these economies.

It should be stressed that in all examples discussed, the optimal environment is not a hazard-free one.

Costly information

When information about environmental circumstances and health risks is costly, individuals may base choices on perceived estimates of health costs. These perceived estimates may differ from actual costs, leading the victims to accept hazard levels which are not optimal. Since victims may either under- or overestimate true hazard levels, the perceived health costs may be lower or higher than actual ones.

In Figure 1 the curve PMHC shows perceived costs to be too high in relation to actual costs; the perceived optimum level of hazard will be too low. In this case, enlightening the victim as to the true costs will lead to an increase in the hazard level from level 1 to level 2, with a consequent reduction in the total cost of environmental hazards. But such an enlightening may involve considerable information resources, the costs of which may be greater than the cost of inefficiencies removed in the process. In such a case, the optimum level of hazard may be closer to the perceived optimum.

The proceeding analysis assumed that the information provided would lead the victim to a more correct assessment of environmental health hazards. Some commentators assert that information sent to potential victims may in fact be systematically biased by attempting to sway the potential victims into believing that the hazard levels are lower than they are. And still others posit that the social environment may systematically bias the values of the victims against environmental impurity.

In both cases, though more in the second than the first, the implications are that individuals are susceptible to influences which may systematically bias their attitudes toward environmental health hazards.

Systematic biases

In the previous view of optimality, the valuations which victims placed on health costs were taken as "given" by the system. Yet these valuations were formed at some stage, and may not be immutable. The degree to which "tastes" toward illness can be influenced is, of course, a critical matter in the present context.

Three different "taste"-influencing processes are of relevance for environmental health hazards. The first is concerned with producer attempts to influence values through advertising. The second relates to tendencies of individuals to emulate those around them. The third deals with the proximity of individuals to specific types of economic systems with the result that certain habits and life-styles fit easily into the system and become reinforced. In all cases, the position of the MHC curve in Figure 1 is influenced, ususally being *lower* than what "otherwise" might be; the health hazards are viewed by victims in a less threatening light.

The advertising mechanism has been associated with products such as cigarettes, various sweet and fatty foods, alcoholic beverages and pharmaceuticals, all instances in which industrial interests can gain sales through promotion. The "taste"-changing mechanism involves convincing the victims to raise their valuations of the beneficial aspects of these goods. It remains undetermined whether such promotional activities actually convince victims to do this, or whether such advertising merely provides the consumer information about where he or she can satisfy underlying needs.

The mechanism of group influence has been cited as a key factor influencing victims *net* valuations of health costs associated with drug and alcohol consumption. The more widespread such consumption is, the higher are the benefits associated with such activities, and consequently, the smaller the health costs will appear in relation to these benefits.

The third mechanism relates to the bias created by the individual's participation in any particular economic system. The bias in a commodity-producing oriented society (capitalism) is toward produced goods and services. Patterns of tastes become oriented toward commodity-intensive activities, and institutions such as the educational system may reinforce the existing reward system. Environmental hazards such as pollution, workplace hazards and product hazards may be a concomitant of such a commodity-intensive organization.

Individuals who become acclimatized to the product-producing milieu may place lower values on the concomitant hazards than they otherwise would. The valuations placed on environmental hazards are thus less, relatively, than under some other system which is less commodity oriented, such as an agrarian society.

Alternative value systems

If the individual's valuations about his own health are not constant, and are perhaps even mercurial, then a social valuation scheme based on individual valuations is a mere will-o'-the-wisp. Yet some system of values must be appealed to if alternative levels of environmental hazards are to be ranked consistently. It is in response to the void in objectives created by seemingly capricious individual valuations that the concept of equity or "fairness" has been brought to the fore.

Recent interpretations of equity goals have been related to specifying a "right" to some beneficial circumstance, such as a hazard-free environment. Referring to Figure 1, this would amount to setting the hazard level at zero, with the result that cleanup costs would be extremely high. A somewhat less extreme goal would be to posit a "right" to a reasonably clean environment, though a definition of "reasonable" would be subject to controversy. Remembering that we can no longer weigh alternative hazard levels in terms of costs and benefits, since valuations of health costs are specious, some other basis must be obtained for deciding on what is reasonable.

The issue is not settled. Some writers refer to a social concensus of what people regard as fair; however, polluters, employers, and consumers do not necessarily have the same notion of fairness as would potential hazard victims.

Other thinkers have attempted to derive theoretical explanations of equity rules on which all members of society might agree. Such models are still in early development stages, however, and do not yet offer a guide to ranking levels of hazards which might be universally regarded as fair.

The dilemma faced in evaluating alternative levels of environmental health hazards becomes one of enormous magnitude. If victims are conditioned to accept environmental hazards to any considerable degree, two problems are produced: One, a health problem ingrained to the core of the society; and two, an absence of a widely acceptable set of values to provide us with some guiding principles to get us out of the dilemma.

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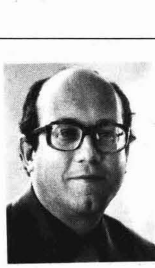

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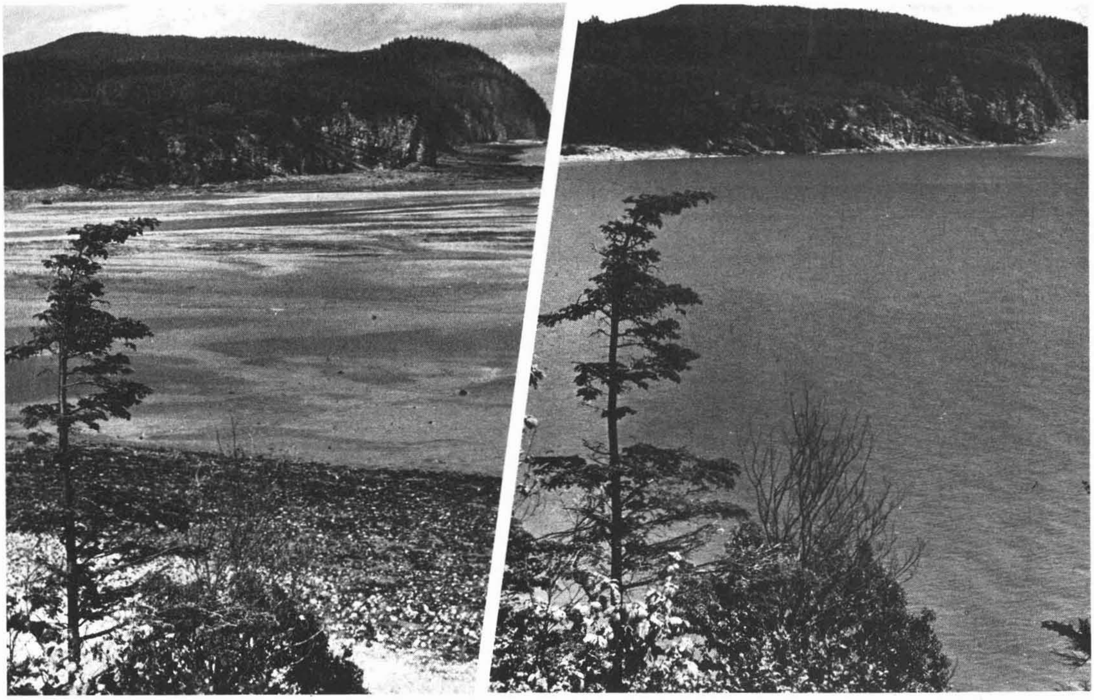
Coordinated by LRE

The changing tides on tidal power



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The installation of a tidal power project in the upper reaches of the Bay of Fundy, now under joint consideration by the governments of Canada, New Brunswick and Nova Scotia, calls for construction of a dam across an inlet, such as the Cumberland Basin, that may produce significant environmental changes. Such changes may affect natural resources over a region larger than the actual tidal basin.

Because of its great tidal range, exceeding 50 feet in places, the Bay of Fundy is one of the few locations in the world where tidal power can be given serious consideration.

One technique for assessing the potential ecological effects of industry on a body of water and its surroundings is analysis of organic carbon and nitrogen found in the water and in its marine life and sediments. Such analyses aid in understanding the cycling of organic matter in marine ecosystems and help predict changes likely to be brought about.

The Marine Ecology Laboratory (MEL) of the Bedford Institute of Oceanography (BIO), in Dartmouth, Nova Scotia, is one of several agencies currently studying the environmental characteristics of the Bay of Fundy. The BIO is operated by the Canadian government and comprises an Atlantic Oceanographic Laboratory, an Atlantic Geoscience Centre, and the Marine Ecology Laboratory. "Within the MEL there are 22 research scientists who range from chemists, physical oceanographers and ecologists, to mathematical theorists," says Dr. Donald Gordon of MEL. "At MEL we are engaged in three basic programs—biological oceanography, fisheries oceanography and environmental quality, part of which is the Bay of Fundy program."

If the tidal power project is pursued, these data will be used in the preparation of an environmental impact statement. Among other instruments MEL is employing to analyze samples from the Bay of Fundy is a Perkin-Elmer Elemental Analyzer, an instrument that analyzes for carbon, hydrogen and nitrogen automatically and simultaneously.

Environmental changes

"The major environmental modification in the case of the proposed Bay of Fundy tidal power project will be caused by the dam, with its sluices and powerhouses," says Dr. Gordon. "Environmental modifications would also result from transmission lines, quarries and temporary features associated with construction. Within certain limits, damage could be minimized by careful planning during the

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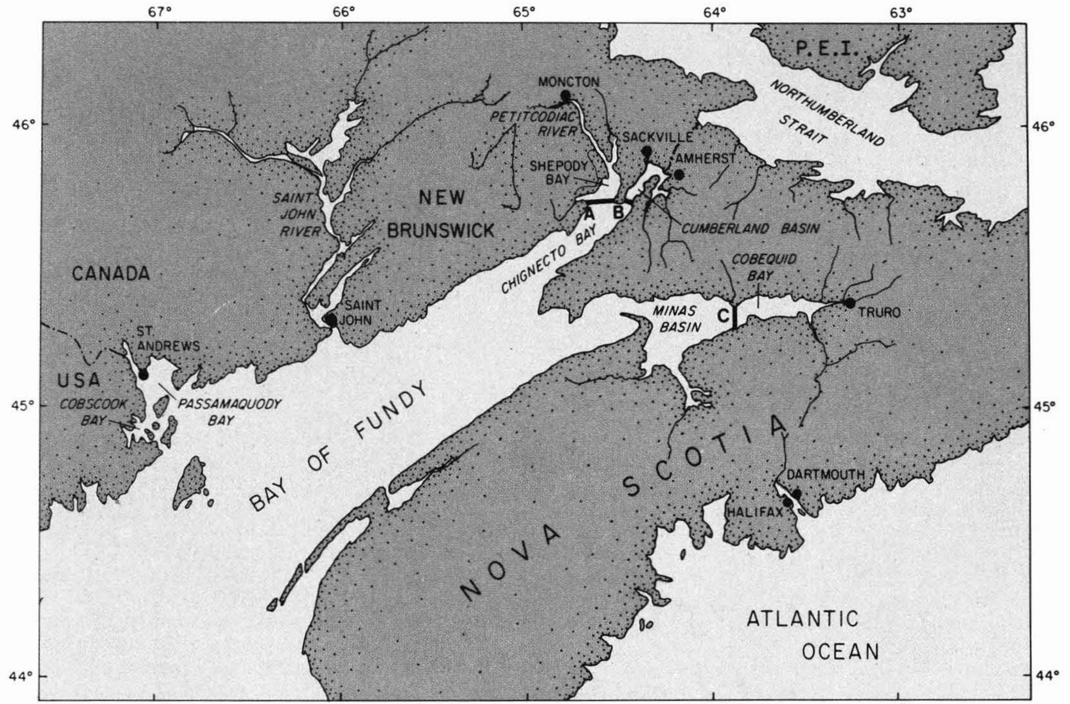
Scientists at the largest Canadian marine oceanographic research laboratory are assessing baseline data before any construction begins on a new tidal dam



Tidal power: A perspective

What? The possibility of a tidal power project in the Bay of Fundy goes back to the early 1900's, with Canada and the U.S. being jointly interested, when the first serious proposals were made in Passamaquoddy Bay. Franklin D. Roosevelt was in favor of a tidal plant and started such a project near Eastport, Maine, in the late 1930's, but this lacked funding and was interrupted by World War II. After the war, joint studies between the U.S. and Canada found the Passamaquoddy project feasible, but uneconomical.

When? As a result of dramatic increases in oil prices in the early 70's, new interest was stimulated, and the governments of Canada, New Brunswick, and Nova Scotia jointly created the Bay of Fundy Power Review Board, in 1972, which initiated a program of further study. In 1977, this Board concluded that a tidal power project in the upper reaches of the Bay of Fundy could be economically feasible.

Where? The map.

How soon? At present, the Bay of Fundy tidal power project is waiting for governments to decide if a proposed 3-y, $33 million pre-investment program should be undertaken. A decision to build or not to build could be made early in the 1980's.

On-going plants. If built, the Bay of Fundy tidal power plant would be the world's second large-scale tidal power station, with almost five times the capacity of the only extant operation large-scale tidal power station, commissioned in 1967 (240 megawatts), located in the Rance Estuary on the cost of Brittany, France. A small experimental station (about 400 kilowatts) was completed in 1968 by the Soviet Union in a gulf of the White Sea, near Murmansk.

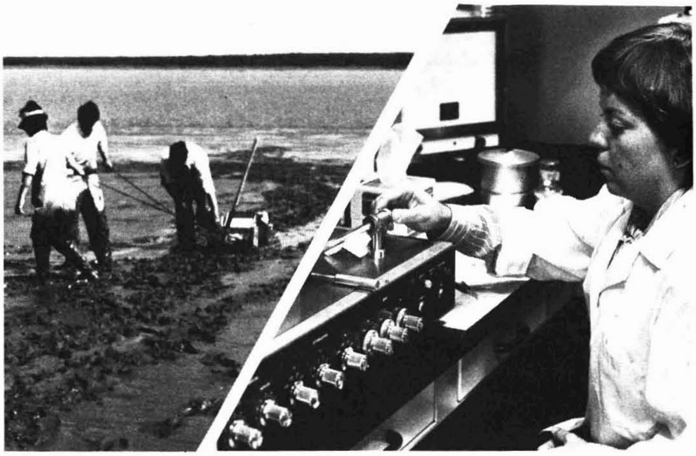
final design stage, especially in regard to selecting the exact mode of operation and location of structures.

"We are now gathering data which describe the ecosystems in the Bay of Fundy," says Dr. Gordon, "to determine what kind of animals live there, their production rates and what they feed on. Carbon and nitrogen are convenient elements to use in studying ecological systems. They are easy to measure and are key elements in every organism."

Ecosystems unaffected by man do not remain static, but evolve as their environments gradually change, usually over time scales in the range of decades to millenia, according to Gordon. He points out, however, that an environmental modification, such as a tidal dam, or barrage, changes the environment importantly and much more rapidly. The ecosystem will adjust to these changes and continue to function in a modified form, but the consequences may be far reaching and difficult to predict.

"Changes in the physical environment will influence water and sediment chemistry and through them the biological components of the ecosystem. At present, very little is known about nutrient recycling processes in the upper reaches of the Bay of Fundy, or about nutrient exchange with outside waters, and barrage construction could modify these. The Bay of Fundy receives limited amounts of municipal, agricultural and industrial wastes. The assimilation capacity of a basin of water is dependent upon many factors, but, most important, its flushing time would be reduced behind a barrage, thereby perhaps producing effluent disposal problems in the future. There is also the possibility that a new pollution problem could occur, for instance, through construction wastes, or if construction were to expose a geological formation containing toxic trace metals which could enter the food chain," Gordon says.

MEL scientist Gordon
sampler for suspended matter



Sampling and analysis. *Samples are collected and analyzed for nitrogen and carbon*

Impact statement

According to this scientist, the environmental impacts possible from the proposed project—to be identified by the environmental impact statement—are both natural and social; positive and negative. Part of the impact statement will be recommendations for design and operation of the project that will reduce negative influences. Project investigators are looking at all areas of the Bay of Fundy, especially at the upper reaches, which are least understood.

"These are quite rural areas, with low population density," says Dr. Gordon. "They contain muddy waters and have a high tidal range, extensive intertidal flats and strong currents. Until quite recently, very little scientific information was available from these regions. To be able to assess the impact of the contemplated power project, we must first know today's environment. This means understanding such topics as physical oceanography, hydrology, sedimentology, chemistry, climatology and ecology of the area.

"We and our colleagues are attempting to construct a carbon and nitrogen budget of the area," says Dr. Gordon, "by following the cycle of carbon and nitrogen through the ecosystem and discovering what the key mechanisms are." Among the mechanisms in which MEL is interested are:

- those in which inorganic nutrients are converted to organic material by plants
- the utilization and transfer of organic matter by animals within the ecosystem; for example, what portions are respired, or exported from the ecosystem under study.

"We propose to describe, quantitatively, the cycling of organic matter through the ecosystems," says Dr. Gordon. "On the smallest scale, we hope to do this for an intertidal mud flat (an area exposed at low tides) and, in time, we hope to do it for the entire Cumberland Basin.

"With the Model 240 Elemental Analyzer, we are able to measure organic carbon and nitrogen in various compartments of the ecosystem," Dr. Gordon says. "Organic carbon and nitrogen in sediments is one of these. Intertidal sediment samples are collected on foot, scooped up with a spatula, while grabs, or corers, are deployed from boats and are used to sample sediment under water. Suspended matter in seawater is collected with a sampling device that collects a five-liter volume of water. Seawater is then filtered through a silver filter, which retains suspended matter larger than about 1 μ."

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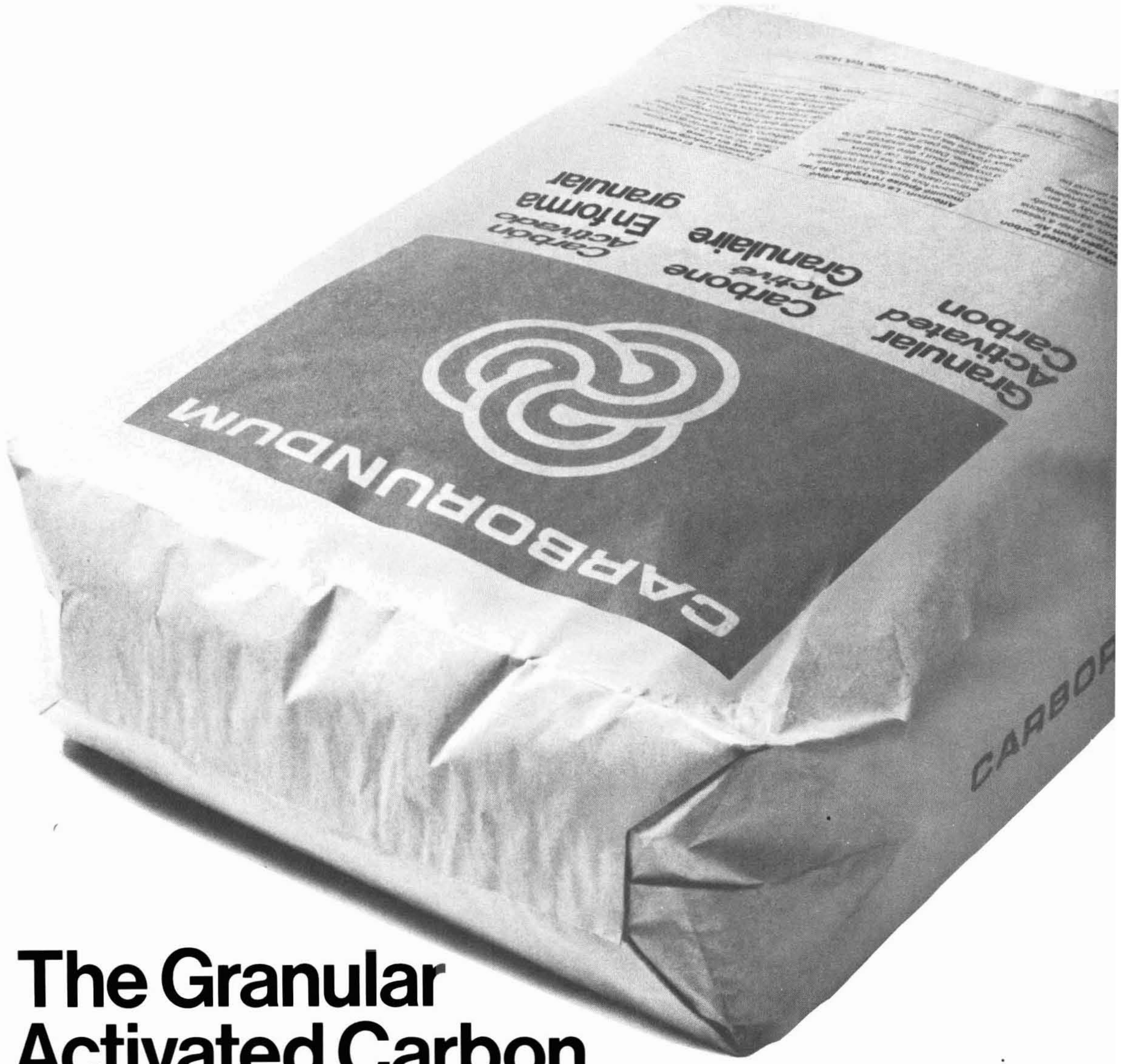
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SPECIAL REPORT

Priority pollutants
II—cost-effective analysis

This list of 129 toxic pollutants includes 114 organic chemicals (with 17 pesticides and 7 PCBs) and 15 inorganic metals or ions. While not yet an approved EPA method, automated gas chromatography/mass spectrometry (GC/MS) is obviously the coming trend

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Question: Can the gas chromatograph/mass spectrometer (GC/MS) compete with the gas chromatograph (GC) as a cost-effective tool for the detection, identification, and quantitation of priority pollutants in industrial effluents?

Answer: Surprisingly, *yes*—even the sophisticated $150 000 GC/MS systems in use today are less costly than GC on a cost per analysis basis. Powerful new GC/MS systems dedicated to the analysis of organics in water have recently been introduced. These highly automated systems are moderately priced and show promise of yielding significantly higher analysis throughputs even from relatively unskilled operators. This should further tip the cost-effectiveness scale in favor of GC/MS.

Our conclusion is based on results which were gathered during months of visiting and interviewing more than 100 chemists, managers, and officials in industrial, government, and independent laboratories who use GC and GC/MS for the analysis of organic compounds in industrial effluents.

In order to differentiate between a gas chromatograph operated with a conventional detector as opposed to a GC with a mass spectrometer as the detector, the convention of GC and GC/MS, respectively, will be used throughout this report.

These interviews have been made to help understand the phenomenal growth of GC/MS over the past decade. In particular, it was observed that environmental analyses for organic compounds are almost always performed by GC/MS. Is this entirely a matter of the reliability of GC/MS data, that is, its ability to provide unambiguous compound identification? Or, could GC/MS in fact be less expensive than GC, despite the apparent disadvantages of higher equipment and operating cost, greater complexity, and a dearth of experienced operators?

When we began this study we asked laboratory managers what the relative costs were, and they simply replied that "GC/MS is cheaper." Why is it cheaper, we asked, and by how much? "I don't know why, but it's a *lot* cheaper," was a typical response.

Since this is an important issue, both for laboratories performing the analyses and for government policymakers who write regulations governing effluent analysis, these cost differences were rigorously quantified.

GC/MS is indeed a cost-effective method of performing priority pollutants analyses. Furthermore, GC/MS data show a greater degree of reliability than GC. Finally, an increase in the number of compounds monitored does not significantly affect the cost or reliability of GC/MS analysis, but does substantially increase the cost and decrease the reliability of GC-only analysis.

In describing these finding the following topics are addressed:

- review of the capabilities of GC and GC/MS
- review of the Clean Water Act priority pollutants programs
- the relevant costs of GC and GC/MS analyses
- performance considerations

Respective roles: GC & GC/MS

The gas-liquid chromatograph (GC) has long been recognized as an important tool for the analysis of environmental samples. Its principal virtue is the ability to physically separate a sample mixture into its individual components. This is done by partitioning the sample constituents between a stationary (liquid) phase and a mobile (gas) phase as the components move through a column. The different solubilities of the sample constituents in the liquid phase are responsible for the partitioning and the resulting separation.

The most widely used GC detector is the flame ionization detector (FID) which yields a current output to most organic compounds in proportion to their respective concentrations in the sample. Consequently, GC with an FID detector is a very useful quantitative analytical instrument.

The principal drawback of GC is its limited identification capability. It achieves identification by presuming that two substances having the same elution times under identical operating parameters are identical. An unknown GC peak is thus identified by matching its retention time with those of a number of known compounds until the retention times are perfectly matched.

In a "quality control" application, this is a particularly effective analytical technique. In this use, the identity

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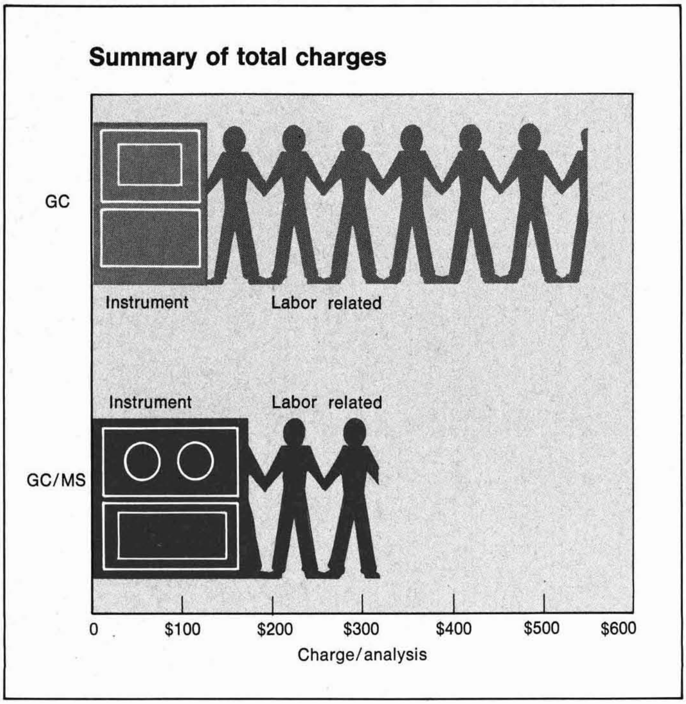
of each peak is known in advance, the interferences are few, and the quantities can be determined directly from the detector output.



In contrast, applications where there is little or no previous knowledge about the components of a sample mixture or the sample is complex, the effectiveness of GC is reduced. It may take the operator days or weeks to iteratively match the retention time of each unknown peak with the various possible candidate compounds. If there are a large number of these unknowns in the mixtures, GC may be overwhelmed as an analytical tool.

A number of techniques have been developed in recent years to bolster the identification capability of GC. The high-efficiency glass capillary column achieves a superior separation between peaks compared to the traditional packed column. These columns provide greater compound resolution and sharp peak shapes, which provide more definitive retention times.

Specific detectors have been developed which respond preferentially to a class of compounds, thus giving the analyst additional information about the identification of each unknown. These detectors enjoy high sensitivity for their respective classes of compound, but suffer from the lack of specificity for individual compounds and relatively narrow dynamic range in signal response. Most of these detectors are easily contaminated by high sample concentrations, water or oxygen.

Combining the mass spectrometer, the universal GC detector, with GC opened a number of advantages

When used in the repetitive scanning (RS) mode, several full-mass spectra are generated as each compound elutes from the GC into the MS. These are used for unambiguous compound identification.

In the selected ion-monitoring (SIM) mode, the mass spectrometer produces a continuous output of one or more specific ions. This produces a highly specific and quantitative analysis.

The modern GC/MS, when combined with a minicomputer-based data system, possesses a number of additional virtues, some of which include:

- The sample needs to be chromatographed only once for a particular analysis. Since all the data are permanently collected and entirely retrievable from storage, further qualitative and quantitative analysis may be carried out at any time in the future, without having to rerun the experiment.
- Poorly resolved GC peaks can still be identified and quantitated using appropriate algorithms provided by the data system. The ability to look at changes in specific ions characteristic of a compound of interest, rather than only gross changes, enables many compounds to be identified and quantitated even when they cannot be totally resolved by the GC column.
- The reproducibility of chromatographic retention time is not nearly as critical as in GC in achieving good results.
- Identification and quantitation are superior to GC at very low sample concentrations.

These factors help explain some of the cost differences in priority pollutant analysis which were observed between GC and GC/MS. These differences are primarily a result of the decreased time required for both the operator and the instrument to do the analysis.

The legal requirement

The Federal Water Pollution Control Act of 1972 (Clean Water Act) required the EPA to establish a program to limit the discharge of "toxic pollutants." These limits were intended to protect potential victims of pollution with an "ample margin of safety." They were to be implemented through the National Pollutant Discharge Elimination System (NPDES) permit program established by the Act. Unfortunately, scientific and practical difficulties led to very little success in fulfilling the objectives of the program.

In the Clean Water Act Amendments of 1977, Congress included the provisions of the Consent Decree, changing several deadlines, including the deadline for final compliance (to July 1, 1984—an extension of one year). These amendments supplemented the Consent Decree but did not replace it. Recently, a 22nd industry, the publicly owned treatment works (POTW), was unofficially added to the list of industries covered by the Consent Decree program. POTWs treat municipal and industrial wastes and have extremely complex effluents which cause particular problems for analysis.

Several industrial groups have asked the court to withdraw the Consent Decree, allowing the Clean Water Act alone to be the basis of EPA toxic effluent regulations. However, in December 1978, EPA and the Natural Resources Defense Council (NRDC), the principal environmental group in the 1976 Consent Decree, asked the court to modify the Decree. The pro-

Dedicated instrument. *The Organics-in-Water analyzer, a GC/MS system with 9-track magnetic tape drive, can be operated by laboratory technicians after a short training period*

posed modifications would extend certain deadlines so that the Decree would conform to the 1977 Amendments, but would also strengthen several aspects of the Decree. For instance, it would require the EPA to investigate and regulate additional toxic substances which are discharged into POTWs, and also would require tougher controls of toxics which are not sufficiently controlled by previously proposed limits.

Implementation of toxics program

The toxics program is being implemented in three phases. In Phase I, the "screening" phase, samples are taken from a small number of plants in each industry. These samples are being analyzed, qualitatively and "semiquantitatively" using GC/MS, following a protocol issued by the EPA. Phase I is still underway in some industries.

In Phase II, the "verification" phase, greater emphasis is being given by EPA to those industries and sites which showed relatively high levels of toxic pollutants in Phase I. The objectives in this phase are to verify the identifications made in Phase I and to provide more accurate quantitative data. In order to do this, EPA has supplemented the Phase I protocol with quality assurance procedures which yield more accurate quantitative data. In parallel, EPA is conducting trial studies in the organic chemicals industry to determine if realiable analyses can be done by GC alone, or with a combination of GC/MS and GC. The results of this work will be used in actually setting the effluent guidelines, including the specification of monitoring and analytical protocols.

Phase III, the "compliance and enforcement" stage, will begin when the effluent guidelines are promulgated. The regulations require regular reporting of the priority pollutants in each discharge stream.

While the government has been busy attempting to comply with the provision of the Clean Water Act and the Consent Decree, industry has not been idle. They have been busy analyzing their effluents in order to determine what the effect of the regulations will be on them.

Certain industries have found that less than 10% of the organic chemicals in their wastewater discharges are on the current priority pollutant list

Industrial people told us many times, "we don't like surprises." They don't like to be surprised by an EPA analysis of their effluents showing results they don't expect. Therefore, they do their own monitoring using the EPA protocol as well as "in-house" protocols developed specifically for their waste streams. They also don't like to be surprised with possible changes in the regulations, so they monitor potentially toxic compounds which are not currently on the EPA list. As a result, many companies are effectively in the Phase III monitoring stage at the present time, even though it is not yet required by law and has no final analytical protocol.

Analysis methodology

In March 1977, the EPA issued a protocol for the Phase I analysis of priority pollutants entitled "Sampling and Analysis Procedures for Screening of Industrial Effluents for Priority Pollutants," which was revised in April 1977. The protocol specifies the use of atomic absorption for elemental analysis, GC/MS for organic analysis, and electron capture GC (with GC/MS confirmation) for pesticides and PCBs.

The analysis of organics in water is broken down into three parts. All samples are concentrated to achieve adequate sensitivity using GC or GC/MS. First, *volatile* organic compounds are concentrated using a purge and trap technique developed by two EPA-Cincinnati chemists, Tom Bellar and James Lichtenberg. Following concentration in the purge-and-trap device (often referred to as a "liquid sample concentrator"), the volatile organics are desorbed from the Tenax trap by flash heating and are introduced into the GC/MS (or GC) for analysis. This is referred to as the volatile organic analysis (VOA). Two volatile compounds, acrolein and acrylonitrile, are analyzed using the direct aqueous-injection technique.

A second group of chemicals is extracted and divided into a base/neutral and an acid fraction for analysis by GC/MS or GC and high pressure liquid chromatography (HPLC). Finally, the pesticide/PCB group is extracted and analyzed by GC, with confirmation by GC/MS.

Table 1 summarizes the analyses which must be performed. The compounds are divided into 11 different "compound types." Organics within each compound type lend themselves to GC analysis by a common detector as noted in the table. All compound types can be detected by GC/MS.

Cost effectiveness is defined as the cost per sample analyzed

This cost effectiveness—GC vs. GC/MS—recognized all the relevant costs in owning and operating a GC or GC/MS system. Particular concern is devoted to the cost of analyzing relatively complex samples that have many unknown compounds or any samples which have significant contamination. Most environmental samples reported to us fall into one or both of these categories. The objective is specifically to establish the cost of performing a priority pollutant analysis by GC and GC/MS.

In doing this comparison, both methods have been placed on an approximately equivalent basis in terms

TABLE 1

Equipment needed for Priority Pollutant analysis

Analysis	Compound type	Number of compounds	Detector GC	Detector GC/MS
VOA	Halocarbons	23	ECD, HD	MS, HD
	Aromatic hydrocarbons	4	FID	FID
	Acrolein/acrylonitrile	2	NPD	
Base/neutrals	PNAs	13	HPLC/FLUOR	
	Chlorinated hydrocarbons	20	ECD	
	Nitrosamines	3	NPD	
	Hydrocarbons	14	FID	
Acid extractables	Phenol	2	FID	
	Chlorophenols, nitrophenols	9	ECD	
Pesticide/PCBs	PCBs	7	ECD	
	Pesticides	17	ECD	
	Total	**114**	**4 plus HPLC/FLUOR**	**1 GC/MS/DS plus 1 GC**

FID, Flame ionization detector; ECD, Electron capture detector; NPD, Nitrogen phosphorus detector; HD, Hall detector; HPLC/FLUOR, High pressure liquid chromatograph with fluorescence detector.

of both analytical quality and sample throughput. Because of the inherent ambiguity of GC data when analyzing samples with unknown constituents, this has not been entirely possible. The assumptions made regarding methods employed to maximize the analytical capabilities of GC to do these analyses are based on actual methods used by laboratories performing these analyses.

Capital cost: GC. In order to attempt to analyze a priority pollutant sample using GC, four separate detectors are required. These are: flame ionization detector (FID), electron capture detector (ECD), nitrogen phosphorus detector (NPD), and Hall or Coulson detector (HD). The preferred assignment of these detectors to each of the 11 compound types is shown in Table 1. In addition to these multiple detectors, the GC laboratory will require an HPLC equipped with a fluorescence detector to identify polynuclear aromatic hydrocarbons (PNAs). This group does not lend itself to analysis by conventional GC but can be analyzed by GC/MS. In order to place GC and GC/MS on a comparable sample throughput basis, the comparison must be based on an equivalent analysis time. This is determined in both GC and GC/MS by the time required for the sample to elute from the GC. Therefore, in an equivalent GC system, the required multiple analyses are performed in parallel. Based on the GC requirements shown in Table 1, we find that four GCs operating in parallel, with multiple detectors arranged as shown in Table 2, can approximate the sample throughput of a single GC/MS.

An integrator is assigned to each GC and a laboratory data system is provided which can accept and process data from each integrator on a time-shared basis, correlating the multiple detector outputs to improve the reliability of the identification. These are required to aid in the identification and quantitation of unknown compounds.

GC/MS. In order to carry out a priority pollutant analysis using this method, a GC/MS system with an electron impact ionization source controlled by a minicomputer/disc drive-based data system is required. An optional GC equipped with FID and a Hall detector is desirable for the occasional analysis of the halocarbons, especially in the event of contamination by hydrocarbons. The second GC also serves as an oven for column conditioning and can be used to establish or optimize chromatographic parameters.

TABLE 2

Equipment required to complete a GC laboratory[a]

GC No.	Detector	Integrator	Lab data system
1	FID ECD	1	
2	HD FID	1	
3	NPD FID	1	
4	ECD HD	1	
HPLC	FLUOR		
4 + 1	9	4	1

[a] Four GC's operating in parallel with multiple detectors approximates the sample throughput of a single GC/MS.

In order to be cost effective, it is imperative that the GC/MS data system have "priority interrupt foreground/background" capability. This feature enables data to be acquired from the MS on a priority basis in the foreground mode. When time is available, the acquired data are then processed in the background mode. Depending on the acquisition requirements, a large amount of the computer's capability, often up to 90%, can be used to process data while still obtaining complete acquisition of new data from the MS. The priority interrupt feature is often confused with "time-shared foreground/background," in which 50% of the computer's time is allotted to each mode. Time-shared systems sacrifice both processing capability and acquisition integrity.

When the priority interrupt foreground/background capability is combined with the automated data processing procedures available today, they can reduce the time required to acquire and process data during a priority pollutant analysis from over 9 hours to approximately 2.5 hours. This results in a cost savings of over $300 per sample.

Until recently, a GC/MS, complete with a data system incorporating such foreground/background capability, has sold for approximately $140 000 (including nine-track magnetic tape drive). This system will be used in the cost analysis. In the past few months a dedicated GC/MS with data system, the Organics-in-Water Analyzer (OWA), has been introduced which sells for approximately $85 000, yet provides all the essential features required for priority pollutant analyses. It will significantly reduce the capital cost requirement as well as the operator costs, but because the instrument is so new, we have not used it as the basis for our comparison.

GC/MS vs. GC: Yes, the costs for capital equipment and operator time differ

The capital costs of these two configurations are summarized in Table 3. We have included the cost of installation, laboratory modification, and the initial training of the operator(s).

Analysis time. The cost of analyzing a sample depends on the amount of time required from both the operators and the equipment. This time can be evaluated by breaking the analysis into three separate tasks:

- sample extraction and concentration
- sample cleanup
- sample analysis and data processing.

The latter can be further broken down into three separate phases of the task: calibration of the instrument, qualitative analysis, and quantitative analysis.

A comparison of the times required to perform each of these tasks in GC and GC/MS analysis is shown in Tables 4 and 5. Whereas solvent extraction and concentration can be performed by a laboratory technician (Tech), a bachelor level chemist (Chem I) is required to perform all other GC functions, and a master's level chemist (Chem II) is required to perform all other GC/MS functions. The more recent highly automated GC/MS systems (OWA) should reduce the qualifications for GC/MS operators to the Chem I grade, thus reducing operator cost by approximately one-third.

The hourly operator costs shown in Table 4 are "unloaded" costs; they do not include fringe benefits, sick pay, etc., which are factored in later (the "overhead" costs shown in Table 6).

Table 4 shows that much more time must be spent in extracting, concentrating, and cleaning up effluent samples which are to be analyzed by GC. This is primarily because sample contamination is the single most limiting factor to correct identification of unknowns by GC, and thus much care and time must be spent in these operations. This is not nearly so critical when performing the analysis by GC/MS. Most GC/MS data systems incorporate "cleanup" routines which recognize and remove interfering contaminants and background. Further, the data system can correctly find and identify the pollutant of interest even when it is masked by co-eluting, interfering peaks, by looking at changes in specifications. When significant contamination by hydrocarbons affect the analysis of halocarbons, the GC with HD would be used to augment the GC/MS identification.

A consideration amount of time is required for the calibration and validation needed for the quantitation of priority pollutants, whether using GC or GC/MS. Normally, an extensive calibration (including a 3-point standard curve) is performed at the start of each day's operation.

At various intervals throughout the day, a validation is performed in order to assure that the initial calibration is still correct. Approximately 15 analyses can be run between the initial calibration and the subsequent validation, whether performing VOA,

TABLE 3

Capital costs of GC and GC/MS

GC Item	GC $	GC/MS/DS Item	GC/MS/DS $
4 GCs with multiple detectors	40K	1 GC/MS/DS (includes 9-track magnetic tape)	140K
1 HPLC	15K		
4 Integrators	12K	Installation Training Room modules	2.5K
1 Lab data system	30K		
Installation Training Room modules	4.5K	1 GC with HD and FID	10K
Total	101.5K	Total	152.5K

TABLE 4

Operator time and cost

		GC				GC/MS			
Phase	Operation	Time (h)	Operator level	Operator cost/h	Cost ($)	Time (h)	Operator level	Operator cost/h	Cost ($)
Sample extraction	Extraction	6	Tech	4.67	28.02	3	Tech	4.67	14.01
	Concentration	2	Tech	4.67	9.34	1	Tech	4.67	4.67
	Purge and trap	0.5	Chem I	7.00	3.50	0.5	Chem II	9.33	4.67
	Pentane ext.	0.5	Chem I	7.00	3.50	—	—	—	—
Sample cleanup	Column chro.	3	Chem I	7.00	21.00	0.5	Chem II	9.33	4.67
	concentration	2	Tech	4.67	9.34	0.5	Tech	4.67	2.34
Calibration	Calibrate inst. (1 per 15 samples)	—	—	—	—	0.3 ÷ 15	Chem II	9.33	0.19
Qualitative analysis	Sample analysis	5	Chem I	7.00	35.00	2.5	Chem II	9.33	23.33
	Std and sample analysis	5	Chem I	7.00	35.00	—	—	—	—
Quantitative analysis (time per 15 samples)	Std analysis and std curve (3 pts)	15 ÷ 15	Chem I	7.00	7.00	7.5 ÷ 15	Chem II	9.33	4.67
	Validate curves	10 ÷ 15	Chem I	7.00	4.67	5 ÷ 15	Chem II	9.33	3.11
Direct operator cost per sample:					**$156.37**				**$61.66**

base/neutral, acid extract, or pesticide analysis. This results in an assignment of approximately 0.8 hours of calibration/validation time per analysis when using GC/MS, and approximately 1.5 hours when using GC. The total sample analysis time when using GC/MS is shortened considerably compared to GC because the internal standard used for quantitation can be run simultaneously with the sample. In GC analysis, two runs are required.

The instrument times shown in Table 5 for GC are instrument-hours. In other words, four instruments running in parallel for one hour are counted as 4 instrument-hours. The total instrument times for the GC system are then divided by 4 to put them on an equivalent basis, since four GCs are used in parallel to perform the analyses.

Use of an expensive instrument with lower operator costs is more economical than less expensive instruments with considerable operator costs

We have found that the unloaded operator costs are $95 per sample lower for GC/MS compared to GC (Table 4). This is a result of the decreased operator time required in spite of the higher operator cost per hour.

This difference is magnified when the additional costs to support the operator are included. As we can see in Table 6, overhead (fringes, vacation, etc.), general and administrative expenses, and the fee charged by contract laboratories on the basis of direct labor, increase the total labor-related savings to $264 per analysis when using GC/MS.

The instrument times required are shown in Table 5. In order to place a value on this time, some assumptions must be made. The capital cost of the equipment has been written off over a period of seven years on a straight-line basis. Usage is assumed to be 1500 hours per year for GC/MS, and 1800 hours per year for each GC. These figures reflect one-shift operation (2080 hours per year available). In actual practice, two-shift operation is not uncommon.

These assumptions result in an instrument cost per hour of $8.06 for GC, and $14.52 for GC/MS. These are then multiplied by a service factor which reflects maintenance, spares, utility usage, other related costs and profit. The total amount charged per instrument-hour by a contract laboratory based upon these costs is then determined to be $26.09 for GC and $47 for GC/MS, using the same service factor for both. These figures may vary greatly from laboratory to laboratory depending on the perceived risk of the investment. Changes in the hourly GC/MS instrument charge, however, cause only small changes in the final cost of the analysis because of the small amount of instrument time required.

When the instrument usage time and hourly charges are used to determine instrument charge per analysis, we can see from Table 5 that the instrument charges are approximately $35 lower per analysis using GC.

The total amount charged per analysis, including both operator-related charges and instrument charges, is $229 lower per analysis when performed by GC/MS (Table 6). This confirms the assessment of laboratory managers who knew that "GC/MS is cheaper" but couldn't explain exactly why. The answer is in reduced operator time to make the analysis and therefore lower operator costs.

GC/MS is very reliable in most all analyses whereas GC was unreliable in many and unsuitable in a few analyses

In performing our questionnaire study, we asked for an assessment of the reliability of the data generated by GC and GC/MS. The results are shown in Table 7. It is worth noting that in every case GC/MS was judged to be more reliable, and was called "very reliable" in most cases. GC was viewed as "unreliable" in most cases, and "unsuitable" for 4 of the 11 compound types.

Reliability of the data is important when one considers the effects of environmental sample analyses. The re-

TABLE 5

Instrument charge per analysis[a]

Phase	Operation	Instrument time (h) GC	Instrument time (h) GC/MS
Qualitative analysis	Sample analysis	8	2.5
	Std and sample analysis	8	
Quantitative anal. (1 per 15 samples)	Std analysis and std curve (3 pts)	24 ÷ 15 = 1.60	7.5 ÷ 15 = 0.50
	Validate curve	16 ÷ 15 = 1.07	5 ÷ 15 = 0.33
Total instrument hours per analysis		18.67	3.33
Total instrument time—4 GC's running in parallel		4.67	3.33

Instrument charge per analysis: Time (h) × charge/h = total instrument charge

GC: 4.67 × $26.09 = $121.84

GC/MS: 3.33 × $47.00 = $156.51

[a] Assumption: The capital cost of the equipment has been written off over a period of seven years on a straight line basis. Usage is assumed to be 1500 h/y for GC/MS and 1800 h/y for each GC.

TABLE 6

Total charges

	GC		GC/MS	
Direct labor	$156.37		$61.66	
Overhead At 126% of direct labor	197.03		77.69	
General and administrative At 14% of direct labor and overhead	49.48		19.50	
Fee at 8% of total cost	32.23		12.71	
Total labor related		435.11		171.56
Instrument		**121.84**		**156.51**
Total per analysis		**$556.95**		**$328.07**

TABLE 7

Data quality by GC and GC/MS

Qualitative	Code	Quality	Accuracy, %
	1	Very reliable	>90
	2	Reliable	80–90
	3	Unreliable	60–79
	4	Unsuitable	<60

Analysis	Compound type	Number of compounds	GC	GC/MS
VOA	Halocarbons	23	2–3	1
	Aromatic hydrocarbons	4	3	1
	Acrolein/acrylonitrile	2	2	1
Base/neutrals	PNAs	13	3	1–2
	Chlorinated hydrocarbons	20	3–4	1
	Nitrosamines	3	3	1
	Hydrocarbons	14	3–4	1
Acid extractables	Phenol	2	2	1
	Chlorophenols, nitrophenols	9	3	1
Pesticides	PCBs	7	4	1–2
PCBs	Pesticides	17	4	1–2

sults of effluent monitoring can include fines for violating discharge permits, the closing of a plant, or lengthy legal actions. Precision and reliability of GC/MS data are invaluable when unreliable data can lead to challenges in court. Many of the companies we visited are acutely aware of this risk.

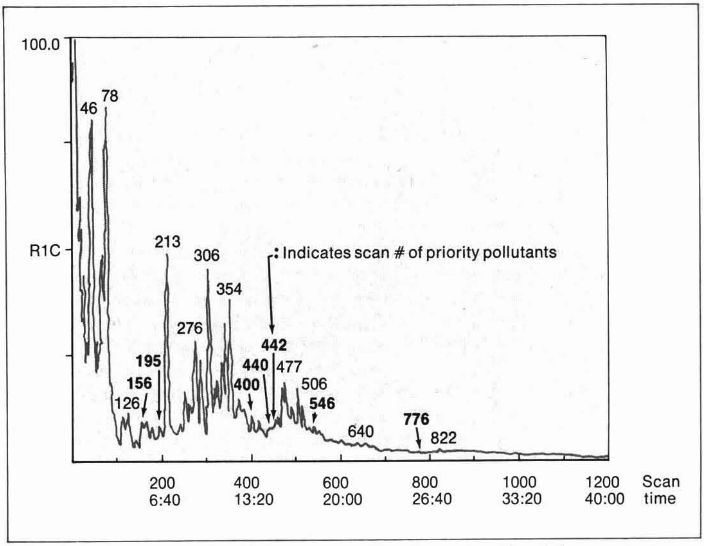
A second factor frequently mentioned is the number of compounds in the sample which must be monitored. As noted earlier, many chemical companies reported that only 10% of the organic compounds found in their effluents were on the EPA priority pollutant list. Many effluents from industry were found to have 100 or more total compounds present. Figure 2 is an example of this. It is a computer-plotted output showing the separated components of the base/neutral fraction of a wastewater sample obtained by GC/MS/DS analysis. This output is similar to a tracing obtained by GC with FID.

The companies we visited are concerned about *all* of the compounds they find. They want to know how they stand if more compounds should be regulated. They also have stated that they want to make sure they don't discharge hazardous chemicals even if the chemicals aren't regulated. Moreover, they want to know what the nature of their effluent is, because it can often provide information about the performance of their process.

Government and contract laboratories are also concerned about the number of compounds which must be monitored. The ability to monitor more than the present 129 compounds must be considered before decisions regarding the regulation of additional compounds are made—because the question is not if, but when.

As more compounds are monitored, there is little change in the time or cost to perform the analysis by GC/MS. The time and costs required by GC increase dramatically, however, when more compounds are analyzed. In fact, for complex samples such as those from chemical plant or POTW effluents, GC alone cannot perform a complete analysis. (A few industries such as the electric power and the explosives industries have very simple effluent streams with few organic compounds. For these industries GC may be sufficient and is often the preferred approach, provided there is not serious sample contamination.) The survey results showed that:

- GC/MS is less expensive than GC on a cost per sample basis.
- GC/MS has greater reliability in compound identification.
- The cost per analysis using GC/MS will not increase significantly if more compounds than those currently on the EPA priority pollutant list are required to be monitored. On the other hand, the costs per GC analysis would be expected to rise dramatically if more compounds were added, presuming the analysis could be done at all using only GC.



Pollutants peaks. *Many chemical companies find that only 10% of the organic compounds in their effluents were on the EPA priority pollutant list. Of 65 discrete peaks, only seven are priority pollutants*

Acknowledgment

The authors are indebted to the numerous individuals in governmental, industrial, contract and research laboratories, who so generously donated their time to make this study possible. Particularly, we wish to thank Mr. Dwight G. Ballinger, Director, Environmental Monitoring and Support Laboratory, U. S. Environmental Protection Agency, Cincinnati, Ohio, who first suggested the need for this study.

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Robert E. Finnigan *is the founder of Finnigan Corporation, a manufacturer of high technology products for worldwide scientific and industrial markets, where he directs the company's market development, market research, and new venture activities. He is also President of the Finnigan Instruments Division. Prior to the founding of Finnigan, he founded the Scientific Instruments Division of Electronic Associates, Inc. Earlier, he was head of process control and instrumentation at Lawrence Livermore Laboratory, and at Stanford Research Institute. While at SRI, he carried out market research studies for a number of analytical instrument manufacturers.*

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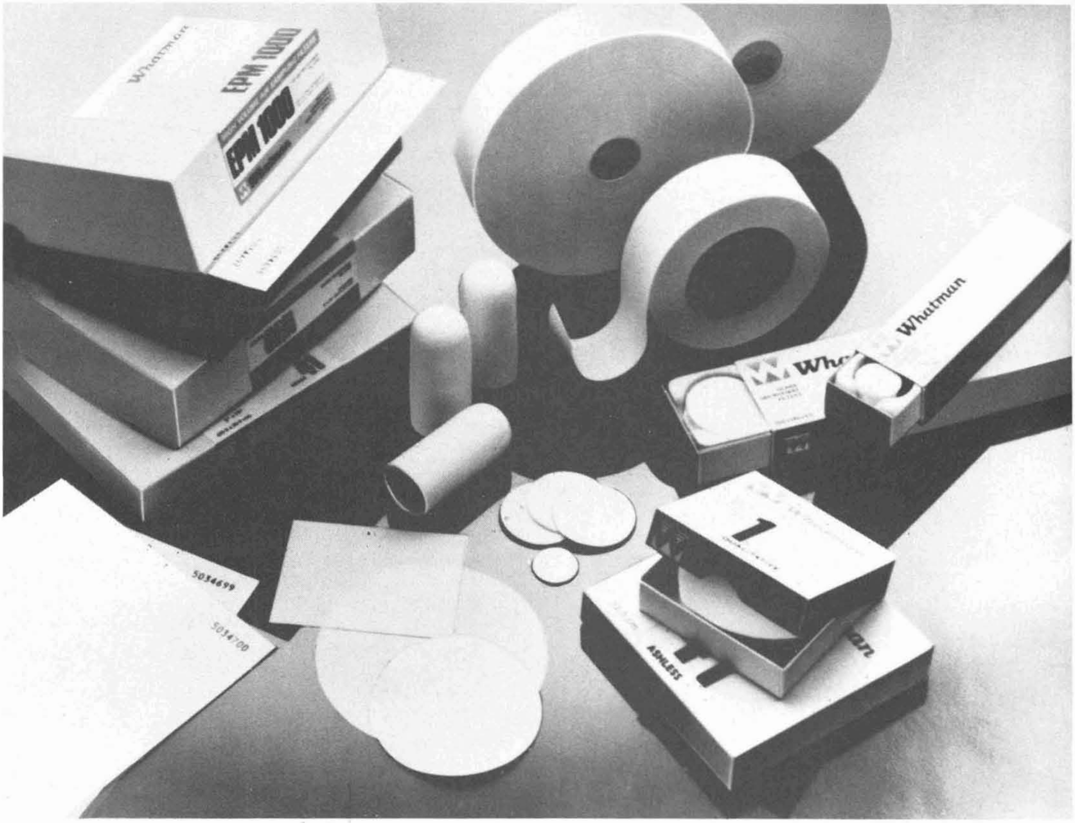

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RESEARCH

Copper Association with Aquatic Fulvic and Humic Acids. Estimation of Conditional Formation Constants with a Titrimetric Anodic Stripping Voltammetry Procedure

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■ An amperometric titration–anodic stripping voltammetry procedure was used to estimate conditional formation constants of copper with fulvic and humic acids isolated from a North Carolina coastal lake. Conditional constants of 4.7×10^5 for copper–fulvic acid and 9.2×10^5 for copper–humic acid were obtained at pH 7. Rate constants of 2.7 and $0.1\ s^{-1}$, respectively, were estimated and used to correct the titration for kinetic dissociation.

Metal association with organic materials can affect the chemical state and availability of metals in natural waters. Among their other characteristics, organics mask metal toxicity to phytoplankton (*1*), increase metal solubility (*2*), and act as metal buffers via their so-called "complexation capacity" (*3*). Anodic stripping voltammetry (ASV) combined with various procedures is used to investigate metal–organic interactions, taking advantage of its high sensitivity and its selectivity for easily reducible metal species. Often the procedure is to add commercial "humic acid" to metal solutions and observe the effect on metal stripping current magnitude or stripping peak potential (*4*). Matson (*5*) combined ASV with a complexometric titration that allowed observation of metal–organic interactions at natural water levels. This titration provided a basis for defining complexation capacity of water samples (*6*) and was further developed and applied by Shuman and Woodward (*7, 8*) to estimate conditional formation constants of metal–organic complexes. Shuman and Woodward (*8*) calculated constants of about 10^5 for copper in aquatic samples. These constants increased with pH, suggesting association with weak acidic sites. Comparison of these values with estimates made by other methods is difficult or impossible, although there is a considerable literature of copper–organic formation constants for many different soil extracts and a few aquatic samples. The difficulty is not simply the nature of the organic material, but is the inability to relate measured quantities of one method with those of another method, e.g., some methods measure displaced protons (*9*), others measure metal activity or uncomplexed metal concentration (*10*), still others measure metal in equilibrium with ion exchange resins (*11*). In addition, definitions and assumptions about organic molecular or equivalent weight used in calculations vary widely.

The work reported here was designed to determine whether humics and/or fulvic fractions isolated from a natural water sample gave copper stability constants comparable to those found in raw water samples. Total acidity of the isolated materials was also determined and compared with their apparent capacity to bind metals. Finally, the titration itself was tested with a criterion established earlier (*7*) and corrected for kinetic dissociation of the complex.

Methods

A 5-L sample of Black Lake (a coastal North Carolina lake containing about 30 mg/L dissolved organic carbon) was filtered through an acid-washed 0.45-μm Millipore membrane filter and concentrated to approximately 1 L in a Virtis freeze concentrator. The pH of the concentrate was lowered with the addition of concentrated HCl to less than 1.0 and coagulated humic acids were separated by centrifugation. The supernate containing the fulvic fraction was extracted following a procedure similar to Christman and Ghassemi (*12*), first into 200 mL of 1-butanol and then into two separate 100-mL quantities. The dark amber butanol fraction was collected in a round-bottomed flask and taken to dryness on a rotary evaporator with reduced pressure and 95 °C. The residue was dissolved in acetone to separate organic material from inorganic salts and brought to dryness under N_2. Typical yields were 100 mg of fulvic acids and less than 20 mg of humic acids. The total acidity (phenolic + carboxylic) of fulvic acid was estimated to be 8.47 mequiv/g by the barium hydroxide–hydrochloric acid titration procedure of Schnitzer and Gupta (*13*).

Solutions were prepared by dissolving the isolated and desiccator-dried fulvic acid and humic acid in 0.5 mM sodium carbonate (Baker-Adamson). The complexometric titration was carried out with a 50-mL sample of the organics in carbonate. This was deaerated in the electrochemical cell with a mixture of seaford grade N_2 and CO_2 which controlled pH 7.00 ± 0.03. Aliquots of a standard copper solution made from the metal were added with Eppendorf micropipets. ASV analysis was performed in triplicate after each addition and after about 10 min of deaeration and mixing. The three-electrode cell and associated instrumentation were described previously (*7*). Pre-electrolysis was 5 min at −0.700 V vs. SCE followed by a voltage scan of 10 mV/s.

Stripping current was plotted vs. added copper, C_M, and analyzed by fitting the data to the theoretical equation:

$$i_s = \frac{S_u}{2}\left[C_M - C_L - \frac{1}{K_{ML}'} + \sqrt{\left(C_L - C_M + \frac{1}{K_{ML}'}\right)^2 + \frac{4C_M}{K_{ML}'}}\right] \qquad (1)$$

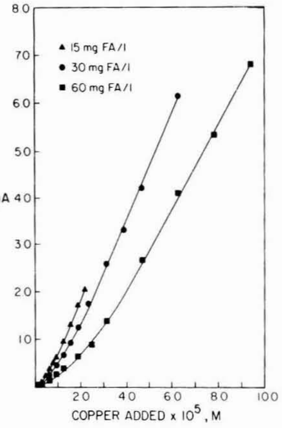

Figure 1. Titration of three concentrations of fulvic acid with copper. Solid lines are fitted curves

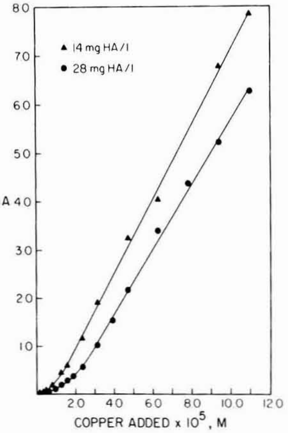

Figure 2. Titration of two concentrations of humic acid with copper. Solid lines are fitted curves

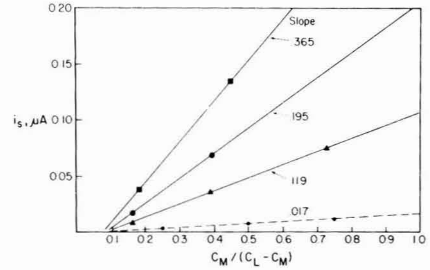

Figure 3. Stripping current as a function of $C_M/(C_L - C_M)$ for fulvic acid concentrations: (■) 60 mg/L; (●) 30 mg/L; (▲) 15 mg/L. Dotted line is slope of hypothetical diffusion current at zero fulvic acid concentration

Table I

	$C_L \times 10^5$, M Cu	$S_u \times 10^{-5}$, μA/M Cu	$K_{ML}' \times 10^{-5}$
A. Titration Curve Parameters without Kinetic Correction			
fulvic acid, mg/L			
15	0.56	1.22	5.5
30	1.11	1.15	2.6
60	2.08	0.90	2.0
	$\bar{K}_{ML}' \pm s = 3.4 \pm 1.9 \times 10^5$		
humic acid, mg/L			
14	0.80	0.77	10.1
28	1.61	0.67	8.1
	$\bar{K}_{ML}' = 9.1 \times 10^5$		
B. Titration Curve Parameters with Correction for Kinetics			
fulvic acid, mg/L			
15	0.88	0.86	7.8
30	2.10	0.85	2.7
60	3.59	0.51	3.5
	$\bar{K}_{ML}' \pm s = 4.7 \pm 2.7 \times 10^5$		
humic acid, mg/L			
14	0.96	0.74	9.8
28	1.87	0.63	8.5
	$\bar{K}_{ML}' = 9.2 \times 10^5$		

where C_L is the titration end point expressed in molar Cu concentration, K_{ML}' is the conditional formation constant, and S_u is the "upper slope" of the titration curve past the end point corresponding to the ASV sensitivity to reducible copper in μA/M Cu (*7, 8*). A Fortran IV nonlinear least-squares regression program (*14*), executed on an IBM OS/360, fit experimental data to Equation 1 and returned values of C_L, S_u, and K_{ML}'. Carbonate solutions containing no organics gave a mean value and range of the upper slope, $1.65 \pm 0.05 \times 10^5$ μA/M Cu.

Results and Discussion

Titration curves for fulvic acid are shown in Figure 1 and those for humic acid are in Figure 2. Fitted parameters are summarized in Table I, part A.

The procedure is based on the assumption that the organic ligands titrated form complexes which do not dissociate at a rate sufficient to contribute metal to the electrode (*8*). A criterion for no dissociation is constant slope of i_s vs. $C_M/(C_L - C_M)$ for points near the beginning of the titration and for all values of C_L. In this region, and provided there is no kinetic dissociation, the ratio $C_M/(C_L - C_M)$ corresponds to a single reducible metal concentration producing a single stripping current independent of C_L. Slopes of i_s vs. $C_M/(C_L - C_M)$ for the three fulvic acid concentrations titrated were not identical, but increased with fulvic acid concentration indicating kinetic dissociation (Figure 3).

If metal is supplied to the electrode by diffusion and by kinetic dissociation of the complex, the pre-electrolysis current can be separated into two components:

$$i_R = i_d + i_k \tag{2}$$

where i_R is the reduction current during pre-electrolysis, i_d is its diffusion component, and i_k is its kinetic component. Stripping current, i_s, is related to the pre-electrolysis current through the accumulation coefficient, γ_M, so that:

$$i_s = \gamma_M i_d + \gamma_M i_k \tag{3}$$

where $\gamma_M i_d$ represents the diffusion stripping current and $\gamma_M i_d$ represents the kinetic stripping current. This formalism was used together with the regression program to correct the titration curves for the kinetic stripping current. First, diffusion stripping currents were estimated from plots of i_s vs. C_L for several values of $C_M/(C_L - C_M)$. Extrapolation of these data to $C_L = 0$ (Figure 4 for fulvic acid) gives the hypothetical current due to convective diffusion alone (*7*). These diffusion stripping currents for fulvic acid are indicated by the dotted line in Figure 3 and the kinetic stripping currents were estimated by measuring differences between the solid and dotted lines.

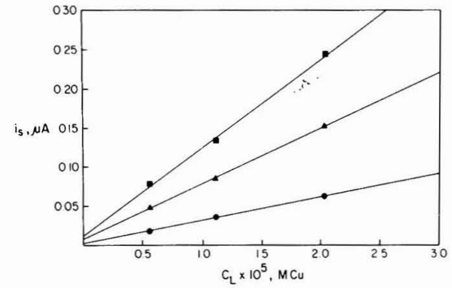

Figure 4. Stripping current as a function of copper concentration equivalent to fulvic acid at three values of $C_M(C_L - C_M)$: (■) 0.75; (▲) 0.50; (●) 0.25

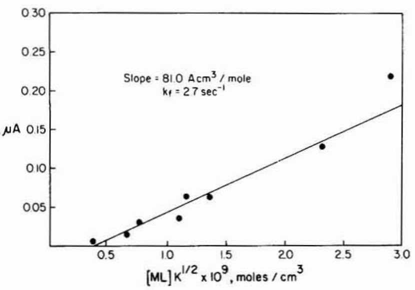

Figure 5. Kinetic stripping current as a function of $[ML]K^{1/2}$ for estimation of kinetic dissociation rate constant

Pre-electrolysis current arising from kinetic dissociation:

$$ML \underset{k_b}{\overset{k_f}{\rightleftarrows}} M + L \qquad (4)$$

is related to the concentration of the complex by:

$$i_k = nFAD^{1/2}[ML]K^{1/2}k_f^{1/2} \qquad (5)$$

where D is the diffusion coefficient of the complex in cm^2/s, [ML] the complex concentration in mol/cm^3, K is the ratio of uncomplexed to complexed metal, k_f is the first-order rate constant of the dissociation reaction in s^{-1}, k_b is the rate constant for association, and n, F, and A have their usual meanings (*15*). Stripping currents ($\gamma_{Cu}i_k$) obtained from Figure 3 were plotted as a function of $[ML]K^{1/2}$ for the three concentrations of fulvic acid to obtain the kinetic rate constant. The product $[ML]K^{1/2}$ was calculated from previously estimated C_L and K_{ML}' values (Table I, part A). A new equation for the titration formulated by adding $\gamma_{Cu}i_k$ in Equation 1 was incorporated into the regression program. Titration data were fit to this new equation using the slope for Figure 5 and D of 10^{-5} cm^2/s.

End points after correction (Table I, part B) were larger than those before corrections, whereas upper slopes were smaller. Nevertheless, values of K_{ML}' were not significantly different from the uncorrected values. The correction was still an approximation since [ML] was calculated from a previous estimate of K_{ML}' and C_L; however, after several iterations, K_{ML}' did not differ significantly from those in Table I, part B, even when convergence on C_L was not obtained. Equation 5 and the experimental slope from Figure 5 were used to estimate a copper–fulvic acid dissociation rate constant of k_f = 2.7 s^{-1} ($D = 10^{-5}$ cm^2/s and $\gamma_{Cu} = 1.71$).

If a theoretical capacity of fulvic acid to bind copper is calculated from the total acidity by assuming bidentate bonding of all acidic sites (8.47/2 = 4.24 mmol/g), then the mean end point of 0.63 mmol of Cu/g of fulvic acid is only 15% of theoretical. This low value is typical of humic materials in general and undoubtedly reflects the simplicity of the assumption (*16*).

The upper slope reflects the technique's sensitivity to reducible copper; it decreased as C_L increased, and was always smaller than the slope in carbonate alone. Several reasons for this trend were considered, the most likely among them being a decrease in the copper diffusion coefficient brought about by changes in viscosity with organic content or by formation of reducible organic copper complexes.

Both Figures 3 and 5 show positive x intercepts and indicate a fraction of added metal is nonreducible and dissociates at a much lower rate than the principal species. Formation of a 1:2 complex, CuL_2, or complexes with binding sites other than the predominant ones could explain this intercept.

Humic acid also showed kinetic dissociation, but to a smaller degree. The iterative procedure described above was also carried out for humic acid and the fitted parameters are given in Table I, part B. Values of C_L and K_{ML}' changed very little with kinetic correction and convergence was rapid. The estimated rate constant for the humic acid complex was k_f = 0.1 s^{-1}.

Conclusions

Isolated fulvic acids give conditional formation constants for Cu similar in value to those obtained in raw water samples (*8*) and isolated humic acids give larger constants. Kinetic dissociation of Cu–fulvic acid complexes affects the titration procedure principally by contributing to the observed current and producing a negative titration error. Kinetic correction is necessary for accurate end points, but is less important for estimation of conditional constants. Although kinetic rate constants can be estimated from the titration, a more direct technique such as the rotating disk electrode (*17*) is preferred.

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Received for review June 16, 1978. Accepted November 17, 1978. This work was supported by the Oceanographic Section, National Science Foundation (Grant No. OCE 73-21045).

Release of Trace Metals by Sewage Sludge and the Subsequent Uptake by Members of a Turtle Grass Mangrove Ecosystem

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■ This research was initiated to determine the rates of uptake, by a *Thalassia testudinum* König/mangrove ecosystem, over a 125-day period, of Cd, Cr, Cu, Ni, Pb, and Zn. The metals were leached from sewage sludge by flowing seawater (8.4 L $\min^{-1}$) and subsequently traversed the model system. The largest net uptake of metals occurred in the "fouling organisms" where Cd, Pb, and Zn uptake closely paralleled the net loss of metals from the sewage sludge. *Thalassia* leaves showed a net uptake for Cr, Pb, Ni, and Zn. The urchin *Lytechinus variegatus* (Lamarck), a grazer of *Thalassia* leaves, also demonstrated a net uptake of Cu, Cr, Pb, Zn, and Ni. The sea cucumber *Holothuria mexicana* (Ludwig) showed a net uptake of Cr, Cu, Pb, and Zn. Net uptake of metals was shown by the roots of the red mangrove *Rhizophora mangle* Linne. Because of insufficient sample mass, no consistent metal uptake was found for the clam *Codakia orbicularis* (Linne), oyster *Crassostrea rhizophorae* (Guilding), or the snail *Nerita tessellata* (Gmelin). The results indicate that the dumping of sewage sludge in coastal tropical waters can lead to the uptake and concentration of toxic trace metals by members of a turtle grass community.

The deposition of sewage sludge in the marine environment may adversely affect the resident organisms by the release of toxic materials into water in forms that may be incorporated into the organisms. The mass dumping of treated sewage sludge into oceans and shallow inshore areas is occurring in a number of areas. In the New York Bight, an area receiving large quantities of solid waste for almost a century, Carmody, Pearce, and Yasso (*1*) determined that there was a definite increase of Cr, Cu, Pb, Ni, and Zn in the sediment due to the dumping of sewage sludge. The uptake of metals by marine organisms and concentration within the food web have been demonstrated numerous times (*2–7*).

Schroeder (*8*) demonstrated, using radioactive isotopes, that *Thalassia testudinum* König would concentrate cobalt and manganese in the leaves rather than the root structure (excluding rhizomes) and that the incorporation of cations in *Thalassia testudinum* was primarily accomplished through the leaves.

Very little has been published regarding the rates of release and subsequent uptake of potentially toxic trace metals from sewage sludge into complex tropical ecosystems. The necessity for this type of controlled field experiments was explained by Menzel (*9*).

Our objectives in this research were to use a flow-through system of sufficient size and complexity so as to nearly duplicate a tropical marine ecosystem and also allow repeatability over varying seasons. This system would allow us to determine the rates of uptake of Cu, Cd, Cr, Zn, Ni, and Pb which were leached from sewage sludge by seawater. The community investigated was comprised of turtle grass (*Thalassia testudium* König) with its associated benthic infauna, the sea urchin (*Lytechinus variegatus* (Lamarck)), the sea cucumber (*Holothurea mexicana* (Ludwig)), attached "fouling organisms", plankton, and the red mangrove (*Rhizophorae mangle* Linne).

This ecosystem was chosen for three reasons: (a) the system comprised a tightly bound community with strong interaction between the members, (b) the important role of the seagrass/mangrove ecosystem in the overall tropical near-shore environment, (c) the possibility of the active concentration of these trace metals in the higher trophic levels with passage of the materials through the food webs.

Methods

Construction of Ecosystem Tanks. The seawater system and tanks were located at Mayaguez, Puerto Rico (18° 15′ N, 67° 12′ W). Two wooden, fiberglass coated tanks (9.2 m × 0.9 m × 1.1 m) were constructed and housed in an open-sided, roofed (translucent plastic) structure.

Seawater System. Each tank was filled to a depth of 0.5 m with calcareous beach sand with an additional 0.1 m of sand over the last 3 m of tank.

The seawater for the system was pumped through a prefilter and gravity fed to the two seawater tanks. The flow rate in each tank was 8.2 to 8.7 L $\min^{-1}$. The total water volume per tank was 3.1×10^3 L.

Sampling. At 1, 5, 25, 50, 85, and 125 days after activated sludge was added to the experimental tank samples of organisms, sediment, sludge, and water were taken from both tanks. A presample was taken prior to addition of any sludge; in this study it is referred to as day 0.

The initial stocking quantity or density for the biological organisms used ranged from 52 to 57 for the urchins and Holothurians, 230 mangrove seedlings, and from 106 to 180 for the snails, clams, and oysters. Exact physical data on stocking density are shown in Montgomery et al. (*10*).

The organisms were allowed to equilibrate for 2 weeks in the flowing seawater system. The turtle grass (*Thalassia testudinum*) density was 400 erect shoots m^{-2}.

Sewage Sludge. The sludge was allowed to settle and the overlying liquid decanted. The sludge (0.7 m^3) was added to a depth of 7.6 cm over the sediment, at the incurrent end of the experimental tank.

Sample Analysis. All reagents were reagent ACS grade. All glassware was cleaned with detergent and rinsed with water (Milli-Q System). Samples for trace metal analysis were digested in previously refluxed, covered beakers. Only nonmetallic instruments and materials were used.

Biological and Sediment Samples. National Bureau of Standards (NBS) bovine liver and orchard leaves were analyzed using the same methods as the regular samples.

The number of organisms sampled per day of experiment is shown in ref *10*. The samples were defrosted after collection, dissected, dried at 105 °C, and homogenized with a ceramic mortar and pestle.

A wet chemical digestion procedure was used for all biological samples (*10*).

The experiments were replicated. Experiment I began on March 11, 1975 and ended July 15, 1975; experiment II began on December 12, 1975 and ended April 26, 1976.

Seawater. Seawater samples were collected in 2.5- or 4-L glass bottles (reagent acid bottles). Samples were immediately filtered through precleaned 142 mm diameter, 0.45 mm pore size filters, then frozen.

Analysis of Trace Metals. Extraction and preconcentration procedures using chelating resins (*10*) were used. Flame atomic absorption spectrophotometry with background cor-

Table I. Results in $\mu g\ g^{-1}$ Dry Weight for Determination of Metals in NBS Bovine Liver and Orchard Leaf Standards[a]

	Cd	Cu	Cr	Pb	Zn	Ni
		Experiment I, Bovine Liver				
MDC	0.3	8.9	3.4	0.5	2.8	0.9
$\bar{x}$	0.56	177	<MDC	2.5	132	
SD	0.26	20.2		0.96	31.7	
N	9	10		10	12	
		Experiment II, Bovine Liver				
$\bar{x}$	0.55	187.4	<MDC	<MDC	131.7	1.0
SD	0.45	15.50			17.59	0.69
N	49	41			53	48
NBS values	0.27 ± 0.04	193±		0.34 ± 0.08	130 ± 10	
		Experiment I, Orchard Leaves				
$\bar{x}$	<MDC	12.3	2.6	44.8	26.1	3.9
SD		3.9	0.63	2.82	5.4	0.6
N		11	6	6	11	3
		Experiment II, Orchard Leaves				
$\bar{x}$	0.66	11		45.0	25.6	4.0
SD	0.34	1.5		3.6	7.64	1.3
N	17	20		23	26	24
NBS values	0.11 ± 0.02	12 ± 1	(2.3)	45 ± 3	25 ± 3	1.3 ± 0.2

[a] The results are shown with mean (±), standard deviation (SD), and our computed minimum detectable concentration (MDC).

Table II. Mean Concentration of Metals in Seawater[a]

	Cd	Cr	Cu	Ni	Pb	Zn
particulate						
mean	0.1	3.8	2.1	4.5	<MDC	2.1
SD	0.1	3.6	1.6	3.9		1.3
soluble						
mean	0.6	0.9	1.9	4.9	2.9	18.0
SD	0.3	0.8	0.8	2.2	1.8	17.8
total	0.7	4.7	4.0	9.4	2.9	20.1
no. of samples	28	28	28	28	28	28

[a] Results are pooled values from experimental and control tanks for experiment II in $\mu g/L$.

rection was used to analyze the concentrate for trace metals.

Results

NBS Standards. The results for our analysis of the NBS bovine liver and orchard leaves standards are shown in Table I.

When experiment I was compared to experiment II no discernible difference was detected; therefore, the results for experiment II are the only results discussed. The net uptake for each metal was computed as the mean experimental results (μg of metal/g dry weight of organisms) minus the mean control results for each sample. The results were checked for statistically valid differences (*t* test, $p < 0.05$).

Seawater. The temperatures ranged from 21 to 26.5 °C with a salinity range from 24 to 35‰ ($\bar{x} = 30.0$, SD 4.2‰, $N = 18$).

No significant differences were noted between metal concentrations in the water of the experimental tank and those in the control tank. The results were pooled and are shown in Table II.

Sewage Sludge. To facilitate comparison, the reciprocal of the trace metal concentration in the sewage sludge was used. A two-stage decline in Cd and Zn concentrations in the sewage sludge (Figure 1) and Ni (not shown, *10*) was seen. The first decrease in metal concentration was nearly instantaneous with a further, smaller decrease after day 50.

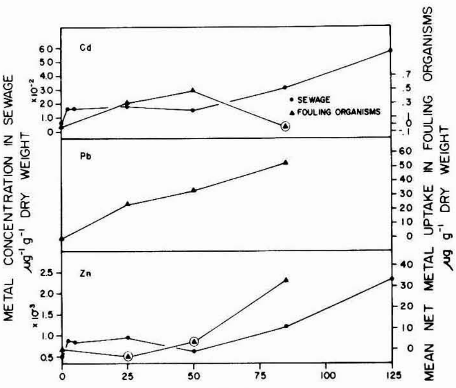

Figure 1. Reciprocal concentration ($[\mu g\ g^{-1}$ dry weight$]^{-1}$) of cadmium, lead, and zinc in sewage sludge and concentration of Cd, Pb, and Zn ($\mu g\ g^{-1}$ dry weight) in fouling organisms over a 125-day sampling period

Fouling Organisms. Lead showed (Figure 1) a steady uptake to the end of the sampling period (85 days). Cadmium (Figure 1) and Ni (not shown, *10*) demonstrated a steady uptake until day 50, and then a decline in the net uptake. Zinc (Figure 1) and chromium (not shown, *10*) indicated a net uptake after day 50.

Thalassia. *Leaves.* Chromium, copper, lead, and zinc showed the same overall trend of increasing net uptake (Figure 2). Nickel and zinc did not show a significant uptake up to day 50, but the net uptake was significant at days 85 and 125 (Figure 2).

Roots. A significant net uptake for Cr and Zn, with Pb, Ni, and Cu showing peaks of significant net uptake, was demonstrated at day 5 and/or 25 days. Cadmium uptake was significant only at day 25. These data are not shown (*10*).

Urchin. Chromium, Cu, and Pb show a steady and rapid increase in net uptake (Figure 2). Zinc shows a steady increase with a decrease in net uptake at day 50, followed by a rapid increase in Zn uptake to day 125 similar to nickel (Figure 2).

Sea Cucumber, Internal Organs. Chromium, Cu, Pb, and Zn showed net uptakes over the 125-day period. The peak net uptake occurred at day 50 or 85. Nickel showed a spike of uptake at days 5 and 50 and a smaller spike at day 125 (Table III).

Mangrove Roots. The net Ni uptake increases rapidly up to day 5 and levels off at day 50 (Table III). Chromium indicated a linear net uptake from day 50 to day 125. No net lead uptake was shown in either experiment I or II, except for the final sample for experiment II. Zinc demonstrated a constant net uptake. Copper appeared to show a gradual uptake after day 50, followed by a decline to original level.

Other. No significant net uptake was shown for oysters, clams, mangrove stem or leaves, snails, holothurian body or muscle, or sediment.

In all cases the mean net uptake of metals, by *Thalassia* leaves and then urchin guts, occurs within 5 days. The *Thalassia* leaves also show periodic decreases in mean uptake with subsequent gains to equal or higher levels. This was true for all the metals except Pb. This closely parallels the results of

Table III. Mean Net Uptake of Metal in Holothurian Soft Parts and Mangrove Roots[a]

expt, day	metal									
	Cr		Cu		Ni		Pb		Zn	
	H	M′	H	M′	H	M′	H	M′	H	M′
1	−13.8**	1.1	0.0	2.8	19.3**	9.7**	0	3.0	−7.5**	3.9**
5	−7.8**		−2.6**		37.9**		2.1		10.6	
25	10.9**		4.6**		1.7		14.9		5.5**	
50	41.2**	9.1**	5.4**	5.8**	41.8**	6.0**	3.4**	0.0	9.7**	3.5**
85	14.6**		10.3**		4.5**		31.7**		22.9**	
125	20.8**	23.3**	3.1**	0.0	15.5**	1.3	7.1**	5.8**	10.5**	3.6

[a] Units are $\mu g/g^{-1}$ dry weight. The mean net uptake was computed as the mean concentration in the experimental organism minus the mean concentration in the control organisms. H refers to Holothurian and M to the mangrove. **, significant difference between experimental and control $P < 0.05$.

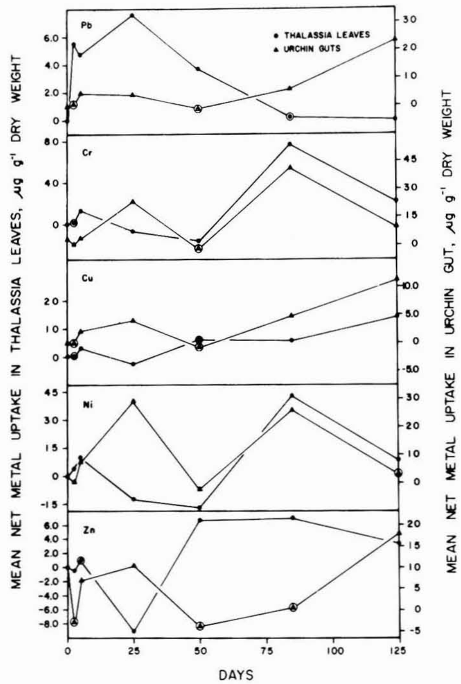

Figure 2. Mean net metal uptake in *Thalassia* leaves and urchin gut (μg g^{-1} dry weight) for Pb, Cr, Cu, Ni, and Zn over a 125-day sampling period.

Parker (*11*) where *Thalassia* leaves showed very similar patterns in uptake of ^{60}Co.

Discussion

Bivalves, in general, show uptake and concentration of most trace metals (*3–6, 12*). However, oysters and clams in our research showed no consistent nor significant net uptake of metal, except possibly zinc and copper. The pooled wet weights of the clam, oyster, and snail soft parts, Holothurian muscle parts, and zooplankton samples were too small to allow an adequate sample size for the trace metal analyses.

The concentrations of metals in the seawater for the experimental tank were very seldom higher than the concentrations in the control tank. Obviously, metals were released from the sludge to the water as shown by the results in Figures 1 and 2 and also by the significant net uptake of metals by *Thalassia* leaves and roots, urchin and sea cucumber internal parts, and fouling organisms. The problem in interpretation of the water results was due to the "point sampling" of the water vs. the "integrated" sampling for the organisms, sediment, and sludge. Shuster and Pringle (*6*) demonstrated that the concentration of metal in the water, at any one time, may not be the best indicator of the total contamination by metal. Parker (*11*) also showed very low levels of radioactive cobalt in the water within 72 h after addition of a radioactive cobalt "spike".

The net uptake of Cd, Pb, and Zn by "fouling organisms" was clearly shown and closely followed the loss of metals from sewage sludge. The uptake of Ni and Cr by fouling organisms was also significant. The fouling organisms were integrated samples.

The net uptakes by *Thalassia* leaves and urchin internal organs closely parallel each other for Cr, Cu, Ni, Pb, and Zn. Significant cadmium uptake by *Thalassia* leaves and urchin internal organs was also seen (*10*). Schroeder (*8*), using radioactive ^{57}Co, ^{60}Co, ^{54}Mn, and ^{65}Zn in seawater, showed that in *Thalassia testudinum* the rhizomes had the highest uptake followed by leaves and then roots. We show significant net metal uptake for Cr, Cu, Pb, and Ni in *Thalassia* roots. Cadmium and zinc had a net uptake in *Thalassia* roots. The close correlation between the urchin's mean net uptake of metals and the uptake in *Thalassia* leaves was not surprising, as the urchins were voracious foragers on *Thalassia* leaves and epiphytes. This was also shown in the field by Camp et al. (*13*). The net uptake of some metals in leaves was closely coupled to the uptake in the roots of *Thalassia*. The results for Cd, Ni, and Cr indicate a translocation of these two metals from roots to leaves. The translocation of metal was also indicated for Zn from day 85, where the net uptake decreases in the roots with an increase in the leaves and vice versa at day 125. In general, the maximum net uptake in *Thalassia* leaves was slightly greater than the uptake in roots.

The interpretation of the significant net uptake for mangrove roots indicates that only Cr showed a linear response over time, whereas Zn and Cu showed an increase in net uptake followed by attainment of apparent equilibrium and then loss of the metal. Lead shows no net uptake until day 85. These results appear to be loosely correlated with the fact that the sediment never showed a net uptake until day 85, when Ni, Pb, and Zn begin to show a slight net uptake in the sediment (*10*). Since no other part of the mangroves sampled indicated a significant uptake of metal, then the only source for the metals in the mangrove roots must be the sediments. If that is so, then only Ni, Pb, and Zn should show net uptake in mangrove roots and then only after day 85. This lack of significant uptake of metals by the sediments could be due to the pooling of whole sediment samples from a 2.5 cm diameter × 25 cm core. Parker (*11*) found that radioactive cobalt was concentrated in the upper 2 cm of the sediment. The *Thalassia* leaves in Parker's research showed the highest concentration of metal with respect to the roots. Parker combined roots with rhizomes and leaves with stems as we did in this experiment. If the gradient of trace metal concentration in the sediment was very steep, then the pooling of the core could have diluted the higher surface metal concentrations with the much lower metal concentrations in the bottom of the core.

The sewage sludge showed a two-stage release. The first stage occurred at day 1, followed by a slow constant release until day 50 when another release occurred. A slow but steady release would more likely result in a higher maximum uptake, whereas a two-stage release due to the estimated 6-h residence time for the water in the tanks and 8.5 L min^{-1} flow rate produce a lower maximum net uptake.

A definite net uptake of trace metals was measured in members of a *Thalassia testudinum/Rhizophorae mangle* community in the two replicated experiments over the period from March 1975 to April 1976. The net uptake was especially significant in: *Thalassia testudinum* leaves and roots/rhizomes, internal organs of the urchin *Lytechinus variegatus*, "fouling organisms", internal organs of *Holothurea* sp., and for some metals in *Rhizophorae mangle* roots. In general, the net uptake pathways followed the trophic levels in the food webs. This pathway was especially noticeable from the sludge to the fouling organisms and from the sludge to the *Thalassia testudinum* leaves and thence to the urchin herbivore *Lytechinus variegatus*. The net uptake in the *Holothurea* sp. was closely related to the net uptake in the fouling organisms and the trace metal loss rate of the sludge. The food web in this artificial system was dominated by the fouling organisms as would be expected. The uptake of trace metals, leached from the sludge, was always greatest in this complex group.

The results of long-term exposure, in a simulated tropical ecosystem, to toxic trace metals more closely approximate the situation in nature than static laboratory experiments. Our results show that chronic exposure to toxic metals can lead to uptake and concentration of these metals in marine organisms. We were able to duplicate our results using this complex simulation of a marine ecosystem.

The authors would not recommend, based on the results of this research, the dumping of sewage sludge in shallow, tropical marine environments. The potential exists for rapid concentration of toxic trace metals by members of the food web high on the trophic scale.

Acknowledgments

The authors express their appreciation to the following organizations: the Puerto Rico Department of Agriculture for wet laboratory facilities and Harbor Branch Foundation Inc. and the Smithsonian Institution for use of facilities for completion of this research. The technical support of the following people was invaluable for the completion of this research: Ms. Gina deCastro, Ms. Luz Cruz, Ms. Dee Zimmerman, Mr. John Thurston, Mr. Pedro Acosta, Mr. Jon Cole, Mr. Jose Echeverria, Mr. Thomas Prinslow, Mr. Jose Ramirez, Ms. Arlene Ramirez, Mr. Bob Quinn, and Dr. Kenneth Waters. We extend our sincere thanks to Dr. Frank Lowman for the initial conception of this project.

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Received for review May 3, 1978. Accepted December 5, 1978. The research was funded under a joint EPA/ERDA grant (IAG-D4-0541/40-468-74). We thank Harbor Branch Foundation Inc. and the Smithsonian Institution for financial support. This is Harbor Branch Foundation, Inc. Contribution No. 115.

Kinetics of Desulfurization of Hot Fuel Gas with Calcium Oxide. Reaction between Carbonyl Sulfide and Calcium Oxide

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In developing coal gasification processes, removal of the sulfur compounds has been of great concern because of their detrimental effects on air quality, corrosion of equipment, and poisoning of the catalysts used in the processes. The sulfur compounds existing in the fuel gases are mainly hydrogen sulfide (H_2S) and carbonyl sulfide (COS) (*1*). Over the past few years, work on the use of metal oxides as sorbents for H_2S removal has been reported in the literature, e.g., in ref *2–5*. In particular, studies have been made on the kinetics of the reaction between CaO and H_2S (*4–7*). It is known that H_2S exists in a greater concentration than does COS in the fuel gases from the coal gasifiers. The thermodynamic equilibrium ratio of H_2S over COS is normally high under the gasification conditions. For example, the ratio is about 50 for the Lurgi process. Nevertheless, the equilibrium is not rapidly reached and, therefore, significant amounts of COS do exist in the raw gases from gasifiers. In addition, COS also exists in the effluents of other industrial processes. For the commercially available coal gasifiers, the typical concentration of COS is 0.01% (*1*).

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■ Rates of sorption of COS by CaO were measured in the temperature range of 500 to 900 °C at a total pressure of 1 atm. The CaO sample was a reagent-grade fine powder with particle size of 1–5 μm. The overall rates in the temperature range of 600 to 900 °C were correlated satisfactorily with the grain model (with a shape factor of 1.5), where chemical reaction was the rate-limiting step. The correlation with the grain model was also supported by the SEM observation of the physical structure of the CaO particles. Using the initial rates as the surface chemical rates, the temperature and concentration dependencies were determined and a rate expression was derived. The rate of sorption of COS by CaO was slightly higher than that of H_2S, using the literature data on the H_2S sorption. Significant sorption of COS takes place parallel to the sorption of H_2S in the coal gasification processes in which lime is used.

Removal of COS from hot gases with metal oxides has yet to be investigated. In this paper, we report the results of a kinetic study of the sorption of COS with CaO. Since lime is used in several promising second generation coal gasification processes, e.g., the CO_2-acceptor and the Westinghouse fluidized-bed processes, the results of this study will be useful in understanding the sulfur removal mechanism in these processes.

In studying the reaction between CaO and COS, we first consider the thermodynamic equilibria of the following reactions:

$$2COS = 2CO + S_2 \tag{1}$$

$$CaO + COS = CaS + CO_2 \tag{2}$$

Equilibrium constants of the two reactions are shown in Figures 1 and 2. Now we shall examine the feasibility of removing COS from the hot fuel gases with CaO. Using the Lurgi process as an example, the temperature range is 1000–1400 °F and the CO_2 composition is 15%. From Figure 2, the equilibrium composition for COS is 7×10^{-7}, or 0.7 ppm. Therefore, calcium oxide is thermodynamically a good sorbent for COS removal from hot fuel gases. The equilibrium curve in Figure 1 will be used in the experimental work as a guide to determine the maximum decomposition of COS.

Experimental

The reaction rates were measured gravimetrically. The detailed experimental and calculation procedures have been described elsewhere (8) except that a Sartorius microbalance was used in this investigation. Also different in this work was the fact that the sample holder was a porous alumina pan suspended with a quartz rod instead of a platinum wire because it was found early in the work that platinum was attacked by COS.

Because COS decomposes at high temperatures, a sufficient amount of CO was introduced into the system to prevent the decomposition. This was confirmed from the mass spectrometric analyses of the COS compositions in the inlet and outlet gases. To test if the measured weight gain was indeed due to Reaction 2, the solid product samples were analyzed by X-ray diffraction.

In all the rate measurements, about 50 mg of reagent grade calcium carbonate powder (Mallinckrodt) was used. The size of the powder was 1–5 μm as measured with scanning electron micrographs. The calcium carbonate sample was first calcined at 900 °C in a N_2 flow. Subsequently, the system was adjusted to the desired temperature and the rate measurement commenced upon admitting the reactant gas. The purpose of using the fine powder calcined CaO was to eliminate the possible pore diffusion resistance and to obtain the chemical rate.

The gases used were directly obtained from gas cylinders with the compositions: nitrogen (99.99%), carbon monoxide (99.95%), and a custom-made nitrogen–carbonyl sulfide mixture (1.87% COS in N_2). Except where noted, the total gas flow rate was 2000 SCCM.

Results and Discussion

X-ray diffraction analyses using standard powder technique gave the following d spacings (in Å): 2.78, 2.42, 1.71, 1.45, 1.38, and 1.20 for the reactant and 2.87, 2.04, 1.72, 1.66, 1.43, and 1.28 for the product. They correspond to CaO and CaS, respectively. Preliminary experiments were also conducted which showed that the maximum weight gains of the solid reactants corresponded to full conversions of CaO to CaS. It was concluded, therefore, that Reaction 2 was the only reaction attributable to the weight change.

To suppress the thermal decomposition of COS in the reaction zone, CO was used in the reactant gas mixtures. In the preliminary experiments, gas samples from the inlet and outlet of the reaction zone were taken and analyzed with a quadruple mass spectrometer for the COS concentrations. The sensitivity of the mass spectrometer was 30 ppm for COS at a total pressure of 1 atm. It was found that, at the highest temperature of this work, i.e., 900 °C, 10% CO in the reactant gas was sufficient to suppress the decomposition of COS at a concentration of 0.1%. The maximum thermodynamic limit of decomposition under the above conditions was, according to Figure 1, 20% of the COS in the feed gas. However, the mass spectrometric analyses showed that the decomposition was below 3%. Consequently, we used 10% CO in all the reactant

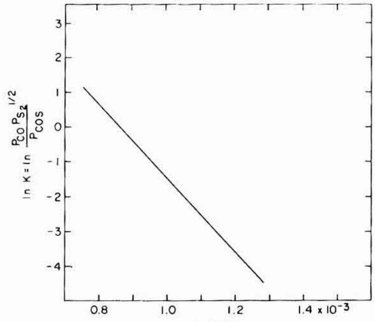

Figure 1. Equilibrium constant for the reaction $COS \rightarrow CO + \frac{1}{2}S_2$

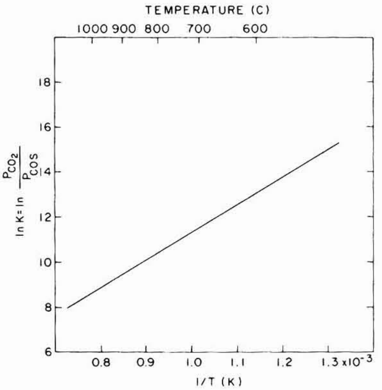

Figure 2. Equilibrium constant for the reaction $CaO + COS \rightarrow CaS + CO_2$

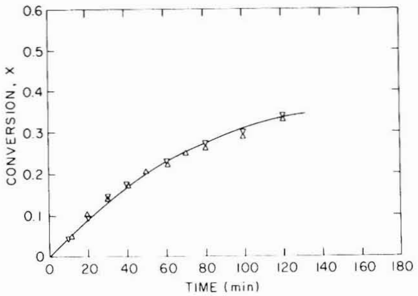

Figure 3. Reaction rate of CaO with COS (0.1%) at 500 °C; in N_2 (△) and in N_2 with 10% CO (▽)

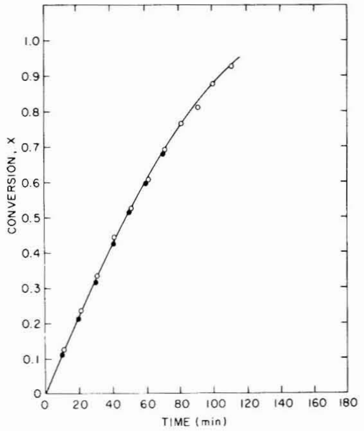

Figure 4. Effect of flow rate on reaction rate at 900 °C with 0.1% COS and 10% CO in N_2; with flow rates of 1000 SCCM (O) and 2000 SCCM (●)

gas mixtures and assumed that the COS concentrations were the true values in all the subsequent experiments.

To ensure that the introduction of CO into the reactant gases did not affect the kinetics of Reaction 2, the rates of this reaction were measured at 500 °C with and without 10% CO. The rates were then compared as shown in Figure 3. Since no difference in the rates was detected, CO may be regarded as a true inert in the reaction system.

To eliminate the resistance due to the gas film, or the external mass transfer effects, a certain minimum velocity of the reactant gas had to be exceeded. This was done by comparing the rates measured at two gas flow rates. In Figure 4, we compared the rates at 900 °C at flow rates of 1000 and 2000 cm^3/min (STP), or SCCM. Inasmuch as the rates were the same in Figure 4, the flow rate of 2000 SCCM was used throughout this work, and the rates measured did not include the external mass transfer effect.

Figure 5 shows the results of conversion of CaO to CaS, X, as a function of time at various temperatures, with 0.1% COS in CO and N_2. Figure 6 gives the rates at 800 °C with the concentration of COS varying from 0.02 to 0.2%. The initial rates, $(dX/dt)_{t=0}$, in this kind of rate curves approximate the intrinsic chemical rates. The initial rates obtained from Figure 6 were plotted against the concentration of COS and are shown in Figure 7. It is seen that, in the range of COS concentration below 0.2%, Reaction 2 is first order with respect to COS. The first-order rate dependence, in the low partial pressure range, was also observed for the reaction of CaO with SO_2 (*9*), H_2S (*3*), and NO (*10*).

To interpret the rate curves such as those shown in Figures

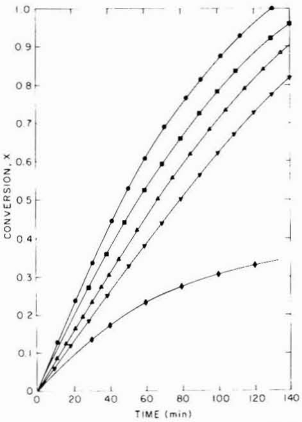

Figure 5. Effect of temperature on reaction rate with 0.1% COS and 10% CO in N_2 at 900 (●), 800 (■), 700 (▲), 600 (▼), and 500 °C (♦)

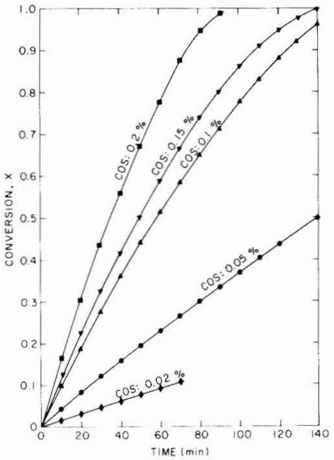

Figure 6. Effect of COS concentration on reaction rate at 800 °C with 10% CO and the marked COS compositions in N_2

5 and 6, the interplay between the chemical rate and the diffusion rate would have to be understood. Mathematical models exist for several simplified and idealized reaction systems (*11*). Before using the models to interpret the rate data, we examined the physical structure of the solid particles with a scanning electron microscope. The micrographs showed that most of the CaO particles had an overall size of 1–5 μm, and each particle consisted of randomly stacked grains, most of which were shaped as flakes. The pores or void in the particles were of the same dimensions as the grains. With the above physical observation, the grain models (*11, 12*) appeared to be well suited for correlating the data.

In the case where chemical reaction limits the overall rate, the following solutions to the grain model (*11*) are used:

$$t/\tau = 1 - (1 - X)^{1/F_g} \qquad (3)$$

In the case where diffusion of COS through the reaction product layer is the limiting rate step, we have the following solutions to the model (*11*):

$$t/\tau = X^2 \qquad F_p = 1 \qquad (4)$$

$$= X + (1 - X)\ln(1 - X) \qquad F_p = 2 \qquad (5)$$

$$= 1 - 3(1 - X)^{2/3} + 2(1 - X) \qquad F_p = 3 \qquad (6)$$

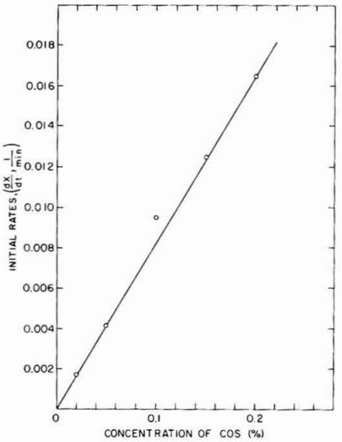

Figure 7. Analysis of the reaction order with respect to COS at 800 °C

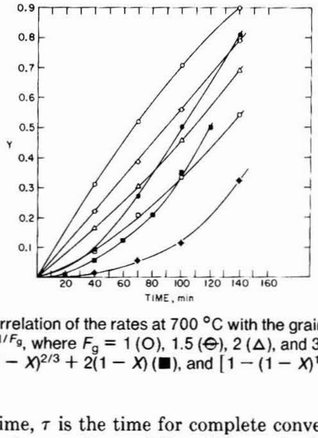

Figure 8. Correlation of the rates at 700 °C with the grain model. $Y = 1 - (1 - X)^{1/F_g}$, where F_g = 1 (○), 1.5 (⊖), 2 (△), and 3 (□). $Y = X^2$ (●), $1 - 3(1 - X)^{2/3} + 2(1 - X)$ (■), and $[1 - (1 - X)^{1/3}]^2$ (◆)

Here t is time, τ is the time for complete conversion, X is the fractional conversion, and F_g and F_p are the shape factors for grain and particle, respectively. F_g has the values of 1, 2, and 3 for, respectively, slab, cylinder, and sphere. In addition to the above equations, Jander's equation (*11*) was also used. Figure 8 shows the results of correlating the data at 700 °C with these equations. As shown in the figure, all the diffusion-limited models (Equations 4–6) failed to correlate the data whereas Equation 3 with a shape factor of 1.5 fit the data satisfactorily. The same equation also correlated the data in the temperature range of 600 to 900 °C (Figure 9).

The satisfactory correlation of the rate data with Equation 3 indicated that the reaction front progressed linearly with time within each "grain", as postulated in the original model.

The shape factor of 1.5 lies between the shapes of slabs (F_g = 1) and cylinders (F_g = 2). As mentioned, the shapes of the "grains" in the CaO sample were close to the slabs. In the model which results in Equation 3 with F_g = 1, the grains were assumed to be slabs of infinite widths and of a uniform thickness. The deviation of the measured rates from the ideal model was attributed to the facts (1) that the slabs were not infinite and (2) that the grain size was nonuniform. The latter factor may be further explained as follows. During the reaction, the smaller "grains" reached completion first and the overall rate would slow down and hence the rate curve would convex, as shown in Figure 8.

The rate at 500 °C exhibited somewhat different features than those at higher temperatures in that the rate fell off rapidly. The same phenomenon has been observed for the reaction between CaO and H_2S at temperatures below 550 °C (*4, 5*). The rate at 500 °C could not be explained with the aforementioned grain models, as shown in Figures 9 and 10. Although the reason for the above rate behavior at 500 °C is not known, it is possible that, at such a low temperature, an impervious layer of CaS formed on the CaO crystallite which prevented further reaction (*5*).

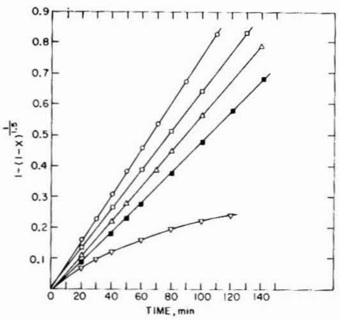

Figure 9. Correlation of rates with the grain model with the chemical reaction limiting case at 900 (○), 800 (□), 700 (△), 600 (■), and 500 °C (▽)

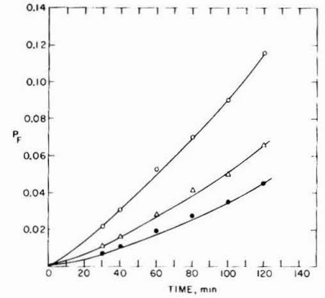

Figure 10. Correlation of the rates at 500 °C with the grain model where diffusion in the product layer is the limiting step. $P_F = X^2$ (○), $X + (1 - X)\ln(1 - X)$ (△), and $1 - 3(1 - X)^{2/3} + 2(1 - X)$ (●)

The activation energy of Reaction 2 was obtained from the temperature dependence of the initial rate. The value of 4.3 kcal was calculated from the data shown in Figure 11.

The surface area of the CaO sample was 7.5 m^2/g as measured with a Micromeritics dynamic surface area instrument. Taking this value as the area of the initial reaction, the chemical rate of Reaction 2 assumed the following form:

$$\frac{dX}{dt} = 78e^{-2160/T}P_{COS}(1 - X) \qquad (7)$$

Finally, because COS normally coexists with H_2S, as in the fuel gases, it is interesting to compare the rates of the reactions of the two compounds with CaO. The initial rates at 700 °C of the two reactions with 0.1% both of COS and H_2S and a total pressure of 1 atm are compared as the following:

CaO + COS:

$$\left(\frac{dX}{dt}\right)_{t\to 0} = 1.3 \times 10^{-4}\ s^{-1} \text{ (reagent powder, this work)}$$

CaO + H_2S:

$$\left(\frac{dX}{dt}\right)_{t\to 0} = 1.0 \times 10^{-4}\ s^{-1} \text{ (reagent powder, ref 3)}$$

$$\left(\frac{dX}{dt}\right)_{t\to 0} = 0.6 \times 10^{-4}\ s^{-1} \text{ (dolomite powder, ref 4)}$$

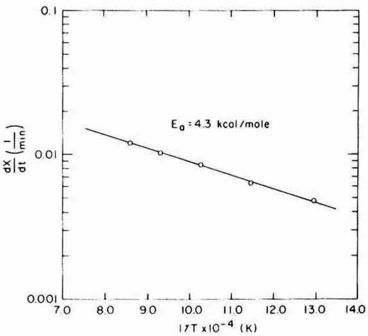

Figure 11. Arrhenius plot of the initial rates

The comparison shows that, under the same conditions, the rates for COS and H_2S are similar. As discussed, both rates are first order with respect to the concentration of the reactant gas. Therefore, with the ratio of compositions of COS and H_2S known, the relative rates of reaction may also be known. Or, alternatively, knowing the rate of the reaction $COS + H_2 \rightarrow H_2S + CO$, and given the ratio H_2/CO, the relative rates of reaction may be calculated. A conclusion may be drawn from this comparison that lime is an equally effective sorbent for COS as for H_2S.

Acknowledgment

We are grateful for the assistance provided by O. F. Kammerer (X-ray diffraction analyses), J. Forrest (mass spectrometric analyses), and I. W. Still, Jr. (scanning electron microscopic observations), all of the Brookhaven staff.

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Received for review July 31, 1978. Accepted December 6, 1978.

Concentration Dependence upon Particle Size of Volatilized Elements in Fly Ash

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■ Fly ash, collected from a coal-fired steam plant, has been separated into 17 well-defined size fractions and analyzed for 29 elements using X-ray fluorescence techniques. The results show that the concentrations of volatile trace elements increase as particle size decreases in the 1- to 10-μm size range. For submicron particles, the concentration becomes independent of particle size. A volatilization–condensation model, which is capable of explaining these results, is suggested.

The particulate emissions from coal-fired steam plants, equipped with modern pollution control devices, consist primarily of submicron particles. A large body of recent work (*1–7*) has shown that the smaller fly ash particles resulting from coal combustion may be considerably enriched in several toxic trace elements. The most widely accepted model (*1*) for trace element enrichment in fly ash formation involves the volatilization of these elements during combustion, followed by condensation or adsorption over the available matrix material (composed primarily of the nonvolatile oxides of Al, Mg, and Si). Fly ash surfaces have been found to be enriched in several of the same trace elements showing enrichment in the smaller particles, supporting this mechanism (*8–10*). The smaller particles, which show the highest concentration of several trace metals, are not efficiently collected by pollution control devices. These particles, enriched in potentially toxic trace metals, also have the highest atmospheric mobilities and are deposited preferentially in the pulmonary and bronchial regions of the respiratory system (*1*).

Two models have been proposed to rationalize the concentration vs. particle size dependence in fly ash resulting from a volatilization–condensation mechanism. Several years ago, Natusch and co-workers (*1*) were able to rationalize their data by assuming that volatilized material condensed evenly over the surfaces of all particles (i.e., a surface layer thickness independent of particle size). They were able to obtain reasonable fits to their data using the equation:

$$C = C_m + \frac{6C_s}{\rho D} \tag{1}$$

where C_m is the concentration in the matrix upon which the volatiles condense, C_s is the surface concentration, ρ is the density, and D is the particle diameter. Flagan and Friedlander (*11*), however, have recently suggested that a direct dependence of C on D^{-1} should exist only in the free molecule regime where the Knudsen number (K_n) is greater than 1. At lower values of K_n, in the continuum regime, they suggest that the total concentration will be proportional to D^{-2}. Physically, this model is essentially the same volatilization–condensation model proposed by Natusch and co-workers but is quantitatively quite different, predicting much greater concentration increases for volatilized elements in the smaller size fractions. While Flagan and Friedlander were able to fit Natusch's data (*1*) equally well with their model, the analytical results and fits to these simple models are of limited value since the data were limited to size fractions greater than 1 μm.

In this work, we report the results of concentration vs. particle size measurements for sized fly ash fractions ranging from 0.15 to 200 μm median diameter. These results allow a direct examination of fly ash for the large enrichments pre-

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Table I. Concentrations of Elements in Fly Ash Determined by X-ray Fluorescence

Size Fraction**		Al (%)	Si (%)	P (%)	S (%)	K (%)	Ca (%)	Ti (%)	V	Cr	Mn	Fe (%)	Ni	Cu	Zn	Ga	As	Se	Ge	Rb	Sr	Y	Zr	Nb	Mo	Sn	Ba	La	Ce	Pb
< 0.2	a	15.2	21.0	1.0	0.29	0.38	4.21	2.33	670	190	970	5.02	99	570	610	160	66	5.1	27	19.4	2480	116	1440	182	89	77	1480	78	177	92
(0.15)	b	12.2	18.9	1.6	0.34	0.33	3.97	2.21	925	172	953	4.74	82	540	620	149	67	2.6	29	23.9	2470	115	1430	183	85	50	1420	90	172	76
0.2-0.5	a	13.0	23.2	1.0	0.55	0.41	4.81	2.59	1060	220	1160	5.32	111	620	700	167	70	3.7	34	21.9	2330	113	1390	178	92	48	1540	96	211	84
(0.4)	b	9.6	22.1	1.1	0.61	0.37	4.51	2.56	830	200	1140	5.05	99	633	660	162	72	3.0	33	20.5	2290	110	1360	176	91	50	1480	89	191	77
0.5-0.9	a	12.6	23.4	1.3	0.36	0.41	4.84	2.64	1140	230	1180	5.41	115	650	740	177	68	3.6	34	20.5	2240	106	1320	167	88	45	1450	91	179	80
(0.75)	b	10.6	21.8	0.7	0.66	0.37	4.50	2.56	860	240	1150	5.07	101	640	680	161	77	5.4	31	19.8	2200	106	1300	165	90	46	1390	82	180	80
	c	11.6	21.9	0.9	0.51	0.39	4.48	2.51	790	218	1090	4.99	99	620	660	159	74	4.1	32	21.1	2280	110	1360	170	90	48	1470	90	181	78
0.9-1.5	a	12.3	23.9	1.2	0.28	0.41	4.82	2.59	890	240	1140	5.28	108	610	690	168	68	3.6	34	21.3	2270	107	1350	171	91	49	1480	99	193	83
(1.3)	b	9.6	22.0	0.8	0.42	0.39	4.52	2.53	880	221	1110	5.04	93	600	650	161	71	2.7	33	21.2	2260	110	1350	172	93	45	1410	100	169	76
	c	10.3	22.7	1.1	0.31	0.40	4.52	2.54	900	215	1090	5.06	95	620	670	164	77	5.1	33	20.2	2310	111	1370	175	91	52	1480	102	188	79
1.5-3.0	a	11.3	21.8	1.2	0.26	0.32	4.91	2.40	890	150	860	4.88	110	610	490	114	29	2.2	15.7	13.2	2340	113	1360	180	47	32	1510	100	187	51
(2.5)	b	10.7	21.1	0.7	0.24	0.34	4.62	2.34	790	137	788	4.60	90	600	470	109	31	1.8	15.4	11.2	2310	112	1350	177	41	25	1460	96	181	50
	c	10.5	21.3	0.6	0.25	0.34	4.81	2.44	850	113	823	4.79	89	620	440	109	33	1.6	15.3	13.9	2290	111	1320	178	44	24	1420	84	172	116
3-6	a	11.3	21.9	1.0	0.24	0.35	5.08	2.44	760	130	790	4.87	72	530	370	106	23	1.6	13.2	9.1	2360	114	1410	186	40	18	1450	86	178	39
(5)	b	9.9	21.1	0.6	<0.17	0.32	4.89	2.43	790	106	728	4.73	68	540	360	105	28	1.3	12.3	8.5	2330	118	1380	182	39	22	1430	93	168	40
	c	9.5	20.9	0.7	0.23	0.32	4.84	2.40	780	58	752	4.66	64	530	360	104	29	1.6	12.5	9.8	2350	116	1400	187	42	20	1420	93	166	35
6-10	a	9.5	22.1	<0.7	0.17	0.32	4.83	2.24	680	50	680	4.57	52	390	220	73	12	1.8	7.8	13.6	2420	110	1270	169	28	11	1530	98	190	23
(8)	b	8.5	21.9	0.8	<0.18	0.29	4.78	2.22	740	39	653	4.42	41	380	210	74	14	1.4	7.7	13.7	2410	110	1260	170	27	17	1450	84	171	24
	c	9.1	20.5	1.0	0.27	0.29	4.69	2.19	680	55	647	4.35	45	380	210	74	15	<0.8	7.5	15.2	2350	108	1220	164	27	12	1460	76	177	21
10-12	a	10.9	22.1	0.9	<0.15	0.29	4.45	1.99	490	45	600	4.09	44	380	170	54	5.7	0.8	3.2	10.1	2320	100	1060	142	20	3.0	1470	85	167	16
(11)	b	7.8	20.1	<0.6	<0.19	0.26	4.19	1.95	500	35	570	3.89	39	380	160	51	8.5	<0.7	4.3	9.1	2330	101	1060	142	18	10.9	1470	77	169	16
	c	8.6	19.0	0.9	<0.19	0.27	4.50	2.08	400	65	638	4.17	42	380	170	53	11.6	<0.8	3.7	10.6	2540	108	1170	162	22	5.3	1530	88	181	14
12-18	a	9.6	21.8	<0.7	<0.16	0.27	4.35	1.97	500	23	600	4.16	42	390	150	44	5.4	<0.9	3.1	13.8	2530	105	1090	143	21	12	1550	99	188	17
(15)	b	8.8	22.2	<0.6	<0.20	0.28	4.58	2.14	370	33	638	4.29	37	410	150	47	8.4	0.9	3.0	14.4	2550	107	1100	145	20	14	1510	95	180	15
	c	9.7	20.4	<0.6	<0.20	0.27	4.40	2.08	380	45	636	4.19	37	340	140	44	9.2	1.4	3.2	13.5	2580	104	1100	150	18	8	1440	83	174	11
18-22	a	6.9	17.6	<0.8	<0.18	0.24	3.72	1.75	360	20	530	3.64	37	270	105	32	4.9	<0.9	1.9	13.2	2500	97	980	120	15	5.8	1540	91	191	8.9
(20)	b	10.3	24.5	<0.7	<0.21	0.28	4.14	1.94	250	29	591	3.78	36	280	107	33	4.9	<0.7	<1.2	11.8	2500	96	990	124	10	3.4	1410	84	164	9.1
	c	8.3	21.4	<0.7	<0.21	0.28	4.05	1.99	290	39	564	3.90	33	240	97	32	4.8	<0.7	<1.2	10.4	2540	102	1010	122	12	14.2	1410	86	180	10.6
22-30	a	11.3	18.1	<0.9	<0.20	0.27	4.26	2.05	490	50	600	4.48	54	290	105	29	5.3	<0.9	<1.3	10.9	2950	109	1080	129	13	14	1570	111	259	8.7
(26)	b	8.9	17.2	<0.7	0.25	0.24	4.11	2.07	500	28	617	4.36	53	300	100	28	6.0	<0.7	1.3	11.6	2920	108	1070	129	14	19	1520	97	176	11.1
	c	9.8	21.5	0.9	<0.24	0.29	4.54	2.24	380	32	653	4.66	40	290	101	27	4.4	<0.8	<1.2	12.5	3110	114	1160	137	16	20	1640	93	203	8.3
30-35	a	12.1	16.7	1.1	<0.21	0.25	4.92	2.43	470	37	740	5.06	53	220	74	28	3.2	<0.9	<1.3	13.3	3640	128	1290	149	19	18	1710	115	269	14.5
(33)	b	7.2	13.9	<0.8	<0.25	0.23	4.72	2.36	310	41	709	4.79	43	210	68	23	5.7	<0.7	<1.2	14.6	3650	126	1310	150	17	26	1650	113	238	11.6
	c	10.0	19.2	1.0	<0.26	0.24	4.98	2.42	350	42	700	4.98	32	220	72	23	5.4	<0.8	<1.2	13.5	3550	123	1260	142	16	15	1540	119	214	9.8
35-50	a	8.2	22.4	<1.0	<0.22	0.35	4.30	2.09	410	34	670	3.95	49	280	105	39	6.8	<0.9	4.1	17.6	2570	101	1040	121	20	14	1470	100	198	10.3
(42)	b	9.0	21.2	1.0	0.39	0.31	4.31	2.11	380	45	680	3.88	36	290	104	35	8.6	<0.7	4.3	17.8	2600	103	1060	121	19	20	1470	98	194	9.7
	c	11.2	23.4	<0.9	<0.28	0.36	4.68	2.30	360	36	668	4.20	43	330	117	42	10.1	1.3	4.1	18.0	2650	103	1090	128	17	35	1500	108	180	13.9
50-60	a	7.9	22.2	<1.0	<0.23	0.40	3.99	1.96	360	28	580	3.56	41	240	64	25	5.8	<0.9	2.1	19.5	2400	93	980	110	17	31	1510	79	184	5.5
(55)	b	10.0	21.0	<0.9	<0.29	0.37	3.81	1.93	330	52	535	3.42	25	240	58	21	5.6	0.8	1.5	19.1	2410	98	980	112	14	33	1490	84	172	7.3
	c	9.8	19.7	<0.9	<0.27	0.37	3.79	1.92	320	27	558	3.39	23	220	62	21	7.3	1.2	<1.3	17.2	2320	92	940	110	13	33	1490	84	175	8.6
62-74	a	9.5	23.8	<1.1	<0.24	0.45	4.80	2.16	280	73	670	3.87	52	280	87	28	6.9	<1.0	2.9	17.8	2430	97	1000	110	18	32	1510	94	164	12.4
(68)	b	10.1	23.8	<1.0	0.32	0.40	4.45	2.19	380	53	611	3.75	39	280	80	28	7.1	0.9	3.5	19.5	2520	101	1040	115	14	39	1490	91	180	13.2
	c	10.7	22.7	1.0	<0.31	0.39	4.34	2.14	270	58	612	3.65	49	230	77	28	7.7	<0.8	2.7	18.7	2480	100	1030	111	16	26	1470	83	174	13.3
74-149	a	11.6	23.7	<1.2	0.46	0.51	4.63	2.30	280	59	630	3.68	35	160	70	24	5.0	<1.0	<1.4	22.7	2120	90	890	102	14		1440	80	168	7.5
(100)	b	8.2	21.7	<0.9	<0.32	0.50	4.28	2.19	270	43	584	3.46	18	160	63	23	6.2	<0.8	<1.2	20.6	2130	89	890	100	12	37	1390	70	152	7.3
	c	8.1	19.8	<0.9	<0.30	0.45	4.30	2.19	190	51	574	3.47	24	160	61	23	5.7	<0.8	2.1	20.4	2010	89	880	96	14	6.8	1420	72	141	7.4
>149	a	10.9	23.1	<1.1	0.46	0.68	5.77	2.96	390	56	800	4.54	38	210	78	28	6.2	4.1	<1.7	26.9	2090	93	940	105	13	7.3	1440	68	151	27
(200)	b	8.0	20.1	<0.9	0.65	0.63	5.06	2.62	270	50	703	3.96	26	190	71	24	7.3	3.1	1.8	26.5	1990	91	900	99	18	17.4	1360	73	140	30
	c	8.5	19.5	<0.9	0.55	0.57	4.96	2.62	370	57	663	3.93	25	300	84	28	8.8	3.9	1.6	25.3	1870	84	870	96	16	3.5	2470	79	129	30
NBS	a	14.0	23.4	<0.8	0.89	1.68	5.25	0.725	247	114	498	6.12	99	132	217	42	67	8.1	20	112	1480	69	322	27	29	5.5	2630	79	144	71
Standard	b	12.2	21.0	<0.8	0.86	1.67	5.15	0.791	186	112	483	6.00	101	134	217	41	66	8.5	19	108	1412	67	307	26	27	6.1	2630	66	151	69
Fly Ash	c	11.3	21.5	<0.8	0.87	1.68	5.10	0.784	120	142	498	5.97	96	137	214	40	65	10.6	19	110	1416	68	306	26	28	6.5	2650	77	152	66
	d	9.2	20.0	<0.7	0.97	1.60	4.93	0.772	145	129	454	5.74	90	138	202	39	64	8.3	18	111	1430	68	308	27	29	8.6	2590	68	148	67

* PPM unless otherwise noted (%).

** Size fractions checked using both optical analysis and a Coulter counter.
Estimated mass median diameter (in microns)

dicted for submicron particles by previous models. We show that the concentrations of volatilized elements in submicron particles are much less than expected and, in fact, appear to be independent of particle size for particles less than a few microns in diameter. A possible explanation of these results is presented, formulated in terms of a volatilization–condensation model which also considers an alternate mechanism for the formation of submicron particles. Our observations indicate that submicron particles, for the coal-fired plant under investigation, are composed in large part of elements unlikely to be volatilized during combustion, but yet are much more homogeneous than larger particles. A reasonable mechanism involves the formation of large numbers of very small particles by the bursting of larger particles due to gas evolution. The submicron particles would then result from a combination of processes involving both coagulation of the smaller particles concurrent with the condensation of volatilized elements.

Experimental

A 50-lb sample of fly ash was collected from the precipitators of a coal-fired steam plant located at Centralia, Wash. Fly ash of a given particle size collected from the precipitators is assumed to be identical with fly ash emitted from the plants, except for the most volatile components (i.e., mercury, organic compounds, etc.). Scanning electron micrographs showed a negligible degree of agglomeration of the spherical particles. Thus, while the bulk composition of emitted fly ash and fly ash collected in the precipitators may be quite different, there is no reason to expect any significant differences in the two samples of fly ash if sufficiently well-defined size fractions can be obtained.

A total of approximately 20 lb of fly ash was sized for these analyses. The fly ash size classifications used in this work were obtained using a Bahco microparticle classifier and an air elutriation technique. Each fraction was passed through the classifier several times to ensure sample cleanup and a narrow size distribution of the collected fraction. The final cleanup was completed in an air elutriation apparatus using a fluidized bed to remove the fine particles adhering to the larger particles. Sized samples had physical median diameters (determined using electron and optical microscopy) of approximately 0.15, 0.4, 0.75, 1.3, 2.5, 5, 8, 11, 15, 20, 26, 33, 42, 55, and 68 μm. Size fractions having (physical) mean diameters of approximately 100 and 200 μm were obtained using a sonic sifter. The accuracy of the size fractions was examined using a Coulter counter and electron microscopy. These results indicated the size fractions to be very well defined and strongly centered about the given particle size. Further details of the separation techniques are given elsewhere (*6*).

Three separate samples of each size fraction (with the exception of the two smallest size fractions due to the limited amount of sample) were prepared for X-ray fluorescence (XRF) analysis. Aliquots of the sized fly ash samples were mixed with an equal mass of cellulose (TLC Reagent Grade, J. T. Baker, Phillipsburg, N.J.) in a polyethylene vial containing a 1-cm tungsten carbide ball. The vial was vibrated with a Vortex mixer for ~15 s, after which 500 mg of the mixed powder was pressed into a pellet under 27 000 kg of pressure in a 3.2-cm diameter press and analyzed. National Bureau of Standards Fly Ash (SRM 1633) was prepared in a similar fashion for comparison. A zirconium secondary source and filter were used for measurement of As, Ca, Cu, Cr, Fe, Ga, Ge, K, Mn, Ni, P, S, Si, Ti, Zn, Se, Pb, V, and Zn; a silver secondary source and filter were used for Mo, Nb, Rb, Sr, Y, and Zr; and a filtered ^{241}Am source (100 mCi) was used for Ba, Ce, La, and Sn. All samples were analyzed for 60 min. The secondary sources were excited by a 1.3-kW tungsten X-ray tube. Both the tube and isotope-excited systems were equipped with similar 80-mm^2 Si(Li) detectors with a fwhm of 200 eV at 6.4 keV (Kevex, Inc., Burlingame, Calif.).

The X-ray spectrometer was calibrated with thin single or dual element standards (Micromatter, Inc., Seattle, Wash.) which provided multielement sensitivity curves for each of the three excitation methods. An automatic peak analysis/data reduction program (*12*) related the thin foil calibrations to the thick samples by an iterative matrix correction procedure which accounted for self-absorption, enhancement, and particle size effects in the secondary source-excited spectra. The matrix correction method (*13*) used the back-scattered exciting radiation to help define the total sample matrix and thus permitted calculation of the required sample absorption parameters. The isotope-excited spectra were corrected only for self-absorption using experimentally measured absorption factors. The basic validity of the XRF technique for fly ash analyses has been established previously in this laboratory in a detailed comparison with atomic absorption and instrumental neutron activation techniques (*6*). Good agreement was also noted in the analyses of NBS standard fly ash (see ref *6* and Table I). The precision and accuracy of XRF analyses of fly ash have been discussed previously (*6*); for most of the heavier elements reported in Table I, the uncertainty is less than 5% of the reported value. Somewhat larger error limits must be attributed to the low Z elements; this is particularly true for Al where we estimate error limits of ±50%. A significant portion of the analytical scatter may be ascribed to sample heterogeneity. Possible uncertainties related to sampling statistics and sample heterogeneity have also been examined previously (*6*). These studies have eliminated the possibility of any systematic error or artifact related to particle size (*6*).

Results

The XRF results are collected in Table I. Limited amounts of sample for the two smallest size fractions allowed only two analyses. For the remaining size fractions three separate analyses were carried out. The experimental scatter between samples is due to a combination of factors related to experimental uncertainties and statistical considerations (i.e., the smaller number of particles analyzed for the larger size fractions); these factors have been examined in detail elsewhere (*6*). In addition to the results reported in Table I, the following elements were examined and not observed in concentrations above their detection limits (in ppm): Cl (530), Co (90), Br (1), I (10), Ru (6), Rh (5), Pd (5), In (11), Cd (8), Sb (8), Te (5), Cs (7), Pr (20), Nd (65), Sm (30), Eu (35), U (10), and Hg (10).

The primary concern of the present work is with elements which appear to be volatilized during the combustion process. These elements are readily recognized in Table I by their characteristic enrichment in the smaller size fractions. If a volatilized element does not undergo significant condensation, adsorption, or reaction with the fly ash surfaces, the enrichment between the smallest and largest particles may not be particularly large (e.g., S which escapes primarily as SO_2). Elements which clearly appear to be volatilized during combustion include P, S, Cr, Ni, Cu, Zn, Ga, As, Se, Ge, Mo, Sn, Pb, and perhaps significant amounts of K and V. The remaining elements have concentrations relatively independent of particle size, although some trends well outside experimental error limits are observed. The possible geochemical origin of these phenomena, such as the apparent correlation of Fe and Ti concentrations, has been discussed in our previous work (*6, 7*).

Discussion and Conclusions

The models of Natusch and co-workers (*1*) and Flagan and Friedlander (*11*) predict the dependence of the concentration of volatilized trace elements to be fit by Equations 2 and 3, respectively:

$$C = a + b/D \tag{2}$$

$$C = a + b/D^2 \tag{3}$$

The predicted dependences are illustrated in Figure 1 by the dashed and dotted lines, assuming complete volatilization of the given trace element (i.e., $a = 0$).

The present work clearly shows that the concentrations of important trace elements do not increase dramatically for submicron particles, as implied by previous work (*1*). This result is also supported by the results of an earlier study from this laboratory (*7*), which fit the concentration profiles for nine size fractions (ranging from 0.5 to 50 μm) to the simple models of Natusch and co-workers and Flagan and Friedlander. This work found correlation coefficients of 0.75 and 0.67 for a suite of 27 elements (which were apparently at least partially volatilized) using the two models, respectively. By removing

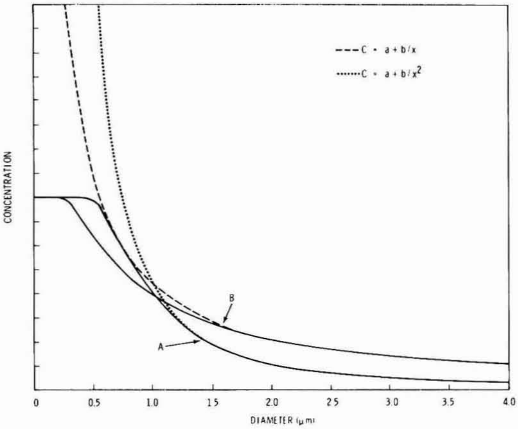

Figure 1. Comparison of the concentration profiles predicted for volatilized elements by the models of Natusch and co-workers (- - -), Flagan and Friedlander (• • •), and two versions of our present model, Equations 6 (A) and 7 (B). Each curve assumes $C_m = 0$, or $a = 0$

the two smallest size fractions (0.5 and 2 µm), the correlation coefficients increased to 0.95 and 0.91, respectively (*7*). Additionally, all reasonable fits using the two simple models yielded curves which predicted much greater concentrations in the two smallest particle sizes than found by our analyses. These previous results may now be viewed as providing support for the present observations.

The implicit assumption of both models is that the surface layer thickness is infinitesimally thin. This, however, contradicts work by Natusch and co-workers (*8, 9*), which suggests surface layers on the order of 0.01 to 0.1 µm thick. Surface analyses at this laboratory indicate the surface layer thickness may be in excess of 0.1 µm in some fly ash samples (*10*).

To apply a volatilization–condensation model (VCM) to a larger range of particle sizes, it is advantageous to generalize the model by assuming a surface layer of thickness L to be deposited over all particles and to assume that all particles are perfectly spherical. By adopting the surface layer thickness predicted by the models of Natusch and co-workers (L independent of D) and Flagan and Friedlander ($L \propto D^{-1}$), one can derive an equation which explicitly accounts for the effect of the surface layer. For the case where L is independent of diameter, the relationship between the bulk concentration (C) of particles of diameter D, the concentration in the matrix (C_m), and the concentration in the surface layer (C_s) of thickness L is given by Equation 4:

$$C = \frac{C_m\rho_m \frac{1}{6}\pi(D - 2L)^3 + C_s\rho_s \frac{1}{6}\pi D^3 - C_s\rho_s \frac{1}{6}\pi(D - 2L)^3}{\rho_m \frac{1}{6}\pi(D - 2L)^3 + \rho_s \frac{1}{6}\pi D^3 - \rho_s \frac{1}{6}\pi(D - 2L)^3} \tag{4}$$

$$\text{for } 2L \le D$$

and

$$C = C_s \qquad \text{for } 2L > D$$

where D = particle diameter, $D - 2L$ = diameter of matrix material before condensation, ρ_m = density of matrix material, ρ_s = density of surface layer, or simply:

$$C = \frac{C_m\rho_m(D - 2L)^3 + C_s\rho_s D^3 - C_s\rho_s(D - 2L)^3}{\rho_m(D - 2L)^3 + \rho_s D^3 - \rho_s(D - 2L)^3} \tag{5}$$

This equation may be simplified by assuming $\rho_m = \rho_s$ to give Equation 6:

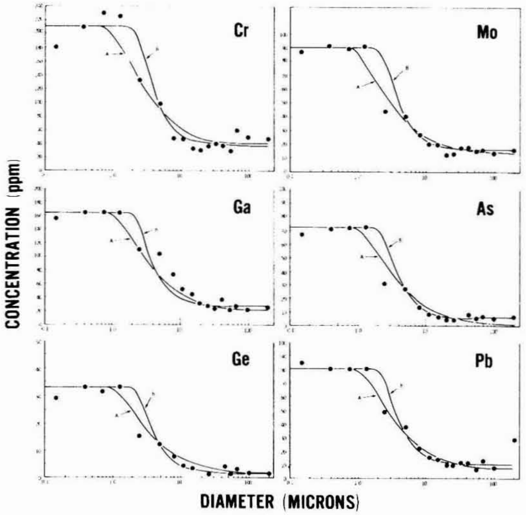

Figure 2. Average concentration vs. particle size profiles for six elements apparently volatilized during combustion. The solid lines give visual fits determined using Equations 6 (A) and 7 (B), and correspond to surface layers of 0.32 ± 1 µm and 1.5 D^{-1} (µm), respectively

$$C = \frac{C_s D^3 + (C_m - C_s)(D - 2L)^3}{D^3} \tag{6}$$

Similarly, a form of the VCM incorporating the assumption that $L \propto D^{-1}$ yields an equation of the form:

$$C = \frac{C_s D^3 + (C_m - C_s)(D - f/D)^3}{D^3} \tag{7}$$

when $2L < D$ (*11*) and where f = a constant and $L = f/2D$. This approach is only an approximation for particle sizes where the surface layer comprises the bulk of the particles, since changes in the particle size (growth) are not considered. A more rigorous analysis shows that not only is the continuum approximation good well into the transition regime, but also that Equation 7 is adequate over most of the particle size range (i.e., $D < \sqrt{f}$), and that $\sqrt{f}$ defines the maximum particle size composed solely of surface material (*14*).

The concentration profiles for volatilized elements can be described by these simple equations, as illustrated in Figure 1. By assuming $C_m = 0$ (equivalent to $a = 0$ in Equations 2 and 3), one can calculate the concentration profiles given by the solid lines A and B from Equations 6 and 7, respectively. In Figure 2, we have used Equations 6 and 7 (curves A and B, respectively) to obtain a visual fit to the data for six elements which are volatilized during the combustion process. It should be noted that the best fits are obtained when C_m is somewhat greater than zero. This implies only partial volatilization of the element under consideration. One should note that the enrichment between the smallest and largest particles is proportional to C_s/C_m.

Our previous analytical results (*6, 7*) for fly ash collected at a separate coal-fired plant were found to fit the assumption that L is independent of D, slightly better than $L \propto 1/D$. Flagan and Friedlander (*11*) have shown that the data of Natusch and co-workers (*1*) may be fit equally well with either Equation 2 or 3. The present results also appear to be fit reasonably well using either Equation 6 or 7. Since one predicts (*11*) a transition from the continuum to free molecule regimes of particle growth to occur on the order of 0.01 µm, one must favor Equation 7 because of its stronger theoretical basis (*14*).

The present analyses, however, suggest the actual mechanism for submicron particle formation is more complex. The results in Table I show that the submicron particles are composed, to a large extent, of elements often assumed to be nonvolatile or having limited volatility under the conditions of coal combustion (e.g., Si, Al, Mg, Ca, etc.). In fact, the concentrations of these elements are not appreciably smaller in the submicron particles than in the large particles. However, the fits illustrated in Figure 2 suggest that particles smaller than approximately 1 μm are composed entirely of volatilized materials (i.e., have a surface layer thickness equal to the particle radius). These results imply either an extremely fortuitous set of volatilities or that the submicron particles are not composed primarily of volatilized materials.

The resolution of this apparent contradiction between the simple volatilization–condensation model and the present results is most likely related to the mechanism for formation of the submicron particles. The results suggest that the majority of submicron particles result from a different mechanism than the larger particles. We presently believe the most reasonable model involves bursting of larger particles during gas release, resulting in formation of a large number of very small particles which coagulate and form a substrate for condensation. This mechanism is consistent with our recent scanning electron micrographs which indicate particles below a few microns in diameter are much less heterogeneous than the larger particles (*14*). Thus, it is unlikely that the bulk of submicron particles result from condensation of volatilized materials on submicron particles resulting from individual submicron molten mineral inclusions; there is no reason to expect submicron mineral inclusions to be any less heterogeneous than the larger mineral inclusions which form the larger fly ash particles. Additionally, other workers have suggested that the number distribution resulting from mineral inclusions is too small for submicron particles to be consistent with observed fly ash number distributions (*11, 15*). A process involving coagulation of many smaller liquid particles, to form a single spherical particle in the 0.1- to 1.0-μm range, would lead to the type of interparticle homogeneity suggested by our electron microscopy results. This mechanism would also be completely consistent with the elemental analyses and the observed concentration vs. particle size profiles.

The "bursting" mechanism for formation of large quantities of submicron particles is suggested by the physical characteristics of larger fly ash particles. A large fraction of particles in the 5 to 100 μm size range consists of either empty (hollow) spheres, known as cenospheres, or hollow spheres packed with large numbers of smaller spheres (plerospheres). The hollow spheres apparently result from H_2O, CO_2, and SO_2 evolution during rapid heating, which causes a "ballooning" of the liquid particles (*16*). The inner smaller spheres apparently result from an internal process also related to the gas release. At temperatures slightly higher than that required for cenosphere formation, the viscosity of the liquid particles will be sufficiently small that the particles may burst, resulting in a shower of much smaller particles. Ramsden (*17*) has obtained experimental evidence for the validity of this particle formation mechanism and observed the formation of large numbers of droplets in the 0.1-μm size range. Since most particles in the larger size fractions from these two plants are either cenospheres or plerospheres, the bursting mechanism is a likely mode of formation for submicron particles. Additionally, sputtering experiments show that hollow particles are extremely rare in the smaller size fractions (*18*), consistent with a different mechanism of formation than the larger particles and possibly involving coagulation of smaller particles.

The observed concentration profiles for volatilized elements (Figure 2) may be qualitatively rationalized in terms of this mechanism. Particles resulting from the simple volatilization process followed by condensation on the surface of a distribution of particle sizes will give concentration profiles which continue to increase with size. This mechanism appears to dominate for particles larger than a few microns. However, as pointed out by Flagan and Friedlander (*11*), the size distribution of mineral inclusions in coal would produce too few particles in the submicron size range and this mechanism might be unimportant compared to other processes producing submicron particles (such as the "bursting" mechanism). Particles resulting from the bursting–coagulation mechanism will have concentrations of volatilized elements determined by the relative amounts of condensation occurring before the bursting process, between bursting and coagulation, during coagulation, and following completion of coagulation. If all condensation occurred prior to the completion of coagulation, the concentration of volatilized elements would be nearly independent of particle size in the size range dominated by the coagulation process.

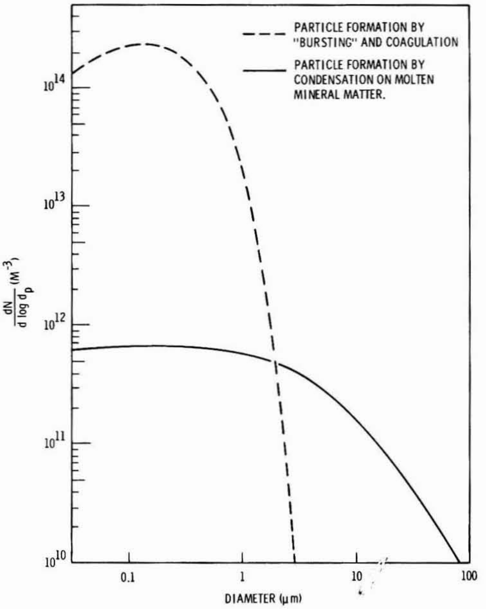

Figure 3. Number distributions of fly ash particles which might be formed by two different mechanisms: (- - -) particles resulting from bursting of larger particles during gas release followed by both condensation of volatilized materials and coagulation to form particles which dominate the submicron size range, and (—) a distribution of particle sizes resulting from the particle size distribution of mineral matter in coal as determined by Padia (*15*)

The type of concentration profiles expected from this mechanism may be demonstrated in a more quantitative manner. We first assume two distinct distributions of particles, one which dominates in the submicron size range due to the bursting mechanism, and a second simply due to condensation on molten mineral inclusions. The first has a concentration, to a first approximation and as discussed above, independent of particle size. The latter concentration may be described by Equation 7 for the most reasonable case of $L \propto D^{-1}$. Thus, the bulk concentration for any given particle size is:

$$C = X_1 C_b + (1 - X_1)\,\frac{C_s D^3 + (C_m - C_s)(D - f/D)^3}{D^3} \qquad (8)$$

where C_b is the concentration of the element in the particles formed by coagulation and X_1 is the fraction of particles of diameter D due to coagulation of particles formed by the bursting process.

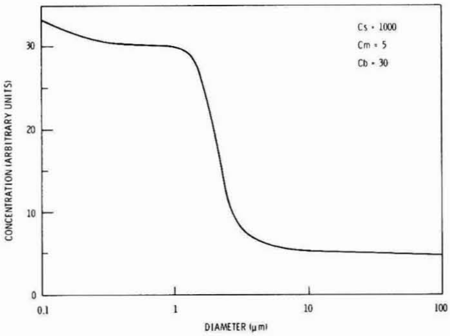

Figure 4. Concentration vs. particle size behavior predicted using the number of distributions given in Figure 3 and applying Equation 8 and setting C_s = 1000, C_m = 5, and C_b = 30

The application of Equation 8 may be illustrated by assuming a particle size distribution for the two mechanisms discussed above. In Figure 3, we approximate the distributions which might be expected. The solid line approximates the mineral size data of Padia (*15*) and the dashed line approximates a hypothetical distribution of particles due to coagulation of many smaller particles in the 0.01 to 0.2 μm size range. We now apply Equation 8 assuming a small surface layer (f = 0.01), C_s = 1000, C_m = 5, and C_b = 30. Figure 4 gives the concentration profile predicted from the two distributions using Equation 8. It should be noted that this profile is quite similar to those obtained by application of Equation 7 where the surface layer thickness is much greater (as in Figure 2), and where it is necessary to assume that the submicron particles are composed completely of volatilized material. The reasons for this similarity are not coincidental; by considering the coagulation of submicron particles on the entire range of particle sizes, instead of gas-phase species, the two models are almost identical. Thus, the model involving bursting followed by coagulation can be consistent with the observed concentration profiles.

Two important conclusions may be drawn from the present results. First, the increase in concentration of volatilized trace elements in the smallest particles is much less than would have been predicted by previous work. This is important since submicron particles are emitted most efficiently [the collection efficiency drops significantly in the 0.1- to 1-μm size range for most pollution control devices presently employed (*19–21*)], have the highest atmospheric mobility, and the greatest potential toxicity. Second, the results suggest a mechanism for formation of the submicron particles. This mechanism involves "bursting" of larger particles during gas expansion and production of a very large number of very small particles which ultimately form particles in the 0.1- to 1.0-μm size range by coagulation. The condensation of volatilized material would then proceed concurrently with the bursting and coagulation process.

Acknowledgments

We wish to thank A. L. Roese of Battelle—Columbus for assistance in obtaining the size fraction separations and W. D. Felix for helpful comments during the preparation of this paper.

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Received for review February 3, 1978. Accepted December 8, 1978. This paper is based on work performed under U.S. Department of Energy, formerly Energy Research and Development Administration, Contract No. EY-76-C-06-1830.

Atmospheric Chemistry of Automotive Lead

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■ Techniques based upon X-ray powder diffraction (XRD) have been developed for the identification of lead compounds present in ambient air polluted by vehicle exhaust. Three of the compounds identified are known to be present in automobile exhaust: PbBrCl, $PbBrCl \cdot 2NH_4Cl$, and α-$2PbBrCl \cdot NH_4Cl$. The other compounds analyzed were $PbBrCl \cdot (NH_4)_2BrCl$, $PbSO_4$, and $PbSO_4 \cdot (NH_4)_2SO_4$, the latter being the predominant form of lead at four of five sampling sites. In laboratory experiments designed to elucidate the formation of these compounds, vehicle-generated PbBrCl was exposed to a range of gaseous and particulate pollutants and the products were examined by XRD. The major process affecting primary lead particulates was found to be coagulation with ambient aerosol accompanied by reaction of PbBrCl with neutral and acid sulfates.

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Table I. Summary of Site Conditions

site description	environment	approx. traffic flow, vpd	ambient particulate Pb, $\mu g\ m^{-3}$	mass median equiv diam, μm		% $\leq$ 2.1 μm	
				TSP	Pb	TSP	Pb
Lancaster Town Hall (A6 Rd.), Lancs.	urban	20 000	1.0–6.0	2.6	0.9	45	69
Preston, Fulwood (A6 Rd.), Lancs.	urban	20 000	0.5–1.6	1.7	0.8	56	74
Barton Green (A6 Rd.), Lancs.	rural	14 000	0.1–0.4	1.8	0.3[a]	54	89
M6 Motorway, Red Scar nr. Preston, Lancs.	suburban/ rural	70 000	0.1–1.7	1.9	0.5	54	85
H.S.E. Cricklewood Labs., London (A5 Rd.)	urban		0.4–2.0	2.8	0.8	43	70

[a] Extrapolated value.

The use of tetraethyl- and tetramethyllead as antiknock additives in gasoline is largely responsible for the presence of lead in the urban atmosphere (*1–3*). Concern over possible adverse health effects has led to a wealth of research activity on various aspects of lead as an environmental pollutant, but one area which hitherto has been poorly understood is the atmospheric chemistry of automotive lead.

The lead compounds emitted in the exhaust gases from spark ignition engines have been identified in laboratory studies using X-ray powder diffraction (*4, 5*). It has been shown that lead bromochloride, PbBrCl, is the principal lead compound in exhaust emissions when leaded petrol containing the scavengers 1,2-dichloroethane (EDC) and 1,2-dibromoethane (EDB) is burned in the combustion chamber.

As the major anthropogenic source of atmospheric lead and bromine is automobile exhaust (*3*), the Br/Pb ratio has been used as an indication of aging of the lead aerosol and also as an indirect estimate of nonautomotive sources of lead (*6*). Various workers have determined particulate Br/Pb ratios in ambient air (*7–10*), finding both geographical and seasonal variations. The measured Br/Pb ratio is generally lower than that expected for primary exhaust particulates, with a greater loss of bromine in summer than in winter reported by workers in California (*8*), Perth, Australia (*9*), and in Britain (*10*).

There have been various attempts to elucidate the atmospheric chemistry of PbBrCl and hence to explain the phenomenon of bromine loss. Pierrard has reported a slow photochemical breakdown of PbBrCl causing release of bromine and chlorine (*11*). Other reports, however, have indicated that light is not essential for the decomposition of PbBrCl. Robbins and Snitz (*12*) investigated the halogen loss from fresh exhaust particles contained in a large bag and found that within the first 0.5 h the halogen component was lost rapidly in the absence of light. This finding was confirmed by the black bag experiment carried out by Ter Haar and Bayard (*13*). The latter workers suggested that the halogen loss from the lead halide compounds emitted from the exhaust was due to simple acid–base reactions involving carbonate or hydroxide ions, rather than a photolytic process, but did not explain the source of these ions in the atmosphere. This mechanism was further investigated by Boyer and Laitinen (*14*), who examined the reaction of laboratory-pure lead halide aerosols with CO_2 and H_2O vapor and found that the lead halide was quite stable with respect to reaction with these species, both in the presence and absence of light of wavelength 300–400 nm. They exposed PbBrCl to 9% CO_2 in moist air at 50 °C in the dark over a 72-h period and found only 0.4% halide loss during decomposition, with slight enhancement during illumination, concluding that the large halogen losses observed from automobile exhaust particulates could not be replicated in the absence of the automotive exhaust environment.

The discrete analysis of individual airborne particles has been carried out as another approach to yield information on the types of lead compounds in the atmosphere. A qualitative elemental analysis has been performed using a scanning electron microscope coupled to an X-ray energy dispersive spectrometer (SEM/XES), upon individual particles collected from the atmosphere (*15–17*). Ter Haar and Bayard (*13*), using an electron microprobe (EMP), reported the identification of 14 different lead compounds in atmospheric samples. However, the limitations of the EMP technique used by these workers have since been pointed out by Heidel and Desborough (*18*) and considerable doubt must attach to the structural assignments. A drawback of both SEM/XES and EMP techniques is that only individual particles may be examined and, hence, it is extremely difficult to examine sufficient particles to determine the overall chemical nature of the lead particles in the bulk sample.

A technique which is capable of providing unequivocal characterization of major crystalline components of a mixture is X-ray powder diffraction (XRD). A previous attempt at identification of lead compounds in urban atmospheres using XRD was unsuccessful (*19*). The main problem encountered was the low concentration of lead present in the overall particulate matter (about 1%) and the interference of quartz, clays, and other minerals. It is generally accepted that the atmospheric size distribution of particulate matter is bimodal, with a minimum abundance at about 1–2 μm aerodynamic diameter (*20, 21*). Particles above this aerodynamic diameter are usually derived from natural erosion processes and reentrained dust. Particles below 2 μm are mainly generated by combustion processes and secondary aerosol formation. Research work has shown that the lead particles are predominantly in the smaller size fraction, whereas interfering particles containing minerals and compounds of iron and calcium are in the larger size range (*22–25*). Sampling only the ambient particulates below 2 μm serves to concentrate the lead compounds for analysis. On this basis, Biggins and Harrison (*26*), using X-ray diffraction on a qualitative level, have recently successfully identified lead compounds in urban air. They reported the predominance of $PbSO_4 \cdot (NH_4)_2SO_4$, a hitherto unknown lead compound in the atmosphere. This paper reports the continuation of that study, with the aim of elucidation of the atmospheric chemistry of PbBrCl, and hence the mechanism of formation of $PbSO_4 \cdot (NH_4)_2SO_4$ and other atmospheric lead compounds of automotive origin.

Experimental

(a) Airborne Particulate Sampling and Analysis. A sampling program was established to identify the lead species in ambient air at five locations, described in Table I. Andersen 2000 cascade impactors were modified so that all particulate material below 2.1 μm would be collected on a single stage. The sampling period was 1 week to collect sufficient material for analysis. The particulate on the collection medium (Gelman binderless glass fiber filter paper) was ultrasonically stripped

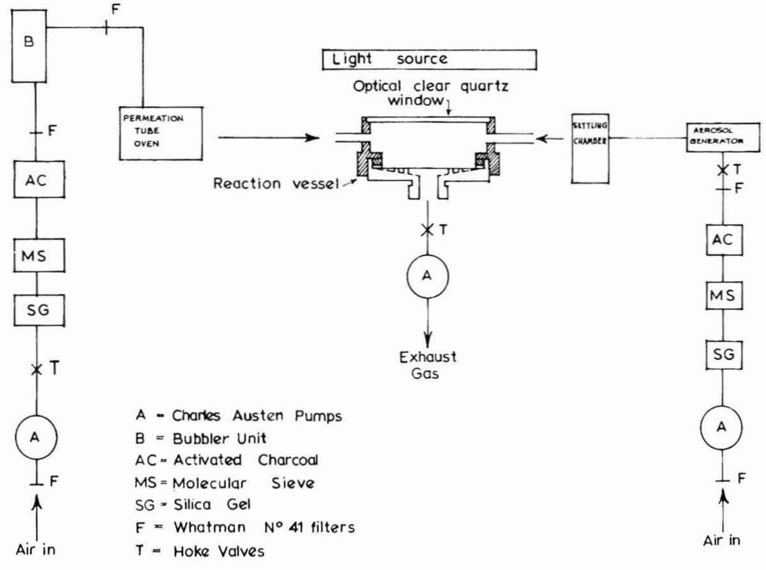

Figure 1. Schematic layout of exposure system for use with gaseous and aerosol droplet pollutants

into aromatic-free *n*-hexane for 30 min and then filtered onto a 0.22-μm Millipore cellulose ester filter. In addition, 48-h Hi-Vol filter samples were collected on Whatman GF/A glass fiber filter paper using a Staplex Hi-Vol pump. The particles were stripped ultrasonically from the filters and those of density >3.32 g cm^{-3} were separated by centrifugation in diiodomethane (*27*).

The samples were analyzed by XRD with a Philips XDC700 Guinier camera using totally monochromatized Cu Kα_1 radiation. The resultant photograms were identified by matching of both *d* spacings and intensities using a Fink search manual (*28*), comparing with standard films, and verifying the matchings with the JCPDS diffraction files (*29*). Identification of some of the unknown photograms was facilitated by the use of standard films obtained from powder samples of ammonium lead halides which were generously donated by Dr. L. M. Niebylski of the Ethyl Corporation. Synthesis of the $(NH_4)_2Pb(SO_4)_2$ standard was accomplished by a modification of the method of Møller (*30*).

(b) Laboratory Study. This study was set up to investigate the chemical reactions involved in formation of the lead compounds observed in the ambient air. As PbBrCl is the principal exhaust component, it was decided to use the lead halides generated direct from a test engine to provide a representative sample in terms of size, morphology, and chemical composition. A sampling probe was positioned near the exhaust manifold of a 1.3-L Ford Cortina engine, which was linked to a Froude-Heenan Hydraulic Dynamometer DPX. The engine was run under constant conditions of 1500 rpm with a load of 40 N·m, and sampling was carried out when the exhaust gas temperature prior to sampling had stabilized between 580 and 600 °C. The sampling probe temperature immediately preceding the filter was approximately 220 °C. Preweighed Whatman GF/A glass fiber filters were used as the collecting medium and samples were stored in individual Petri dishes within a desiccator in the dark. The filters were weighed and then analyzed directly with a Philips powder diffractometer using Cu Kα radiation, the output being in a chart of 2θ angles against intensity. In most cases, PbBrCl was the only crystalline phase identified with all the interplanar *d* spacings being assigned, while in a few cases PbO was also detected at a very trace level. The finding of only PbBrCl, which had a consistent Br/Cl ratio of 1.0 as indicated by the diffraction pattern (*14*), must reflect the engine sampling conditions. The fuel used was commercial Texaco 3-star with a mole ratio of Pb:EDB:EDC of 1:0.5:1.

A reaction vessel shown in Figure 1 was designed to subsequently accommodate the vehicle exhaust filter such that air, pollutant gases, and aerosol droplets could be drawn through or onto the filter. Samples from the engine were obtained in batches and quality control checks were carried out with XRD to confirm the purity of PbBrCl. In some cases, as an additional safeguard, filters that had been identified as having only PbBrCl present were exposed in the reaction vessel to verify the reaction that had taken place. The light source used in the photolysis experiments was a 20 J s^{-1} Philips Actinic Blue 05 Lamp with a spectral range between 300 and 500 nm, yielding an irradiance of 6.2 mW cm^{-2} on the filter surface. Known concentrations of SO_2 and NH_3 were supplied by a permeation tube system, and a relative humidity of 100% was achieved by the passage of clean air through two bubblers of deionized distilled water in series. The air to the bubblers and the permeation tube system was cleaned by passage through Whatman 41 filters, silica gel, molecular sieve 13X and 5A, and activated charcoal (see Figure 1).

A series of experiments was performed in which the vehicle exhaust filter was exposed to an aerosol of H_2SO_4, NH_4HSO_4, or $(NH_4)_2SO_4$. For this purpose a specially designed aerosol generator was used, allowing a known volume of solution of the reagent to be atomized into a 2-L polyethylene flask from which a portion of the fine droplets could be drawn off onto the filter via a settling chamber. The output of the aerosol generator was evaluated using a Casella cascade impactor and the droplets were found to be <10 μm diameter, and predominantly ≤1 μm. The amount of SO_4^{2-} from the aerosol generator collected on the filter was analyzed by the barium chloride turbidimetric method (*31*). The amount of PbBrCl on the filter was determined by analysis of Pb by flame atomic absorption spectrometry. Since the ratio of the mass of total particulate matter on the filter to that of lead was found to be almost constant, the filter weight was used to estimate the amount of PbBrCl present.

Exposed filters were dried in a desiccator for 24 h and analyzed directly using the Philips powder diffractometer. To

Table II. Ambient Lead Compounds Identified by XRD at Various Sites

site	date	chem phases identified
	1977	
M6 Motorway	Oct 26–31	$PbSO_4 \cdot (NH_4)_2SO_4$
	Oct 31–Nov 7	$PbSO_4 \cdot (NH_4)_2SO_4$
	Nov 7–14	$(NH_4)_2SO_4$
	Nov 14–21	$PbSO_4 \cdot (NH_4)_2SO_4$; $PbBrCl \cdot (NH_4)_2BrCl$
	Nov 21–28	$PbSO_4 \cdot (NH_4)_2SO_4$; $PbBrCl \cdot (NH_4)_2BrCl$
Preston, Fulwood	Aug 1–8	$PbSO_4 \cdot (NH_4)_2SO_4$; PbBrCl (minor phase)
	Aug 8–15	$PbSO_4 \cdot (NH_4)_2SO_4$
	Sept 12–19	$PbSO_4 \cdot (NH_4)_2SO_4$
	Sept 20–27	$PbSO_4 \cdot (NH_4)_2SO_4$
	Oct 4–11	$PbSO_4(NH_4)_2SO_4$; $PbSO_4$
Barton Green	Oct 4–11	$PbSO_4$
	1978	
H.S.E. London	Feb 28–Mar 7	$PbSO_4 \cdot (NH_4)_2SO_4$
	Mar 21–28	$(NH_4)_2SO_4$
	Apr 4–11	$PbSO_4 \cdot (NH_4)_2SO_4$; $(NH_4)_2SO_4$

Table III. Ambient Lead Compounds Identified by XRD at the Lancaster Town Hall Site

date	chem phase identified
1977	
May 5–7[a]	$PbSO_4 \cdot (NH_4)_2SO_4$; $PbSO_4$
May 17–24	$PbSO_4 \cdot (NH_4)_2SO_4$; PbBrCl; $(NH_4)_2SO_4$
May 17–19[a]	$PbSO_4 \cdot (NH_4)_2SO_4$; $PbSO_4$
May 24–31	$PbSO_4 \cdot (NH_4)_2SO_4$
May 31–June 8	$PbSO_4 \cdot (NH_4)_2SO_4$
July 1–8	$PbSO_4 \cdot (NH_4)_2SO_4$
1978	
Jan 30–Feb 6	$PbSO_4 \cdot (NH_4)_2SO_4$; α-$2PbBrCl \cdot NH_4Cl$; $PbBrCl \cdot 2NH_4Cl$; NH_4Cl
Feb 6–13	$PbSO_4 \cdot (NH_4)_2SO_4$; $(NH_4)_2SO_4$; [b]
Feb 13–20	$PbSO_4 \cdot (NH_4)_2SO_4$; $(NH_4)_2SO_4$; [b]
Feb 20–27	$PbSO_4 \cdot (NH_4)_2SO_4$; α-$2PbBrCl \cdot NH_4Cl$
June 30–July 7	$PbSO_4 \cdot (NH_4)_2SO_4$; α-$2PbBrCl \cdot NH_4Cl$; PbBrCl
July 7–14	$PbSO_4 \cdot (NH_4)_2SO_4$

[a] These results were obtained using the Hi-Vol sampler. [b] Diffraction pattern identical with a product of $PbBrCl \cdot (NH_4)_2SO_4$ (excess) reaction (see text).

ensure comparability, some reaction products were also examined using the Guinier camera.

Results and Discussion

(a) Analysis of Atmospheric Particulates. The MMEDs of lead and total suspended particulates were determined at each site, the results appearing in Table I. The values for lead of 0.3–0.9 μm are in good agreement with those reported by Skogerboe et al. (*32*) and other workers.

The compounds identified by XRD are listed in Tables II and III. The majority of samples were collected using Andersen impactors, as the size fractionation afforded by this technique was thought to be valuable in the context of respiratory exposure to lead. At four of the five sites the dominant lead compound was $PbSO_4 \cdot (NH_4)_2SO_4$. This compound has not, to our knowledge, been reported previously as occurring in the environment, and its repeated presence led to some speculation as to the mechanism of formation. Other lead compounds identified were $PbSO_4$, reported by Olsen and Skogerboe (*27*) to be the predominant compound of lead in street dusts and roadside soils, PbBrCl, and the ammonium lead halides, α-$2PbBrCl \cdot NH_4Cl$, $PbBrCl \cdot 2NH_4Cl$, and $PbBrCl \cdot (NH_4)_2BrCl$, identified by comparison with standard samples provided by the Ethyl Corporation.

In general, the atmospheric samples exhibited rather broad diffraction lines, consistent with the small size of the crystalline particles. The excellent degree of matching between environmental samples and standards is exemplified by Figure 2, showing the sample collected at the Lancaster Town Hall site on Jan 30–Feb 6, 1978 (sample LT1), compared with standard Guinier camera photograms of $PbSO_4 \cdot (NH_4)_2SO_4$, $PbBrCl \cdot 2NH_4Cl$, and α-$2PbBrCl \cdot NH_4Cl$, and with the three photograms superimposed. Only three major diffraction lines are left unassigned, and these are due to NH_4Cl.

The most comprehensive data are available for the urban Lancaster Town Hall site where sampling was carried out over a period of a year (Table III). This was the only site at which the two ammonium lead halide salts α-$2PbBrCl \cdot NH_4Cl$ and $PbBrCl \cdot 2NH_4Cl$ were observed, and this is consistent with the observation of Hirschler et al. (*4*) that in a city driving cycle these compounds are emitted from vehicles in a greater degree than under full-throttle conditions. Hence, their presence at the motorway and Preston sites, at which traffic moved far more freely, would not be expected. The typical lead additive composition used in gasoline in Britain over the sampling period was a mole ratio of Pb:EDC:EDB of 1:1:0.5, giving a probable excess of HCl within the exhaust system. Hence, the formation of the two ammonium lead halide salts may be explained by reaction of lead bromochloride with NH_4Cl, formed by reaction of HCl with ammonia either within the vehicle exhaust system, as suggested by Hirschler et al. (*4*), or in the ambient air as Habibi (*5*) proposed:

$$HCl + NH_3 \rightarrow NH_4Cl \tag{1}$$

$$PbBrCl + 2NH_4Cl \rightarrow PbBrCl \cdot 2NH_4Cl \tag{2}$$

$$2PbBrCl + NH_4Cl \rightarrow \alpha\text{-}2PbBrCl \cdot NH_4Cl \tag{3}$$

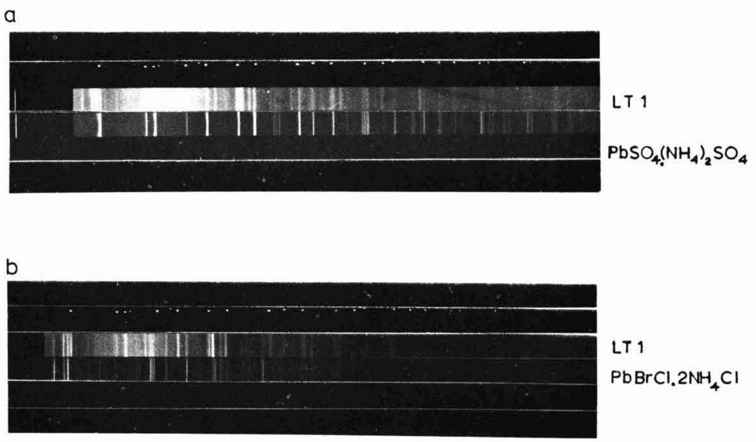

Figure 2. Comparison of sample, LT1, with standard compounds: (a) LT1 and $PbSO_4{\cdot}(NH_4)_2SO_4$; (b) LT1 and $PbBrCl{\cdot}2NH_4Cl$; (c) LT1 and α-$2PbBrCl{\cdot}NH_4Cl$; (d) LT1 and $PbSO_4{\cdot}(NH_4)_2SO_4$, $PbBrCl{\cdot}2NH_4Cl$, and α-$2PbBrCl{\cdot}NH_4Cl$

The presence of NH_4Cl in one sample from the Lancaster Town Hall site lends support to this mechanism. The PbBrCl–NH_4Cl reaction was the subject of a laboratory study (vide infra).

It should be emphasized at this stage that all sites, other than the London site, were selected for their freedom from industrial sources of lead, and it may be said with confidence that the lead compounds encountered arise from vehicle emission, or the chemical amendment of vehicle-emitted lead. Hence, PbBrCl, $PbBrCl{\cdot}2NH_4Cl$, and α-$2PbBrCl{\cdot}NH_4Cl$ are compounds observed in automobile exhaust analysis studies (*4, 5*), but the existence of $PbSO_4{\cdot}(NH_4)SO_4$, the predominant atmospheric lead compound, $PbSO_4$, and $PbBrCl{\cdot}(NH_4)_2BrCl$ all required explanation.

(b) Laboratory Study. (*i*) *Reactions of PbBrCl with Atmospheric Gases.* Photolysis in a stream of nitrogen or air at either zero or 100% relative humidity caused no change over 24 h, as detectable by XRD, consistent with the findings of Boyer and Laitinen (*14*). The addition of 3 ppm of SO_2 also caused no change, hence indicating that any reaction of PbBrCl with SO_2 was very slow, although since the residence time of SO_2 in the reaction vessel was very short, no inference could be drawn regarding reactions with SO_2 oxidation products.

No reaction with ammonia at 1.1 ppm was observed at zero relative humidity, but in saturated air in light or dark after 40 h the presence of α-$2PbBrCl{\cdot}NH_4Cl$ and Pb(OH)Br at a trace level was detected together with unchanged PbBrCl. We postulate a reaction pathway as follows:

$$PbBrCl + NH_3 + H_2O \rightarrow Pb(OH)Br + NH_4Cl \quad (4)$$

$$NH_4Cl + 2PbBrCl \rightarrow \alpha\text{-}2PbBrCl{\cdot}NH_4Cl \quad (5)$$

In a similar experiment, when water droplets were carried over from the humidifier in the presence of ammonia, an enhanced formation of Pb(OH)Br occurred, but in the absence of NH_3 no reaction ensued. Hence the presence of both NH_3 and H_2O appears to be essential, suggesting the intermediate formation of NH_4OH. Exposure of PbBrCl to an aerosol mist of ammonia solution caused the same reaction to occur.

The reaction of PbBrCl with NH_4Cl was investigated in the laboratory using an aerosol mist of 1 M NH_4Cl solution, and the formation of α-$2PbBrCl{\cdot}NH_4Cl$ was demonstrated by XRD (reaction 5).

(*ii*) *Reaction of PbBrCl with H_2SO_4.* Since the reaction with ammonia and water had achieved the introduction of ammonium chloride into a double salt with lead bromochloride, we felt it possible that subsequent reaction with sulfuric acid

Table IV. Products of the Reaction of PbBrCl with 1 M NH_4HSO_4 and 1 M $(NH_4)_2SO_4$, Identified by XRD

mole ratio NH_4HSO_4:$(NH_4)_2SO_4$	products identified[c]
1:0	$PbSO_4$ (m); *b*; *a*
2:1	$PbSO_4$ (m); *a*; *b*
1:1	$PbSO_4$ (m); *a*; *b*
1:2	$PbSO_4$ (min); *a*; *b* (t)
1:3	$PbSO_4$ (t); $PbSO_4 \cdot (NH_4)_2SO_4$; *a*, *b* (t)
0:1	$PbSO_4 \cdot (NH_4)_2SO_4$ (m); *b*, *a*

[a] α-2PbBrCl·NH_4Cl. [b] 2PbBrCl·NH_4Br; postulated structure. [c] m = major phase; min = minor phase; t = trace level.

Table V. Products of the Reaction of PbBrCl with Varying Mole Ratio $(NH_4)_2SO_4$

mole ratio of PbBrCl:$(NH_4)_2SO_4$	products identified[c]
3:1	α-2PbBrCl·NH_4Cl (m); PbBrCl (m); $PbSO_4 \cdot (NH_4)_2SO_4$ (t)
1.5:1	α-2PbBrCl·NH_4Cl (m); $PbSO_4 \cdot (NH_4)_2SO_4$ (min); *a*
1:1	PbBrCl·$(NH_4)_2BrCl$ (m); $PbSO_4 \cdot (NH_4)_2SO_4$ (m)
1:1.5	$PbSO_4 \cdot (NH_4)_2SO_4$ (m); *a*
1:2	$PbSO_4 \cdot (NH_4)_2SO_4$ (m); *b* (m)

[a] Other diffraction lines were unassigned. [b] Possibly PbBrCl·2$(NH_4)_2BrCl$ (see text). [c] t = trace level; min = minor phase; m = major phase.

aerosol would produce $PbSO_4 \cdot (NH_4)_2SO_4$. The laboratory experiment did not in fact produce this product, but $PbSO_4$ was identified together with other unassignable diffraction lines.

When lead bromochloride itself was exposed to a mist of 1 M H_2SO_4 in light or dark, lead sulfate was the sole product, indicating the reaction:

$$PbBrCl + H_2SO_4 \rightarrow PbSO_4 + HBr + HCl \quad (6)$$

(iii) Reaction of PbBrCl with NH_4HSO_4 and $(NH_4)_2SO_4$. Having now gained an impression of the pattern of reactivity of PbBrCl, our next step was to examine the dark reaction with aerosol mists of NH_4HSO_4 and $(NH_4)_2SO_4$, both of which exist in the atmosphere in some abundance (*33–37*), being derived from the neutralization by ammonia of sulfuric acid formed from sulfur dioxide oxidation. These two reagents were used either singly or in combination, and the reaction products are shown in Table IV. In reaction with pure 1 M NH_4HSO_4, the major product was $PbSO_4$, accompanied by diffraction lines characteristic of lead ammonium halides. One product was the same as that generated by reaction of PbBrCl with NH_4Br, believed to be of structure 2PbBrCl·NH_4Br, unconfirmed due to the absence of a standard. Trace amounts of α-2PbBrCl·NH_4Cl also appeared to be present. Hence the reaction appears to be:

$$6PbBrCl + 2NH_4HSO_4 \rightarrow 2PbSO_4 + 2PbBrCl \cdot NH_4Br + \alpha\text{-}2PbBrCl \cdot NH_4Cl + HCl + HBr \quad (7)$$

A decrease in the ammonium bisulfate relative to ammonium sulfate caused a progressive decrease in $PbSO_4$ formation, accompanied by the appearance of $PbSO_4 \cdot (NH_4)_2SO_4$. With pure 1 M $(NH_4)_2SO_4$, the major product was $PbSO_4 \cdot (NH_4)_2SO_4$, although repetition of the experiment was accompanied by changes in the other diffraction lines. To examine this effect, a group of PbBrCl filters was selected such that each had a similar mass loading. These were then exposed to different quantities of 1 M $(NH_4)_2SO_4$, the experimental results being shown in Table V.

The most significant reaction is that occurring at a 1:1 mole ratio, which formed two compounds which are found together at the motorway site (Table II):

$$2PbBrCl + 2(NH_4)_2SO_4 \rightarrow PbSO_4 \cdot (NH_4)_2SO_4 + PbBrCl \cdot (NH_4)_2BrCl \quad (8)$$

Reaction with excess ammonium sulfate led to the formation of a compound with an identical diffraction pattern to the unidentified compound encountered in the presence of unreacted $(NH_4)_2SO_4$ at the Lancaster Town Hall site on Feb 6–13 and Feb 13–20, 1978. The structure was not established due to the lack of a standard, but we postulate that it may be PbBrCl·2$(NH_4)_2BrCl$. Other reactions also gave rise to unassigned diffraction lines, apparently similar to those of the known lead ammonium halides. The formation of α-2PbBrCl·NH_4Cl in experiments with excess PbBrCl offers an alternative explanation of the existence of this compound in the atmosphere.

One point which emerged in this latter work arose from experiments in which the concentration of the $(NH_4)_2SO_4$ reagent solution was varied from 0.25 to 4 M, while maintaining a similar total mass exposure to the compound. When solutions of 0.25 M were used, the formation of $PbSO_4$, rather than $PbSO_4 \cdot (NH_4)_2SO_4$, was observed. This is apparently a result of the known high solubility of $PbSO_4$ in ammoniacal solutions, but not in water. Hence in a strongly ammoniacal solution PbBrCl and $(NH_4)_2SO_4$ react with the ultimate formation of $PbSO_4 \cdot (NH_4)_2SO_4$ and lead ammonium halides, while in dilute solutions $PbSO_4$ rapidly precipitates and this appears as the major product.

(c) The Atmospheric Reactions of PbBrCl. It is now well established that neutral and acid sulfates are important chemical constituents of the atmosphere (*35–37*). Indeed, in a recent paper Tanner and Marlow (*36*) have shown that in samples collected at Glasgow, Ill., about 40% of the total aerosol mass was comprised of sulfate and in suboptically sized particles sulfate accounted for an average of 98% of the aerosol mass, in association principally with the cations NH_4^+ and H^+.

Both H_2SO_4 and NH_4HSO_4 are hygroscopic and form aqueous solution droplets at all humidities from 30 to 100% (*37*, *38*), while $(NH_4)_2SO_4$ is a deliquescent salt which undergoes a transition from the dry crystal to the solution droplet at 81% relative humidity (*37*). Since $(NH_4)_2SO_4$ is probably formed within a solution droplet of NH_4HSO_4 by reaction with ammonia, it may remain as a solution droplet for some considerable time at lower humidities (*39*), especially if the droplet lacks crystallization nuclei (*40*). Hence in Britain, where high relative humidity is common, it might be expected that sulfates exist predominantly as solution droplets of extremely small diameter.

Chamberlain et al. (*23*) have shown that primary vehicle exhaust lead particulate is approximately 0.015 μm in diameter. Measurements of particle size close to a rural section of a motorway showed a mass mean diameter for lead of 0.03–0.05 μm, while close to the same motorway within a heavily urbanized area there was a substantial shift toward larger particle sizes, which these workers attributed mainly to coagulation with the general urban aerosol. The coagulation process arises from adhesion of particles colliding as a result of Brownian diffusion. Such processes are highly dependent upon particle size and number density, being extremely rapid for particles as small as 0.015 μm in diameter, but very much slower for large particles, becoming unimportant for particles of >0.5 μm diameter (*41*).

It is therefore clear that the vehicular lead is exhausted into an environment where the most rapid physical process is one of coagulation with other fine particles, which are predominantly sulfate droplets. Hence, our laboratory experiments in which lead bromochloride particles are exposed to an aerosol mist of sulfates are a realistic expression of the physical process occurring within the atmosphere, and hence the chemical processes are likely also to be a close parallel.

A question of considerable current interest is that of filter artefacts: substances formed on the filter during air sampling. We have considered the possibility that the compounds which we observed are formed, at least in part, on the surface of the filter. We reject this possibility, since although lead and sulfate represent a substantial proportion of the submicrometer aerosol, their contribution to the total aerosol volume (in Hi-Vol sampling), and to the $\leqslant 2.1$ μm size range (in Andersen impactor sampling) is far smaller. Hence, in a random deposition of lead bromochloride and sulfate particles on a filter surface, the probability of deposition in contact is small, and reaction occurring in this manner is likely to be only a minor contributor to product formation, since coagulation in the atmosphere is such a rapid process. It should also be mentioned that the possibility of chemical reaction during the filter-stripping process was eliminated using standard samples. The co-existence of $(NH_4)_2SO_4$ and PbBrCl in the atmospheric sample collected at Lancaster Town Hall on May 17–24, 1977, lends further support to our argument. We have also analyzed the lead components of street dusts by XRD and have found $PbSO_4{\cdot}(NH_4)_2SO_4$ in a sample collected from the A6 road (*42*). This cannot have been a filter artefact and presumably arose from deposition of atmospheric particles.

As indicated in the introductory statement, one experimental observation made in various locations is that of a decrease in the Br/Pb ratio of atmospheric particulates during summer months. This may be readily explained by our results. Photochemical processes play a major role in the atmospheric oxidation of sulfur dioxide, and hence the rate of oxidation and the resultant formation of sulfuric acid are considerably enhanced during the summer months. Consequently, the abundance of H_2SO_4 and NH_4HSO_4 relative to $(NH_4)_2SO_4$ in the atmosphere is increased and Reactions 6 and 7 involving halogen loss as a hydrogen halide become more important relative to Reaction 8, in which the halogens are conserved. Thereby, the particulate Br/Pb ratio is diminished.

In very recent work, Eldred and co-workers (*43*) have identified several factors important in aerosol bromine loss in samples collected at 20 sites from 1973 to 1977 in California. They confirm the aforementioned seasonal variation in bromine loss, and report a greater loss in Southern California than in Northern California, which is presumably a consequence of the greater photochemical activity of the Southern Californian atmosphere causing more rapid formation of acid sulfates. These workers also report that bromine loss was approximately constant within a given air basin. We interpret this finding as due to the dependence of the Br/Pb ratio upon the degree of acidity of ambient sulfate close to the point of emission of the lead. Hence, whereas during transport of gaseous air pollutants across the air basin, continuing photochemical reactions will cause changes in the concentrations of primary and secondary pollutants, the Br/Pb ratio will be fixed by rapid reactions close to source and will change little with aerosol transport. Perhaps the most interesting finding of these workers is that bromine loss was greater for particles <0.65 μm than for those between 0.65 and 3.6 μm. This is clearly a result of the far greater susceptibility of the smaller particles to coagulation, and hence to reaction with ambient sulfates.

Conclusions

The lead compounds encountered in atmospheric sampling may be accounted for as either vehicle-emitted or formed by reaction with atmospheric sulfates. In the first category come PbBrCl, $PbBrCl{\cdot}2NH_4Cl$, and $\alpha\text{-}2PbBrCl{\cdot}NH_4Cl$.

Compounds formed within the atmosphere are $PbSO_4{\cdot}(NH_4)_2SO_4$ (usually the major lead component), $PbSO_4$, and $PbBrCl{\cdot}(NH_4)_2BrCl$, as well as other unidentified lead ammonium halides. The formation of these compounds is explained by reaction of vehicle-generated PbBrCl with neutral and acid sulfate droplets following coagulation by Brownian diffusion. The most important process appears to be the equimolar reaction of PbBrCl with $(NH_4)_2SO_4$ (Reaction 8). This process explains the finding of $PbSO_4{\cdot}(NH_4)_2SO_4$ at four out of five sampling sites, while both products of the reaction were found in two successive air samples at the motorway site.

The presence of $PbSO_4$ is explained by reaction of PbBrCl with acid sulfates, either H_2SO_4 (Reaction 6) or NH_4HSO_4 (Reaction 7). The loss of halogen as hydrogen halide in these latter reactions explains the known bromine loss from lead halide aerosols, and the decrease in Br/Pb ratio during summer months is explained in terms of a more rapid atmospheric oxidation of SO_2 and hence a greater proportion of acid sulfate.

In our atmospheric sampling program, five sites were used, including one in London. The formation of the compounds encountered at each could be explained by the above-described mechanisms, and we believe that certainly within Britain similar processes are likely to dominate the atmospheric chemistry of automotive lead. The ubiquity of sulfate aerosols ensures that these processes will also be operative in other locations, although other reactions with reagents such as HNO_3 and NH_4NO_3 may also be important. Indeed, we have recently found a rapid reaction between PbBrCl and gaseous HNO_3 to form $Pb(NO_3)_2$ (*42*).

Acknowledgments

The authors are indebted to Dr. I. F. Ferguson of the UKAEA, Springfields, for assistance in interpretation of the diffraction data, to Dr. G. G. Johnson, Jr., of Pennsylvania State University for running some data on the Johnson-Vand Search Program, and to Professor H. W. Edwards, Colorado State University, for valuable discussions. They also wish to thank Dr. L. M. Niebylski of the Ethyl Corporation, Ferndale, Mich., for the provision of standard compounds, Mr. T. Meredith, Environmental Health Department, Preston Borough Council, and Dr. D. R. Middleton, Health and Safety Executive, Cricklewood Laboratories, London, for assistance in arranging sampling sites, and Dr. D. C. Anderson, University of Lancaster, Department of Engineering, for the provision of engine dynamometer facilities.

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Received for review September 29, 1978. Accepted December 8, 1978. The provision of a Science Research Council studentship (to P.D.E.B.) is acknowledged.

Environmental Poly(organosiloxanes) (Silicones)

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■ Poly(organosiloxanes) (silicones), which are totally synthetic polymers, were measured in the sediments of the Potomac River, Washington, D.C., and Delaware Bay, Delaware–New Jersey. The Potomac sediments exhibited an average of 1.38 ppm (range 0.46–3.07 ppm) of extractable silicone. The Bay sediments showed an average of 0.61 ppm (range 0.10–1.56 ppm) of extractable silicone. Data from both locations are based on a 35% recovery efficiency for the solvent extraction technique using diethyl ether to recover silicones from dried solids. Extracts, converted to methyl isobutyl ketone solution, were analyzed by nitrous oxide–acetylene flame atomic absorption spectrophotometry. Furthermore, the aqueous surface microlayer in a boat harbor on the Chesapeake Bay contained an average of 30 ppb of silicone, and microlayer from Delaware Bay contained an average of 34 ppb of silicone. All data are on a weight/weight basis, and are reported as organic silicon. Due to the ubiquitous occurrence of silicones seen in this study, silicones are offered as excellent tracers for anthropogenic additions to the environment.

Poly(organosiloxanes) (silicones) are totally synthetic, linear organic polymers finding wide industrial application, especially since World War II. Silicones possess many desirable properties, such as surfactant characteristics, thermal and chemical stability, resistance to ultraviolet radiation, and presumed biological inertness (*1–3*). Silicones are extremely inert hydrocarbon analogues and feature a central chain of alternating silicon and oxygen atoms, with various organic substituents attached to the silicon atoms. Dimethylsilicones comprise the most common type, on the basis of amounts produced. Between 22 000 and 24 000 metric tons of silicone materials were estimated to have been produced by the West, and Japan, in 1965 (*1*). Production figures since then have increased (*4*).

Many uses of silicones are open ended, in that the silicones are released unaltered upon consumption of a silicone-containing product. Often, the silicone is utilized as a trace additive to a bulk material (*5*). Examples are silicone antifoam formulations added to cooking oil, fruit juices, and beer. However, silicones are not biodegradable, and must be considered persistent in the environment (*2*).

Silicones are, in many respects, similar to hydrocarbon oils. It is hypothesized that silicones would tend to accumulate at phase boundaries in aqueous systems as do hydrocarbons (*6, 7*). The phase boundaries of importance are the atmosphere–hydrosphere boundary, characterized by the surface of a body of water, and the lithosphere–hydrosphere boundary, characterized especially by seston. Silicones, like many hydrocarbons, should occupy the former boundary as a constituent in the organic- and trace metal-enriched surface microlayer found on most bodies of water (*8–10*). As materials collecting at the latter boundary, silicones could occur as coatings on particles in the water column and thus be added to the sediments as the seston settles out of the water column.

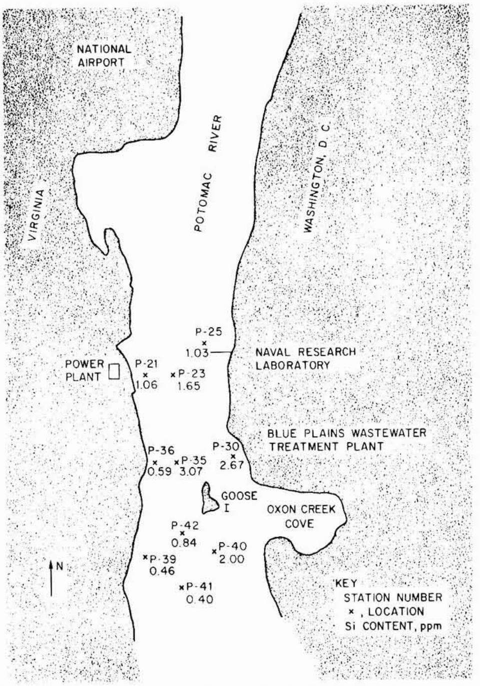

Figure 1. Sampling locations and organic silicon contents in the surface sediments of the Potomac River, Washington, D.C. Silicones are 37.9% silicon

In this study, samples collected from these two silicone-accumulating phase boundary regions were examined to provide information concerning the environmental dispersal of silicones. All data in this report are in terms of organic silicon content. Silicones are 37.9% silicon.

Experimental

Sampling Locations and Techniques. Early in 1978, samples of filter cakes, aqueous sludge, and aqueous effluent were obtained from the Blue Plains Wastewater Treatment Plant, Washington, D.C. (see Figure 1). These solid and liquid samples were stored in glass and were used for methods development and to quantify the silicone from one major source in the Potomac River watershed. Filter cake and sludge were frozen, then freeze-dried soon after collection, pending final processing. The effluent was stored at 4 °C.

In early May, 1978, surface microlayer samples were collected at Chesapeake Beach, Md., roughly due east of Washington, D.C., on the western shore of the Bay, using an aluminum mesh screen washed with distilled chloroform prior to use (*11*). Samples were drained from the screen into 1-quart glass Mason jars which had been washed with acetone and diethyl ether, covered with ether-washed aluminum foil, and then sealed using the lids provided. Samples were stored at 4 °C prior to final processing. All sampling was from an oar-propelled fiberglass boat, with samples being collected upwind of the boat.

In mid-May, 1978, surface sediment samples were collected in the Potomac River using an all aluminum clam-shell sampler with a surface area of approximately 375 cm^2 (see Figure 1). The sampler was cleaned and operated, lubricant-free. The interior of the bulk sample was subsampled using a chloroform-washed stainless-steel spoon, and the subsamples were placed into cleaned, 1-pint glass Mason jars, and sealed as for the microlayer samples. Samples were frozen soon after collection, then freeze-dried prior to final processing.

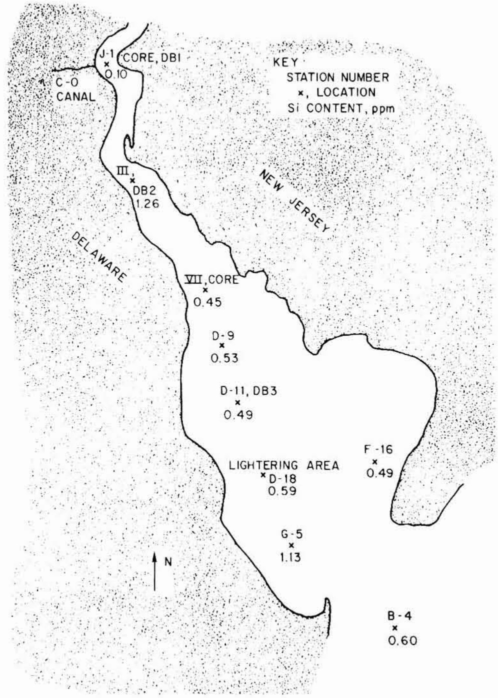

Figure 2. Sampling locations and organic silicon contents in the surface sediments of Delaware Bay, Del.–N.J. Silicones are 37.9% silicon

In late May, 1978, samples of water-surface microlayer, surface sediment, and sediment cores were collected in Delaware Bay (see Figure 2). The microlayer samples were collected upwind and uptide from the R/V *Ridgely Warfield*, using an aluminum skiff propelled by an electric trolling motor. Microlayer samples were collected with both the screen and with a chloroform-cleaned PVC boom (*8*). Surface sediment samples were gathered with a steel Shipek grab (the grease on the grab contained no detectable silicone), with a surface area of approximately 815 cm^2. Cores from the Bay were collected with a plastic-tube-liner equipped gravity corer, and were split and subsampled to preclude contamination of the core interior.

Sample Processing. Liquid samples used in the study (approximately 800 mL each of Blue Plains effluents and screen microlayer samples) were extracted with two aliquots (100, 50 mL) of ether in all-glass separatory funnels with glass closures. Combined ether extracts were rotary evaporated to dryness, and the samples were taken up to 5 mL with glass-distilled methyl isobutyl ketone (MIBK). The samples were stored in 5-mL volumetric flasks with ground-glass stoppers.

Freeze-dried solids were extracted for 2 h with 300 mL of diethyl ether in all-glass Soxhlet apparatus, holding preextracted cellulose Whatman thimbles. Extracts were rotary-evaporated to dryness, then taken up to 5 mL with MIBK, and stored in glass volumetric flasks pending final analysis. All solvents used (ether and MIBK) were redistilled from glass prior to use. Each batch of six samples to be processed included two blanks. All data reported later have been corrected for blank silicone.

Instrumental. Sample extracts in MIBK were analyzed by atomic absorption spectrophotometry (*5, 12, 13*). This study used Perkin-Elmer Models 303 and 460 spectrophotometers with nitrous oxide–acetylene flames. All instruments were equipped with recorders (Texas Instruments Servo-riter

Table I. Extractable[a] Silicones in Blue Plains Materials

	sample	organic Si, ppm	
A. filter cake[b]	A	26.3	
	B	42.3	
	C	45.7	
	D	27.6	$\bar{X} = 36.2$ ppm
	E	27.6	$\sigma = 9.0$
	F	38.6	
	G	32.8[c]	
	H	48.6[c]	
	(S_{1-5})	(22.6)[d]	
B. sludge[b]	I	103.8	
	J	89.1	
	K	96.4	$\bar{X} = 96.1$ ppm
	L	94.4	$\sigma = 5.3$
	M	96.7[c]	
	N	97.5[c]	
		ppb	
C. aqueous effluent	O	4.3	
	P	4.8	$\bar{X} = 4.5$ ppb
	Q	4.1	$\sigma = 0.3$
	R	4.7[e]	

[a] Based on 35% recovery of silicones in the dried sample. Silicones are 37.9% silicon. [b] Freeze-dried solids. [c] Analyzed by X-ray fluorescence. All other analyses by atomic absorption spectrophotometry. [d] Extracted with CH_2Cl_2. All others with diethyl ether. [e] Data from oven-dried residue of effluent, extracted as per solid.

II). Instrumental parameters were as recommended in the manufacturer's literature. Octaphenylcyclotetrasiloxane (Eastman) dissolved in MIBK was used as a primary standard; dilutions of the stock solution were used to produce working curves (*12*), yielding data in terms of organic silicon.

As a check on the analytical procedure, selected extracts of Blue Plains filter cake and freeze-dried sludge were analyzed by wavelength-dispersive X-ray fluorescence, on a Philips Model 1410/70 X-ray spectrometer. Two-hundred-microliter aliquots of extracts and standards, in MIBK, were evaporated onto 6.3-μm polypropylene film (Chemplex Industries) held in poly(methacrylate) rings for X-ray analysis.

Results and Discussion

Analytical Technique Evaluation. Analytical methods development relied heavily on samples of filter cake, sludge, and aqueous effluent obtained from the Blue Plains Wastewater Treatment Plant. The cake appears to consist largely of moist matted cellulose fibers, and is ultimately discarded into a landfill. The sludge is a black suspension (~4% solids), which is an intermediate product of the treatment process at Blue Plains. Both filter cake and sludge were freeze-dried in bulk, and ground to a uniform small particle size with a porcelain mortar and pestle, prior to use. The freeze-drier (Virtis) and sample storage desiccator were sealed with hydrocarbon-based Apiezon L grease to preclude contamination from more contemporary silicone vacuum greases.

Solvents used for trace lipid analysis of environmental samples include aromatic hydrocarbons, ethers, volatile aliphatic fluids, and halogenated materials (*6, 14–16*). Because of toxicity problems, benzene was not considered for use in this study. Diethyl ether (ether) and methylene chloride (CH_2Cl_2) were considered appropriate volatile lipid solvents. Multiple aliquots of filter cake were extracted with ether and CH_2Cl_2 (Table I). This test showed that ether extracted an average of 65% more silicone than did CH_2Cl_2, so that ether was selected for use in this study. Blue Plains filter cake had an average of 36.2 ppm of extractable organic silicon, the sludge 96.1 ppm of silicon, and the aqueous effluent 4.5 ppb of silicon, on a weight-to-weight basis.

Table II. Silicones[a] in the Aqueous Surface Microlayer of Two Estuarine Locations

A. Chesapeake Beach, Md.		B. Delaware Bay, Del.–N.J.	
sample	org Si content, ppb	sample	org Si content, ppb
CB1	41.1	DB1	22.8
CB2	24.2	DB2	35.4
CB3	24.2	DB3	44.2

[a] Based on 100% recovery of silicones in the aqueous sample. Silicones are 37.9% silicon. Tests on aqueous effluent from Blue Plains showed that ether extracts ~100% of silicone from aqueous samples. See text for details.

The extraction efficiency of the technique was evaluated by processing solid materials spiked with known quantities of Dow Corning 704 silicone fluid. Weighed quantities of silicone fluid dissolved in ether were combined with quantities of molecular sieve (Linde, Type 13X, pellets), silica gel (Fisher, 60–200 mesh), and USGS standard rock (Analyzed Granite, G-2). The samples were rotary-evaporated to dryness, then extracted as detailed earlier. An average of 35% of added silicone was recovered from the spiked solids. This figure is taken to be an estimate of silicone recoveries from environmental samples. Additional work also established 2 h as being an optimal extraction time (see Table II).

The possibility of interferences from inorganic silicon during organic solvent extraction was examined. Commercial silica gel (Fisher) was extracted with ether and then reextracted with a second portion of ether for 24 h. In neither case was a silicon signal detectable by atomic absorption spectrophotometry. Furthermore, samples of silica gel, molecular sieve, and filter cake were extracted and analyzed as outlined before. Aliquots of the extracts were filtered with mild vacuum through preextracted 0.2-μm pore size silver filters (Selas Flotronics, Spring House, Pa.). In all cases, analysis of the aliquots before and after filtration gave the same results in terms of organically soluble silicon content. The infrared spectra of selected aliquots of some sample extracts were obtained on a Perkin-Elmer Model 337 infrared spectrophotometer. The samples exhibited the highly characteristic absorption found at 7.95 μm, which is attributed to deformations in the silicon–carbon bonds of the silicone (*14, 17, 18*). Thus, the samples contained silicone; there was no detectable interference from inorganic silicon. In summary, the technique used in this study appears to be rapid, specific for organic silicon, and interference free.

The extraction efficiency for recovery of silicones in aqueous samples was examined by extracting aqueous samples with two aliquots of ether (100, 50 mL) and measuring the silicone in the combined extracts. Duplicate aliquots of aqueous Blue Plains effluent were oven dried at 60 °C; the residue was collected and then extracted as for a solid sample. The solid residue from the aqueous effluent will contain all the silicone in the original effluent. Results from both whole and dried effluent were comparable (see Table I).

Silicones in the Surface Sediments of the Potomac River, Washington, D.C. Silicone contents found in the surface sediments from the Potomac River are presented in Figure 1. The sediments exhibited an average of 1.38 ppm of extractable organic silicon, ranging from 0.46 to 3.07 ppm. The riverine sediments with the higher silicone contents occurred near station P-30, which is just off the dock near the outfall of the Blue Plains Wastewater Treatment Plant. The water there was odoriferous, and was releasing many bubbles of what

Table III. Silicone [a] in Sediment Cores from Delaware Bay

depth, cm	org Si content, ppm	notes
core J-1		
3–8	0.39	distinct petroleum odor
12–14	∼−0	sandy layer
30–33	0.45	grey-black, gelatinous
60–63	∼−0	grey-black, gelatinous, some sand
core VII		
4–6	0.12	tan-brown, very fluid, small particle size
15–17	∼−0	gelatinous, no petroleum odor
56–58	1.13	black, fibrous with plant fragments
80–82	1.20	black, distinct petroleum odor

[a] Based on 35% recovery of silicones in the dried sample. Silicones are 37.9% silicon.

was presumably methane, from anoxic sediments near the outfall. Station P-35, which exhibited the highest sedimentary silicone content, is close enough to the outfall to be influenced by it. Silicone in sediments above the outfall at Station P-30 could accumulate for a number of reasons. The Potomac is tidal upstream to Great Falls, Md., and material released in the tidal region, while undergoing a net transport downstream to the Chesapeake Bay, will oscillate up- and downstream with the tides, to deposit upstream of the Blue Plains point source. Cities such as Cumberland, Md. may also serve as silicone sources in the Potomac watershed, and would supply silicone to downstream sediments.

Silicones in the Microlayer at Chesapeake Beach and on Delaware Bay. Marinas, which concentrate small boat activity, can serve as sources of silicones. Organic silicon was found in samples of microlayer collected in a small-boat harbor at Chesapeake Beach, Md. (see Table II). Sample CB1 was collected near the junction of the Bay and the harbor, and the surface film there had a markedly lowered surface tension, as measured in situ by calibrated spreading oils, after the technique of Barger et al. (*19*). Surface tension lower than that of distilled water implies the presence of surfactant materials; silicones appear to have been among the surfactants causing the lowered surface tension.

The Delaware Bay microlayer samples were collected within established foam lines, well away from any obvious sources of contamination and showed an average organic silicon content of 34.1 ppb (Table II). The foam lines collect along the boundaries of different water masses, and are common and persistent in Delaware Bay (*8*), and tend to concentrate organics and trace metals.

Silicones in the Sediments of Delaware Bay. Figure 2 and Table III document organic silicon contents of the sediments of Delaware Bay. All locations sampled show a measurable, low silicone content with an average of 0.61 ppm of silicone, about half that found in the Potomac. The low value found at station J-1 may be due to scouring present at that location, with silicone-laden sediment and seston being carried down-bay for deposition there. In this context, note that a sediment with a high silicone content occurred at station G-5, which is in a region of rapid sediment accumulation. Station G-5, too, is down-bay from the tanker lightering area in Delaware Bay, so that abundant hydrocarbons released from lightering operations, mixing with environmental silicones, may augment entry of silicones into the sediments northwest of Cape Henlopen. Clean sands are to be found in many places off the mouth of Delaware Bay (personal observation), but the sediment at station B-4 was fine-grained and clayey, typical of Bay sediments. Whether or not more characteristic off-shore sediments would contain detectable silicones is a question still to be answered.

The cores taken in Delaware Bay show more interesting trends. The sandy layer at 12–14 cm in core J-1 showed no detectable silicones, and may be similar to off-shore sediments in this regard. The lower portion of this core was very homogeneous in gross appearance, yet silicone content varied with depth, being lower near the bottom of the core.

It is significant to note, however, that the deepest layer in core VII had the highest silicone content for that core. The layer at 56–58 cm had high silicone, and a fibrous texture, which included plant fragments. Silicone, as a component of the microlayer, could coat plant fragments and be rapidly sedimented in certain situations, carrying the silicone to the sediments (see ref *20*, for a more complete discussion of this process).

Conclusions

This study has shown silicones, measured in terms of organic silicon, to be a ubiquitous component of the sediments and of the water-surface microlayer of widely spaced and differing aqueous environments. Initial work concentrated only on silicone that occupies phase boundaries in fresh- and saline-water regimes, though it is conceivable that the silicones could occur as a dilute solution in water, too. Future work will address this possibility.

Silicones, which are totally synthetic, are offered as an excellent tracer for anthropogenic additions to the aqueous environment. Recent work (*21*) has shown that such compounds as steroids are useful as indicators of, and tracers for, such materials as sewage sludge released to the environment. It is proposed that silicones, too, may be useful tracers in such a context.

In spite of many studies which have examined the short-term effects of large doses of silicones in biotic systems (*2, 3, 22*), there is apparently nothing known of the effects of long-term, low-level exposure. Recent work has shown that dimethylsilicones can methylate mercury in abiotic systems (*23*), so that the implications of the widespread dispersal of a methyl source such as the most commonly used dimethylsiloxane are significant. Furthermore, it is proposed that silicones could act as very stable mobilizers of lipid-soluble bioactive compounds, such as pesticides, making these materials more readily available to the biota than would normally be the case. Further investigations of silicones in the environment and, more specifically, of their effects in the environment are imperative.

Acknowledgments

Mr. David Conlon and other individuals at the Blue Plains Wastewater Treatment Plant, Washington, D.C., are thanked for help in procuring samples from the Plant, and the Potomac River. Dr. Thomas Church, of the University of Delaware, is gratefully acknowledged for providing the opportunity to sample in Delaware Bay.

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Received for review August 30, 1978. Accepted December 11, 1978. Work supported in part by Postdoctoral Research Associateship from the National Research Council. Ship time aboard R/V Ridgely Warfield provided by National Science Foundation Grant No. NSF-OCE-77-2079 to Dr. Church, University of Delaware.

Accumulation of Polychlorinated Biphenyls (PCBs) in Surficial Lake Superior Sediments. Atmospheric Deposition

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■ Sediment cores were obtained from Lake Superior by means of an oceanographic box corer and analyzed for polychlorinated biphenyls (PCBs). Concentration of PCBs in the top 0.5 cm averaged 0.17 ± 0.13 μg/g of sediment on a lakewide basis. The maximum PCB concentrations were found in surficial sediments between the Keweenaw Peninsula and Thunder Bay in the prevailing downwind direction of Thunder Bay, Ontario. Depth-fractionated sediments yielded no detectable PCBs at depths greater than 3 cm below the sediment–water interface, and they often were not detected below a burial depth of 1 cm. The depth of sediment turbation by biotic or physical processes appears to be less than 1 cm. PCB input to Lake Superior from the atmosphere (dry, wet, gaseous) is estimated as $3\text{–}8 \times 10^6$ g·year^{-1}, and can account for sedimentary PCB concentrations. The PCB sedimentation rate in Lake Superior is estimated as $\sim$0.3–0.4 μg·m^{-2}·year^{-1}. The results of this study suggest that atmospheric transport and deposition may dominate PCB input to the Lake Superior ecosystem.

The introduction of polychlorinated biphenyls (PCBs) and other chlorinated hydrocarbons (e.g., DDT group pesticides, aldrin, dieldrin, mirex) into the Great Lakes has resulted in their accumulation in every level of the food chain. Measured concentrations of PCBs in some fish species in Lake Michigan (*1–3*) and the other Great Lakes (*1, 4*) have confirmed that levels exceed the U.S. Food and Drug Administration's current guidelines of 5 μg/g. As a result of high PCB concentrations in Lake Michigan fish, the commercial fishing industry has been curtailed and warnings of the hazards of human consumption of fish obtained by recreational activities have been issued. The potential hazards of PCB intake to human health and the well being of the ecological system have been aptly described (*5*).

Atmospheric deposition has been implicated as the major source of PCB input to Lake Michigan (*6*) and other natural waters (*7–11*). The effect of such input has been the accumulation of PCBs in water, phytoplankton, zooplankton, abiotic particulates, fish, and lake sediments. The atmosphere is likely to be the major source of PCBs to Lake Superior, since the lake has a large surface area compared to its drainage basin, has minimum tributary inflow, lacks industrial and urban activity in the basin, and greater than 50% of total water budget occurs in the form of rain. Although recent studies (*1, 4, 11, 12*) indicate the PCB concentrations in certain commercial fish species are approaching or are greater than the FDA action limit of 5 μg/g, the water concentrations remain at or below detection levels (*12*).

Since lake sediments act as sinks for PCBs entering the lake system (*2*) (and PCBs may be recycled by the biological community inhibiting permanent burial (*13*)), a study was conducted of the PCB content of surficial bottom sediments in Lake Superior and compared to estimated PCB inputs to the lake from the atmosphere and tributary inflow.

Experimental

Sediment cores were collected at nine deepwater locations in Lake Superior from aboard the USCGC Woodrush in July 1977 (Figure 1). Collection sites were chosen to correspond to areas where sediment was accumulating at different rates in the lake. Sediment does not accumulate in Lake Superior in most areas where the water depth is less than 110 m, apparently due to surface wave action at depth (*14*). Depositional environments were located in this study with a seismic–reflection–profiling system, and sediment cores were collected with an oceanographic box corer (0.25 m^2 surface area). The box corer is ideal for collecting sediments for determination of PCBs in lakes with low sedimentation rates because surface sediment disturbance is minimized and sample volume in the top 0.5 cm of sediment is sufficient for extensive analysis.

Sediment cores were fractionated carefully into 0–0.5, 0.5–1, and 1–3 cm depth intervals below the sediment–water interface, and sediment at greater depths was obtained in some cores for evaluation of natural, precultural concentrations of PCBs, sampling and analytical blanks, and PCB recovery from spiked samples. The fractionated sediments were stored in all-glass, hexane–acetone washed containers and stored at 4 °C aboard ship and frozen on return to the laboratory.

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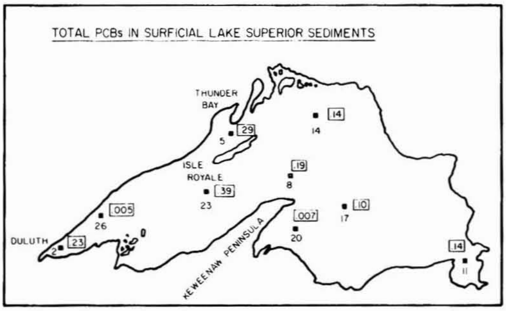

Figure 1. Distribution of PCBs in surficial bottom sediments in Lake Superior. PCB concentrations in cores noted are in units of $\mu g/g$ (ppm) dry weight, in the top 0.5 cm, and represent total values

The sediment samples were extracted and concentrated by the exhaustive steam distillation procedure described by Veith and Kiwas (*15*). Approximately 50–100 g of representative wet sediment was obtained from each sample by inserting an 8 mm i.d. glass tube to the bottom of the sediment container. The sediment was first homogenized in a Waring Blendor with distilled water, and the slurry was then transferred quantitatively to a 3-L round-bottomed flask and diluted to the 2.5-L mark with distilled water. The sediment–water slurry was boiled vigorously for 5 h in a modified Dean-Starke apparatus, with the distillate being extracted in 25 mL of toluene. The toluene was dried over anhydrous Na_2SO_4, fractionated on silicic acid (*16*), concentrated in a Kuderna-Danish apparatus, and finally analyzed for PCBs by electron-capture gas chromatography (GC).

Each sediment extract was chromatographed on at least two different columns using a Varian Aerograph 2700 GC equipped with a Sc^3H electron capture detector and Varian A-25 strip chart recorder. The liquid phases used were 2.5% DL 200/55 + 2.5% QF-1 and 5% DL-200/500, both coated on Chromosorb W. The chromatographic conditions were as follows: column temperature 190 °C, injection temperature 225 °C, detector temperature 250 °C, and nitrogen flow 30 mL/min. The nitrogen was passed through a series of adsorbents to remove any residual water, oxygen, halogenated hydrocarbons, or organics prior to entering the GC. In addition to dual column identification, standard addition using known Aroclor 1242 and 1254 standards was used to further quantify the unknown peaks. Blanks carried through the experimental procedures and sediment samples collected at depths greater than 4 cm yielded PCB concentrations below the detection limit of 0.001 $\mu g/g$. Sediment-spiked PCBs were subjected to steam distillation and GC analysis and gave recoveries of 80–90% for Aroclor 1221, 1232, 1242, and 1254 isomer mixtures.

Results and Discussion

Polychlorinated Biphenyls in Lake Superior Sediments. The distribution of total PCBs in surficial Lake Superior sediments is shown in Figure 1. The concentration of PCBs was determined by the method of Webb and McCall (*17*) and the total PCB concentration is reported as the sum of Aroclor 1242 and 1254 isomers. The reported results of PCB concentrations in the top 0.5-cm layer of collected sediment represent ~15–25 years of sediment accumulation (*18–21*). The concentration of total PCBs in the upper 0.5 cm of Lake Superior sediments ranged from 0.005 to 0.39 $\mu g/g$ with an arithmetic mean of 0.17 ± 0.13 $\mu g/g$ ($n = 9$). The highest concentrations were noted near Duluth-Superior (extreme western end) and in the central part of the lake between the Keweenaw Peninsula and Thunder Bay. Swain (*4*) has shown that elevated concentrations of PCBs have been found in fish, water, and precipitation in Siskiwet Lake on Isle Royale. The lack of man's influence on the island and the predominance of industrial activity in the prevailing upwind direction suggest that Thunder Bay and vicinity may be a major source of airborne transport and deposition of PCBs to Isle Royale and surrounding Lake Superior.

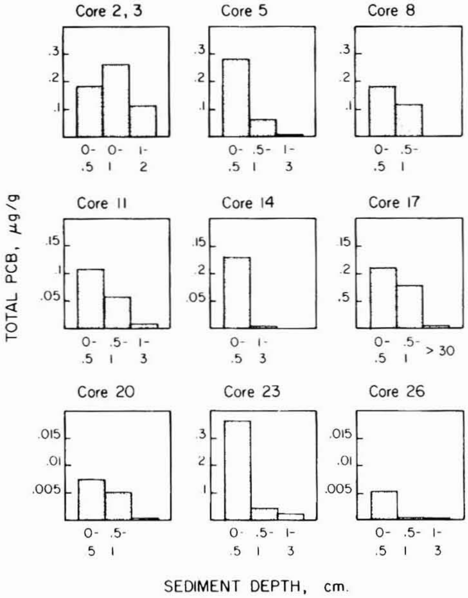

Figure 2. PCBs in depth-fractionated surficial sediments in Lake Superior. Core number refers to samples obtained at sites noted in Figure 1

The minimum PCB value of 0.005 $\mu g/g$ was obtained in box core no. 26 collected ~18 km southeast of Silver Bay, Minn. Sediment at this site is dominated by taconite tailings discharged by the Reserve Mining Co. over the past 25 years, and which presently cover much of the lake bottom offshore (*22*). PCBs entering the sediment via the atmosphere in this area may be diluted by the rapidly accumulating tailings, and therefore PCB concentrations in the tailings do not reflect natural sedimentary conditions in the lake. Other minimum values occur in the eastern sector of the lake.

The arithmetic mean concentration of 0.17 μg of PCB per g of sediment exceeds by 2 to 10 times the values of 0.06 and 0.007 μg of PCB/g observed for sediments in Lake Superior by Glooschenko et al. (*11*) and Veith et al. (*12*), respectively. This may be attributed in part to the superior sampling capabilities of the box corer used in this study. Sediment collection with a grab sampler or gravity or piston corer may result in the loss of the fluffy, low density, organic floc representing the recently deposited material.

In southern Lake Michigan, which potentially receives considerably more atmospheric input from urban and industrial centers, PCB concentrations in the sediment vary from 0.012 to 10 $\mu g/g$ (*2, 3, 11*). In every study a gravity or grab sampler was used in sample collection, suggesting that actual concentrations may be 2–10 times higher than reported. If not, PCB concentrations in surficial sediments of Lakes Superior and Michigan are comparable. If this is the case, regional dispersion, transport, and deposition of airborne PCBs must be dominating PCB concentrations and cycling in the Great Lakes.

The concentration of PCBs found in various sediment fractions is given in Table I, with site-specific profiles of

Table I. PCBs in Lake Superior Sediments

box core no.	sediment depth, cm	water depth, m	PCB, µg/g		
			1242	1254	total
2	0–0.5	60	0.14	0.05	0.19
3	0–1	60	0.20	0.06	0.26
3	1–3	60	0.09	0.01	0.10
5	0–0.5	185	0.27	0.02	0.29
5	0.5–1	185	0.05	0.01	0.06
5	1–3	185	ND[a]	0.01	0.01
7	15	215	ND	ND	ND
7	30	215	ND	ND	ND
8	0–0.5	250	0.16	0.03	0.19
8	0.5–1	250	0.12	0.02	0.14
11	0–0.5	130	0.05	0.08	0.13
11	0.5–1	130	0.03	0.03	0.06
11	1–3	130	ND	0.004	0.004
14	0–0.5	230	0.12	0.02	0.14
14	0.5–1	230	ND	ND	ND
17	0–0.5	305	0.07	0.04	0.11
17	0.5–1	305	0.06	0.02	0.08
17	30	305	ND	ND	ND
20	0–0.5	230	ND	0.007	0.007
20	0.5–1	230	ND	0.005	0.005
20	4	230	ND	ND	ND
23	0–0.5	200	0.34	0.05	0.39
23	0.5–1	200	0.02	0.01	0.03
23	1–3	200	0.004	0.009	0.01
26	0–0.5	256	ND	0.005	0.005
26	0.5–1	256	ND	ND	ND
26	4	256	ND	ND	ND

[a] ND, not detectable.

sediment PCBs shown in Figure 2. There is a rapid decrease in the PCB concentrations in sediment with depth, with no detectable values (<0.001 µg/g) occurring at depths greater than 3 cm, and in several instances at depths greater than 1 cm. These profiles suggest that mixing of surficial sediments by benthic organisms or bottom currents is a negligible factor in downward mixing of PCBs below a depth of 1 cm in the sediments. This conclusion is supported by ^{210}Pb profiles (*19*), interstitial water profiles of dissolved silica (*23*), and dissolved organic carbon, Ca, Mg, K, Cd, Pb, Cu, Fe, Mn, and Al (*24*) observed in these same cores from Lake Superior. The bioturbated depth has been estimated for most of the lower Great Lakes as ranging from 3 to 8 cm and from 1 to 3 cm for Lake Michigan (*25*, *26*). The absence of surficial sediment turbation in Lake Superior reflects the low level of primary productivity in the surface waters.

Lake Superior has a mean deep-water sedimentation rate estimated to be ~0.3 mm·year^{-1} (*18–21*). In contrast, Lake Huron has a sedimentation rate of 0.2–3.1 mm·year^{-1} (*27*), while Lake Erie has a rate of 0–7.4 mm·year^{-1} (*28*). The low level of sediment turbation in Lake Superior permits the historical evaluation of PCB inputs to the lake in the form of tributary inflows and atmospheric deposition. In addition, it may be possible to differentiate between natural and anthropogenic inputs of materials such as polynuclear aromatic hydrocarbons by examining the precultural (pre-1890) influences in sediment composition. The commercial production and distribution of PCBs in the U.S. have occurred over the last 50 years, and therefore in the absence of sediment turbation, PCBs should be present only in the top ~1.5 cm if the sedimentation rate is ~0.3 mm·year^{-1} or 33.3 years·cm^{-1} sediment accumulation. In general, PCBs can be detected at sediment depths only less than 1 cm, adding credence to the above conclusions.

The composition of the PCBs found in Lake Superior sediments may add insight as to their source(s). Using the operational identification and quantification scheme devised by Webb and McCall (*17*), ~60% (SD 35%) of the PCBs detected in the top 0.5 cm of sediment were similar to Aroclor 1242. Omitting cores 20 and 26 from the calculation, in which no Aroclor 1242 was detected, the portion of Aroclor 1242 increased to 75% (SD 18%) of the total. Isomeric mixtures of PCBs such as Aroclor 1260 and lower molecular weight, more volatile products were not observed. Murphey and Rzeszutko (*6*) recently found that particulates scavenged by precipitation over Lake Michigan were ~29% Aroclor 1242, 56% Aroclor 1254, and 15% Aroclor 1260. In contrast, air samples contained a high proportion of Aroclor 1242 (~84%), while precipitation samples overall had a much lower contribution, 42%. Andren and Doskey (*29*) found that the composition of air particulates and vapor collected over Lake Michigan favored Aroclor 1242 (70–80%) over the less volatile Aroclor 1254 (20–30%). The high proportion of PCBs observed in Lake Superior sediments as Aroclor 1242 is consistent with the composition of PCBs in precipitation and air over Lake Michigan. The information suggests that PCBs emitted as a mixture such as Aroclor 1242 may be transported in the vapor or particulate phase to Lake Superior from local and regional sources and deposited by dry, gaseous, or wet deposition.

Atmospheric Input of PCBs to Lake Superior. PCBs can enter the Lake Superior ecosystem by dry, gaseous, or wet deposition. Recent work on the atmospheric chemistry of PCBs suggests that greater than 90% is transported in the vapor phase (*10*), which is deposited primarily by turbulent impaction. However, little information is available on the PCB content of air particulates, vapor, or rain in the Lake Superior region. Therefore, the atmospheric deposition of PCBs to Lake Superior will be estimated based on measurements made

Table II. Concentrations of PCBs in Rain and Air

location	concn	note	ref
	rain, ng/L		
Chicago (Lake Michigan)	177	arith $\bar{x}$	6
Beaver Island (Lake Michigan)	215	arith $\bar{x}$	6
Lake Michigan	119	wt $\bar{x}$	6
Saginaw Bay	19	rain and snow	40
Duluth (Lake Superior)	50	snow	4
Isle Royale (Lake Superior)	97.5	snow	4
North Atlantic	6.5		38
	air, ng/m^3		
Chicago (Lake Michigan)	8 ± 3.8	arith $\bar{x}$	6
Lake Michigan	0.12–1.46		29
Arizona	<0.02–0.41		10
La Jolla, Calif.	0.5–1.4		39
Mass.	4–5		8
Bermuda	0.15–0.5		8
Grand Banks	0.05–0.16		8
Bermuda	0.19–0.66	1973	10
Bermuda	0.08–0.48	1974	10
Chesapeake Bay	1.0–2.0		10
Atlantic	0.72–1.6		10

Table III. Atmospheric Input of PCBs to Lake Superior

component	atm input, g·year^{-1}
rain	3–6 × 10^6
particulate	0.1–1 × 10^6
vapor	0.1–1 × 10^6
total	3–8 × 10^6

	sediment concn in top 0.5 cm, μg/g	
	range	median
calcd[b]	0.09–0.2	0.15
calcd[c]	0.2–0.4	0.3
obsd[d]	0.005–0.39	0.17

[a] Corresponds to 0.4–1 × 10^{-5} g·m^{-2}·year^{-1}. [b] Calculated on the basis of lake surface area – 8.21 × 10^{10} m^2. [c] Calculated on the basis of sediment surface area where sediment is accumulating –4.5 × 10^{10} m^2. [d] Mean of 9 sampling locations; 0.17 ± 0.13 μg of PCB/g of sediment.

in similar environments.

Table II presents a list of typical concentrations of PCBs determined in rain and air in continental and marine environments. A PCB concentration range of 50–100 ng·L^{-1} in rain was chosen as typical for the Lake Superior region, based primarily on the measurements in northern Lake Michigan (*6*) and in the Thunder Bay–Isle Royale locale of Lake Superior (*4*). Assuming an annual precipitation volume over Lake Superior of 0.8 m·year^{-1}, a concentration range of 50–100 ng·L^{-1}, and a lake surface area of 8.21 × 10^{10} m^2, input to Lake Superior by rainfall is estimated as 3–6 × 10^3 kg·year^{-1}.

The concentrations of PCBs in air listed in Table II for remote continental or marine environments relatively uncontaminated by local sources range from ~0.1 to 1.6 ng·m^{-3}. The range chosen for calculation of particulate and vapor phase input to Lake Superior was based primarily on measurements by Andren and Doskey (*29*) over Lake Michigan and by Bidleman et al. (*10*) in the marine environment.

The calculation of particulate input of PCB to Lake Superior assumed that 10% of measured PCB air concentrations were particulate (*10*) and occurred in submicron-sized particles to which a deposition velocity of 0.005 ms^{-1} was applied. The particulate PCB input was calculated as:

$$\text{flux} = V_d C_{\text{air}} \qquad (1)$$

where flux is deposition per unit area per time (g·m^{-2}·year^{-1}), V_d is the deposition velocity (m·s^{-1}), and C_{air} is the concentration of PCB in air (ng·m^{-3}). Thus, the input of PCB to Lake Superior by dry deposition was estimated as 0.1–1 × 10^3 kg·year^{-1} using a lake surface area of 8.21 × 10^{10} m^2.

The vapor phase input of PCBs to Lake Superior was calculated by the two methods of Bidleman et al. (*10*) and Cohen et al. (*30*). Using the gaseous deposition velocity (V_g) chosen by Bidleman et al. of 0.19 cm·s^{-1} and using Equation 1 with 90% of the 0.1–1 ng·m^{-3} PCB air concentration as vapor phase, a gaseous input of ~0.4–4 × 10^3 kg·year^{-1} was calculated. Cohen et al. (*30*) studied the liquid-phase controlled volatilization rates of PCB isomeric mixtures in the presence of wind waves. The authors suggested that a mass transfer coefficient of ~30 cm·h^{-1} or 0.008 cm·s^{-1} be used for environmental wind speeds (3–10 m·s^{-1}) typical for Lake Superior. A PCB flux to Lake Superior, based on the mass transfer coefficient of 30 cm·h^{-1}, a PCB concentration range of 0.1–1 ng·m^{-3}, and assuming 90% of air concentration was in the vapor phase, was calculated as 0.02–0.2 × 10^3 kg·year^{-1}. The choice of a deposition velocity or mass transfer coefficient for vapor-phase PCB input to Lake Superior is critical to the estimation of the lake's budget. The lower mass transfer coefficient of 0.008 cm·s^{-1} determined by Cohen et al. (*30*) is better than that chosen by inference by Bidleman et al. (*11*). However, PCBs do not behave as isomeric Aroclor mixtures in their interactions with aqueous and solid surfaces, but rather as individual compounds. Mass transfer coefficients for individual PCB isomers are therefore needed to refine our calculations. In addition, information on the PCB interaction and accumulation of PCBs in surface organic microlayers (SOM) may favor deposition to the lake surface by depleting the PCB vapor-phase concentration at the air–water interface. Data obtained on Lake Superior SOM to be published elsewhere show a mean PCB enrichment of ~100% over bulk water levels (*31*). Consideration of the bulk water dilution problems introduced by the screen sampler used suggests that surface enrichment may be 10^3–10^4 times greater than observed. Interestingly, Aroclor 1242 represented ~64% on the average of the total PCB in the SOM. Based on the above calculations, a vapor phase input of 0.1–1 × 10^3 kg·year^{-1} PCB to Lake Superior was selected. Therefore, the estimated atmospheric flux of PCBs to Lake Superior is estimated at 3–8 × 10^3 kg·year^{-1} or 0.41–1 × 10^{-5} g of PCB·m^{-2}·year^{-1} (Table III). This compares to the measured PCB input to Lake Michigan of 5 × 10^3 kg·year^{-1} or 8.6 × 10^{-5} g of PCB·m^{-2}·year^{-1} (*6*). The similarity between the calculated input to Lake Superior and the measured input to Lake Michigan may be coincidental or may be indicative of dispersion and transport of airborne PCBs on a regional scale.

The estimated annual input of PCBs to Lake Superior from the atmosphere may be compared to the concentrations found in surficial sediments. For this calculation, it is assumed that all PCB in the sediment was derived from the atmosphere. Assuming a deepwater lake sedimentation rate of ~0.03 cm·year^{-1}, a bottom surface area of 8.21 × 10^{10} m^2, and a sediment density of 1.5 g·cm^{-3}, the concentration range calculated for PCBs in the top 0.5 cm is 0.09–0.2 μg of PCB/g of sediment (Table III). This compares to the observed concentration range of 0.005–0.39 μg/g. Accounting for the fact that sediment does not accumulate at water depths less than 110 m or 45% of the lake surface area (*14*), the expected concentration is increased to $\sim$0.2–0.4 μg of PCB/g in areas of sediment accumulation. The calculated concentration of PCBs in surficial sediments of Lake Superior based on atmospheric deposition alone agrees with that observed in the field. If the elevated sediment concentrations near Isle Royale are excluded from the comparison because local sources may be important, the agreement between calculated and observed concentrations improves. Within the level of certainty of the calculations and field measurements, we conclude that atmospheric deposition of PCBs to Lake Superior accounts for the PCB concentrations observed in surficial sediments. Elevated concentrations near Isle Royale and Duluth-Superior can be attributed to more localized industrial and urban sources. The contribution of tributary inflow to the PCB budget of the lake is negligible. This conclusion is based on an assumed mean background concentration of 1 ng$\cdot$L^{-1} in tributary inflow and an annual inflow to the lake of 4.9×10^{10} m$^3\cdot$year^{-1} yielding 49 kg$\cdot$year^{-1}. Tributary input therefore represents less than 2% of atmospheric input.

Bickel and Carlson (*32*) have estimated that the deepwater mass sedimentation rate in Lake Superior is $7.2–10.8 \times 10^{12}$ g$\cdot$year^{-1} or $1.6–2.4 \times 10^2$ g$\cdot$m$^{-2}\cdot$year^{-1} over the $\sim 4.5 \times 10^{10}$ m^2 of lake bottom where sediments are accumulating (*21*). This corresponds to a mean PCB sedimentation rate of $\sim$0.3–0.4 μg of PCB$\cdot$m$^{-2}\cdot$year^{-1} obtained by multiplying the mean PCB concentration in surficial sediment by the mass sedimentation rate. Edgington and Robbins (*33*) have estimated the mass sedimentation rate in southern Lake Michigan to be $\sim$70 g$\cdot$m$^{-2}\cdot$year^{-1} based on ^{210}Pb dating. Based on this value, atmospheric PCB loading of $5 \times 10^6\cdot$year^{-1} (*6*) and a surface area of 5.8×10^{10} m^2, the estimated PCB sedimentation rate for Lake Michigan is calculated to be $\sim$0.5–0.7 μg of PCB$\cdot$m$^{-2}\cdot$year^{-1}. The similarity between the two values suggests that the atmospheric processes contributing PCBs to the Great Lakes and the aqueous phase processes responsible for transporting PCBs to sediments are similar. The processes responsible for PCB accumulation in sediments include sorption on biotic and abiotic particles followed by sedimentation (*34–36*), or penetration of fecal pellets from zooplankton or larger organisms into deep water (*37*). PCBs in surficial sediments may be recycled by benthic organisms increasing their effective residence time in the system (*13*).

Acknowledgments

The assistance of M. Henderson and P. Choitz in the preparation of this manuscript is acknowledged.

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Received for review September 5, 1978. Accepted December 12, 1978. This research was supported in part by National Science Foundation Grants ENG7609432 and OCE 7602255 and by the Petroleum Research Fund administered by the American Chemical Society. We are indebted to the U.S. Coast Guard for use of the USCGC Woodrush, the U.S. Environmental Protection Agency for providing funds for a large winch, and the Graduate School of the University of Minnesota.

Sources and Movement of Organic Chemicals in the Delaware River

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■ The transport of industrial organic chemicals from their source, into the Delaware River, through various treatment facilities, and into Philadelphia's finished drinking water was studied using water samples collected in August 1977. Solvent extraction, liquid chromatographic cleanup, and gas chromatographic mass spectrometry were used for compound separation and identification. Results confirmed discharge sources for many previously identified compounds. Furthermore, it was shown that many of these compounds circulated into Philadelphia's drinking water, and that the various water and waste treatment facilities had a minimal effect on the organic levels. For all chemicals, dilution processes were responsible for the largest reduction in organic concentrations. Results were substantiated by a 10-week sampling program designed to monitor seven selected waste chemicals.

Nearly 100 organic compounds of biological, municipal, and industrial origin have been identified in the Delaware River (*1*). Among the industrial contaminants, several compounds seemed to be coming from a specific plant in the Philadelphia area. Furthermore, relatively high levels of anthropogenic chemicals were observed in the river near the Philadelphia area (*1*), indicating that they may be entering the city's drinking water. We have, therefore, traced the movement of various industrial chemicals from their origin, through the river, and into Philadelphia's drinking water. We have also conducted a 10-week, continuous sampling program to monitor seven selected compounds in the aquatic system. This paper is a report on these studies.

The Sampling Area. Only a small segment of the Delaware River, lying just north of Philadelphia, was studied. A schematic diagram of the complete sampling area is shown in Figure 1. General flow and hydraulic characteristics of the river have been discussed previously (*1*). The box in the upper left-hand corner of Figure 1 represents a plant in the Philadelphia area which we will refer to as plant A. This plant does not discharge its wastewater directly into the river, but rather into the city sewer along with several other industrial users. These combined industrial wastes are treated at the City of Philadelphia's Northeast Sewage Treatment plant using classical secondary treatment methods (*2*). The treated effluent is then discharged into the Delaware River at river mile 104.

Water flow in this segment of the river is dominated by tidal movement rather than by downstream river flow; tidal volumes are an order of magnitude greater than downstream river flows. During periods of normal flow, effluents discharged into the river travel approximately 7 miles upstream during high tide (*3*). Under these conditions, water flow in the upstream direction is sufficient to transport industrial chemicals from the sewer outfall upstream to the intake pipes of Philadelphia's Torresdale drinking water facility at river mile 110 (*4*). Intake valves for this plant are open only during high tide, making industrial waste contamination of the city's drinking water not only possible but probable (*4*). Water entering the drinking water plant is treated using standard techniques (*4, 5*): prechlorination; settling; coagulation (ferric chloride, alum, and lime); disinfection; flocculation; and filtration (rapid sand filters). After a final chlorination step, drinking water is distributed throughout the city. Water from this treatment facility provides the city of Philadelphia with approximately 50% of its finished drinking water (*4*). All present drinking water standards are being met at this water treatment plant (*6*).

Experimental

Samples were collected in late August 1977 from sites a to h, as shown in Figure 1. Our purpose was to follow a 24-h slug of industrial wastes through the cycle from plant A to the finished drinking water. The sampling scheme was designed to account for retention times between the various sampling locations, as well as for tidal movement in the river (*3, 4*). Details of this sampling regime are outlined in Table I.

The composite sample from plant A was taken from a 5-gal continuous sampler after the 24-h sampling period. All other samples were composites of individual grab samples collected at a particular location. River water samples were collected approximately 100 yards from the western shore at the designated river mile and at a depth of about 0.5 m.

Another set of samples was collected weekly over the 10-week period extending from January 15 to March 28, 1978, from points c, g, and h (see Figure 1) and from the center channel of the Delaware at river mile 98. Samples from sites c, g, and h were composites of 200-mL grab samples collected every 8 h beginning Tuesday 8 a.m., Tuesday 8 p.m., and Wednesday 8 a.m., respectively. River samples were 1-gal grab samples taken every Wednesday morning.

All samples were collected in glass bottles fitted with Teflon-lined screw caps. Methylene chloride and hydrochloric acid were added to the water samples at the collection site in order to minimize biological degradation and to start the extraction process. Since waste effluents from plant A do not support microbial activity (*6*), sample preservation in the 24-h continuous sampler was not needed.

All samples were stored in the dark. Small samples were kept on ice during transport to the laboratory. Larger samples were refrigerated as soon as possible after collection.

Analytical techniques and instrumentation for the concentration, separation, and identification of sample components have been discussed in detail elsewhere (*1*). In general, analytical techniques used in this study included solvent extraction, liquid chromatographic fractionation, high-resolution gas chromatography, computerized gas chromatographic mass spectrometry (GC–MS) in both the electron impact (EI) and chemical ionization (CI) modes, mass spectrometric selected ion monitoring (SIM), and high-resolution mass spectrometry (HRMS).

For the initial phase of this study (August, 1977), concentration values were semiquantitative and were based on standard curves for selected compounds. Estimated errors in quantitation are approximately ±20% in plant A's waste effluent, ±50% in the Northeast influent and effluent and the river water, and an order of magnitude in the finished drinking water.

During the second phase of this study (January–March, 1978), experimental procedures were developed to more precisely quantitate seven previously identified compounds. Concentration values were measured using selected ion monitoring (SIM) performed on the unfractionated, combined neutral and acidic extracts for each sample. Sample concentrations were calculated by comparing the computer-integrated peak areas of selected masses with those obtained from standard solutions containing the seven compounds.

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Table I. Sampling Scheme Giving Details of Timing, Volumes, Types, and Locations (See Figure 1)

location	collection period [a]	total vol, L	sampling interval, h	no. of samples	type
(a) plant A effluent	8/23 12 p.m. to 8/24 12 p.m.	0.5		1	continuous
(b) Northeast influent	8/24 2 a.m. to 8/25 2 a.m.	0.5	4	7	grab
(c) Northeast effluent	8/24 8 a.m. to 8/25 8 a.m.	1	4	7	grab
(d) river mile 106	8/25 10 a.m.	23		1	grab
(e) river mile 108	8/25 10:30 a.m.	23		1	grab
(f) river mile 118	8/25 11 a.m.	23		1	grab
(g) Torresdale influent	8/25 8 a.m. to 8/26 8 a.m.	4	4	7	grab
(h) Torresdale effluent	8/25 8 p.m. to 8/26 8 p.m.	4	4	7	grab

[a] All samples taken in August, 1977.

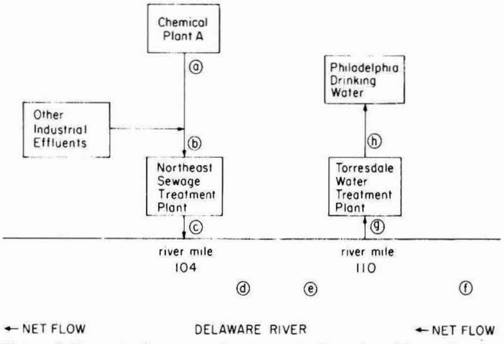

Figure 1. The sampling area, showing collection sites. River mileages are measured upstream from the mouth; net flow proceeds from right to left

Solvent extraction efficiencies were measured for these seven compounds. Preextracted water samples were spiked with a known aliquot of a standard solution. Spiked samples were extracted and quantitated using the above procedures. Tests were run in triplicate using water samples from all four sampling locations. Recoveries were better than 75% in all cases. Reported concentration values were corrected for solvent extraction efficiencies and have errors of less than ±20%, excluding sampling errors.

Results and Discussion

All of the compounds identified in the industrial wastewater, the municipal sewage effluent, the river water, and Philadelphia's finished drinking water are listed in Table II. Some structures are given in Figure 2. Estimated concentrations have been included for most of the abundant compounds. The compounds in Table II are listed according to location of first appearance. Within each of these groups, chemicals have been subdivided by compound type. This arrangement allows for both a quick identification of specific pollution sources and for a facile appraisal of the movement of these chemicals in the aquatic system.

For an overview of the occurrence and environmental significance of many of the compounds listed in Table II, the reader is referred to our previous paper on the Delaware River (*1*). During the following discussion, only those compounds which were not previously identified in the Delaware River or which gave some insight into the movement of chemicals through the various treatment processes and in the Delaware River will be considered.

Identification of Contamination Sources. The first objective of this study was to verify that plant A was the specific source for a set of previously identified compounds. These compounds included 1,2-bis(chloroethoxy)ethane (**6**), the phenyl glycols (**7–11**), the chlorinated phenyl glycols (**12** and **13**), DDE (**17**), dichlorobenzophenone (**16**), and the binaphthyl sulfones (**37**).

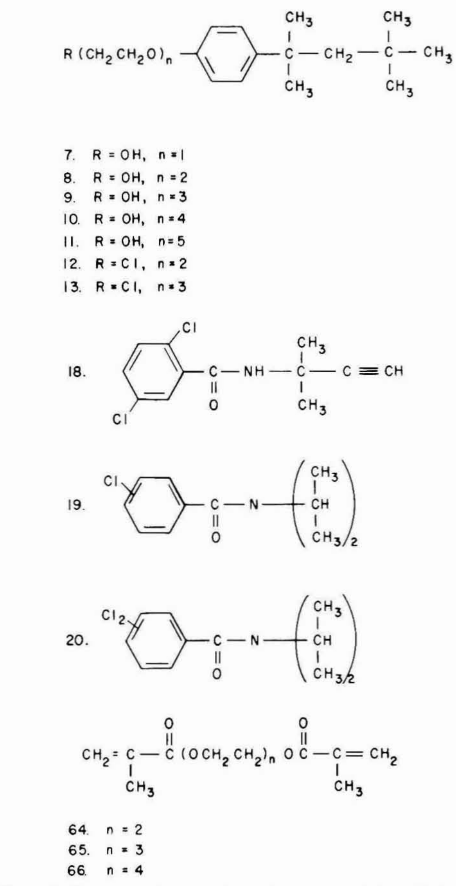

Figure 2. Structures of selected organic compounds found in the Delaware River (see Table II)

Our data (see Table II) verify that these chemicals are, in fact, being discharged from plant A along with various other phenolic compounds (**1–5**), chlorinated compounds (**18–20**), and esterified species (**25** and **26**). All of the above compounds are either commercial products manufactured at plant A or are process byproducts.

The commercial herbicide (*7*) 2,5-dichloro-*N*-(1,1-dimethyl-2-propynyl)benzamide (**18**) was discharged in plant A's waste effluent in relatively high concentration (500 ppb). We should point out that this compound was not detected during our earlier work (*1*), but plant A operates in a batch mode (*6*) and does not consistently discharge the same mix

Table II. Compounds and Their Concentrations (ppb) Observed at the Various Sampling Sites (See Figure 1)

	plant A	NE in	NE out	RM 106	RM 108	Tor in	Tor out	RM 118
I. plant A								
A. phenols								
1. phenol	7000	60	20	0.3	0.3	t[a]	t	–[b]
2. cresol	50	un[c]	20	–	–	–	–	–
3. octylphenols[d]	5000	400	200	3	2	0.4	0.01	–
4. nonylphenols[e]	600	un	40	1	0.02	0.02	–	–
5. 4-octyl-2,6-di-*tert*-butylphenol	200	un	un	–	–	–	–	–
B. ethylene glycol derivatives								
6. 1,2-bis(2-chloroethoxy)ethane	100	un	un	1	1	t	t	–
7. 2-(*p*-1′,1′,3′,3′-tetramethylbutylphenoxy)ethanol[m]	200	50	10	un	un	un	0.02	5
8. 2-[2-(*p*-1′,1′,3′,3′-tetramethylbutylphenoxy)ethoxy]ethanol[m]	100	un	un	0.6	0.3	un	0.02	5
9. 2-(2-[2-(*p*-1′,1′,3′,3′-tetramethylbutylphenoxy)ethoxy]-ethoxy)ethanol[m]	400	un	un	0.4	0.2	un	0.002	t
10. 2-[2-(2-[2-(*p*-1′,1′,3′,3′-tetramethylbutylphenoxy)ethoxy]-ethoxy)ethoxy]ethanol[m]	200	un	un	un	NA[f]	NA	NA	–
11. 2-(2-[2-(2-[2-(*p*-1′,1′,3′,3′-tetramethylbutylphenoxy)ethoxy]-ethoxy)ethoxy]ethoxy)ethanol[m]	un	un	NA	NA	NA	NA	NA	NA
12. 1-chloro-2-[2-(*p*-1′,1′,3′,3′-tetramethylbutylphenoxy)-ethoxy]ethane[m]	2000	200	80	0.6	0.4	0.3	0.2	–
13. 1-chloro-2-(2-[2-(*p*-1′,1′,3′,3′-tetramethylbutyiphenoxy)-ethoxy]ethoxy)ethane[m]	1500	120	50	0.6	0.5	0.3	0.2	–
C. chlorinated compounds								
14. tetrachlorostyrenes[e]	400	60	20	0.5	0.06	–	–	–
15. hexachloroethylbenzene[g]	un	un	–	–	–	–	–	–
16. dichlorobenzophenones[g]	1000	110	60	1	0.2	0.1	0.1	–
17. 1,1-bis(chlorophenyl)-2,2-dichloroethylene (DDE)	1800	200	30	0.4	0.3	un	un	–
18. 2,5-dichloro-*N*-(1,1-dimethyl-2-propynyl)benzamide[m]	500	40	20	0.4	0.2	0.02	0.01	–
19. chloro-*N*-(1,1-diisopropyl)benzamide[g,m]	50	t	t	t	t	–	–	–
20. dichloro-*N*-(1,1-diisopropyl)benzamide[g,m]	un	un	un	0.2	0.06	0.04	0.02	–
21. dichlorobenzenes[e]	100	100	t	v[h]	v	v	v	v
22. chlorotoluene[g]	un	t	t	v	v	v	v	v
23. trichlorobenzenes[e]	200	20	10	t	t	–	–	–
24. tetrachlorobenzenes[e]	200	t	t	t	t	–	–	–
D. plasticizers								
25. bis(2-ethylhexyl) adipate	2000	90	10	0.2	0.04	0.02	0.002	–
26. dioctyl sebacate	200	–	–	–	–	–	–	–
27. tris(*tert*-butyl) phosphate	50	un	un	0.5	0.4	0.3	0.4	0.8
E. hydrocarbons								
28. C_2 benzenes[e]	1000	100	v	v	v	v	v	v
29. C_3 benzenes[e]	un	40	10	2	0.6	–	–	–
30. naphthalene	un	20	4	t	t	t	–	–
31. methylnaphthalenes	500	un	0.4	0.2	0.02	t	t	t
32. C_2 naphthaienes[e]	t	t	t	t	t	t	–	t
33. C_3 naphthalenes[e]	un	t	t	t	t	t	–	t
34. C_4 benzenes[e]	un	200	40	2	t	–	–	–
35. $C_{14}H_{28}$[i]	200	10	un	–	–	–	–	–
36. $C_{16}H_{32}$[i]	2000	30	10	–	–	–	–	–
F. others								
37. binaphthyl sulfones[e]	0.6	un	un	un	–	–	–	–
38. isophorone	un	100	10	3	0.6	t	t	–
II. Northeast influent								
A. phenols								
39. phenylphenol	–	un	un	un	un	–	–	–
40. cumylphenol	–	t	t	0.3	0.01	0.01	–	–
41. *tert*-butylmethoxyphenol	–	t	t	t	t	t	t	t
C. chlorinated compounds								
42. dichlorophenols[e]	–	un	0.4	0.4	t	t	un	–
43. trichlorophenols[e]	–	t	0.1	0.1	t	t	un	t
44. bis(chlorophenyl)methanol[g]	–	3	5	0.7	0.2	0.1	0.002	–
D. plasticizers								
45. triphenyl phosphate	–	16	2	0.3	0.2	0.2	0.03	t
46. dibutyl phthalate	–	50	25	0.6	0.4	0.1	0.1	0.3
47. butylbenzyl phthalate	–	40	100	0.6	0.3	0.3	0.1	0.4
48. bis(2-ethylhexyl) phthalate	–	200	100	1	1	0.5	0.6	0.5

Table II. Continued

	plant A	NE in	NE out	RM 106	RM 108	Tor in	Tor out	RM 118
E. hydrocarbons								
49. pyrene	–	t	t	t	t	t	–	t
50. fluoranthene	–	t	t	t	t	t	–	t
51. anthracene	–	t	t	t	t	t	–	t
52. phenanthrene	–	t	t	t	t	t	–	t
53. methylphenanthrene	–	t	t	t	t	t	–	t
54. chrysene	–	t	t	t	t	t	–	t
F. others								
55. cholesterol	–	400	200	2	1	0.6	–	0.9
56. cholestanol	–	600	300	3	2	1	–	0.9
57. α-terpineol	–	80	80	–	–	–	–	–
58. 2-phenyl-2-propanol	–	70	70	2	0.5	–	–	–
59. stearic acid	–	h[j]	h	h	h	h	–	m[k]
60. palmitic acid	–	h	h	h	h	h	–	m
61. benzil	–	t	un	0.4	0.2	un	0.02	–
62. bornyl acetate	–	100	50	1	1	0.1	0.002	–
63. *N*-(*n*-butyl)benzenesulfonamide	–	un	un	0.6	0.3	t	t	–
III. Northeast effluent								
B. ethylene glycol derivatives								
64. diethyleneglycol dimethacrylate[m]	–	–	10	0.2	t	t	–	–
65. triethyleneglycol dimethacrylate[m]	–	–	35	0.5	0.1	5	–	–
66. tetraethyleneglycol dimethacrylate[m]	–	–	700	10	3	0.5	0.02	–
67. chlorophenylphenylmethanol[g]	–	–	t	0.1	0.1	0.1	un	–
F. others								
68. menthol	–	–	8	un	–	–	–	–
IV. river								
B. ethylene glycol derivatives								
69. bis(2-[2-(*n*-butoxy)ethoxy]ethoxy)methane	–	–	–	un	1	2	t	3
70. triethyleneglycol bis(2-ethylhexanoate)	–	–	–	0.2	0.1	–	–	0.1
71. tetraethyleneglycol bis(2-ethylhexanoate)	–	–	–	2	3	t	–	2
C. chlorinated compounds								
72. dimethyl 2,3,5,6-tetrachloroterphthalate	–	–	–	un	un	un	0.03	t
D. plasticizers								
73. 2,2,4-trimethylpentane-1,3-diol-1-isobutyrate	–	–	–	0.2	0.2	t	t	–
74. 2,2,4-trimethylpentane-1,3-diol-3-isobutyrate	–	–	–	0.2	0.3	t	t	–
75. 2,2,4-trimethylpentane-1,3-dioldiisobutyrate	–	–	–	0.5	0.3	t	t	–
F. others								
76. chlorophyll[l]	–	–	–	2	7	4	–	9
77. fluorenone	–	–	–	0.04	0.02	un	un	t
78. ethylthiopyridine[g]	–	–	–	t	t	t	t	t
79. 1,1-bis(chlorophenyl)-2,2,2-trichloroethane (DDT)	–	–	–	t	t	t	un	–
V. drinking water								
C. halogenated compounds								
80. dichloroisopropenyltoluene[g]	–	–	–	–	–	–	un	–
81. bromochlorophenol[g]	–	–	–	–	–	–	un	–
82. dibromophenol[g]	–	–	–	–	–	–	un	–
83. dichlorobromophenol[g]	–	–	–	–	–	–	un	–
84. dibromochlorophenol[g]	–	–	–	–	–	–	un	–

[a] t indicates that only trace levels were detected. [b] – indicates not detected. [c] un indicates that compound was not resolved gas chromatographically and, therefore, was not quantitated. [d] The predominant species was *p*-1,1,3,3-tetramethylbutylphenol, although other isomers were present. [e] Several isomers present. [f] NA indicates that analysis for these compounds was not carried out (not analyzed). [g] Isomer unknown. [h] v indicates volatile compound; these compounds would not be retained in the water column during the summer months. [i] Structure unknown, mol wt from CI, present in hexane fraction. [j] h indicates very high concentrations; these compounds give broad unresolved peaks which could not be quantitated. [k] m indicates moderate concentration. [l] Chlorophyll was observed as a series of phytadienes (see ref *1*). [m] See Figure 2 for the structure of this compound.

of waste chemicals. Concentrations of compound **18** around 0.003 ppb were found in drinking water samples during our 10-week quantitation study (see below).

An interesting case is presented by several of the multichlorinated aromatic compounds (**14**–**17**): tetrachlorostyrene, hexachloroethylbenzene, DDE, and dichlorobenzophenone. None of these compounds are produced commercially; however, plant A did manufacture the pesticide 1,1-bis(*p*-chlorophenyl)-2,2,2-trichloroethanol. This pesticide was produced commercially using the reaction scheme outlined in Figure 3 (*8*). DDE is the unreacted starting material; tetrachlorostyrene and hexachloroethylbenzene are probably cleavage byproducts formed during the initial chlorination step or from the reaction intermediate 1,1-bis(*p*-chlorophenyl)tetrachloroethane. Dichlorobenzophenone could form during alkaline hydrolysis of either the tosylate ester intermediate or the pesticide itself. Two other structurally related compounds, bis(chlorophenyl)methanol (**44**) and chloro-

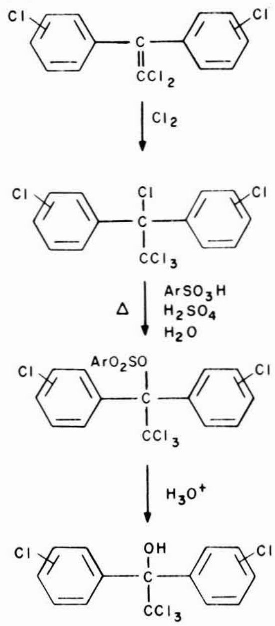

Figure 3. Reaction pathway for the commercial production of 1,1-bis(*p*-chlorophenyl)-2,2,2-trichloroethanol (see ref *8*)

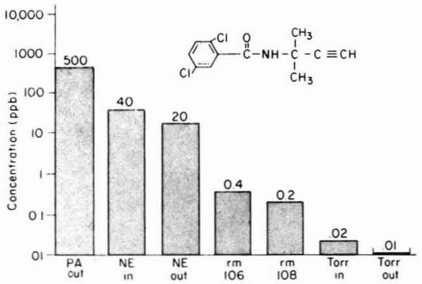

Figure 4. Concentration levels of 2,5-dichloro-*N*-(1,1-dimethyl-2-propynyl)benzamide (**18**) throughout the sampling system

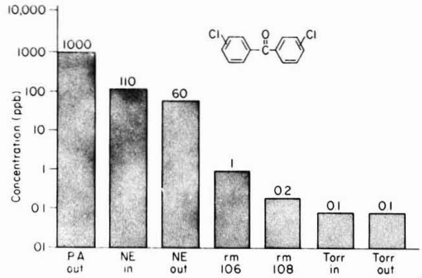

Figure 5. Concentration levels of dichlorobenzophenone (**16**) throughout the sampling system

phenylphenylmethanol (**67**), first appear in the Northeast influent and effluent water, respectively. We think that these are probably degradation products of one of the above chlorinated species. We should point out that the pesticide itself was not detected in any of the wastewater or river water samples.

Although some of the methyl substituted compounds (**28–34**) and chlorinated aromatics (**21–24**) and the solvent isophorone (**38**) first appear in plant A's waste effluent, they are common industrial chemicals which could also be entering the water system at various other points. This was confirmed by comparing concentration data for these compounds with the same data for the compounds specific to plant A. The former compounds show much smaller changes in concentration between sampling locations, suggesting multiple discharge sources.

Most of the compounds which appear for the first time in the Northeast treatment plant's influent (**39–63**) are common industrial or municipal contaminants. They are not unusual and have been discussed in detail elsewhere (*1, 9–11*). *N*-(*n*-Butyl)benzenesulfonamide (**63**) is interesting because it has never been identified in environmental samples. Its major commercial use is as a plasticizer for polyamide materials (*12–14*). It has also been patented as a starting material in the production of sulfonyl carbamate herbicides (*15*). The exact source of this contaminate is not yet known.

Those compounds originally appearing in the treatment plant's effluent water (**64–68**) were, of course, not present in the influent water; this suggests that they were formed during the treatment process. The most striking example is the poly(ethylene glycol) derivative, tetraethyleneglycol dimethacrylate (**66**). This particular chemical is commonly used as a copolymer in many synthetic materials (*16–18*). It seems possible that a polymer entering the Northeast treatment plant is being degraded to monomer units during treatment, or that residual monomer is being washed off polymers during treatment. This compound was the most abundant chemical discharged in the Northeast treatment plant effluent; this leads to correspondingly high river water values. The di- and triethyleneglycol homologues (**64** and **65**) were also identified.

Compounds first appearing in the river water (**69–79**) may be categorized into three groups according to source: first, those entering the river system from other industrial discharges such as various ethylene glycol derivatives (**69–71**) and various plasticizers; second, those compounds formed by the natural biological activity in the river, for example, chlorophyll (**76**); lastly, compounds which enter the river via rainwater runoff, most notably the herbicide dimethyl 2,3,5,6-tetrachloroterphthalate (**72**) (*19*).

In the finished drinking water a series of halogenated compounds appears which were previously undetected. It seems logical that these compounds, especially the halogenated phenols (**81–84**), are formed during the chlorination process (*20*).

Movement of Compounds through the System. It is easiest to assess concentration changes as various compounds travel from industrial wastewater to finished drinking water if the data are presented graphically. Figures 4 to 7 are a series of bar graphs showing concentration data for several compounds at each of the seven sampling locations. These particular compounds were chosen because: (a) they are unique chemicals entering from a single, well-defined source, and (b) they complete the sample loop and were found at all sample locations. This second characteristic makes it possible to assess the effects of all treatment processes and of dilution during upstream river movement.

Figures 4 to 7 indicate several trends. Large changes in concentration (approximately four orders of magnitude) were observed between plant A's effluent and the finished drinking water. Obviously, this large decrease in organic concentration is important when considering allowable discharge levels and treatment processes. For all four compounds, a definite concentration pattern developed over the sample system. The greatest concentration decreases occurred between plant A's effluent and the Northeast Treatment plant's influent (sites a to b) and between the Northeast Treatment plant's effluent and the first upstream river sampling location (sites c to d). It is interesting that these large decreases in concentration are

Table III. Median Concentrations [a] and Relative Concentrations for the 10-Week Study (January to March, 1978) and Grab Sample Concentrations (August 1977)

	10-week concn, ppb				relative concn				grab concn, ppb			
compd [b]	NE eff	river [c]	Torr inf	Torr eff	NE eff	river [c]	Torr inf	Torr eff	NE eff	river [d]	Torr inf	Torr eff
3	200	8	0.4	0.2	100	4	0.2	0.1	200	3	0.4	0.01
7	8	0.3	0.03	0.03	100	4	0.4	0.4	10	un	un	0.02
8	10	0.5	0.05	0.06	100	5	0.5	0.6	un	0.6	un	0.02
12	20	0.3	0.02	0.04	100	2	0.1	0.2	80	0.6	0.3	0.2
13	20	0.5	0.07	0.04	100	3	0.3	0.2	50	0.6	0.3	0.2
17	20	0.3	0.04	0.02	100	2	0.2	0.1	30	0.4	un	un
18	4	0.2	0.003	0.003	100	5	0.08	0.08	20	0.4	0.02	0.01

[a] The range of the individual measurements is usually a factor of 3 above and below the median; for example, for a median of 20 ppb, the range is 7 to 60 ppb. [b] See Table II. [c] River mile 98. [d] River mile 106.

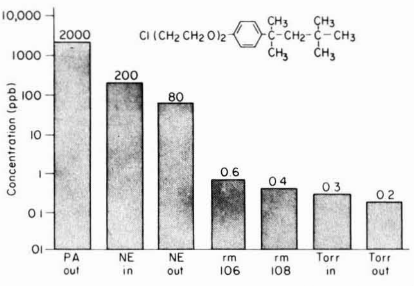

Figure 6. Concentration levels of 1-chloro-2-[2-(*p*-1′,1′,3′,3′-tetramethylbutylphenoxy)ethoxy]ethane (**12**) throughout the sampling system

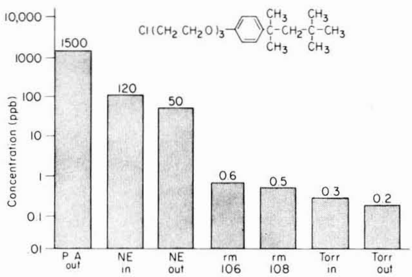

Figure 7. Concentration levels of 1-chloro-2-(2-[2-(*p*-1′,1′,3′,3′-tetramethylbutylphenoxy)ethoxy]ethoxy)ethane (**13**) throughout the sampling system

caused solely by dilution. In the first case, plant A's effluent was diluted with other industrial wastewaters; in the second case, the municipal waste effluent was diluted with river water. In the two areas where treatment was performed, namely between the Northeast Treatment plant's influent and effluent (sites b to c) and between the Torresdale drinking water plant's influent and effluent (sites g to h), only small concentration decreases occurred. For these four compounds, at least in this system, dilution is the most effective treatment process.

On the other hand, the data in Table II show that there are several compounds where treatment processes, especially at the Torresdale plant, are effective. These include the hydrocarbons, sterols, palmitic and stearic acids, some of the ethylene glycol compounds, the phenols, and chlorophyll. Unfortunately, it appears that the compounds of greatest environmental significance may be the least affected by the waste treatment processes.

Table III presents *median* concentration values for seven compounds which were found in plant A's effluent. These data were collected over a 10-week period using selected ion monitoring GC/MS techniques. Table III also lists the concentration data for the summer grab samples (see Table II) and *relative* concentration values for the 10-week study. A comparison between the concentration values for the 10-week study and the summer grab measurements shows good agreement (within the estimated error) for the two data sets. Data on the relative concentration levels in the 10-week samples demonstrate again that dilution is the most important treatment process for reducing industrial waste levels in this aquatic system. No more than a 50% reduction in concentration is achieved at the Torresdale water treatment plant for any of the compounds. For the phenyl glycols (**7** and **8**), a chlorinated phenyl glycol (**12**), and 2,5-dichloro-*N*-(1,1-dimethyl-2-propynyl)benzamide (**18**), the treatment process appeared to have no effect at all.

Acknowledgments

The cooperation of the Delaware River Basin Commission and the help of the Water Department of the City of Philadelphia are gratefully acknowledged.

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Received for review July 14, 1978. Accepted December 22, 1978. This project was supported by the Chemical Threats to Man program of the National Science Foundation (Grant No. ENV-75-13069).

Adsorption of Polychlorinated Biphenyl onto Sea Bed Sediment, Marine Plankton, and Other Adsorbing Agents

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■ Adsorption of PCB onto sea bed sediment, sand, and previously dehydrated samples of plankton and other adsorbing agents was experimentally examined and compared with the results of field observations. Samples of zooplankton and phytoplankton were observed to reach their maximum PCB adsorption capacity within 100 to 200 min. However, the desorption rate was very slow. Batch studies, as well as field observations, indicate that PCB adsorption of various adsorbing agents correlates well with the PCB concentration in brine, and could be described by a Freundlich isotherm. The PCB concentration factors of the adsorbents were found to be inversely related to their average particle size and linearly related to their specific surface area for adsorbents of the same constituent. However, the organic content of the adsorbent also appeared to influence the PCB concentration factor.

In recent years, an increasing number of analyses of polychlorinated biphenyls (PCBs) in marine plankton, sediments, and fishes have been conducted because of pollution by PCBs and their relation to accumulation phenomena (*1–5*). However, little is known about the mechanism of transport of PCBs in the marine environment. According to the few available studies, horizontal distributions of PCBs in water and in the sediment surface suggest that the role of sediment or suspended matter upon the transport of PCBs in coastal waters is important (*5*). PCBs were shown to accumulate more on suspended matter than on plankton (*6*). At the same time, PCB accumulation onto suspended matter and plankton in the marine environment was found to be correlated to PCB concentration in water, and could be described by a formula analogous to that of a Freundlich plot (*6*). Concerning the latter, a forecast has been already given by an adsorption experiment using clay minerals, sand, and soil samples (*7*). The capacity of PCB adsorption upon suspended matter was also suggested to be mainly dependent upon particle size (*6*).

As we have seen, the problem has been reduced to an experimental examination of PCB adsorption on marine sediment, plankton, and other adsorbing agents. This will complement the above-stated findings of the field observation, and the relevant characteristics of particles for PCB adsorption will also be determined.

The objectives of this study are threefold:

- To measure the PCB adsorption rate onto adsorbents, or to estimate the time necessary for attaining the equilibrium concentration through batch adsorption studies.
- To ascertain experimentally PCB adsorption equilibrium between solid and aqueous phases, which has been observed in the field.
- To examine the general relationship between particle size, specific surface area, and PCB concentration factor of the adsorbent agents.

Hopefully, an outgrowth of this work will be the development of a model to predict the behavior of PCBs in the marine environment, taking into account the sorption of sediments and suspended matter and the hydraulics of their transport.

Methodology

Materials. The PCB, KC-500, was a sample from Kaneka Chemical Co., and was used without further purification. The sediment, sand, plankton, activated carbon, and acid clay samples used in this study and their sources are given in Table I. Various types and contents of the sediment were chosen to examine their effect upon the adsorbing ability of PCB. Activated carbon and acid clay were chosen for the sake of contrast.

Experimental Studies. The adsorption studies were carried out by mixing an aqueous solution of PCB with a known amount of adsorbent agents. An *n*-hexane solution of PCB was mixed with 2 mL of ethanol and added to 400 mL of seawater. *n*-Hexane was used to rapidly disperse the PCB in the water phase, and ethanol was added to emulsify and dissolve it in the aqueous phase. A separatory funnel was kept on a shaker for 10 min to disperse and emulsify the mixture. The various amounts of the added ethanol (0.03, 0.1, 0.5, and 2 mL) were examined, but the difference of the added amount was ascertained not to have any influence upon PCB partition between solid and aqueous phases. In these studies, the PCB concentration in the aqueous phase was controlled within 100 ppb. This value was less than the solubilities of PCB in the range of 0.3–3 ppm given by Zitko (*8*), but two times higher than the solubility of ~56 ppb given by Haque et al. (*7*).

The adsorption experiment was performed with the concentration of PCB varied and the amount of adsorbent agent held constant. A known quantity of adsorbing agent was weighed and added to the aqueous solution prepared in a funnel. The funnel was kept on the shaker for a certain period; the period of time for adsorption rate measurement varied with its stage, while the time for the adsorption equilibrium test was fixed. The samples for rate measurement were then centrifuged at 3000 rpm, and those for equilibrium testing were allowed to settle for 24 h. The PCB content of 200 mL of the supernatant liquid was extracted in two stages using 25 mL each of *n*-hexane. The extract was concentrated to 3 mL by blowing down under a dry air stream after rectification. The adsorption of PCB on the surface of the container and loss of PCB by volatilization were accounted for by running a blank through the experiment. Loss by volatilization was negligible.

The concentration of PCB remaining in solution was determined with a Hitachi series gas chromatograph (equipped with a Ni^{63} electron capture detector). The quantity of PCB was determined by taking into account the sum of all gas chromatographic peaks (*9*). The analytical procedure followed the method established by the Environment Agency of Japan (*10*).

The amount of PCB adsorbed, x, was calculated by the formula:

$$x = V(C_2 - C_1) \tag{1}$$

where V is the volume of the aqueous solution, and C_2 and C_1 are the original and final net concentrations of the adsorbate. The net concentration of the adsorbate was determined through the use of a blank run.

The specific surface area of the adsorbents was estimated by the vapor phase chromatographic method. The volume of adsorbed nitrogen upon the adsorbent was measured by sorptionmeter (Shimazu series), and the specific surface area was calculated by the equation of Brunauer, Emmett, and Teller (*11*).

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Table I. Source of Materials under Investigation

surface	source
Izumisano sediment	fine sea bed sediment collected off Izumisano in Osaka Bay, particle diameter is <70 μm, ignition loss content 10.1%
Tarui sediment	sea bed sediment collected off Tarui beach of Osaka Bay, mainly fine mud, though containing various particle size fractions
Iwafune sand	coarse sand collected at Iwafune beach facing the Japan Sea; particle size of sand ranges from 600 to 700 μm, ignition loss percentage is less than 0.1
phytoplankton	filtrate drawn with sieve GG54 (approximately 330 μm in mesh diameter) after collecting with plankton net XX13 (~95 μm in mesh diameter), collected at Osaka Bay in Aug 1974, and dehydrated once by reduced pressure at room temp
zooplankton	remains from plankton net GG54 (~330 μm in mesh diameter), samples collected at Osaka Bay in Aug 1974, and dehydrated once by reduced pressure at room temp
aged activated carbon	granular charcoal carbon without reactivation for 5 years; original manufacturer was Tsurumi Industries Co., Yokohama, Japan
Japanese acid clay	Wako Pure Chemicals Co., Osaka, Japan
Takasago sediment	fine sea bed sediment collected in the neighborhood of the port of West Takasago, particle size is <70 μm; a typical sample of sediment contaminated with PCBs

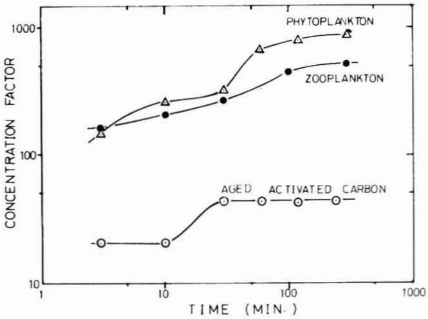

Figure 1. Time-dependent increase of PCB concentration onto adsorbing agents, plankton and aged activated carbon

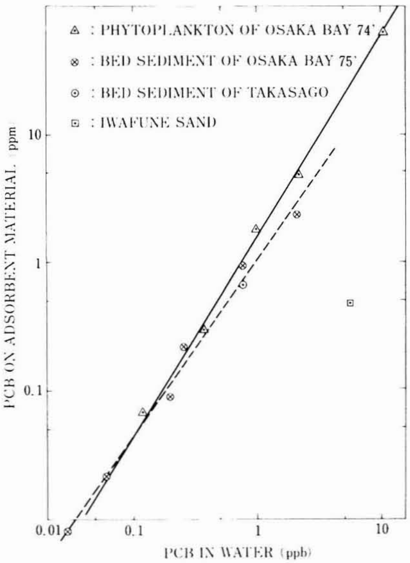

Figure 2. Maximum capacity of PCB adsorption onto sand, sea bed sediment, and once-dehydrated sample of phytoplankton, and maximum capacity of desorption from Takasago sediment

Results and Discussion

Adsorption Rate. The adsorption rate of PCB in brine solution onto phytoplankton, zooplankton, and aged activated carbon was examined (Figure 1). The volume of adsorbed PCB increased with time and finally attained maximum capacity. The time necessary to attain maximum capacity can be estimated from this figure. The aged granular activated carbon attained maximum capacity in approximately 30 min, and the samples of phytoplankton and zooplankton required, respectively, 100 and 200 min to reach maximum capacity. Sediment and suspended matter will probably require an intermediate period of time to attain their maximum capacity.

In contrast, the desorption experiment showed that the rate of PCB loss from the sea bed mud collected off Izumisano was far slower than the rate of adsorption. This was because the rate of PCB loss from the sediment was about 1% for the first day, and 0.8% for the next 5 days. The desorption rate for phytoplankton was also far slower than the rate of adsorption.

Adsorption Equilibrium. Relationships between maximum capacity of PCB on the adsorbing agents and PCB concentration in brine solution were tested (Figure 2). This figure shows a typical Freundlich plot. The quasiequilibrium adsorptions of PCB on plankton and sea bed sediment were assumed capable of treatment by a Freundlich type isotherm equation:

$$q = KC^{1/n} \tag{2}$$

where K and n are constants, and q is the final PCB concentration on the adsorbent. The values of n for phytoplankton and sea bed sediment are 0.67 and 0.77, respectively. In the case of Iwafune sand, its maximum adsorption capacity was far less than those of the other sediments. The state of the adsorption equilibrium of Takasago sediment is also shown in the same figure for contrast. A state of equilibrium was assumed to be maintained between sea bed sediment and its interstitial water. Takasago sediment had the same particle size as Izumisano sediment, and the adsorption test of Izumisano sediment showed that the Izumisano sediment had almost the same capacity of PCB adsorption. The result also suggests this maximum capacity can be reached by the adsorption equilibrium of PCB.

Capacity of PCB Adsorption of Various Adsorbing Materials. The maximum capacity of PCB adsorption onto adsorbing agents is said to differ depending upon the discrepancy in their properties (*7*). However, little quantitative investigation has been reported concerning this point. Our observation of PCB adsorption onto suspended matter and plankton (*5*) and the above stated experiment can provide the means for this analysis, as illustrated in Figure 3.

Figure 3 shows typical Freundlich plots of various adsorbing agents. On the same figure, the data for PCB accumulation to the activated sludge (*12*) and some data for PCB adsorption to industrial adsorbents (activated carbon, macroreticular resin (*13*)) are added for reference. The adsorption tests for Woodburn soil, illite clay, montmorillonite, and kaolinite (*7*)

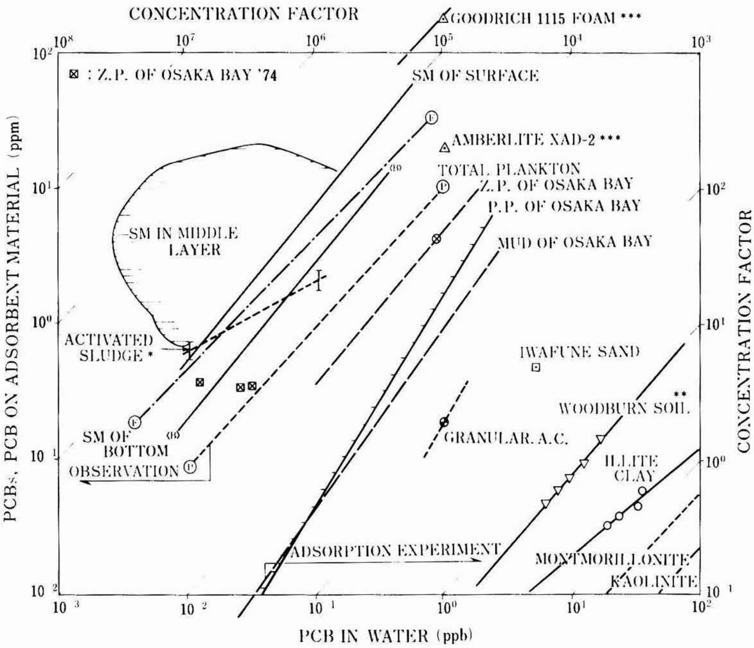

Figure 3. Freundlich plot showing adsorption of PCBs onto several adsorbing agents and suspended matter (SM): SM in middle water layer, SM in bottom layer, total plankton - - - observation; sand, sea bed mud, phytoplankton, zooplankton, aged activated carbon, – – – in vitro experiment. (*) Adsorption experiment by Aizawa et al. (*12*). (***) Experiment by Lawrence and Tosine (*14*). (**) Experiment by Haque et al. (*7*). F in circle refers to overall PCB accumulation in fish (*5*)

Table II. Freundlich Constants and Concentration Factors of Adsorbing Agents

agent	method	Freundlich constant, *n*	concn factor	source
suspended matter	in situ, obsd			
in surface layer		1.2	0.5×10^5 to $\sim 10^5$	*6*
in middle layer			10^5 to $\sim 3 \times 10^6$	*6*
in bottom layer		0.9	0.2×10^5	*6*
total plankton		1.0	10^4	*5*
zooplankton of Osaka Bay			10^4 to $\sim 5 \times 10^4$	*6*
fish in Harimanada		1.0	0.4×10^5	*5*
activated sludge	in vitro, exptl	0.6	2×10^4 to $\sim 7 \times 10^4$	*12*
zooplankton of Osaka Bay			0.5×10^5	present work
phytoplankton of Osaka Bay		1.6	2×10^2 to $\sim 2 \times 10^3$	present work
mud of Osaka Bay		1.4	4×10^2 to $\sim 10^3$	present work
Iwafune sand			10^2	present work
granular activated carbon			2×10^2	present work
Woodburn soil		1.1	(8 to ~10)	*7*
illite clay		0.81	(2 to ~1)	*7*
montmorillonite clay		(1.0)	(0.5)	*7*
kaolinite clay		(1.0)	(0.2)	*7*
Goodrich 1115 foam			0.2×10^6	*14*
Amberlite XAD-4			0.2×10^5	*14*

are also given in the same figure. Each oblique line represents a constant concentration factor (q/C). Concentration factors range from 10^{-1} to 10^6 due to different adsorbing agents, as tabulated in Table II. Maximum capacities of PCB adsorption given by the in situ observation and by the in vitro experiment do not always coincide, especially for the case of phytoplankton. One explanation may be attributed to the state of the plankton; in the former it was living, in the latter it was not. The PCB concentration factor of soil and clay minerals (7) was very small compared with those of our samples. The reason for these differences is subject to further investigation.

Average Particle Size and Specific Surface Area. Adsorption to the surface probably plays an important role in PCB accumulation to a particle. In fact, PCB accumulation onto sea bed sediment was found empirically to correlate to the content of the fine particle portion of sediment (5). The percentage of the fine particle portion of the sediment, i.e., the ratio of the fine mud under 50 μm in particle diameter to the whole sediment, was found to be proportional to the specific

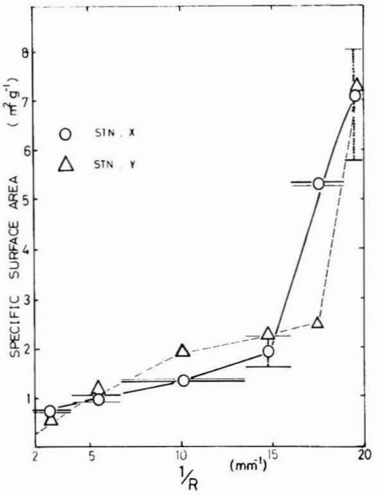

Figure 4. Relationship between specific surface area of sieved fractions of sediment and reciprocal number of the representative particle diameter. Samples collected at stations X and Y off Tarui beach in Osaka Bay. The horizontal bars indicate the ranges of particle size

surface area of the sediment (*13*). In this connection, the size and properties of the particle must be examined thoroughly. As to Tarui sediment, the representative particle size of every sieved fraction was also observed to have an inverse relation to its specific surface area (Figure 4). This fact suggests that the average particle size correlates to its specific surface area among the adsorbing materials of similar properties.

The same relationship was examined for various adsorbing agents, including heterogeneous ones: phytoplankton, zooplankton, fine sea bed sediment and coarse sand collected at the sea shore, aged activated and Japanese acid clay (Figure 5). Irrespective of the vast differences in particle properties, the specific surface area of the particle seems to be proportional to the reciprocal of the average particle size, with Japanese acid clay as an exception.

Concentration Factor of Adsorbing Materials. Considering Figures 3 and 5 (see also Table II), the relationship between PCB concentration factors and the specific surface area of adsorbing agents is arranged in Figure 6. The specific surface area of particles not capable of having their size measured, for example, suspended matter in the marine environment, is estimated on the basis of the average particle size. The specific surface areas of particles of similar organic content are recognized to have a good correlation to the PCB concentration factor, and the specific surface area can be assumed to dominate the concentration factor as a first-order approximation. But the effect of organic content upon the magnitude of the concentration factor cannot be denied. Provided that the specific surface areas of every adsorbing agent are equal, the descending order of PCB concentration factors is given: zooplankton (A) > suspended matter in the middle water layer and total plankton (B) > suspended matter in the surface layer and phytoplankton (C) > suspended matter in the bottom layer and fine sea bed mud (D) > coarse sand and Japanese acid clay (E). The basis of this order can be attributed to the organic contents and constituents. A, B, and C are organic materials or materials of supposed organic origin, and this order corresponds to the descending faunal composition. Ignition loss of D is about 10–20%, and that of E is nearly zero.

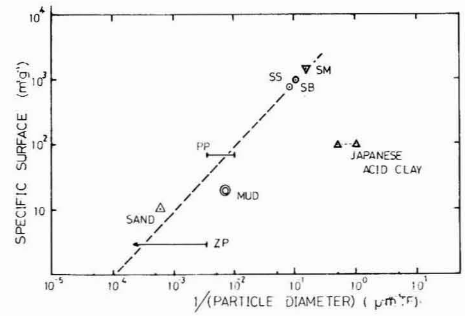

Figure 5. Relationship between specific surface area of adsorbing agents and representative particle diameters: PP, once-dehydrated sample of phytoplankton; ZP, once-dehydrated sample of zooplankton; MUD, sea bed mud collected in Osaka Bay; SAND, Iwafune coarse sand; SS, SM in surface layer; SM, SM in middle water layer; SB, SM in bottom water layer

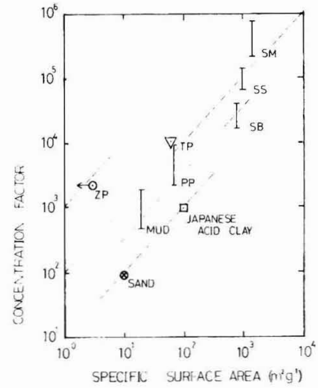

Figure 6. Relationship between PCB concentration factors and specific surface area of adsorbing agents. TP, total plankton

Conclusion

In this paper, the PCB accumulation to adsorbent materials was described in the form of a Freundlich adsorption isotherm. These results coincide with our previous report concerning suspended matter in the marine environment. In regard to the adsorbing agents examined here, correlations were obtained between average particle size and specific particle surface area, and between specific surface area and PCB concentration factor of adsorbing materials.

Analyzing both our observations and experiments, the PCB concentration factors of adsorbing agents in the coastal marine environment can be conjectured to be controlled mainly by their specific surface area, and secondly by their organic content.

Acknowledgment

We express sincere appreciation to Dr. Nicholas C. Kraus, Nearshore Environment Research Center, for a helpful review of the manuscript.

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Received for review July 5, 1978. Accepted December 28, 1978. Presented at the 1976 Autumn Meeting of the Society of Chemical Engineers of Japan, Nagoya, Japan, Oct 1976.

Sampling Parameters for Sulfate Measurement and Characterization

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■ Evaluations of critical sampling parameters have been performed for primary sulfate measurement and characterization with a selective condensation method. It was found that filtration temperature and sampling flow rate were the critical parameters and that sampling conducted using variations of the parameters would result in incomparable data. It was also found that a viable temperature controlled H_2SO_4 collection device could replace the Goksoyr–Ross coil and alleviate H_2SO_4 recovery and pressure drop problems which are common to the methodology.

Increases in the use of sulfur-containing fuels for energy production have resulted in parallel increases in sulfur oxides emissions from power plants. While environmental concerns over these sulfur oxides formations were to surface much later, the corrosive effects of the oxides have been a persistent problem from the onset. Just as persistent have been the problems related to measuring the sulfur oxides quantitatively, particularly the higher oxides of sulfur trioxide (SO_3) and sulfuric acid (H_2SO_4). Depending on the nature of the fuel, boiler design, and firing conditions, the fuel sulfur is oxidized mainly to sulfur dioxide (SO_2). Subsequent to being oxidized to SO_2, or by some alternate oxidation reaction route, from 1% to as high as 25% of the sulfur appears in the sulfate form (*1*). Ordinarily, a large part of the sulfate exists as gaseous H_2SO_4 or absorbed H_2SO_4 on ash particles. It is precisely this phenomenon, the potential of gaseous H_2SO_4 to interact with fuel gas particles, that has not only complicated corrosion difficulties, but has made the measurement of the sulfate species so difficult.

In order to address the problems and parameters involved with acid formation in these combustion systems, extensive work was performed in Western Europe during the middle of this century. This work involved the study of acid formation as a function of excess air (*2*), sulfur content of the fuel (*3*), and effects of ash deposits (*4*). For potential control approaches, the effects of fuel additives were also investigated (*5*). Regardless of the objectives of the studies, difficulties were common and numerous when attempts were made to sample and quantitate the H_2SO_4 present in the flue gases.

Basically, all of the measurement attempts involve the extractive sampling of the flue gas, followed by the attempted separation of the particulate related sulfate from the unassociated (or gaseous) H_2SO_4. This separation attempt ordinarily involved either placing some type of porous plug in the inlet end of the sampling probe or passing the flue gas sample through a flat filtering pad following the probe. By assuming that all of the gas-phase H_2SO_4 had passed the filter, the acid was then collected by an impinger train or by collecting the acid in aerosol form following its condensation. For most corrosion studies the filter was discarded, since the primary objective was measuring the H_2SO_4 (to which the corrosion was attributed). The success of these studies was contingent upon both the collection efficiency of the impingers or aerosol collector, as well as the success of passing the H_2SO_4 gas through the filtering device.

With the shift of energy production in the U.S. from coal to the less expensive crude oil during the last decade, a resurgence of interest in sulfur oxides measurements has occurred. Notwithstanding the corrosion problems which have remained persistent, the more recent emphasis has been directed toward environmental aspects. These interests were spurred by both the correlation of total suspended particulate in the Northeast with increased crude oil usages (*6*) and by the considerably higher than predicted ratio of H_2SO_4 to SO_2 for oil-fired units (*7*). A recent study (*8*) of sulfate presence in the total suspended particulate (TSP) in the atmosphere near an oil-fired plant has suggested a significant local impact caused by emissions of primary sulfates. Contemporary studies involving primary sulfates include both H_2SO_4 corrosion and emission control strategy, particularly flue gas desulfurization type control systems.

Accompanying the resurgence of sulfate emissions concerns was renewed interest in measurement methodology. The emphasis of these measurements has been placed on both a total sulfate sampling approach (*9*) and a characterization approach (*10, 11*), which would distinguish between unassociated gaseous H_2SO_4 and particulate related sulfate. The particulate related sulfate consists of both metal sulfate and absorbed H_2SO_4. In the Gaseous Emissions Research Section of EPA's Environmental Sciences Research Laboratory, we have addressed the problems of sulfate measurement technology. Our initial work (*9*) involved total water-soluble sulfates (TWSS) measurements for fossil fuel fired boilers and culminated in a recommended procedure for such sampling. Refinement of primary sulfate emissions measurements from these sources ultimately led to examining methodology for measuring gaseous H_2SO_4 separately from particulate related sulfates. Upon examination of previous work it was found that the approach used for this type of measurement ordinarily involved the selective condensation method. Former users of the method have apparently overemphasized the collection efficiency of the condensation coil, while neglecting attention to the filtration process. While considerable effort (*12, 13*) has been expended on the reaction of sulfur trioxide (SO_3) with fly ash to increase the efficiency of electrostatic precipitators, the potential for the same reaction during sampling has apparently been ignored. Work (*14*) has also shown that when the SO_3 (which exists as gaseous H_2SO_4 in combustion gases)

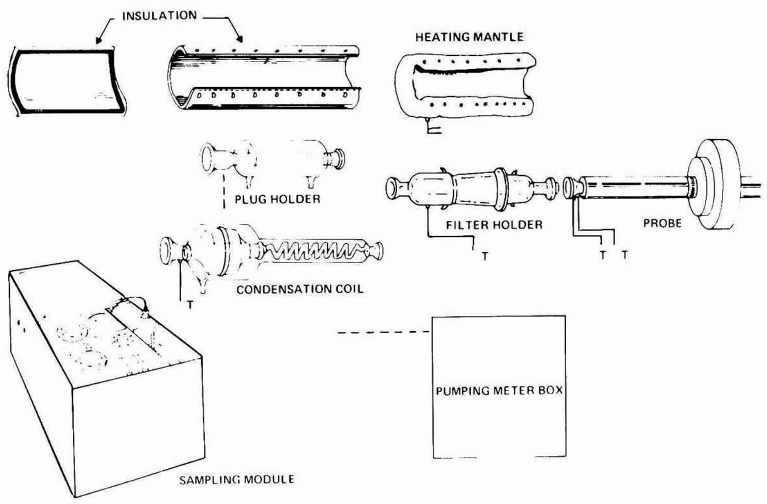

Figure 1. Schematic drawing of manual acid condensation system

reacts with fly ash particles, the reaction is only partially reversible, as indicated by the observed hysteresis. When attempts are made to distinguish unassociated gaseous H_2SO_4 from particulate related sulfates, the methodology must account for this potential interference due to H_2SO_4 absorption at the particulate filtration interface.

Further problems with the selective condensation approach were encountered during our own field sampling experiences including acid recovery from the backup frit of the Goksoyr–Ross (*15*) coil and the high pressure drop introduced into the sampling system by the frit. The high pressure drop from the frit along with the continuously changing pressure drop at the filter during particle collection resulted in difficulties in maintaining a consistent and repeatable sampling rate.

This work involves the development and evolution of a selective condensation system which would serve as a primary sulfate characterization method for combustion source measurements. A thorough study of the sampling parameters of flow rate and filter temperatures and their effects on separating gaseous H_2SO_4 from particulate-related sulfate was performed. Also investigated were the frit retention of sulfate ion during sample recovery and a viable equivalent acid aerosol collection method. Predictions from the results indicate that comparisons of such sulfate characterization measurements, which attempt to distinguish gaseous H_2SO_4 from particulate sulfate, cannot be acceptable unless sampling guidelines are adhered to.

Experimental

A sulfate measurement and characterization system which uses a Goksoyr–Ross type condensation coil was designed for field sampling as shown in Figure 1. The system consists of a high-temperature heated quartz probe, which includes a sheathing which slides snugly into a custom made "Swagelok" fitting adapted to a standard 4-in. port cap. Following this is a high-temperature quartz filtering device, enclosed within a custom made heating mantel, and which has a coarse quartz support frit for holding the filtering pad. Following the filtration, the H_2SO_4 is converted to the aerosol form in the temperature-controlled collection device, which for this work consisted either of a Goksoyr–Ross condenser or glass wool plug holder. For some experiments, the plug holder preceded the condenser. In order to prevent moisture condensation in the condenser or plug holder, which would enhance the potential for SO_2 oxidation, the temperature is maintained near 60 °C by circulatory water from a hot water bath. Following the H_2SO_4 collection device is an 80% 2-propanol (IPA)–H_2O Greenburg–Smith bubbler, followed by a 3% peroxide (H_2O_2) impinger for SO_2 collection. Accompanying the ice bath containing the impingers, the sampling module also contains the water bath, along with voltage controls for heating the probe and filter. The module also contains a four-position pyrometer for reading the temperature potentials from four strategically located copper–constantan thermocouples, as indicated by "T" in Figure 1. The sample is acquired by a standard Research Appliance Corporation (RAC) sampling unit, such as used for method 5 particulate sampling. The weight of the sampling module, less water in the bath, is 30 lb (13.6 kg), and it can be easily transported by an individual sampler.

At the initiation of each sample, all temperatures and the time are recorded. At the termination of sampling, the same parameters are recorded. For the results presented here, all temperatures are presented as averages of the initial and final ones recorded. In actuality, one must observe these temperatures nearly continuously and, when fluctuations occur, make appropriate control adjustments in order to maintain the desired level. The continuous observation of flow rate is even more necessary as the pressure drop across the filtration device increases as the particulate buildup occurs. Stopwatch timing of the gas meter volume is necessary if a consistent flow rate is to be maintained. The samples are recovered in their respective fractions of the probe wash, filter, and filter wash, condenser and/or plug wash, IPA, and H_2O_2 catch. Additional sample fractionation was performed when the objectives of the measurement dictated. The high-temperature filters used during this work consisted of high-purity quartz as described by ADL (*16*) and were heat treated to 900 °F for 4 h prior to use.

The recovered samples are titrated by the barium–thorin procedure as described in the EPA Compliance Test Method 6 (*17*), except that the probe wash and filter wash are passed through the mixed bed resin to remove metal interfering cations prior to titration.

A series of tests was performed at a local No. 6 residual-oil-fired boiler to establish the effects of flow rate and temperature. During the studies when the flow rate was varied, the filter temperature was maintained at 271 to 282 °C. For samples involving various filter temperatures, sampling was conducted at 10 L/min. During the sampling, the flue gas

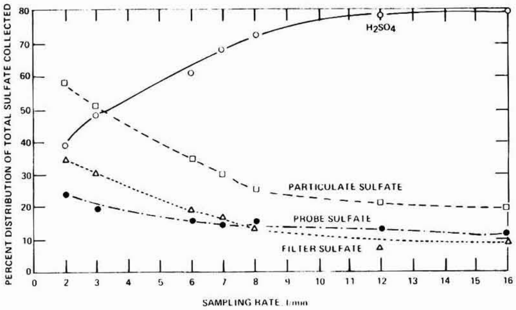

Figure 2. Effects of sampling rate on sulfate distribution

temperature fluctuated between 260 and 288 °C. A series of samples was also performed to examine the extent of sulfate retention in the backup frit contained in the condenser. This was a result of some prior work (unpublished), which indicated that as high as 30% of the H_2SO_4 was being collected on the frit of the condenser regardless of the number or configuration of coils which preceded the frit.

As an equivalent method of H_2SO_4 aerosol collection, a special water jacketed glass wool plug holder was used for a series of samples. During a portion of the samples the plug holder was used as an H_2SO_4 backup collector to the condenser, while some samples were collected solely with the glass plug after filtration. Throughout this work, the temperature of either or both the acid collection devices was maintained at 60 °C. Subsequent sampling at a coal-fired boiler was conducted to establish the feasibility of using the same glass plug for several successive samples without sulfate retention.

Results and Discussion

A series of 16 samples, consisting of duplicate runs of 8 different flow rates, was collected at the oil-fired boiler. For the purpose of establishing flow rate effects it was assumed that all sulfate which passed the probe and high temperature filtration device was H_2SO_4. On this basis the percent H_2SO_4 was calculated as the ratio of sulfate collected past the filter divided by the total sulfate collected in the sampling train × 100%. The results of the various sampling rates are shown in Figure 2. The fraction of H_2SO_4 penetrating the filter is a function of the velocity of the gas stream between 2 and 8 L/min, approaching a plateau between 12 and 16 L/min. For the 8 to 16 L/min flow rate there appears to be little effect of flow rate either on the probe or filter distribution. At the lower flow rate of 2 to 6 L/min, the steeper slope of filter catch indicates the H_2SO_4 is being collected in the front half of the train predominantly at the filter, with a lesser retention by the probe. More than likely some of the particles collected at the filter at higher flow rates dropped out in the probe at lower flow rates, and the ratio of acid on the filter to particulate sulfate was greater than indicated in the figure.

Having confirmed the potential error due to sampling at low flow rates, a second series of samples was collected to establish the effects of filter temperature on sulfate distribution. The results of the series of duplicate runs at each of 5 temperatures using a 10 L/min flow rate are shown in Figure 3. Again the results of the measurements, particularly with respect to sulfate characterization, are dependent on a sampling parameter. There appears to be no effect of sulfate in the probe; this would be expected inasmuch as the probe temperature was maintained above 271 °C. As the filter and filter holder temperature were varied, the effects are seen in these components of the sampling train. While there is a gradual increase in sulfate retention from 260 down to 150 °C, this becomes more profound from 150 down to 82 °C. It is apparent that the condensation of sulfuric acid is occurring and, furthermore, some of the acid is condensing on the filter holder before reaching the filter. The overall effects of filter temperature on the ability of the methodology to distinguish gaseous H_2SO_4 from particulate related sulfate were apparent throughout the temperature range involved. According to the results, maintaining the filter temperature at 260 °C rather than 150 °C reduced, in effect, the particulate ratio of total sulfate from 33.5 to 23.5%. Likewise, assuming the ratio of H_2SO_4 to total sulfate to be 76.4% as it was at 260 °C, it can be calculated that 13% of the H_2SO_4 was retained at the filter at 150 °C and would be included as particulate matter.

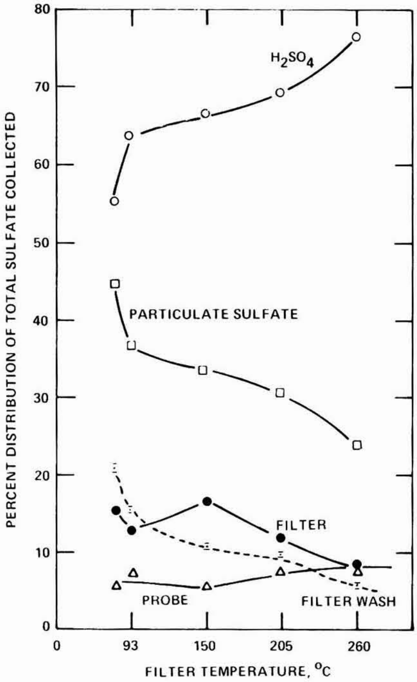

Figure 3. Effects of filter temperature on sulfate distribution

A further series of studies was performed to establish an equivalent method of collecting condensed H_2SO_4. During field measurements a constant flow rate was difficult to maintain with the condensation sampling train due to pressure drops within the system. As the backup frit in the condenser was found to introduce a 7 to 9 in. Hg pressure drop in the sampling system, along with the additional pressure drop due to the filter and collected particulate, a method which would avoid such pressure drops was desirable. In addition, prior experience had proven that a slow buildup of sulfate in the backup frit was occurring over a period of several samples, a buildup which could not be recovered by the routine washing, but required a hot water washing for several hours. The method of collecting H_2SO_4 after the filter should preferably offer both a low-pressure drop and minimal effort for complete sample recovery. From our prior experience with collecting H_2SO_4 with glass wool plugs, enclosing such a plug in a water-jacketed holder appeared to be a feasible approach. The construction of the holder (depicted in Figure 1) was such that the same circulating water bath was used as for the condenser.

Several series of simultaneous samples with the condenser and glass plug holder were performed to determine if the glass plug would collect the H_2SO_4 as efficiently as the condenser.

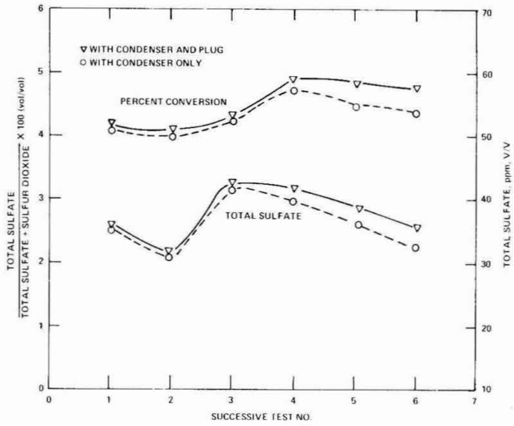

Figure 4. H_2SO_4 breakthrough of frit

For a series of 6 simultaneous samples, the average H_2SO_4 catch in the condenser was 38.2 ± 3.1 ppm, while for the glass plug holder the average H_2SO_4 catch was 37.4 ± 7.4 ppm. (Concentrations are in parts per million v/v.) Within experimental error, it was concluded that the glass plug, at the same temperature and flow rate, would collect the H_2SO_4 as well as the condenser.

A series of six measurements was also performed to ascertain whether the buildup of sulfate in the frit would eventually result in acid breakthrough. A thoroughly cleaned condenser was used for the six measurements, which also involved the glass plug holder just subsequent to the condenser in the sampling train. As the testing proceeded chronologically from test 1 through 6, it can be seen in Figure 4 that a gradual breakthrough of H_2SO_4 is occurring at the condenser frit and is being collected in the glass plug. In the upper portion of Figure 4 the effect can be seen that this breakthrough will have on calculating the percent conversion of SO_2 to SO_4, based on total sulfate/(total sulfate + sulfur dioxide) × 100%.

A final series of sulfate characterization measurements was performed on a coal-fired boiler, using the acid condensation system at various sampling rates. Of interest during this work was the establishment of a relationship between percent H_2SO_4 and the sampling rate at this combustion source, and the subsequent comparison of the relationship with that obtained from the oil-fired boiler. The results of the coal-fired boiler along with the oil-fired boiler results are presented together in Figure 5, along with the 95% confidence intervals. The flue gas temperature during these measurements fluctuated between 150 and 158 °C. It was thought that if the relationship between the percent of H_2SO_4 and sampling rate was the same, corrections could be applied for data obtained at various sampling rates for different sources. This approach appears to be inapplicable, as the slopes of the lines (3.856 for the coal-fired and 5.684 for the oil-fired) vary considerably. It must be concluded that data comparison from one source to another will be meaningful (in terms of sulfate characterization) only if the samples are collected at the same sampling rates.

Conclusions

It has been found from these studies that the selective condensation approach to measuring and characterizing primary sulfate emissions from combustion sources must be used with precaution. In general, when attempts are made to distinguish gaseous H_2SO_4 from absorbed H_2SO_4 and other inorganic sulfates, their success is contingent upon several sampling parameters.

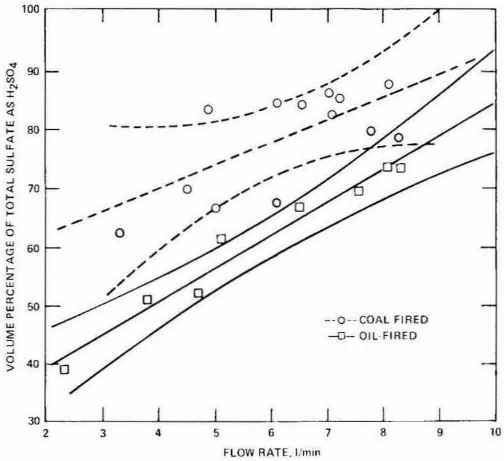

Figure 5. Comparison of coal and oil-fired boilers

Of particular concern is the rate at which the sampling is conducted. While the sample rate results presented in this work consisted of time averages of sample volume per total sampling time, the actual sampling rate was ascertained with a stopwatch throughout the run. Due to the increasing pressure drop in the sampling system from the particulate buildup at the filter, a consistent sampling rate can be maintained only by constant timing of the gas meter. Due to the degree of the slope of the line shown in Figure 2, between 2 and 8 L/min, it is not adequate to "average" 10 L/min, as a lower sampling rate during the latter portion of sampling with still bias the results toward particulate sulfate.

The temperature study indicates that a maximum of 271 to 281 °C is necessary to assure a minimum H_2SO_4 retention at the filter. It would have been of interest to have performed sampling with the filter temperature above this recommended temperature; however, conversion of H_2SO_4 to unassociated SO_3 and ultimately back to SO_2 presents a high temperature constraint on the method. Extending the filter temperature beyond the flue gas temperature in itself presents the potential problem of desorbing H_2SO_4 from some of the particles. Whether this occurs could only be ascertained by the simultaneous in situ measurement of gaseous H_2SO_4, a measurement that currently is not technologically feasible.

It was also found from the study that two serious measurement problems, namely system pressure drop and acid-frit recovery, can be eliminated by a viable H_2SO_4 collection alternative. The temperature-controlled glass plug proved to collect the H_2SO_4 aerosol as well as the condenser, and avoided the pressure drop and acid recovery problems. Furthermore, the glass plug approach is simple, less costly to construct, and does not result in H_2SO_4 buildup and/or breakthrough as does the condenser.

In view of the above results, it is recommended that primary sulfate measurements conducted by the selective condensation approach be done so in excess of 10 L/min and with a filter temperature of 271 to 281 °C. It is further recommended that the awkward Goksoyr–Ross type condenser be replaced in the sampling train with a simple, well-packed 1 cm × 15 cm Pyrex glass plug, in a temperature-controlled holder device. Recovery of H_2SO_4 from this device requires only a simple rinse with the help of a small vacuum; as a precaution, the glass wool must be dried with air prior to its further use.

Finally, in view of several extensive efforts to characterize primary sulfate emissions from combustion sources with this type of measurement approach, it is recommended that the sampling parameters examined in this work along with the recommendations be adhered to, such that data from various sources can be compared at a later point in time. On the basis of sulfate characterization, this can be done only if a consistent sampling rate and filtration temperature for the method are used during the source sampling.

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Received for review October 6, 1978. Accepted December 29, 1978. Mention of brand names does not imply EPA endorsement.

Pollution History of the Savannah River Estuary

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■ Records of natural and pollutant fluxes to the Savannah River estuarine system are found in some river and marsh deposits into which time frames can be introduced by ^{210}Pb or plutonium geochronologies. Plutonium releases from the Savannah River Plant to the environment are evident in only one deposit and in marsh grass, both of which have elevated levels of the ^{238}Pu/$^{239+240}$Pu ratios in comparison to those expected from atmospheric fallout. The highest concentrations of metals were found in deposits upriver; in sediments of the estuary itself, lower concentrations of the metals resulted from their dilution through the entry of oceanic solid phases.

The Savannah River Estuary is one of the large salt marsh estuaries of the world. The Savannah River has received inputs of transuranic elements (about 0.3 Ci of plutonium) from the Savannah River Plant of the U.S. Department of Energy, a part of which entered the Estuary (*1*). Previously, we have studied the histories of heavy metal inputs to a variety of environments—the Southern California Bight (*2*); Narragansett Bay (*3*); and Chesapeake Bay (*4*)—through records in sediments into which a time frame could be introduced. This investigation extends these studies as well as that of Windom (*5*), who prepared a preliminary mass balance of heavy metals entering the Savannah River system to consider the processes occurring in a salt marsh estuary.

Experimental

Samples. The field work was carried out during the period Oct 17–25, 1976 utilizing the Skidaway Institution of Oceanography (Savannah, Ga.) vessel R/V Blue Fin. The sample locations (Figure 1 and Table I) were chosen on the bases that no dredging had taken place in the immediate area, that the river bank and channel were relatively stable and not previously subjected to active erosion, that dredge soil disposal had not taken place, and that the sediments appeared to be anoxic (dark grey or black muds). Marsh grass (*Spartina alterniflora*) and Spanish moss were also collected during this time.

The box cores were frozen on board ship with dry ice. After 24 h in a dry ice reefer, the frozen solid cores were extruded from their liners, trimmed, and cut into longitudinal sections. One section, about 15 mm thick, was used for X-ray pictures (Figure 2) and two or three 60-mm thick sections were cut for chemical analyses.

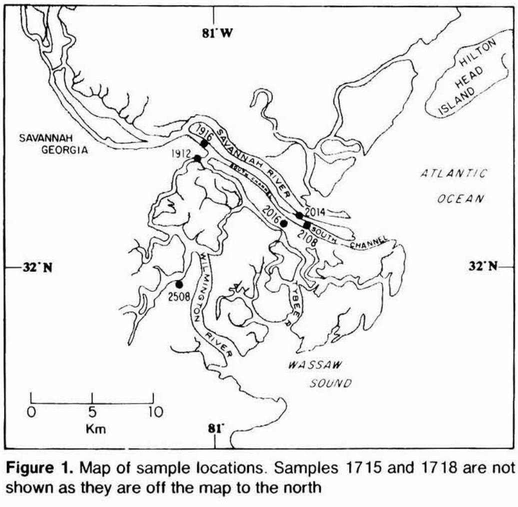

Figure 1. Map of sample locations. Samples 1715 and 1718 are not shown as they are off the map to the north

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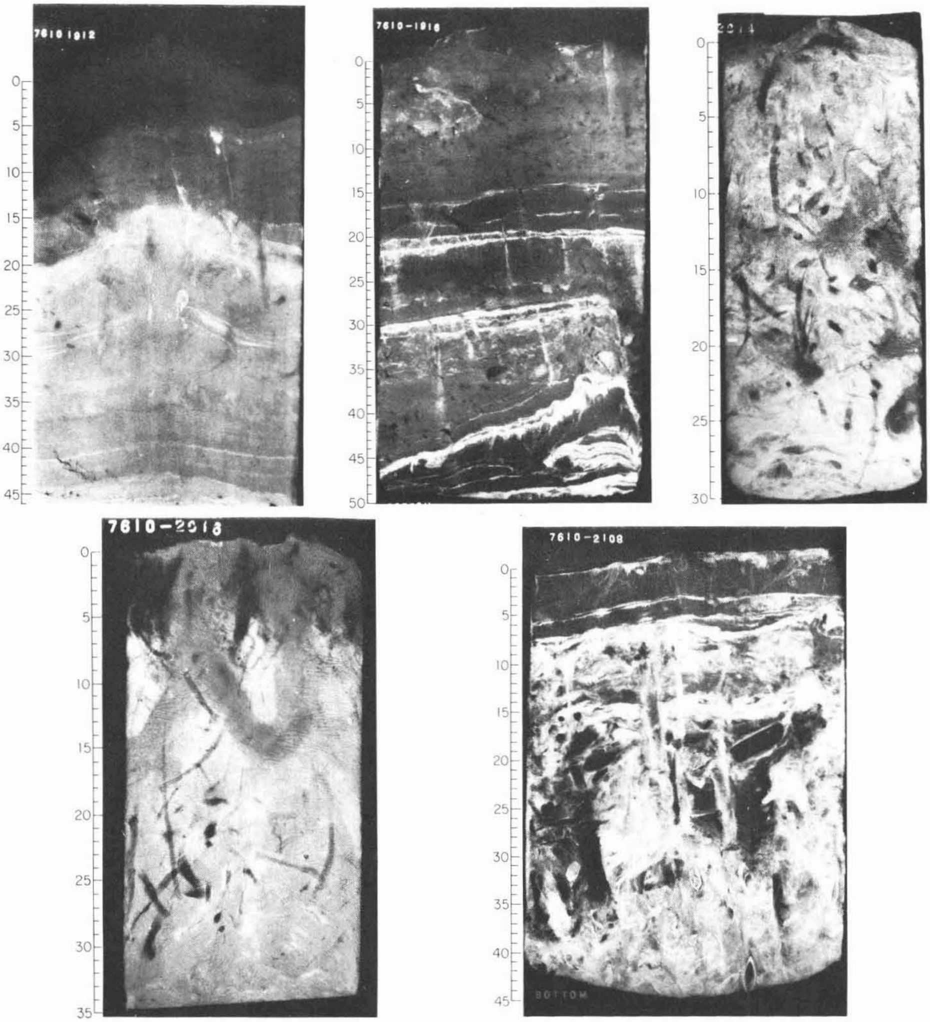

Figure 2. X-ray pictures of core sections. The marsh cores 2014 and 2016 display dark grey, randomly oriented streaks which are the roots of the marsh grass *Spartina alterniflora*. In River Core 1912 the slight density contrast in the upper 20 cm reflects a high water content. The thin white laminae in the middle and lower sections of the core are fine grained sand. Note the small shell at 16 cm. The upper 15 cm of Core 1916 is mottled without any apparent layering, whereas at depth white laminae composed of fine grained sand are present. The top 7 cm of core 2108 has thin white laminae; below this level, the deposit appears chaotic with randomly sited shells and no indications of lamination. The dark objects at 20 cm are wood fragments

Table I. Sample Locations

date collected	no.	latitude	longitude	description
10/19/76	7610-1912	32° 04′ 20″ N	81° 00′ 30″ W	Wilmington River; box core 46 cm long; water depth 3 m
10/19/76	7610-1916	32° 05′ 00″ N	81° 00′ 15″ W	Savannah River; south channel; box core 49 cm long, water depth 4 m, 18 km above the mouth
10/20/76	7610-2014	32° 01′ 30″ N	80° 53′ 45″ W	marsh adjacent to south channel of Savannah River, 15-cm diam, open barrel core, 30 cm long
10/20/76	7610-2014	same location		marsh grass *Spartina alterniflora;* living plant material
10/20/76	7610-2016	32° 01′ 10″ N	80° 54′ 25″ W	marsh adjacent to Tybee River, 15 cm diam, open barrel core, 35 cm long
10/20/76	7610-2016	same location		marsh grass *Spartina alterniflora,* dead plant material
10/21/76	7610-2108	32° 01′ 15″ N	80° 53′ 45″ W	Savannah River, south channel, box core 42 cm long, water depth 4 m, 5 km above the mouth
10/25/76	7610-2508	31° 59′ 20″ N	81° 01′ 20″ W	Spanish moss

Techniques. The analytical techniques used in this investigation have been described in previous publications: lead-210 (*6, 7*); heavy metals (*2*); plutonium (*8*); and quartz (*9*).

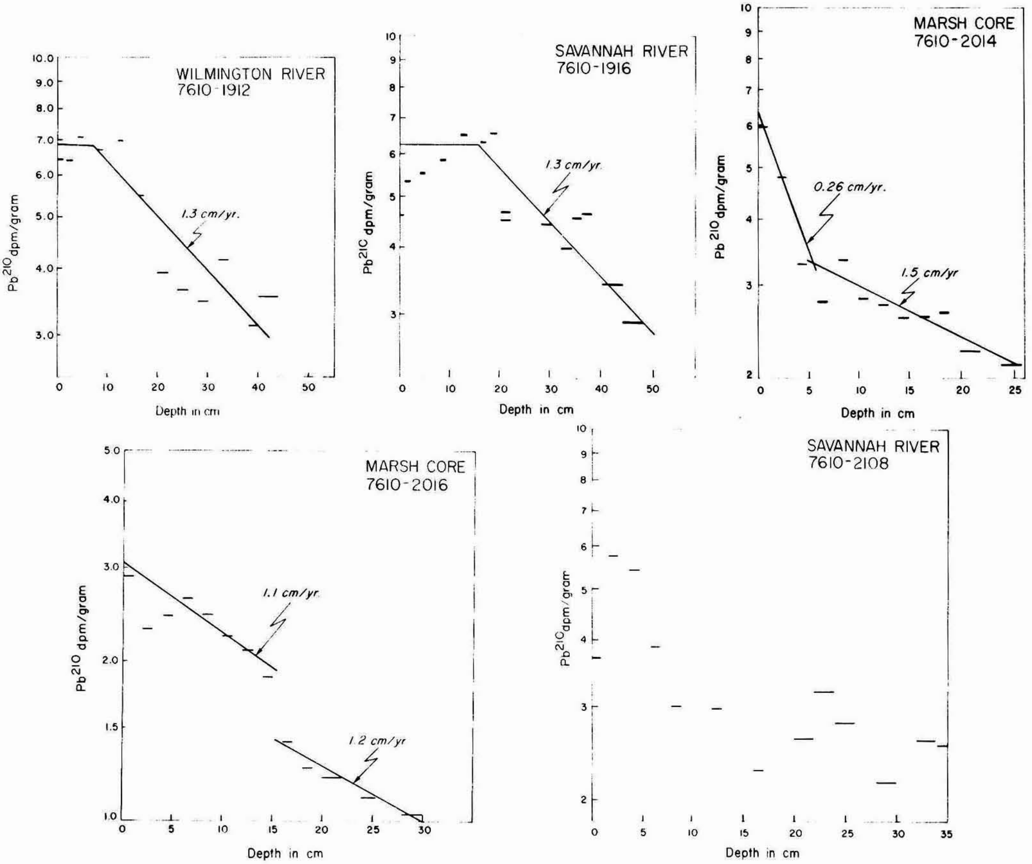

Figure 3. The Pb-210 depth profiles of the box cores

Time Frames for the Sediments

Sedimentary geochronologies were based upon ^{210}Pb and artificial radionuclide depth profiles. ^{210}Pb, with a half-life of 22 years, was assumed to be unsupported in the strata sampled, which covered a time interval of several decades. The artificial radionuclides are first detectable in coastal marine sediments about 1954 (*3, 8*), and this criterion was used also to establish time scales. Only where both methods are in agreement are assigned ages of strata considered reliable.

Marsh Core 7610-2016. The ^{210}Pb profiles (Figure 3 and Table II) indicate a sedimentation rate of 1.1 cm/year over the first 15 cm and 1.2 cm/year over the second 15 cm. Unusual and unexplainable is the break in the ^{210}Pb profile at 15 cm. If the rate is uniform over the 30 cm of core, then the age of the lower strata is computed to be about 1950. $^{239+240}$Pu disappears in the lowest part of the core, the 28–30-cm stratum (Table II), and this would correspond to about 1954. Thus, for the extent of the core, the two techniques appear to be in agreement within several years for any given stratum. The X-ray picture of the core does not show any stratification or any evidence of a discontinuity at 15 cm. The roots of the marsh grass *Spartina* are evident throughout the deposit as dark grey, randomly oriented streaks on the X-ray picture (Figure 2).

Wilmington River Core 7610-1912. The ^{210}Pb profile below 13 cm indicates a sedimentation rate of around 1.3 cm per year (Figure 3 and Table II). The near-uniform values in the upper 13 cm may be a consequence of bioturbation. The plutonium-239+240 disappears between the 30- and 44-cm levels, the former having a ^{210}Pb age of 1953 and the latter, 1943. Bioturbation can result in a transfer of plutonium, as well as ^{210}Pb, to deeper levels. Still, there is reasonable agreement between the two geochronologies and the rate of around 1.3 cm/year appears valid. Stratification is evident in the X-ray picture of the core section (Figure 2) and supports continuous, undisturbed deposition between 13 and 44 cm.

Marsh Core 7610-2014. The two geochronologies are not in accord. The ^{210}Pb profile indicates an initial sedimentation rate of 0.26 cm/year to a depth of about 5 cm (Figure 3; Table II). Then a rate change takes place and the deeper strata accumulate at about 1.5 cm per year. According to the former rate, the 5-cm level is about 20 years old and in adjacent deeper strata, the $^{239+240}$Pu should disappear. However, the transuranic radionuclides are still detectable at the 24- to 26-cm level. The X-ray picture of the core section (Figure 2) indicates an intensive intrusion of plant roots, which may have caused displacements of sedimentary phases.

Savannah River Core 7610-2108. The deposit has somewhat uniform concentrations of ^{210}Pb and $^{239+240}$Pu to the vertical extent of the box core, 34–36 cm (Figure 3; Table II). Higher levels of the nuclides are evident in the 2–3- and 4–5-cm strata. If one neglects the 2–3- and 4–5-cm strata, a ^{210}Pb sedimentation rate of about 2 cm/year results. The strata would then have deposited over about an 18-year interval which could account for the high $^{239+240}$Pb concentrations at the core bottom. Still, the results clearly do not allow the introduction of a geochronology to the sediments. The X-ray

Table II. Plutonium Contents of Savannah Estuary Sediments (on a Dry Weight Basis)

depth in core, cm	$^{239+240}Pu$, dpm/kg	$^{238}Pu/^{239+240}Pu$ (act. ratio)
Marsh Core No. 7610-2014 Adjacent to South Channel Savannah River		
0–1	49.4 ± 2.2	0.06 ± 0.01
2–3	27 ± 1.1	
4–5	14.2 ± 0.9	0.02 ± 0.01
6–7	16.3 ± 1.2	0.04 ± 0.01
8–9	17 ± 0.9	0.05 ± 0.01
10–11	16.2 ± 1.2	0.02
14–15	8.9 ± 0.8	
20–22	8.3 ± 0.7	0.04
24–26	3.2 ± 0.3	
Wilmington River Core No. 7610-1912		
0–1	52.3 ± 2.6	0.05 ± 0.01
2–3	54.8 ± 2.3	0.05 ± 0.01
4–5	54 ± 4	0.05 ± 0.01
8–9	52 ± 2.6	0.05 ± 0.01
12–13	56.3 ± 4	0.04 ± 0.01
16–17	40.3 ± 1.9	0.04 ± 0.01
20–22	7.5 ± 0.7	
28–30	2.3 ± 0.4	
40–44	0.7 ± 0.2	
Savannah River (18 km from Mouth) No. 7610-1916		
0–1	51.7 ± 1.9	0.09 ± 0.01
4–5	66 ± 2.7	0.08 ± 0.01
8–9	84.6 ± 5	0.11 ± 0.02
12–13	75.7 ± 4	0.17 ± 0.02
16–17	70 ± 2.4	0.14 ± 0.01
20–22	61 ± 2.4	0.05 ± 0.01
28–30	58 ± 2	0.03 ± 0.01
34–36	68 ± 2	0.03 ± 0.01
40–44	13 ± 1	0.04 ± 0.02
Marsh Core No. 7610-2016, Adjacent to Tybee River		
0–1	18 ± 2.5	
4–5	26 ± 1.8	0.03 ± 0.01
6–7	36.5 ± 2.3	0.03 ± 0.01
8–9	34.6 ± 1.7	0.03 ± 0.01
14–15	10.9 ± 0.9	0.03 ± 0.015
20–22	2.2 ± 0.1	
28–30	0.9	
Savannah River (5 km from Mouth) Core No. 7610-2108		
0–1	27 ± 0.9	0.04 ± 0.01
2–3	44.7 ± 2	0.05 ± 0.01
4–5	45 ± 4	0.03
6–7	24.5 ± 2	0.05 ± 0.02
8–9	23.2 ± 1.5	0.04 ± 0.01
12–13	26.6 ± 1.5	0.03 ± 0.01
16–17	18.8 ± 2	
20–22	22 ± 1.4	0.04 ± 0.02
28–30	7.6 ± 1	0.06 ± 0.02
34–36	21.8 ± 1.2	0.03 ± 0.01

Table III. Plutonium and Cesium-137 Contents of Plants from Savannah River Estuary System (Activities Given on a Dry Weight Basis)

	$^{239+240}Pu$, dpm/kg	$^{238}Pu/^{239+240}Pu$ (act. ratio)	^{137}Cs, dpm/kg	$^{239+240}Pu/^{137}Cs$ (act. ratio)
Spanish moss (living) 7610 2508	7.5 ± 0.5	0.17 ± 0.03	1114 ± 37	0.007
Spartina grass (detritus) 7610 2016	4.6 ± 0.3	0.17 ± 0.03	201 ± 8	0.023
Spartina grass (living) 7610 2014	1.7 ± 0.1	0.31 ± 0.03	102 ± 3	0.017

picture (Figure 2) indicates some stratification in the upper layers. There are numerous clam shells at depth in the core, indicating the possibility of bioturbution by the living organisms.

Savannah River Core 7610-1916. The ^{210}Pb geochronology yields a sedimentation rate of 1.3 cm/year for depths below 13 cm (Table II; Figure 3). Bioturbation and/or physical mixing appears to take place to depths of about 13 cm. The lowest depth of the box core, 40–44 cm, would then have been deposited between 31 and 34 years ago. With mixing to 13 cm we can account for the presence of plutonium isotopes at these depths. Assuming an overall sedimentation rate of 1.3 cm/year and the first significant appearance of $^{239+240}Pu$ in the environment in 1954 (or at a depth of 28 cm), bioturbation would take the plutonium to strata deposited 10 years previously or a depth of 41 cm. The X-ray picture indicates evident stratification throughout the core below about 13 cm.

Two aspects of these results appear significant. First of all, there is the observation that the riverine deposits have a persistence over decades and thus can reveal sedimentation histories over such time periods.

Secondly, the centimeter/year sedimentation rates found herein do not agree with that of a 1 mm/year based upon eustatic changes of sea level (*10*). There is other evidence that a lower rate may prevail in this U.S. southeastern estuarine system. The 9 rivers which enter this salt marsh zone carry a suspended load of 8.5 × 10^{11} g/year or 4.2 × 10^{11} cm^3/year (assuming a density of 2 g/cm^3) (*5*). If this sediment is uniformly deposited over the salt marsh area of 4 × 10^5 ha, then an accumulation rate of 0.1 mm/year results.

This apparent conflict may be resolved by any of a number of factors. First of all, there may be precipitation of solids from the dissolved or colloidal water phases, a situation which would enhance the sedimentation rates derived solely from the measured particulate load of the rivers. Also, the values determined in this work may be site specific and not truly representative of the entire estuarine system. The coring sites were chosen with the sense that they would be able to maintain precipitated materials more readily than other zones. Finally, there are fluxes of solids of marine origin entering the rivers (see subsequent section) that will increase the accumulation rates based solely upon the river data.

Still, our three measured rates through their consistency appear more reliable than estimated rates based upon regional parameters.

Nonfallout Plutonium

In only one core is there evidence of nonfallout plutonium. The Savannah River Core 1916 displays elevated values of the $^{238}Pu/^{239+240}Pu$ ratios at levels 12–13 and 16–17 cm with values of 0.17 and 0.14, respectively (Table II). At sedimentation rates of 1.3 cm/year, the dates of accumulation of these high values of ^{238}Pu would be a period around 1966 and 1963, respectively. The plant released both ^{238}Pu and $^{239+240}Pu$ with higher levels of the former. Fifty-five curies of plutonium has

Table IV. Metal and Quartz Contents of Cores (Ppm, Except Quartz, Fe, and Al Which Are in Percent Dry Weight)

depth, cm	Pb	Zn	Cr	Cu	Co	Ni	Mn	Al	V	Fe	Qu
Wilmington River Core No. 7610-1912											
0–1	60	103	200	53	12	23	560	11.5	350	5.7	9
1–2	58	109	320	57	13	28	700	13.5	430	7.0	
2–3	44	90	280	45	11	19	520	10.3	340	5.1	8
4–5	48	98	250	53	10	20	550	10.9	460	5.4	
8–9	44	78	190	48	11	23	770	11.4	310	5.7	10
12–13	38	96	144	42	12	23	900	11.1	210	4.8	
16–17	41	85	170	47	14	24	680	10.9	260	5.4	
20–22											10
24–26	41	89	132	48	15	26	970	13.0	150	5.8	
30–32	44	102	124	54	16	30	1000	14.2	180	6.6	
38–40											9
40–44	45	95	122	54	16	31	840	12.6	170	5.7	
Savannah River Core No. 7610-1916											
0–1	48	85	150	49	12	23	310	10.1	290	4.0	20
1–2	42	91	180	49	12	25	330	10.3	300	3.8	
4–5	41	99	170	50	13	24	550	10.5	310	5.3	16
8–9	42	91	230	52	14	26	570	10.8	310	5.4	
12–13	42	105	190	56	14	27	560	11.3	360	5.6	
16–17	45	102	260	56	15	25	550	10.5	360	5.1	12
20–22	42	83	210	42	14	19	510	8.8	320	5.3	
28–30	44	64	160	34	12	18	300	7.4	210	3.8	
36–38	40	88	180	41	11	24	620	9.9	230	4.4	21
44–48	40	67	110	41	11	22	580	9.0	100	4.2	
Marsh Core No. 7610-2014											
0–1											20
1–2	31	31	130	32	9	16	275	8.1	160	4.1	
3–4	30	40	110	37	12	24	190	9.1	160	4.1	
5–6	31	48	100	38	14	24	220	9.0	144	4.2	
7–8	30	61	120	39	12	25	220	9.7	160	4.5	
8–9											15
9–10	30	58	120	38	14	24	250	9.6	160	4.8	
11–12	30	51	110	42	14	24	260	10.2	160	4.4	
13–14	28	63	100	36	13	24	250	10.0	146	3.9	
15–16	30	58	100	42	14	26	280	9.9	160	4.6	
17–18	29	64	100	41	17	28	315	9.9	160	4.7	
19–20	32	73	120	45	21	28	410	12.5	190	5.9	
20–22											12
22–24	25	50	90	36	14	25	340	8.6	123	4.9	
Marsh Core No. 7610-2016											
0–1											38
1–2	24	42	56	13	4	11	170	5.2	71	3.2	
3–4	26	47	59	14	5	11	180	5.4	81	3.5	
4–5											39
5–6	27	58	67	15	6	15	210	6.4	99	4.2	
7–8	27	58	68	16	6	16	220	6.5	100	4.2	
9–10	28	64	77	18	6	18	240	6.7	106	4.6	
14–15											39
15–16	24	51	65	16	7	11	230	6.3	94	4.0	
18–19											37
19–20	23	45	56	14	6	15	210	5.5	80	3.6	
22–24	20	50	55	14	7	17	220	5.5	85	3.6	

Table IV. Continued

depth, cm	Pb	Zn	Cr	Cu	Co	Ni	Mn	Al	V	Fe	Qu
26–28	18	38	48	12	5	12	210	4.7	68	3.1	
28–30											50
30–32	14	23	33	6	3	6	150	3.3	37	2.0	
Savannah River Core No. 7610-2108											
0–1	25	58	80	15	7	13	540	4.4	125	4.0	47
2–3	36	89	148	24	9	25	540	7.1	220	5.9	
4–5	26	70	115	18	8	17	470	5.9	160	4.7	33
8–9	24	65	93	16	8	13	470	4.9	160	4.6	
12–13	22	65	92	18	8	13	450	4.6	160	4.4	
16–17	24	67	94	18	7	13	420	4.5	170	4.9	56
22–24	20	53	81	15	5	19	340	4.0	136	3.8	
24–26	23	99	85	16	4	12	360	4.2	138	4.1	
30–32	29	77	88	19	6	14	420	5.4	150	5.1	
34–36	20	42	81	15	5	12	390	5.0	131	4.1	48

been delivered to the Savannah River watershed by fallout from weapons testing (*1*). Living *Spartina* and dead *Spartina* from stations 2014 and 2016, respectively, had unusually high ratios, 0.17 and 0.31 (Table III). The plutonium-238 may have been brought to the grass surfaces from the atmosphere with suspended soil debris from the area adjacent to the Plant. Spanish moss, which receives its nourishment from scavenging and from rainout and fallout, had a ratio of 0.17. This observation reinforces the argument for atmospheric, rather than riverine, transport for the ^{238}Pu. These soil particles are known to have elevated levels of this transuranic nuclide (*11*).

Metals

For the three cores in which time frames could be introduced, 7610-1916, 7610-2016, and 7610-1912, the manganese/aluminum ratios appear to increase with increasing depth (Figure 4; Table IV). The ratio was used instead of the absolute concentrations, inasmuch as there may be various dilutants of the river-borne solid inorganic phases such as organic matter and tidally introduced minerals such as quartz (see subsequent section). The behavior of manganese has been noted before in anoxic cores where the element enters the deposit in an oxidized form and is subsequently reduced to the mobile, divalent state. This latter form then diffuses molecularly out of the deposits to the overlying waters (*12*). The other two cores did not display such Mn/Al profiles. The concept that these latter cores were mixed and that the other three were continuously accumulated is strengthened.

In the Wilmington River Core (7610-1912), three metals, lead, chromium, and vanadium, appear to decrease with increasing depth, suggesting increased deliveries to the system in recent years (Figure 4). All three of the elements are recognized pollutants, mobilized by man, that often show such behaviors in coastal waters. Cores 7610-1916 and 7610-2016 appear to have near uniform concentrations of all metals measured except manganese.

The highest concentrations of the metals, exclusive of iron, were found in the two cores most distant from the ocean, 7610-1912 and 7610-1916. In estuarine systems, there is an extensive precipitation of metals in the zones where the salinities reach 10–15‰ (*13*). It is precisely in this area that reported salinities achieve such values (*14*). On the other hand, there exists the possibility that ocean-introduced solid phases might be diluting the riverborne materials, as has been suggested by Müller and Förstner (*15*). Meade (*16*) indicates that there is a movement of sand into the Savannah River estuarine system from the coastal zone. To assess this possibility, we analyzed the sediments for detrital marine minerals using quartz as a representative member (Table IV).

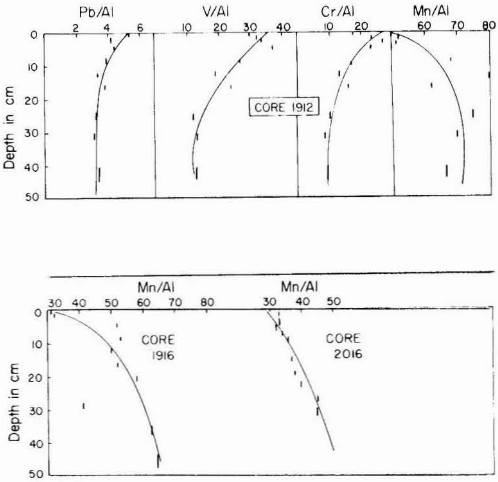

Figure 4. Heavy metal profiles in the box cores

Aluminum was chosen as the metal to test the "dilution hypothesis". Its content in the sediments would be trivially affected through the introduction of aluminum from the quartz, which contains only trace amounts of the light metal. The dilution effect of quartz was evident upon the aluminum concentrations. The absolute values of aluminum in the cores vary between 3.3 and 14.2%, greater than a factor of four (Table IV). When the aluminum concentrations are considered on a quartz-free basis, their range is reduced by a factor of two, to 6.6 to 14.4%. This dilution of the river-borne materials with the quartz can explain the variations in other metals, whose concentrations vary as does aluminum.

The iron concentrations are more uniform than those of aluminum. The reasons for this uniformity are as yet not understood.

The plutonium-239+240 levels in the surface sediments of the Savannah system achieve values up to 85 dpm/kg (level 8–9 cm in core 1916), similar to those of the surface sediments of Narragansett Bay (*3*), where activities of around 125 dpm/kg were observed and to those of Chesapeake Bay with a highest value of around 146 dpm/kg (*4*). The high values in the Savannah deposits are associated with sediments having low-quartz contents.

Overview

In this investigation to ascertain the possible leakages of transuranics from the Savannah River Plant into the Savannah River Estuary, several novel observations have evolved. First of all, some riverine deposits were shown to have maintained solid phases accumulated over periods of decades on the bases of ^{210}Pb and plutonium geochronologies.

Second, the dilution of heavy metal concentrations in the estuarine sediments through entry of tidally mobilized oceanic solid phases, relatively poor in heavy metals, is demonstrated. This observation confirms previous arguments for sand movement into the Savannah River estuarine system from the coastal zone. Thus, the quantitative importance of such oceanic contributions of solid phases to an estuarine system can be determined in principle.

Finally, the impact of man upon the composition of Savannah River is recorded in its deposits. Increased levels of lead, chromium, and vanadium, well-recognized pollutants, in the recently deposited strata provide the evidence for this argument.

Acknowledgments

Director David Menzel of the Skidaway Institution of Oceanography provided material, manpower, and spiritual resources without which this project could not have been carried out and for which we are extremely grateful.

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Received for review March 27, 1978. Accepted December 29, 1978. The research was sponsored by the Nuclear Regulatory Commission under Contract No. AT (49-24)-036 with the University of California.

Degradation of Diazinon by Sodium Hypochlorite. Chemistry and Aquatic Toxicity

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■ This study demonstrated that diazinon is rapidly degraded by sodium hypochlorite between pH 8 and 10. The sequence of reactions was determined and the two principal end products of the reaction were identified as acetic acid and isobutyramidinium trichloroacetate. Treatment with hypochlorite reduced the acute toxicity of diazinon dust formulations to bluegill by at least 3700-fold. Bioassay data indicated that a diazinon emulsifiable concentrate formulation retained considerable toxicity after treatment with sodium hypochlorite. The toxic components of the emulsifiable concentrate reaction mixture were identified as the heavy aromatic naphtha constituent of the formulation and the chlorinated aromatic hydrocarbons produced by the hypochlorite reaction. These components were almost as toxic as the diazinon formulation. A model approach emphasizing the need for bioassay data in development of chemical disposal systems is proposed and discussed.

Chemical treatment appears to be a reasonable means for disposing of small quantities of pesticide formulations and for field decontamination of empty containers (*1*). Therefore, we are investigating methods for chemical detoxification and disposal of organophosphate and carbamate pesticide wastes. The approach used in these studies is designed to provide sufficient data and information to allow an accurate assessment of the environmental impact and acceptability of the use of chemical treatment systems for disposal of pesticides and toxic wastes.

Diazinon was selected for the initial studies because of its widespread use. It is stable at pH 7 and can persist in the environment for as long as 6 months (*2*). The half-life of diazinon as determined by Faust and Gomaa (*2*) was 12, 4436, and 145 h at pH 3.1, 7.4, and 10.4, respectively. Meier et al. (*3*) obtained Arrhenius data for the acid hydrolysis of each diazinon formulation in use by the Army. This allowed prediction of the half-life of diazinon at any temperature between 5 and 50 °C. Although acid hydrolysis was effective in degrading diazinon, the resulting reaction mixtures retained a residual toxicity. This residual toxicity has been attributed to sulfotepp (*O,O,O,O*-tetraethyl dithiopyrophosphate), which occurs as an impurity in formulations of diazinon (*4*).

Preliminary studies with an alternative chemical approach indicated that diazinon in an aqueous 1% suspension of the emulsifiable concentrate was rapidly degraded by addition of sodium bicarbonate and sodium hypochlorite (Clorox, ~1.5 N OCl^-). A detailed study was initiated to determine the rates of the diazinon degradation as a function of pH, to identify the products of reaction, and to evaluate the toxicity and environmental effect of disposal of the final reaction mixture.

The purpose of this publication is not only to furnish spe-

Table I. Recipes for the Degradation of Diazinon Formulations by Clorox

formulation/quantity	water, mL	Clorox, mL	NaHCO$_3$, g
48.2% EC/1 mL	100	30	3
2% D/10 g	100	30	3

cific information on a chemical degradation system for diazinon in pesticide formulations, but also to provide a model (Figure 1) for the approach to be used in evaluation of any method for detoxifying hazardous materials prior to disposal. This model is especially useful where the "detoxified" material may enter streams or waterways. Combined use of chemical kinetics, product identification, and bioassays is essential to this model.

Experimental

Pesticide Formulations and Reagents. Military standard formulations of diazinon, the 48.2% emulsifiable concentrate (EC), FSN 684-782-3925, and the 2% dust (D), FSN 6840-753-5038, were used in this study. The EC contained 48.2% diazinon, 41.4% heavy aromatic naphtha, and 10.4% emulsifiers (Triton X-180 and X-190). Samples of Triton X-180 and X-190 were obtained from Rohm and Haas Corp. A sample of the heavy aromatic naphtha was obtained from the Exxon Corporation. A 100-mg sample of diazoxon, provided by Ciba-Geigy Corp., was used as a reference standard for this compound. The sodium hypochlorite used in this study was a commercial 5% aqueous solution, Clorox, that had a hypochlorite concentration of approximately 1.5 N. All other chemicals were ACS reagent grade.

Analysis of Reaction Mixtures. For a chemical analysis, a 5-mL aliquot of the reaction mixture containing the EC or dust formulation and Clorox was treated with 1 mL of methylene chloride containing hexadecane as an internal standard. The methylene chloride extract was analyzed by gas chromatography with a 6-ft glass column (0.25-in. o.d.) packed with 10% OV-17 on 80/100 Gas-Chrom W. A flame ionization detector was used. Kinetic results for the disappearance of diazinon and the formation of reaction products were obtained from the gas chromatographic data.

Elemental analysis, infrared and UV spectrophotometry, mass spectrometry, NMR, and, in some cases, comparison with gas chromatograms of known compounds provided confirmation of the identity of the isolated reaction products.

Chemistry. In the formulations studied, diazinon was degraded with sodium hypochlorite in solutions buffered with sodium bicarbonate. The proportions of formulation, water, Clorox, and sodium bicarbonate are shown in Table I.

Bioassays. Bluegills (*Lepomis macrochirus*), fathead minnows (*Pimephales promelas*), and daphnia (*Daphnia magna*) were exposed at 20 ± 1 °C to several concentrations of each test sample in static systems. The fish were less than 1 year old, and the daphnia were less than 24 h old. Test solutions were prepared in well water having a total hardness of 192 mg/L, a total alkalinity of 138 mg/L, and a pH of 8.2. A photoperiod of 16 h light/8 h dark was maintained. The fish bioassays lasted 96 h, and the daphnia tests lasted 48 h. The number of survivors in each test concentration was monitored daily (with daphnia, swimming ability was the criterion for survival). The survival data were used to determine the acute toxicity of each material.

Screening bioassays with fish were conducted by exposing a maximum of ten fish per concentration to a range of toxicant concentrations. Intervals between successive concentrations were usually greater than in the full-scale bioassays. The number of fish and volume of toxicant solution varied between bioassays. In some tests as few as two fish were exposed to 2 L of test water, whereas, in others, 10 fish were exposed to 14 L of test solution. At the end of each bioassay, the interval between the highest concentration that killed <50% and the lowest concentration that killed >50% of the exposed animals was reported as the "predicted LC$_{50}$ range".

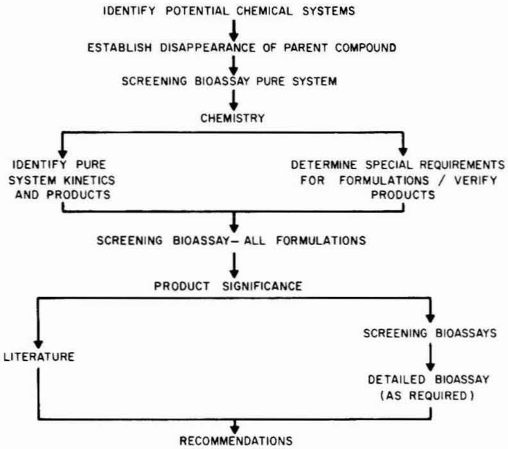

Figure 1. Approach for evaluating detoxification systems

Screening bioassays with daphnia were the same as those for full-scale tests, except that intervals between successive test concentrations were usually larger and only ten daphnia (five animals × two replications) were utilized for each test concentration. "Predicted EC$_{50}$ ranges" were estimated in the same manner as were LC$_{50}$ ranges for fish.

For full-scale bioassays, 20 fish per concentration (10 animals × 2 replicates) or 60 daphnia per concentration (5 animals × 12 replicates) were exposed to 5 or more concentrations of each test sample. Fish tests were conducted in 19-L jars containing 14 L of test solution. Daphnia tests were performed in 250-mL beakers containing 200 mL of test solution. For the bioassays with fish the 96-h LC$_{50}$ (median lethal concentration, i.e., concentration lethal to 50% of the exposed animals) was calculated by means of the method of Litchfield and Wilcoxon (5). For daphnia a 48-h EC$_{50}$ (median effective concentration, i.e., concentration which immobilized 50% of the exposed animals) was calculated by the same method.

The acute toxicities of the pesticide formulations were determined before and after treatment with hypochlorite. The acute toxicities of the separate constituents of the emulsifiable concentrate formulation were also determined. The species were exposed to various concentrations of Triton X-180 prepared from a stock solution of 1.0 g of compound in a liter of distilled water or to dilutions of a suspension of heavy aromatic naphtha (HAN) prepared by suspending 4.14 g of HAN in 1 L of water containing 1.0 g of Triton X-180. The latter suspension simulates the emulsifiable concentrate in the absence of diazinon. Since sodium hypochlorite may act on Triton X-180 to produce toxic products, the toxicity of such reaction mixtures was evaluated. A 100-mL aqueous solution of Triton X-180 (1 g/L) buffered with 3 g of sodium bicarbonate was treated with 30 mL of Clorox for 48 h. Prior to toxicity screening, this solution was treated with sodium thiosulfate to reduce excess hypochlorite.

Results

Reaction Sequence in Diazinon Degradation. The sequence of reactions found for the degradation of diazinon by sodium hypochlorite is shown in Figure 2. The products observed during the first few minutes of the reaction were

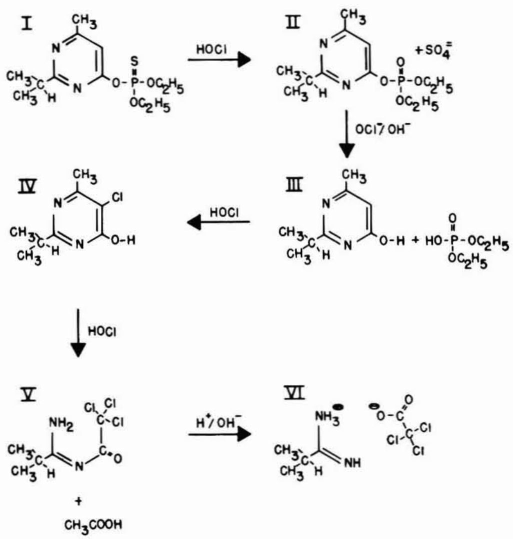

Figure 2. Sequence of reactions and products formed in the reaction of diazinon with sodium hypochlorite

Table II. Diazinon Degradation by Clorox as a Function of pH Using 100 mL of 1% Diazinon EC, 30 mL of Clorox, and 0.5–1.0 M Buffer

pH	buffer	half-life, s	comments
13.1	hydroxide	no reaction	
11.4	carbonate/phosphate	3000	no diazoxon observed
10.3	carbonate/phosphate	110	no diazoxon observed
10.0	carbonate/phosphate	78	no diazoxon observed
8.3	carbonate/bicarbonate	80	no diazoxon observed
6.8	phosphate	5000	diazoxon accumulation
5.8	phosphate	430	diazoxon accumulation
4.0	acetate	600	diazoxon accumulation

identified as diazoxon (*O,O*-diethyl 2-isopropyl-4-methyl-6-pyrimidinyl phosphate) and 2-isopropyl-4-methyl-6-pyrimidinol. These products were observed 2 min after the addition of hypochlorite to the diazinon emulsion. The mechanism by which the P═S bond is oxidized to P═O by hypochlorite was not determined, but sulfate ion was identified as a product in the reaction mixture by ring oven analysis (*6*). Conversion of the P═S moiety of diazinon to P═O (to give diazoxon) increased the rate of phosphate ester hydrolysis. In this study the presence of 0.15 N hypochlorite increased the rate of diazoxon hydrolysis at pH 11.4 by 25-fold as shown in Figure 3. The catalyzed hydrolysis of diazoxon by hypochlorite observed in these studies is similar to the hypochlorite-catalyzed hydrolysis of Sarin (isopropyl methylphosphonofluoridate) described by Epstein et al. (*7*). This agreed with results reported by Gomma et al. (*8*), who found that diazoxon was hydrolyzed 14 times faster than diazinon at pH 10.4. Thus, the rapid formation of 2-isopropyl-4-methyl-6-pyrimidinol observed in the early part of the reaction was probably due to hypochlorite-catalyzed hydrolysis of diazoxon. The pyrimidinol compound underwent further degradation by hypochlorite to yield two products that were initially designated as compounds IV and V. During the oxidation of IV to V, acetic acid was also formed. Compound V was degraded by acid or alkaline hydrolysis to a nonvolatile salt initially designated as compound VI. Authentic samples of compounds IV, V, and VI were prepared and characterized. They were used to aid in the identification of intermediates in the diazinon–Clorox reaction. Trichloroacetate ion was identified among the products and chloroform was detected as a minor reaction product. The yield of chloroform represented 5.5% (on a molar basis) of the diazinon present in the reaction mixtures and is apparently formed in a side reaction. The appearance of chloroform paralleled the formation of trichloroacetic acid.

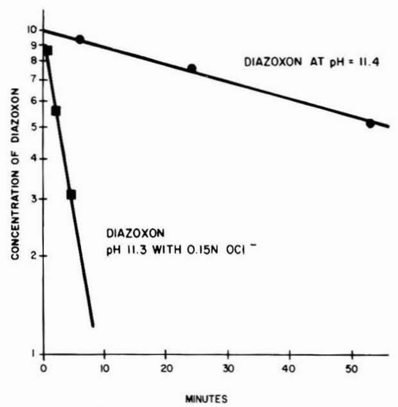

Figure 3. Rate of hydrolysis of diazoxon in the presence and absence of hypochlorite ion

Rate of Clorox Degradation of Diazinon in the Emulsifiable Concentrate and Dust Formulations. The rate of Clorox degradation of a 1% aqueous suspension of diazinon EC was found to be pH dependent. Table II presents a summary of the rates of diazinon degradation by sodium hypochlorite as a function of pH. At pH 13.1 no degradation was observed after 2 h. This is in agreement with Hsieh et al. (*9*), who observed that sodium hypochlorite in 1 N NaOH did not degrade parathion. Between pH 4.0 and 6.8, an accumulation of diazoxon was observed as the diazinon underwent degradation.

In these reactions, 30 mL of 1.6 N sodium hypochlorite was added for every 100 mL of 1% diazinon EC. Although the sodium hypochlorite concentration could be increased without adverse affect on the reaction, a minimum ratio of 1 mL of Clorox (1.6 N NaOCl) to 5 mL of a 1% aqueous suspension of diazinon EC was necessary. The use of less sodium hypochlorite resulted in an incomplete reaction to yield diazinon, and in some cases, diazoxon in the reaction mixture. Reproducible and complete degradation could be achieved with 100 mL of 1% diazinon EC, 30 mL of sodium hypochlorite, and 3 g of sodium bicarbonate. This reaction mixture had a pH of 8.4 ± 0.1 and gave a diazinon half-life between 45 and 85 s with no diazoxon observed during or after the reaction. Figure 4 shows the diazinon disappearance with time in this reaction mixture.

The diazinon dust formulation was readily degraded at pH 8.4 by Clorox (recipe in Table I). Under these conditions the half-life of diazinon at room temperature was 40 s with no diazoxon detected during or after the reaction. Figure 5 shows the diazinon disappearance with time for this reaction mixture.

Bioassay Results. Table III presents the aquatic toxicity data obtained by exposing test animals to diazinon formulations before and after reaction with sodium hypochlorite and to some components of the reaction mixtures. Hypochlorite degradation of diazinon in the dust formulation resulted in a considerable reduction in toxicity to all test animals. However, the reaction mixture from treatment of the diazinon EC formulation with sodium hypochlorite showed no reduction

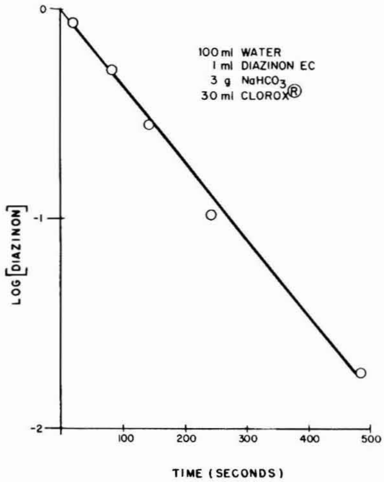

Figure 4. The rate of diazinon disappearance during the reaction of diazinon EC with sodium hypochlorite at pH 8.3

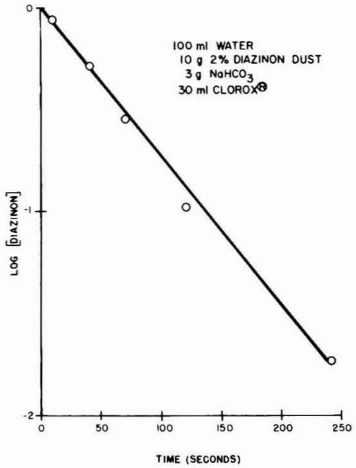

Figure 5. The rate of diazinon disappearance during the reaction of diazinon dust with sodium hypochlorite at pH 8.4

Table III. Calculated LC_{50} [a] or Estimated Range [b] of LC_{50}, in mg/L of Test Material

	fathead minnow	bluegill	*D. magna*
1. diazinon dust formulation	5.6–10.0	0.17	0.00122
2. diazinon dust formulation treated with Clorox	180–320	154	70.6
3. diazinon emulsifiable concentrate	3.7	0.53	0.00125
4. diazinon emulsifiable concentrate treated with Clorox	3.2–5.8	3.1–7.1	5.2
5. Triton X-180		20–50	20–50
6. Triton X-180 treated with Clorox		10–50	7.7–15.4
7. trichloroacetic acid	2000		2000
8. heavy aromatic naphtha (HAN) [c]	4.2–20.8	2.1–4.2	0.42–2.3
9. chlorinated HAN isolated from diazinon EC/Clorox reaction		3.25–5.28	4.2

[a] LC_{50} is the concentration of toxicant which killed 50% of the fish after 96-h exposure or immobilized 50% of the daphnids after 48 h. [b] Range within which LC_{50} or EC_{50} would be expected to fall, based upon preliminary bioassay using 20 daphnids and 10 or fewer fish per concentration. [c] Emulsified with 1 g of Triton X-180 per 4.14 g of HAN.

in toxicity to fathead minnows and only an approximate tenfold reduction to bluegill. The residual toxicity found in the diazinon EC–hypochlorite reaction mixture was apparently due to the formulation's components and not the final products of diazinon degradation.

Sulfotepp (*O,O,O,O*-tetraethyl dithiopyrophosphate) had been identified as an impurity in these formulations (*4*); however, it was readily degraded by sodium hypochlorite in these reactions. Further study demonstrated that the heavy aromatic naphtha (HAN) components of the emulsifiable concentrate were toxic to fish. This heavy aromatic naphtha had an aromatic petroleum fraction, boiling range 168–274 °C, consisting of a mixture of hydrocarbons from C_8H_{10} to $C_{11}H_{16}$. It is evident from Table III that although Triton X-180 is of relatively low toxicity to fish, the mixture of HAN with Triton X-180 was significantly more toxic. The HAN toxicity is sufficient to account for the observed residual toxicity of the hypochlorous acid–diazinon EC reaction mixture. Formation of chlorinated aromatic hydrocarbons was also observed in the reaction of the diazinon emulsifiable concentrate with sodium hypochlorite. These chlorinated products were analyzed by gas chromatography–mass spectrometry. At least 18 chlorinated compounds were separated by gas chromatography and identified by their molecular ion. The molecular ions observed were: $C_8H_9Cl^+$, *m/e* 140; $C_9H_{11}Cl^+$, *m/e* 154; $C_{10}H_{13}Cl^+$, *m/e* 168; and $C_9H_{10}Cl_2^+$, *m/e* 188. The toxicity of this partially chlorinated HAN to bluegill was comparable to that observed with emulsified HAN and may have contributed to the residual toxicity of the reaction mixture.

Discussion

Unlike most other reagents, hypochlorous acid plays a multiple role in the degradation of a variety of organic compounds, especially when it is in equilibrium with hypochlorite ion at a pH near its pK_a (*10*). In this reaction, diazinon undergoes oxidation (sulfur moiety) followed by nucleophile-catalyzed hydrolysis, stepwise chlorination, and probably nucleophilic, carbon–carbon cleavage. Each step is influenced by the presence of hypochlorous acid or hypochlorite ion.

Diazoxon, *O,O*-diethyl *O*-(2-isopropyl-4-methyl-6-pyrimidinyl) phosphate, is formed in the first step of the reaction of sodium hypochlorite with diazinon. Margot and Gysin (*11*) have reported that the cholinesterase inhibiting activity of diazoxon is about 4000 times greater than that of diazinon. This potentially hazardous compound can be produced as a stable reaction intermediate under acidic conditions. However, this hazard can be eliminated by strict control of reaction conditions to maintain the pH between 8.3 and 11.4, where no residual diazoxon is observed in the reaction mixture.

Trichloroacetic acid (Cl_3AcOH), a herbicide, is a major product in the oxidation of diazinon by sodium hypochloride. This study has shown a low acute toxicity for Cl_3AcOH to aquatic species. Johannes and Kemmerling (*12*) reported that trichloroacetic acid presents no hazard to fish and has low acute oral toxicity to warm-blooded organisms. The acute toxicity of Cl_3AcOH to rats occurs at 3200 mg/kg (*13*).

The aquatic bioassays demonstrated that hypochlorite oxidation of the emulsifiable concentrate did not detoxify the sample, even though the pesticide had been eliminated. The residual toxicity was probably due to emulsified aromatic hydrocarbons from the "inert ingredients" of the formulation and/or to chlorinated products from the reaction of hypochlorite with these ingredients.

Hypochlorite oxidation does degrade diazinon at a rate acceptable for use as a field method for disposal of wastes containing this pesticide. It is a simple and inexpensive approach that uses common reagents and would appear to be ideal for field use. However, this study has shown that hypochlorite does not detoxify all formulations of diazinon and that the diazinon–hypochlorite reaction does yield products (i.e., trichloroacetate and chloroform) that may cause environmental problems if disposed of in the field.

These results demonstrate the need for careful study of any chemical disposal system before its use is recommended. Such studies should follow an approach similar to that used in this effort (Figure 1) and must include bioassay comparisons to assure that the degraded material has been acceptably detoxified. As seen in this study, disappearance of the parent compound and identification of nontoxic products are not sufficient justifications for using a specific disposal method. An otherwise acceptable procedure may be unsafe for use because of toxic impurities, unidentified toxic products (from the pesticide and/or formulation), and/or toxic "inert" ingredients that are not detoxified by the chemical system. Screening bioassay of the material before and after chemical degradation should help to determine if the system has been detoxified. The combination of bioassay and chemical data allows a more accurate assessment of the environmental impact and of the acceptability of field disposal of the product waste.

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Received for review September 18, 1978. Accepted January 8, 1979.

Elemental Emissions from a Coal-Fired Power Plant. Comparison of a Venturi Wet Scrubber System with a Cold-Side Electrostatic Precipitator

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■ Emissions of elements in total suspended particles and in discrete particle-size intervals are compared for two coal-fired electrical generating units equipped with venturi scrubbers and one unit with a cold-side electrostatic precipitator (ESP). Coal and particulate emission samples were analyzed by instrumental neutron activation analysis, atomic absorption spectroscopy, and X-ray fluorescence. Emissions of Cr, Mn, Zn, Co, Ni, and Cu from the scrubbers were enhanced, probably because of corroded internal metal surfaces. Concentrations of many toxic elements, including Br, As, Se, Sb, U, V, and Cr, in aerosols emitted from the scrubber were up to 170 times greater than in aerosols from the ESP. The scrubber emitted a greater proportion of aerosol mass in particles of respirable sizes. We conclude that the wet scrubbers reduced the potential inhalation hazard from particulate emissions less effectively than an ESP of comparable efficiency.

Coal use for electric power generation in the United States is expected to increase from 3.6 to 5.1×10^{11} kg by 1980 (*1, 2*). Even now, release of potentially toxic substances to the atmosphere is of concern (*3–6*), and the possibility of adverse effects of these substances has stimulated considerable interest in the control of particulate emissions.

Electrostatic precipitation and wet scrubbing processes are the two major strategies employed to control particulate emissions at coal-fired electrical utility stations. Commercial wet scrubbers are very efficient in removing supermicron particles and reduce plume visibility greatly (*7, 8*). Besides controlling particulate emissions, the units simultaneously reduce SO_2 emissions (*7, 9*). Thus particulate scrubbers can be used both with and as flue-gas desulfurization systems. However, current commercial wet particulate scrubbers rely principally on impaction and interception mechanisms and theoretically should not remove efficiently the smaller, submicron particles (*7, 8, 10, 11*). In addition, resuspension of droplets from mist eliminators can augment the emission of fine particles from scrubbers (*12*). Of the types of scrubbers used on coal utility boilers, high-energy, venturi scrubbers are among the most efficient in removing submicron particles (*7, 10*).

In view of the greater respirability of fine particles (*13*) and the well-established concentration of many elements in fine particles from coal combustion (*5, 14–20*), the emission of substances from wet scrubbers and electrostatic precipitators must be scrutinized. In this work we compare elemental emissions and particle-size distributions from two power units equipped with high-energy, variable-throat, venturi wet scrubbers and a unit equipped with a cold-side ESP. Each of the units was in use at a Western coal-fired power plant at which the same coal was burned in all units. Because fly-ash elutriation and particle-size characteristics of the boilers were

0013-936X/79/0913-0598$01.00/0

Table I. Design and Operating Parameters of the Coal-Fired Utility Boilers Equipped with a Venturi Wet Scrubber or Electrostatic Precipitator System

parameter	scrubber units[a] no. 1	no. 2	ESP unit
boilers			
type	front-fired	front-fired	front- and rear-fired
efficiency, %[b]	87	87	88.7
excess air, %	15	12.5	16
max steam capacity, kg/s	160	203	654
control devices			
flue gas flow rate at inlet, m^3/s[c]	254	322	1026
temp,[d] °C	54	54	117
suspended particle concn at inlet, mg/m^3	20.2	20.2	23
SO_2 concn at inlet, ppm	650	650	800
efficiency of particulate removal, %	99.2[e] (99.7 ± 0.1)[g]	99.2[e]	97[f]

[a] Liquid-to-gas ratio, 1.4 L/m^3 (actual); make-up water for the system, 6.4 to 7.6 m^3/min; liquid delay time in the venturi-cycle loop, about 2 min; liquid temperature leaving the scrubber, 54 °C; pH of liquid in the thickener maintained at 7.5 by the addition of lime; suspended solids in recirculated flow maintained at 6%. [b] At maximum generating capacity. [c] Nominal value at 21 °C. [d] Measured at outlet sampling location. [e] Nominal value. [f] Estimated from elemental penetrations and plant-design data. [g] Measured during February sampling period at a differential venturi pressure of 36.8 mmHg and 95% of maximum electrical generating capacity.

Table II. Typical Coal Consumption and Efficiencies of Energy Conversion

power unit	load factor, %	coal consumption, g/s × 10^4	energy conversion efficiency, Btu/kW·h
scrubber-equipped units			
1 (Feb 76)	100	2.74	1.00×10^4
2 (June 75)	100	3.58	1.02×10^4
ESP-equipped units			
(July 75)	94	9.71	9.47×10^3
(July 75)	82	8.57	9.38×10^3

similar, the relative effectiveness of the two types of control devices can be evaluated for trace element removal by comparing their emissions.

Experimental

Power Units. Three separate units, designated as 1, 2, and 3, with respective maximum steam capacities of 160, 203, and 654 kg/s were tested. Blended, pulverized, surface-mined, subbituminous coal from the same source was burned in each of the units. All three boilers operated dry bottom without fly-ash reinjection. Flue gasses from both of the scrubber-equipped units (1 and 2) were fed through an air heater before entering the scrubber. Gasses from the scrubber passed through a mist eliminator, a wet, induced-draft fan, and another mist eliminator. The scrubbing solution was continuously recycled from the cyclone separator to the venturi. Blowdown from the cyclone was sent to a thickener where lime ($CaCO_3$) was added. The scrubber systems were designed to remove 99.2% of the incident particulate material and also removed 30 to 35% of the SO_2.

Gasses leaving the boiler of the ESP-equipped unit flowed through two cold-side precipitators, which were arranged in a chevron design, before exiting through a 91-m stack. The total specific collecting area of the ESP was 4760 cm^2/m^3. When all sections were operating properly, net removal efficiency of the ESP was typically 97%. Other specifications for the boilers and control devices are listed in Table I.

Sampling. Samples were taken with a modified, EPA-type sampling train as described previously (*20*). The same filter materials (47-mm, 0.4-μm pore, Nuclepore membranes) and University of Washington Mark III and Mark V source test cascade impactors (*21*) were used in each of the units. The impactors, respectively, provided 8 and 12 discrete fly-ash size fractions for chemical analysis ranging from ≤0.1 to ≥30 μm.

Samples were collected at the outlets of the scrubber mist eliminators and in-stack at the 61-m level of the ESP-equipped unit during two periods in June and July 1975. Scrubber maintenance was performed several months before sampling in June. Additional samples were collected from the first scrubber and the ESP unit along with inlet and outlet testing during a third period in February 1976 shortly after scrubber maintenance.

Records of plant-operating data collected hourly include gross generating load, coal consumption, and proximate analyses. Energy-conversion efficiencies (determined monthly), status of ESP sections, and scrubber venturi pressure (hourly) were obtained from plant personnel. Velocity, temperature, and pressure of the stack gas were monitored continuously during each sampling. Samples of coal, ESP fly ash, bottom ash, and scrubber slurry were also taken during the stack fly-ash collections.

Plant Operation. During the sampling period in June, operation of the scrubber-equipped units remained relatively stable. During the sampling period in July, 4 of the 32 precipitator sections were inoperative but compliance with emission standards (215 ng/J) and precipitator efficiency (97% for total suspended particles) were maintained by operating at reduced loads. In February, failure in the precipitator resulted in a 10- to 20-fold increase in emissions. These data are not reported.

Analyses. Stack-, ESP-, and bottom-ash, scrubber-slurry, scrubber-lime, and coal samples were analyzed for up to 43 elements by instrumental neutron activation analysis (INAA) as previously described (*22, 23*). Filter, fly-ash, and coal samples were analyzed for Pb, Cd, and Be by atomic absorption spectroscopy (AAS). Nickel, Pb, and Cd were determined in coal and fly-ash samples by energy-dispersive, X-ray fluorescence analysis (XRF) (*24*). Results from these techniques were verified by analyses of National Bureau of Standards' standard reference materials, coal (SRM 1632) and coal fly-ash (SRM 1633), and through interlaboratory comparisons of SRM samples (*25, 26*).

Size distributions of particles collected on several individual impactor stages, backup filters, and total filters, i.e., 47-mm filter preceded only by an inlet nozzle, were determined by scanning electron microscopy (SEM). The treatment and results of these data were discussed previously (*20*).

Data Normalization. Rates of atmospheric discharge of minor and trace element species in each sample were computed from the stack concentrations and gas velocities. Emission rates were further normalized to the boiler heat input to account for differences in coal consumption, electric power production, and efficiency of energy conversion of each unit. The heat input was computed from the gross generating load and energy-conversion efficiency of each unit. Coal consumption rates were computed from the gross generating load (L), the known thermal efficiency (a monthly average E), and the heat content of the coal (Q_c) as follows:

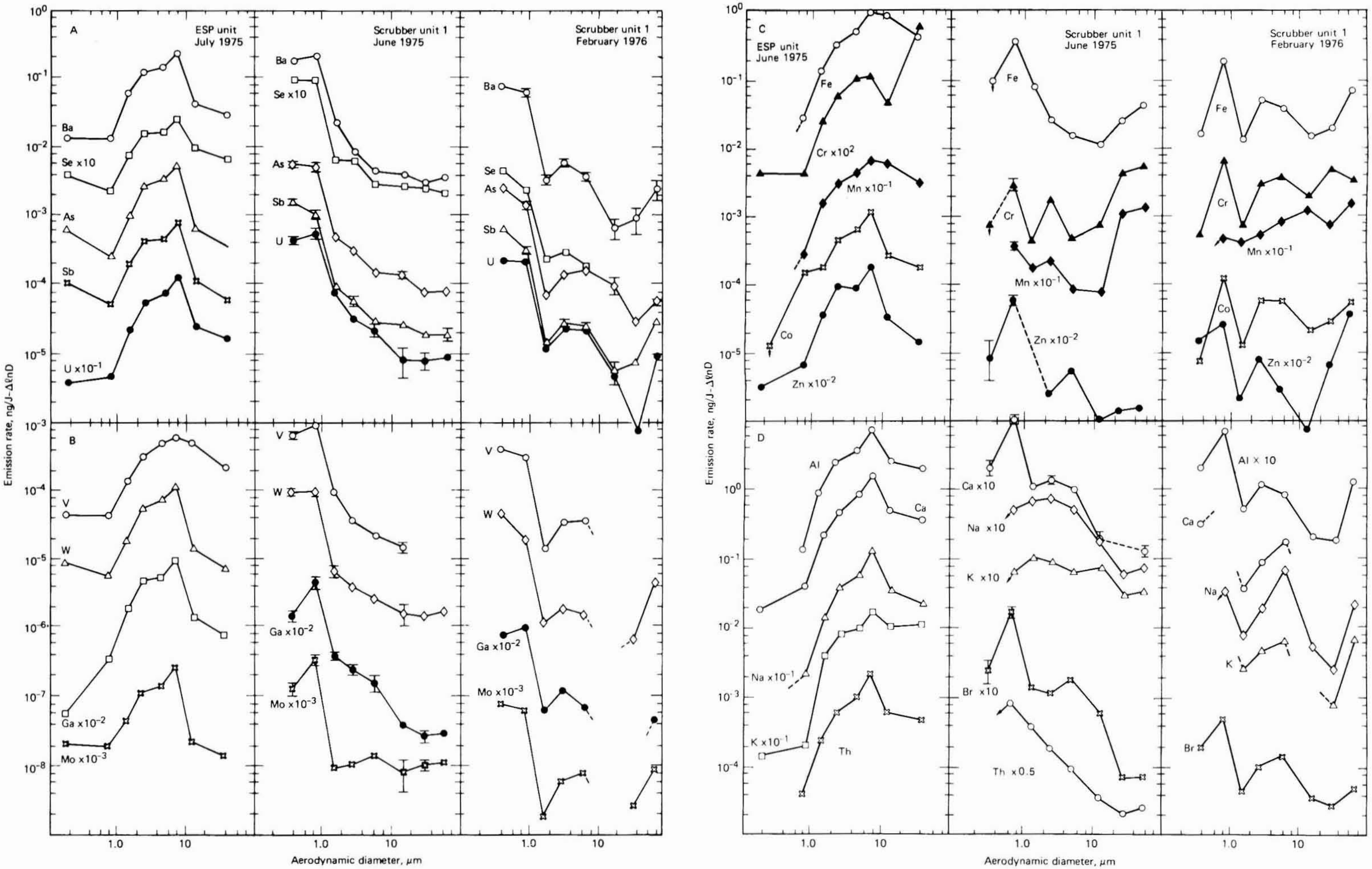

Figure 1. Particle-size distributions of elements emitted from power units equipped with a cold-side ESP and a venturi wet scrubber. The concentration data of individual elements are expressed as emission rate per joule of heat input to the boiler to allow comparison of the two units. The data are normalized to log size intervals (*D* = particle diameter)

Table III. Concentrations of Elements in Coal Burned during Sampling Periods ($\mu g/g$) [a]

elements	June 75	July 75	Feb 76
Al	30 100 ± 4990 (7)	30 300 ± 3600 (15)	29 500 ± 2390 (7)
As	2.03 ± 0.43 (7)	2.73 ± 0.71 (11)	2.84 ± 0.84 (6)
Ba	466 ± 108 (7)	418 ± 88 (14)	420 ± 167 (7)
Be	1.51 ± 0.17 (7)	1.67 ± 0.14 (9)	1.2 ± 0.6 (7)
Br	0.97 ± 0.20 (6)	0.96 ± 0.18 (2)	—
Ca	6 300 ± 1610 (7)	5 360 ± 730 (15)	5 620 ± 860 (7)
Cd	0.053 ± 0.020 (7)	0.061 ± 0.019 (10)	0.17 ± 0.02 (7)
Ce	24.9 ± 2.0 (7)	25.6 ± 1.7 (15)	27.0 ± 2.0 (7)
Cl	54.4 ± 11.5 (2)	71 ± 20 (4)	48 ± 17 (1)
Co	1.94 ± 0.17 (7)	1.98 ± 0.25 (14)	2.08 ± 0.22 (7)
Cr	6.12 ± 0.52 (7)	5.19 ± 0.29 (15)	7.02 ± 1.28 (7)
Cs	0.590 ± 0.084 (6)	0.70 ± 0.08 (15)	0.72 ± 0.16 (7)
Cu	14.0 ± 0.5 (2)	13.4 ± 1.2 (6)	12.7 ± 0.6 (7)
Fe	5 940 ± 740 (7)	5 720 ± 380 (15)	6 470 ± 570 (7)
Ga	8.30 ± 1.72 (2)	8.8 ± 1.4 (11)	8.48 ± 1.25 (7)
Hg	0.25 ± 0.05 (6)	0.065 ± 0.015 (5)	0.10 ± 0.02 (5)
In	0.037 ± 0.007 (4)	0.0415 ± 0.0046 (13)	0.039 ± 0.006 (5)
K	1 690 ± 170 (6)	1 820 ± 250 (14)	1 730 ± 260 (7)
La	13.0 ± 1.0 (7)	14.3 ± 0.8 (15)	13.4 ± 0.8 (7)
Mg	1 950 ± 460 (4)	2 330 ± 470 (11)	2 240 ± 753 (6)
Mo	2.4 ± 0.9 (1)	2.60 ± 0.54 (15)	2.67 ± 0.26 (6)
Mn	56 ± 24 (6)	54.1 ± 1.6 (15)	60.2 ± 20.0 (7)
Na	2 970 ± 370 (7)	2 940 ± 160 (15)	2 930 ± 248 (7)
Ni	4.4 ± 0.5 (2)	—	—
Pb	10.7 ± 0.5 (2)	10.2 ± 1.2 (16)	12.1 ± 0.7 (7)
Rb	9.95 ± 1.96 (7)	9.05 ± 0.53 (15)	12.1 ± 1.8 (7)
S [b]	5 800 ± 1000 (7)	5 200 ± 800 (2)	5 800 ± 600 (12)
Sb	0.656 ± 0.086 (7)	0.572 ± 0.049 (15)	0.614 ± 0.095 (7)
Sc	2.84 ± 0.20 (7)	2.77 ± 0.11 (15)	2.98 ± 0.20 (7)
Se	1.41 ± 0.11 (7)	1.55 ± 0.15 (15)	1.74 ± 0.25 (7)
Sr	88 ± 13 (7)	87.2 ± 8.9 (15)	97.7 ± 8.3 (7)
Ta	0.509 ± 0.038 (7)	0.492 ± 0.038 (15)	0.513 ± 0.056 (7)
Th	5.95 ± 0.41 (7)	5.73 ± 0.32 (15)	6.21 ± 0.67 (7)
Ti	1 120 ± 222 (6)	1 220 ± 200 (14)	1 230 ± 180 (6)
U	2.13 ± 0.11 (7)	1.85 ± 0.19 (15)	2.12 ± 0.25 (7)
V	22.9 ± 3.0 (4)	22.1 ± 3.2 (9)	24.9 ± 3.1 (4)
W	0.99 ± 0.40 (2)	0.80 ± 0.24 (5)	<0.13 (1)
Zn	15.8 ± 1.4 (6)	14.7 ± 1.7 (15)	16.4 ± 3.2 (7)
Zr	55.6 ± 8.7 (7)	52.2 ± 5.9 (15)	66.7 ± 9.8 (7)

[a] Averages and standard deviations; number of samples given in parentheses. [b] Analyses obtained from power plant.

$$\text{coal flow} = L(\text{kW}) \times E\,\frac{\text{Btu}}{\text{kW}\cdot\text{h}} \times \frac{1}{Q_c\,\dfrac{\text{Btu}}{\text{lb}}} \times 0.126\,\frac{\text{g}\cdot\text{h}}{\text{s}\cdot\text{lb}}$$

Rates of coal consumption and the efficiencies of energy conversion are listed in Table II. Consumption rates of individual elements were obtained by multiplying their concentrations in coal (Table III) by the coal consumption rate. Overall penetrations of individual elements were computed by dividing the emission rate by the consumption rate. Penetrations are independent of the concentrations of elements in coal.

Elemental concentrations in particles associated with the observed distributions were determined by INAA of impactor samples. Using SEM analysis, density measurements, and INAA, we corrected elemental mass on impactor backup filters for excess mass resulting from particle bounce-off and reentrainment to provide a more accurate estimate of the small particle component (see ref *20*). Particle-size distributions of several elements from both the scrubber-equipped (unit 1) and ESP-equipped units are shown in Figures 1A through D. Normalized emission rates (ng/J) are plotted vs. the aerodynamic diameters of particles on individual impactor stages and backup filters; aerodynamic diameters were determined from SEM measurements (*20*).

Results and Discussion

Scrubber Emissions. As shown in Table IV, emissions of most elements from the scrubber units agreed closely during June 1975, despite large differences in steam generating loads (about 160 and 203 kg/s in units 1 and 2, respectively). Thus, normalization to gross heat consumption accounts successfully for differences in coal consumption of these units (see Table II). Number vs. size distributions of fly-ash aerosols collected from each of the units were distributed bimodally, reflecting in part particles derived from vapor condensation and from residual mineral matter (fly ash) that is eluted from the boiler (see Table V). A third peak in aerosol size distribution was often observed in particles collected by impaction from scrubbers (Figure 1) in both the June and July experiments and is attributed to liquid aerosols that penetrate the mist eliminators.

In the scrubber experiment in June, ≥90% of the mass of

Table IV. Normalized Emission Rates of Elements in Particulate Emissions from Scrubber- and ESP-Equipped Electrical Generating Units (pg/J) [a]

Element	Scrubber, June 1975[b]		ESP unit, July 1975[c]			Scrubber unit 1, February 1976[d]		
	Unit 1	Unit 2	Sample at 82% Load	Range[e]		Median	Range	
Al	1320 ± 60	1130 ± 60	15,600 ± 500	3860 - 21,700		680 ± 20	367 - 1290	(22)
As	13.5 ± 0.2	9.2 ± 0.2	15.3 ± 0.3	5.77 - 15.3		5.24 ± 0.08	3.53 - 10.6	(23)
Ba	450 ± 20	580 ± 30	807 ± 10	243 - 807		97.9 ± 0.8	50.1 - 240	(23)
Be	—	—	0.72 ± 0.24	0.42 - 0.72	(3)	—	—	
Br	2.00 ± 0.03	0.53 ± 0.04	6.6 ± 3.5		(1)	0.98 ± 0.02	0.355 - 4.16	(21)
Ca	—	—	3400 ± 100	1590 - 3940		782 ± 47	525 - 1150	(15)
Cd	—	0.84 ± 0.34	0.26 ± 0.03	0.097 - 0.26	(4)	—	—	
Ce	0.93 ± 0.05	0.45 ± 0.09	16.0 ± 0.5	8.25 - 21.3		0.48 ± 0.03	0.35 - 0.83	(18)
Cl	63 ± 3	49 ± 3	—	—		37.0 ± 6.1	12.8 - 159	(13)
Co	0.57 ± 0.02	0.30 ± 0.01	2.38 ± 0.04	1.12 - 3.05		0.165 ± 0.005	0.0065 - 2.13	(22)
Cr	20.7 ± 0.2	3.4 ± 0.1	9.58 ± 0.36	3.1 - 30.5		13.4 ± 0.2	1.96 - 124	(22)
Cs	—	—	0.410 ± 0.031	0.209 - 0.615		0.014 ± 0.005	—	(1)
Cu	—	8.8 ± 1.0	—	—		11.6 ± 2.3	4.36 - 23.2	(4)
Fe	455 ± 20	425 ± 7	3670 ± 40	1980 - 5350		239 ± 14	160 - 1200	(21)
Ga	5.3 ± 0.2	2.9 ± 0.1	18.7 ± 1.0	9.74 - 19.8		2.01 ± 0.06	1.18 - 4.03	(20)
I	1.21 ± 0.04	0.82 ± 0.08	—	—		—	—	
In	0.019 ± 0.001	0.014 ± 0.001	0.108 ± 0.008	0.0339 - 0.108		0.0140 ± 0.0009	0.00820 - 0.0203	(17)
K	41 ± 6	49 ± 5	905 ± 200	441 - 1130		27.7 ± 5.0	13.6 - 72.9	(17)
La	0.46 ± 0.02	0.45 ± 0.01	8.96 ± 0.09	4.75 - 12.0		0.275 ± 0.009	0.124 - 0.524	(21)
Mg	230 ± 50	290 ± 110	1360 ± 380	1170 - 3240		112 ± 9	57 ± 11 - 570 ± 320	(15)
Mo	4.3 ± 0.2	2.7 ± 0.2	6.48 ± 0.76	2.26 - 8.61		2.07 ± 0.12	1.20 - 2.87	(20)
Mn	38 ± 1	15.7 ± 0.3	41.2 ± 0.5	9.07 - 41.2		23.0 ± 0.4	1.99 - 137	(22)
Na	230 ± 10	219 ± 6	2210 ± 10	1120 - 2810		170 ± 4	72.5 - 310	(22)
Ni	15 ± 4	—	—	—		13.3 ± 1.1	5.30 - 40.4	(9)
Rb	—	—	5.52 ± 0.57	2.52 - 7.52		—	—	
Sb	3.26 ± 0.06	1.7 ± 0.2	2.15 ± 0.04	0.863 - 2.15		1.38 ± 0.02	0.901 - 1.99	(21)
Sc	0.127 ± 0.005	0.097 ± 0.004	1.96 ± 0.02	1.03 - 2.72		0.0552 ± 0.0009	0.0391 - 0.107	(21)
Se	20.5 ± 0.5	21.0 ± 0.6	5.82 ± 0.16	2.83 - 6.07		12.9 ± 0.2	8.81 - 18.0	(21)
Sr	18.4 ± 0.8	20 ± 1	85.4 ± 8.0	32.2 - 111		9.44 ± 3.6	5.11 - 15.7 ± 3.8	(12)
Ta	0.056 ± 0.005	0.022 ± 0.008	0.323 ± 0.013	0.158 - 0.441		0.017 ± 0.003	0.00898 - 0.288	(11)
Th	0.22 ± 0.01	0.195 ± 0.007	3.67 ± 0.06	1.96 - 5.09		0.102 ± 0.004	0.0603 - 0.203	(19)
Ti	76 ± 9	77 ± 9	892 ± 90	338 - 1150		43.1 ± 9.0	27.2 - 86.8	(10)
U	1.08 ± 0.04	0.58 ± 0.04	3.29 ± 0.15	1.39 - 3.29		0.527 ± 0.008	0.254 - 0.751	(22)
V	16.6 ± 0.4	19.9 ± 0.6	39.7 ± 3.2	17.3 - 39.5	(5)	9.39 ± 0.53	5.84 - 13.9	(20)
W	2.26 ± 0.04	1.72 ± 0.04	2.78 ± 0.18	1.20 - 2.78		1.04 ± 0.03	0.690 - 1.37	(23)
Zn	8.8 ± 0.9	4.6 ± 0.3	44.8 ± 2.4	16.5 - 44.8		5.83 ± 0.52	2.51 - 69.4	(21)
Zr	—	6.6 ± 2.5	34.6 ± 7.1	13.1 - 41.1		2.46 ± 1.00	1.54 - 4.70	(5)
TSP[f]	—	—	123,000 ± 2000	65,000 - 123,000		10,900 ± 2200	10,100 - 16,100	(16)

[a] Uncertainty given is that of counting statistics of samples and blanks; variation among successive samples is generally less than 20% for the ESP unit, but somewhat larger for scrubber units. Uncertainties in the absolute emission rates from the ESP are estimated to be on the order of 30%. [b] Units 1 and 2 were operated at 97 to 100 and 89 to 100% of full generating capacity, respectively. Differential venturi pressure (ΔP_v) for both scrubber units ranged from 34 to 37 mmHg. [c] Unit operating at 83% capacity with four precipitator sections inoperative. Data are from up to eight samples unless indicated by number in parentheses. Wall and interstage losses were severe in impactor samples from ESP units and these samples are not included; data on scrubber units were derived from both filter and cascade impactor samples (see ref *20*). [d] Unit operated at 86 to 100% of full generating capacity with ΔP_v of 23 to 56 mmHg. [e] Unit operated at 69 to 95% of full generating capacity. [f] Total suspended particles.

most emitted elements occurred in particles of diameters ≤1 μm. Several elements, however, including Co, Cr, Fe, Mn, Cl, Br, Na, K, and Ca, often had appreciable or even major portions of their mass in aerosols of large sizes. Therefore, these elements are most probably contained in the liquid droplets. Scanning electron microscope analyses of dried impactor substrates collected in June revealed only submicron fly-ash particles on the uppermost (large particle) stages. However, on filter and impactor substrates collected in February, fly-ash particles with physical diameters as large as 6 μm were present. These larger particles suggest that the scrubber (unit 1) was less efficient in removing supermicron particles of the fly ash in February than in June. Despite this apparent decrease in collection efficiency of supermicron particles, the normalized elemental emission rates (Table IV) of the scrubber-equipped unit in June were 1.5 to 5 times higher than in February. As shown in Figure 1, the increased emission rates in June were generally confined to submicron-size particles. Evaporation of the liquid in entrained droplets can lead to the formation of submicron particles. Hence, the greater emissions in June may have resulted from entrainment problems with the mist eliminators and the high content of dissolved solids in the recycled scrubbing solution. All of the scrubber units were, however, operating within compliance (TSP emission ≤ 21.5 ng/J) during both sampling periods.

ESP and Scrubber Efficiency. Curves of particle collection efficiency vs. particle size for the ESP and unit 1 scrubber were constructed from the data from concurrent inlet–outlet sampling during February. As shown in Figure 2, the collection efficiency of the scrubber unit for supermicron particles is >99%, but below 1 μm drops off rapidly with decreasing particle size. The aerodynamic 50% cut-off diameter for the scrubber was about 0.75 μm, and its efficiency for TSP's was 99.7 ± 0.1% (see Table I). The negative efficiency for the collection of very small particles is attributed to mist entrainment and flash volatilization of liquid droplets that contain dissolved and suspended solids.

Unfortunately, the mechanical failures noted above prevented measuring optimum ESP performance. The ESP efficiency curve, however, agreed qualitatively with that typical of a cold-side ESP shown in Figure 3 (27). These curves are characterized by high collection efficiencies of both supermicron and submicron particles, with a shallow minimum for particles in the 0.1- to 1.0-μm range. Thus, we would expect submicron particles to penetrate the scrubber more effectively than the ESP. As noted above, the relative effectiveness of the two types of control devices may be inferred from particulate emission rates from each, if the particle size distributions of

Table V. Mass Median Aerodynamic Diameters (MMAD) of Elements in Aerosols Emitted from Two Coal-Fired Electrical Generating Units (μm)

ESP unit, July 1975		scrubber unit, Feb 1976	
elements	MMAD,[a] μm	elements	MMAD,[a] μm
Cr, Cs, Rb, Zr	10.7–12.3	Co, Cr, Ni	7.1–12
		Fe, K, Mg, Na, Zn	3.0–4.0
Al, Br, Ce, Co, Dy, Eu, Fe, Hf, K, La, Lu, Mg, Nd, Sc, Sm, Ta, Tb, Th, Ti	9.1–10.0	Al, Br, Ce, Dy, Hf, Lu, Sc, Sm, Th, La	1.4–2.1
		Ca, Ga, In, Mo	1.69–0.81
Ca, Mn, Na, Se	7.9–8.6		
As, Ba, Ga, In, Mo, Sb, U, V, W, Zn	4.4–6.3	As, Ba, Sb, Se, U, V, W	0.49–0.59
total suspended particles[b]			
small mode	0.13 ($\sigma_g{}^c = 1.42$)		0.33 ($\sigma_g{}^c = 1.57$)[d]
large mode	8.1 ($\sigma_g{}^c = 2.2$)		0.80 ($\sigma_g{}^c = 1.20$)[d]

[a] Range of median values of MMADs from distributions of up to six impactor samples. [b] Determined from SEM particle counting techniques (*20*). [c] Geometric standard deviation. [d] Data from SEM analyses of filter sample collected in June 1975.

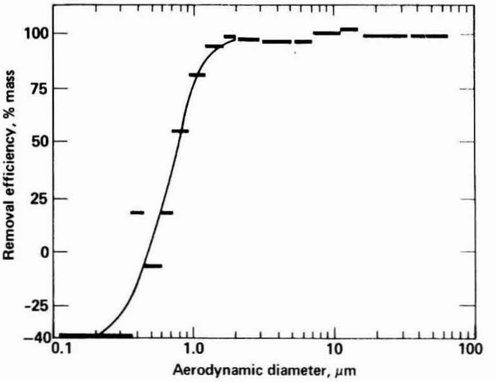

Figure 2. The venturi wet scrubber system is inefficient in removing particles of submicron diameters

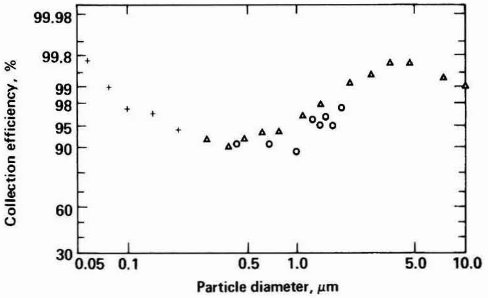

Figure 3. Particle removal efficiency of a cold-side ESP is relatively uniform over the entire range of particle sizes. Reprinted with permission from ref *27*. Copyright 1975 Air Pollution Control Association

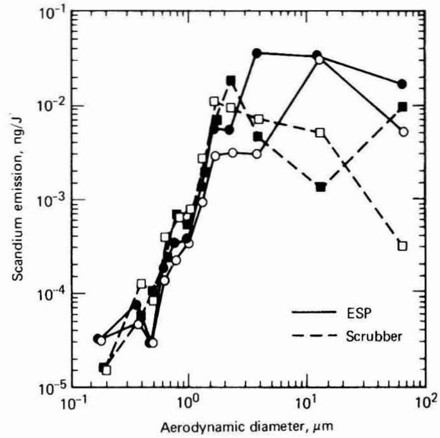

Figure 4. Emission rate of Sc in aerosols collected at the inlet of the precipitator and wet scrubber

aerosols entering the two devices are known.

Size distributions of particles entering both a scrubber system (unit 1) and the ESP were measured with cascade impactors during the February experiment. The distributions of Sc (Figure 4), an element which is independent of particle size, indicate that normalized rates of mass flow (mass/unit heat input) and particle-size distributions are nearly the same for particles <2 μm. The considerable discrepancy in the curves at larger particle sizes probably results from problems associated with turbulence and severe losses on walls of the impactor. The data reflect single-point sampling in turbulent inlet ducts and, hence, difficulties in obtaining truly isokinetic and representative sampling. As shown in Figure 4, the results of successive measurements at the inlet of particles ≥ 5 μm in both control devices generally agreed poorly. Based on the engineering parameters, the normalized fly-ash input (mass/gross boiler heat input) should be equal to that of the ESP. Because the composition of the coal burned during each sampling period was essentially identical (see Table III), emissions normalized to gross boiler heat input may be compared directly.

Neglecting small differences in elemental concentrations in coal ($\leq$7% for Sb), we can estimate the relative efficiencies of the two devices for collecting particles in the submicron and supermicron size ranges from the normalized curves of emission rate vs. particle size (Figure 1). Based on elements such as As and Sb for which concentrations in small particles can be determined most accurately (see ref *20*), scrubber emissions (February data) of submicron particles collected on the backup filter are about six times greater than ESP emissions. Scrubber emissions of these elements in the supermicron particles, however, are only about 1/11 of those in the ESP emissions after accounting for losses on the walls in ESP impactor samples, which were as high as 40% (see ref *20*). Thus, because normalized mass inputs to both devices were the

Table VI. Penetration of Elements Contained in Particles Emitted from a Venturi Wet Scrubber and an ESP-Equipped Coal-Fired Generating Unit (%)

element	ESP unit, July 1975		scrubber unit, Feb 1976	
	sample at 82% load	range[a]	median[a]	range
Al	1.1 ± 0.1	0.26–1.5	0.047 ± 0.004	0.025–0.088
As	11.5 ± 3.0	4.3–11.5	3.7 ± 1.1	2.5–7.5
Ba	4.0 ± 0.8	1.2–4.0	0.47 ± 0.19	0.24–1.2
Be	0.9 ± 0.3	0.5–0.9 (2)	–	–
Br	0.14 ± 0.08		(2.1 ± 0.4)[b]	0.75–8.8
Ca	1.3 ± 0.2	0.61–1.5	0.28 ± 0.05	0.19–0.41
Cd	8.8 ± 3.0	3.3–8.8 (4)	–	–
Ce	1.29 ± 0.09	0.67–1.7	0.036 ± 0.003	0.026–0.062
Cl	–	–	1.6 ± 0.6	0.54–6.7
Co	2.5 ± 0.3	1.2–3.2	0.16 ± 0.02	0.063–2.1
Cr	3.8 ± 0.3	1.23–12.1	3.9 ± 0.7	0.56–36
Cs	1.2 ± 0.2	0.61–1.8	0.040 ± 0.017 (1)	–
Fe	1.32 ± 0.09	0.71–1.9	0.075 ± 0.008	0.050–0.38
Ga	4.4 ± 0.7	2.3–4.6	0.48 ± 0.07	0.28–0.96
In	5.4 ± 0.7	1.7–5.4	0.73 ± 0.12	0.43–1.1
K	1.0 ± 0.3	0.50–1.3	0.032 ± 0.008	0.016–0.085
La	1.29 ± 0.07	0.68–1.7	0.042 ± 0.003	0.019–0.079
Mg	1.2 ± 0.4	1.0–2.9	0.10 ± 0.03	0.051[c]–0.51[d]
Mo	5.1 ± 1.2	1.8–6.8	1.6 ± 0.2	0.91–2.2
Mn	1.6 ± 0.5	0.35–1.6	0.77 ± 0.26	0.067–4.6
Na	1.55 ± 0.09	0.78–2.0	0.12 ± 0.01	0.050–0.21
Pb	5.5 ± 1.1	2.2–5.5 (4)	–	–
Rb	1.3 ± 0.1	0.57–1.7	–	–
Sb	7.7 ± 0.7	3.1–7.7	4.5 ± 0.7	3.0–6.6
Sc	1.46 ± 0.06	0.77–2.03	0.037 ± 0.003	0.027–0.073
Se	7.7 ± 0.8	3.8–8.1	15 ± 2	10–21
Sr	2.0 ± 0.3	0.76–2.6	0.20 ± 0.08	0.11–0.32
Ta	1.3 ± 0.1	0.66–1.9	0.067 ± 0.014	0.035–1.1
Th	1.32 ± 0.08	0.70–1.8	0.033 ± 0.004	0.020–0.066
Ti	1.51 ± 0.03	0.57–1.9	0.071 ± 0.018	0.045–0.14
U	3.7 ± 0.4	1.6–3.7	0.50 ± 0.06	0.24–0.72
V	3.7 ± 0.6	1.6–3.7	0.76 ± 0.10	0.47–1.1
W	7.2 ± 2.2	3.1–7.2	(2.6 ± 0.8)[b]	1.7–3.5
Zn	6.3 ± 0.8	2.3–6.3	0.72 ± 0.15	0.31–8.6
Zr	1.4 ± 0.3	0.52–1.6	0.075 ± 0.032	0.047–0.14

[a] Number of samples was eight unless otherwise indicated. [b] Data based on elemental concentration in coal collected during July 1975. [c] Unusually high uncertainty of ±0.020. [d] Unusually high uncertainty of ±0.34.

same, the scrubber must be much less efficient than the ESP in removing submicron particles. Furthermore, as shown in Table VI, the overall penetration of As (3.7%) in scrubber aerosols of MMAD of 0.51 μm (Table V) is about 80 times larger than the overall penetration of Al (0.047%), which is associated with aerosols with an MMAD of 1.7 μm. Thus, as one would expect, the overall penetration of a specific element is dependent on its concentration in small particles.

Penetrations of Elements. In Table VII, we compare penetrations of elements through the ESP-equipped unit (July data) to those from the scrubber-equipped unit (February data) measured over the entire particle-size range. The penetration ratios are nearly identical with the normalized emission rates except that they account for the small differences in elemental concentrations in coal.

As shown in Table VII, despite an 11-fold greater efficiency in TSP removal, i.e., 1/0.087 or ((1 − 0.997)/(1 − 0.97)), the penetration of elements in the first group through the scrubber was as much as 58% (for Sb) of that through the ESP-equipped unit. Substantial fractions of Br and Se apparently occur in the vapor phase at stack temperatures (*10*). Thus, the very large relative emission of Se and Br probably results from both scrubbing and condensation occurring at the lower gas temperature at the scrubber sampling location (54 vs. 110 °C in the ESP stack).

Most of the elements in group 1 of Table VII are associated with ESP and scrubber aerosols of smaller MMADs (see Table V) on which their concentrations are typically highly enriched (*5, 14, 16–20*). This might be attributed to their presence in coal partly as volatile inorganic or organic species or as fine mineral grains. Considerable evidence of augmented emission via mechanisms of entrainment and droplet evaporation exists (*10, 28, 29*) and suggests that high penetrations of several elements including S, Na, and K, which may be leached into the recycled scrubbing solution, result from the evaporation of droplets to form fine particles. It is likely, therefore, that the emission of lime-associated elements, i.e., Ca, Al, Mg, K, and Fe, present in limestone at 68, 2.4, 0.87, 0.13, and 0.11%, respectively, is especially augmented by these processes and might account to some extent for their presence in fine particles and their enhanced emission from the scrubber-equipped unit.

Scrubber emissions of Cr and Mn, and to some extent Zn and Co (group 2), were also enhanced relative to the TSP. Emission of these elements seems to be enhanced by corrosion of metal surfaces inside the scrubbers. Although independent evidence (*30*) supports this conclusion, the magnitude of the enhancement might be in error because of possible contami-

Table VII. Ratios of Emissions Rates and Estimated Potential Pulmonary Deposition of Elements from a Venturi Wet Scrubber and an Electrostatic Precipitator (February Scrubber Data: July ESP Data)

Element	Penetration ratio[a]		Pulmonary deposition ratio[b]		Concentration ratio[c]	
	Median	Range	Median	Range	Median	Range
			Group 1			
Br	15 ± 0.04	5.4 - 63	27 ± 7	10 - 1100	170 ± 0.5	66 - 250
Se	1.9 ± 0.1	1.2 - 5.5	3.9 ± 0.5	2.7 - 12	22 ± 3	15 - 22
Sb	0.58 ± 0.02	0.39 - 2.1	0.93 ± 0.21	0.63 - 3.5	6.7 ± 0.7	4.8 - 8.4
W	0.36 ± 0.03	0.25 - 1.1	0.61 ± 0.14	0.40 - 1.8	4.1 ± 0.6	3.0 - 4.4
As	0.32 ± 0.01	0.22 - 1.7	0.57 ± 0.07	0.39 - 3.1	3.7 ± 0.4	2.7 - 6.8
Mo	0.31 ± 0.04	0.13 - 1.2	0.65 ± 0.20	0.28 - 2.6	3.6 ± 0.6	1.6 - 4.8
V	0.21 ± 0.02	0.13 - 0.69	0.44 ± 0.04	0.27 - 1.4	2.4 ± 0.4	1.6 - 2.8
Ca	0.22 ± 0.015	0.13 - 0.67	0.41 ± 0.04	0.23 - 1.3	2.5 ± 0.3	1.6 - 2.7
U	0.14 ± 0.01	0.065 - 0.45	0.35 ± 0.05	0.17 - 1.2	1.6 ± 0.2	0.79 - 1.8
In	0.14 ± 0.01	0.080 - 0.65	0.25 ± 0.04	0.14 - 1.1	1.6 ± 0.2	0.98 - 2.6
Ba	0.12 ± 0.005	0.060 - 1.0	0.22 ± 0.03	0.12 - 1.9	1.4 ± 0.2	0.73 - 4.0
Ga	0.11 ± 0.01	0.061 - 0.42	0.24 ± 0.03	0.13 - 0.90	1.3 ± 0.2	0.74 - 1.7
Sr	0.10 ± 0.04	0.042 - 0.42	[d]--	--	1.1 ± 0.4	0.51 - 1.7
			Group 2			
Cr	1.03 ± 0.06	0.046 - 29	2.8 ± 0.2	0.12 - 80	12 ± 2	0.56 - 120
Mn	0.48 ± 0.02	0.042 - 13	1.0 ± 0.04	0.086 - 27	5.5 ± 0.6	0.51 - 52
Zn	0.11 ± 0.01	0.049 - 3.7	0.30 ± 0.07	0.13 - 9.7	1.3 ± 0.2	0.060 - 15
Co	0.064 ± 0.003	0.020 - 1.8	0.11 ± 0.01	0.034 - 3.0	0.74 ± 0.08	0.24 - 7.2
TSP	0.087 ± 0.009	0.082 - 0.25	--	--	≡1.0 ± 0.1	≡1.0 - 1.0
			Group 3[e]			
Mg	0.08 ± 0.03	0.02 - 0.5	0.15 ± 0.07	0.04 - 1.0	0.9 ± 0.2	0.2 - 2.0
Na	0.077 ± 0.003	0.025 - 0.27	0.13 ± 0.01	0.044 - 0.5	0.89 ± 0.10	0.30 - 1.1
Zr	0.05 ± 0.02	0.03 - 0.3	[d]--	--	0.6 ± 0.2	0.4 - 1.2
Fe	0.057 ± 0.004	0.030 - 0.54	0.13 ± 0.03	0.060 - 1.2	0.66 ± 0.09	0.37 - 2.2
Ti	0.047 ± 0.011	0.024 - 0.25	0.080 ± 0.025	0.03 - 0.44	0.54 ± 0.14	0.29 - 1.0
Al	0.043 ± 0.001	0.017 - 0.34	0.082 ± 0.008	0.032 - 0.63	0.49 ± 0.05	0.21 - 1.4
La	0.033 ± 0.003	0.010 - 0.11	0.061 ± 0.006	0.020 - 0.22	0.38 ± 0.05	0.12 - 0.44
K	0.031 ± 0.009	0.012 - 0.17	0.067 ± 0.019	0.026 - 0.37	0.36 ± 0.11	0.15 - 0.68
Ce	0.028 ± 0.002	0.016 - 0.092	0.043 ± 0.004	0.022 - 0.14	0.32 ± 0.04	0.20 - 0.37
Th	0.025 ± 0.001	0.011 - 0.094	0.055 ± 0.004	0.024 - 0.20	0.29 ± 0.03	0.13 - 0.38
Sc	0.025 ± 0.001	0.013 - 0.95	0.054 ± 0.004	0.027 - 0.19	0.29 ± 0.03	0.16 - 0.38

[a] Based on data in Table VI. Uncertainties are derived from analytical uncertainties only. [b] Predicted pulmonary deposition ratio at stack conditions (see ref *13* and *31*). [c] Emission ratio normalized to mass emission rates. [d] Element not determined in cascade impactor samples from both units. [e] Group 3 also includes the elements Nd, Eu, Yb, Sm, Dy, and Lu.

nation by corrosion of the stainless steel samplers.

Matrix elements such as Fe, Al, and Sc (group 3), as well as total particulate mass, are emitted in greater quantities per unit heat input from the ESP unit than from the scrubber unit because of their predominant association with large (MMADs of about 10 µm) silicate fly-ash particles, which are not as efficiently removed by the ESP as by the scrubber.

Lung Deposition. Particles greater than 10 µm are generally not considered respirable and, as indicated by the curve in Figure 5, pulmonary deposition of the smallest sizes is greatest (*13*). Because the MMADs of aerosols emitted from the scrubber-equipped unit (~1.7 µm for group 3 elements; see Table V) are much smaller than those from the ESP-equipped unit (10 µm for group 3 elements), we used the ICRP pulmonary deposition model (*13*) to estimate the relative alveolar deposition of aerosols emitted from the two units.

The predicted deposition (mass/unit heat input) from elemental emissions from both units was computed by numerical integration of the product of the mass vs. size distributions from the cascade impactor and the ICRP deposition data as described in Biermann and Ondov (*31*). Because the data reflect air at stack concentrations, only relative depositions are meaningful; these are listed in Table VII (pulmonary deposition ratios). We note that the ratios listed may change with distance from the plant because of the effects of coagulation and sedimentation. Therefore, the comparison is only qualitative.

Depending on their mass vs. particle-size distributions, the relative depositions of individual elements (pulmonary deposition ratios, Table VII) are about twice the corresponding values of the actual relative emissions (penetration ratios). Thus, the model predicts that the scrubber aerosols are deposited in the lungs to about twice the extent of those from the ESP, because of the smaller particle sizes in the aerosol. Neglecting Se, the median values of the pulmonary deposition of scrubber emissions of group 1 elements ranged from about 20 to 2700% of the ESP emissions; the maximum values were 90 to 11 000% of the ESP emission. The corresponding values

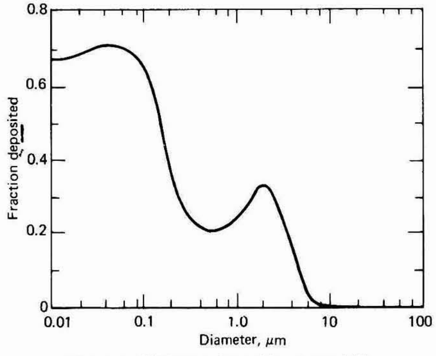

Figure 5. ICRP lung deposition curve (*13*)

for group 2 elements ranged from a low of 3.4%, the minimum value of Co, to a high of 8000% for Cr. The relative potential pulmonary deposition of group 3 elements from scrubber emissions was generally less than 15% of the ESP emissions, but ranged from about 1.6 to 120%. Thus, considering both overall efficiency (relative emission rates) and the distribution of particle sizes (relative potential pulmonary deposition), the venturi scrubber unit when operating properly was typically as effective or better, i.e., at least 50% of the time, in controlling the emissions of most elements associated with fine particles, including both group 1 and 2 elements. The scrubber was also generally much more effective in reducing emissions of the elements in group 3 on large particles. Notable exceptions were Cr, Mn, Ni, and Cu, which were frequently emitted in much greater quantities from the scrubber. During the June experiment (not shown in Table VII), the relative emission and relative potential depositions (pulmonary deposition ratios) of group 1 elements were from 2 to 5 times greater than those listed; and the corresponding values of group 3 elements were from 1.5 to 3 times greater than the listed values. In June, the scrubber was not operating optimally, probably because of mist entrainment problems discussed above, but was, however, operating in compliance with state emission standards (21.5 ng/J). Under these conditions, the scrubber was less effective than the ESP in controlling the emissions of most group 1 and 2 elements.

Specific Concentrations. As noted above, the ESP that was tested was somewhat undersized (4760 cm^2/m^3) and is not nearly as efficient (97 vs. 99.8%) as larger (12 100 cm^2/m^3), more modern units in use at plants burning low-sulfur coal (*32*). Further normalization of the penetration ratios (Table VII) to the respective TSP ratios yields ratios of the specific concentrations of elements (μg of element/g of fly ash). The ratios of the specific concentrations indicate the relative emission of the two devices operating at equal efficiencies (concentration ratios, Table VII). Given equal efficiencies (for TSP), the penetration of group 1 elements through the scrubber would then range from 1.1 to 6.7 times that of the elements through the ESP (median values), neglecting Se and Br for reasons discussed above. The corresponding factors for group 2 elements ranged from 0.74 to 12. Penetrations of group 3 elements are, however, smaller through the scrubber unit.

Elements in group 3 tend to be distributed throughout the volume of the particle, while the available evidence shows that many of the group 1 elements are deposited on the surface of particles (*14, 33–35*) and might therefore have greater biologic availability. Based on the penetrations of Be, Cd, and Pb through the ESP-equipped unit (Table VI), we predict both Cd and Pb to behave as group 1 elements, and Be as a group 3 element. The concentration of Si, a major component of fly ash, shows no dependence on particle size (*26*), and should display group 3 behavior. Elements that are toxic to humans are included in each of the groups (*36*). However, most of the elements for which we have evidence of group 3 behavior, e.g., Si, Al, Fe, Na, K, lanthanides, and Sc, are generally considered less toxic than those in groups 1 and 2, e.g., As, Se, Sb, U, Cd, Pb, V, and Cr (*36, 37*). Thus, compared with an ESP of equal efficiency of TSP removal, the scrubber's enhanced emission of particulate species with greater potential toxicity may offset its advantage of greater efficiency in removing large particles because the latter contain potentially less toxic elements.

Summary and Conclusion

The efficiency of a venturi scrubber system was as high as 99.8% in removing TSP, but was severely reduced for particles <1 μm, and in fact the venturi wet scrubber emitted as much as 40% more submicron particles than entered the system. Comparison of scrubber emissions with those from an ESP-equipped coal utility unit indicates that despite a factor of 11 lower efficiency in TSP removal, the ESP unit was still significantly more efficient in removing submicron particles. Because of concentration enhancements on small particles and the difference in the removal efficiency of small particles, concentrations of many potentially toxic elements in particulate material emitted from the scrubber systems were as much as 250 times greater than those in emissions from the ESP unit. In addition, the particle sizes in emissions from the scrubber units (submicron size) are more efficiently deposited in the lungs of humans. Furthermore, the emission of several metals, as well as elements associated with the scrubbing liquid, seems to be enhanced because of corrosion of metal surfaces inside the scrubbers. Therefore, we conclude that the wet scrubber system tested was less effective in reducing the potential inhalation hazard of those particulate emissions discussed above than an ESP of comparable overall efficiency.

Acknowledgments

The authors gratefully acknowledge the assistance of R. E. Heft, R. W. Wikkerink, D. G. Garvis, and K. O. Hamby in the collection and analysis of samples; W. H. Martin and R. K. Tandy for assistance in data reduction; and B. K. Ishida and H. R. Ralston for assistance in preparing the manuscript.

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Received for review March 13, 1978. Accepted January 12, 1979. Preliminary accounts of the work described in this paper were presented at the 172nd National Meeting of the American Chemical Society, Division of Environmental Chemistry, San Francisco, Calif., Aug 29–Sept 3, 1976, and at the 71st Annual Meeting of the Air Pollution Control Association in Houston, Tex., June 25–30, 1978. Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore Laboratory under Contract No. W-7405-ENG-48. Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that are suitable.

NOTES

Tritium Oxidation in Surface Soils. A Survey of Soils Near Five Nuclear Fuel Reprocessing Plants

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■ The oxidation of elemental tritium into tritiated water by soil microorganisms represents a previously unsuspected pathway for tritium contamination of food. Soils from around potential point source emissions of tritium were tested and all were found to have the capacity of rapidly oxidizing tritium.

Our previous work (*1, 2*) showed that soil microorganisms are responsible for a rapid oxidation of elemental tritium to tritiated water. This laboratory work pointed to a possible hazard and a pathway of food contamination previously unsuspected. Our work also showed that plants rapidly incorporated tritium (*3*) when exposed in a growth chamber and that the route of contamination depended on the oxidation of HT in the soil. In past accidental releases of elemental tritium, very little attention has been given to evaluating soil and plant contamination. However, the present data indicate that soil and plants would be the primary accumulation sites and, therefore, the most sensitive media for sampling.

Elemental tritium is produced in nuclear power reactors and is released during reprocessing of the fuel elements. Currently there are nuclear fuel reprocessing facilities operating near Aiken, S.C., Arco, Idaho, Hanford, Wash., and a small experimental unit near Oak Ridge, Tenn., and a new facility is constructed, but inoperative, at Barnwell, S.C. We undertook the project reported here to determine if the soil microorganisms capable of tritium oxidation existed near these facilities and, if so, to find out if their activity was sufficient to be considered important in the event of a tritium release.

Methods

Tritium oxidation was determined in the following manner. Representative soils were collected from the vicinity of each of these facilities and analyzed for their tritium oxidation potential. The physical and chemical properties of these soils are found in Table I.

The soils (200 g, dry weight basis) were incubated for 7 days at 30 °C in 15-cm petri dishes; daily additions of water were made to maintain them at 50% of their water-holding capacity. The incubation period ensured that the microbial populations in each culture were active and at a stable level of activity. Field conditions were not maintained during the incubation period in order to create optimal conditions for tritium oxidation.

After the incubation period, moist soil equivalent to 20 g on a dry weight basis was removed. The 20-g samples were placed in 1-L round-bottomed flasks and enough water was added to bring each sample to 140% of its water-holding capacity. The flasks were closed with rubber stoppers and the resultant soil slurry was spread over the inner surface by shaking. After the flasks had been flushed with air, 1.5 μCi of elemental tritium was injected through the rubber stopper with a gas-tight syringe (5-cm^3 injection of HT in N_2). These bottles were then stored at 30 °C for various periods of time before analysis.

Table I. Physical and Chemical Properties of Soils

soil type	sand, %	clay, %	org matter, %	cation exchange capacity, mequiv/100 g	pH	HT oxidation rate, V_{max} = % h^{-1}
Clairborne[a] silt loam	22.1	14.4	3.9	4.1	5.7	34 ± 3
Armuchee[a] silt loam	32.1	18.3	4.1	1.0	4.7	59 ± 8
Collegedale[a] silt loam	23.7	19.0	6.2	15.3	5.2	39 ± 3
Fullerton Cherty[a] silt loam	26.2	11.1	3.4	2.9	4.7	65 ± 8
Blanton[b] loamy sand	90.9	1.6	0.4	0.3	5.1	49 ± 9
Fuquay sand[b]	91.7	1.8	0.6	0.3	4.9	44 ± 9
Norfolk[c] loamy sand	90.9	2.6	0.7	2.1	5.0	12 ± 2
Blanton sand[c]	89.0	2.0	0.6	0.3	4.6	15 ± 2
Burbank[d] loamy sand	80.8	3.0	0.5	5.4	7.3	35 ± 3
Quincy[d] loamy sand	84.5	2.2	0.4	7.2	7.4	30 ± 3
Ritzville[d] silt loam	35.1	3.7	0.6	8.9	6.9	31 ± 7
Warden[c] very fine sandy loam	45.8	2.4	0.5	9.6	7.1	48 ± 8
Berniceton[e] sandy loam	47.8	17.5	0.6	12.2	8.1	48 ± 7
Pancheri[f] silt loam	47.6	14.6	1.0	12.4	8.2	66 ± 6

[a] Anderson County, Tenn., near Oak Ridge National Laboratory, U.S. Department of Energy (DOE) reservation. [b] Aiken County, S.C., near Savannah River DOE reservation. [c] Barnwell County, S.C., near Allied Gulf nuclear fuel reprocessing plant, under construction. [d] Franklin County, Wash., near the Hanford DOE reservation. [e] Butte County, Idaho. [f] Jefferson County, Idaho, near the National Engineering Laboratory, DOE reservation.

The reaction was stopped by opening the flask to allow the remaining elemental tritium to escape and by adding 50 mL of benzene. The water was distilled in a benzene and water azeotrope (*4*) and the amount of tritium recovered as water was determined by liquid scintillation.

The reaction rate was determined by analyzing replicate samples at various times. This produced a series of measurements which yielded curves that are described by a regression function known as the exponential growth model:

$$Y = P_1[1 - \exp(-P_2 t)] + E \tag{1}$$

where Y = the amount of tritium converted to HTO at any time, P_1 = the asymptotic tritium concentration (nanocuries), P_2 = the reaction rate parameter (hours^{-1}), t = time in hours, and E = the error function, assumed to be Gaussian. Each data set was fit to this regression model using a nonlinear least-squares program.

The derivative of Formula 1 with respect to time gives the velocity of the reaction:

$$\frac{dy}{dt} = P_1 P_2 e^{-P_2 t} \tag{2}$$

At time zero the velocity is maximal and equals P_1P_2. If the concentration of converted oxidized tritium is expressed in terms of percent or as a fraction, P_1 equals 1.0 and P_2 therefore equals the maximum velocity of the reaction. The dimensions in these tests were in units of the fraction of tritium converted per hour; multiplying by 100 yielded the percent of HT converted to HTO per hour.

Results and Discussion

From the test results we generated a family of curves which represent different rates of tritium oxidation. The maximum velocities occurred at $T = 0$. In these experiments, atmospheric hydrogen, at an accurately known concentration of 0.50 ppm (vol:vol) (*5*), was the dominant source of elemental hydrogen.

Maximum velocities were calculated and are presented in Table I to compare rates for various soils. Because these soils had been incubated at 50% of their water-holding capacity to bring the microorganism populations to a high level of activity, comparisons are of potential activities which do not necessarily represent field activities.

The reaction rates observed ranged from 12% per hour to 66% per hour and were generally independent of the soil type or soil chemical properties. These rates are sufficiently rapid to account for significant oxidation of HT if it were present in the environment. It is probable that significant quantities of tritium would be found in the soil following a release or leakage of HT. The amount would obviously depend not only on microbial activity but also on air mixing near the soil surface, duration of exposure, and HT concentration. Our findings suggest that appropriate sampling schemes should be developed to quantify the importance of microbial oxidation of HT as a factor in plant and water contamination.

Acknowledgment

We thank Darrell L. Gallup, Idaho State Soil Scientist, Rector H. Moneymaker, Anderson, Tenn. Soil Survey Party Chief, Donald C. Hallbick, South Carolina State Soil Scientist, and Richard C. Harriman, Soil Scientist in Pasco, Wash., all of the U.S. Soil Conservation Service, for collection and classification of soil samples and Dr. Robert Kinnison, U.S. Environmental Protection Agency, for statistical assistance.

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Received for review August 21, 1978. Accepted November 13, 1978.

CORRESPONDENCE

SIR: Polasek and Bullin (*1*) have recently concluded that aluminized polyester material is superior to Tedlar for the collection and storage of ambient air samples for subsequent hydrocarbon analysis. Tedlar bags have been used in our laboratory for many years and we have not seen hydrocarbon losses of the order reported by Polasek and Bullin. We have seen losses of highly polar compounds, however, but these compounds are not normally found at significant concentrations in ambient air. We have also observed increases in hydrocarbon concentration after long-term storage in Tedlar. This we speculate to be due to the release of film contamination such as *N*,*N*-diethylacetamide and other compounds left in or on the Tedlar during its manufacture (*2*). In fact, we have observed the release of contamination from every film material we have utilized in the construction of sample containers. Aluminized Scotch Pak is one of the most contaminated materials that we have investigated. These results disagree with those reported by Polasek and Bullin, who found almost ideal storage of hydrocarbons in aluminized Scotch Pak, but they did not test properly for low level contamination, since they used high concentration standards for the study of storage of ambient air.

To check the results of Polasek and Bullin, we constructed and tested identical size bags made from aluminized Scotch Pak, Tedlar, and Teflon. The bags were made by heat sealing using a Vetrode heat sealer. A stainless steel O-seal straight thread adapter and a 1-in. diameter × $1/2$ in. thick Teflon nut were used for the access port. Included in this study were stainless steel cans treated by the "summa process", which is a deplating process used to deactivate the inside surface of the can (*3*).

All containers were filled with hydrocarbon-free air. The cans were pressurized to 30 psig.

All containers were analyzed immediately and again in 5 days (120 h) by a detailed hydrocarbon analysis using a three-column gas chromatographic system described by Lonneman et al. (*4*). This method of analysis differed from the total hydrocarbon analyzer approach used by Plasek and Bullin in that it permitted species separation of the contaminant peaks. The results of the storage study for these four containers are presented in Table I and show that the samples in each container increased in hydrocarbon content with storage time. Apparently this increase was due to desorption from the vessel walls.

These results show Tedlar to be superior to aluminized polyester, but not as good as the steel cans. Two possible explanations for the different results reported by Polasek and Bullin include either the use of leaky bags or compounds in their standard tank more polar than those found in ambient air. The one main difference is that they used NMHC concentrations at 7–10 ppm, for which ppbC contamination cannot be seen. In no case did we ever observe a decrease in NMHC concentration in any of the sampling containers. Release of surface contamination, which would interfere with total nonmethane measurements, was most severe with the aluminized polyester. These results are in complete disagreement with those reported by Polasek and Bullin.

Table I. Comparison of Hydrocarbon Buildup in Various Containers

container	rate of NMHC buildup, ppbC/h
aluminized polyester	26.75–29.40
Tedlar	0.88–1.25
Teflon	0.70–0.85
summa processed cans	0.37–0.41

Table II. Methods of Cleaning Teflon for Storage of Ambient Air to Be Analyzed for Hydrocarbons

pretreatment	av rate of NMHC buildup, ppbC/h
no treatment	0.78
24 h heat at 180 °C	0.19
36 h heat with vacuum of 25 Torr	0.08

Teflon and the steel cans appear to be the best containers for the storage of air samples with low hydrocarbon concentrations. Attempts were made to clean up 5-mil Teflon by both heat and vacuum. Table II shows that this can be done. However, subsequent field use of these bags proved them to be much more fragile after heat treatment and leaks developed during their use.

Since the "summa" processed cans seemed the most promising, they were heated at 140 °C and evacuated at 5 Torr for 24 h. After cooling, these cans were filled with roadside air, analyzed immediately, and again after 5 days. A 20% increase in nonmethane hydrocarbon concentration was observed. All significant increases were in the C_8–C_{10} hydrocarbon range.

The increase in organic component concentration (reported here as nonmethane hydrocarbon) in the Teflon bags may be related to the release of contaminate components from the surface of the film picked up or included during the manufacture of the Teflon film. Permeation of compounds from the outside surrounding air through the Teflon film is another possible consideration. The buildup of contamination in stainless steel containers, however, cannot be as easily explained. This buildup may be due to the slow release of components from the surface of the stainless steel cans or some other unidentified mechanism.

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SIR: Your recently published article, "Evaluation of Bag Sequential Sampling Technique for Ambient Air Analysis" by Polasek and Bullin (*1*), is of great interest to Environmental Measurements, Inc. EMI manufactures the only commercially available sequential bag sampling system, the Air Quality Sampler (AQS-II), and also fabricates air sampling bags for use in the AQS-II, as well as other air sampling systems. The article contains two statements that are of concern to EMI:

- "Tedlar bags are poor for sample storage of ambient air concentration levels" (p 711).
- ". . . the validity of the bag sequential sampling technique has not been established" (p 709).

Regarding the storage of air samples in Tedlar bags, it must be said that there are bodies of data which contradict the findings of the Texas study. For example, a more recent EMI

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study was performed last year (2). Standard EMI air sampling bags made from Tedlar PVF Film (Du Pont Type no. 200SG40TR) were used. California urban ambient air samples were kept for 500 h and the loss in CO concentration was 9% or less. (The same instrumental methods were used as in the Texas study.)

These results are in sharp contrast to the Texas study, which shows a 43% loss of CO in only 100 h for Tedlar bags (type not specified). The 5× greater loss in CO in one-fifth the time suggests that there may be effects caused by differences in bag material, manufacturing techniques, preconditioning of the bags, ambient air constituents, methods of bag storage, or other unknowns.

Additional work using Tedlar bags can be cited. For example, Lonneman et al. recently reported (3) that Tedlar bags can be used successfully for hydrocarbon sampling when care is taken to prevent sunlight from photooxidizing the sample. (Other references are available on request.)

We submit, therefore, that Tedlar air sampling bags can be—and are being—used as air sample containers when proper precautions are followed in the choice of PVF film, heat sealing of the bags, and storage of air samples.

Regarding the validity of bag sampling, it must be pointed out that the sequential sampler that was evaluated by the authors, which showed poor correlation with continuous analyzers because it had rubber diaphragm pumps and gum rubber tubing, is *no longer on the market*. The EMI AQS-II, which uses piston pumps and Tygon tubing, was not part of this evaluation and does not exhibit the poor performance characteristics of the obsolete unit (see ref 2; other references available on request).

AQS-II systems have been produced for a wide variety of uses in North America and Europe. Many units are in daily operation collecting carbon monoxide samples; others are used in special studies of more exotic pollutants such as benzene and radon.

We submit, therefore, that the validity of the bag sequential sampling technique has been—and is being—established by continuing practical application. EMI would welcome further evaluations of the AQS-II by qualified researchers.

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SIR: This is in reference to the paper on the bag sequential sampling technique for ambient air analysis by J. C. Polasek and J. A. Bullin [*ES&T*, **12**, 708–12 (1978)].

The authors indicated that when the intakes for the bag samplers and the continuous analyzer were placed side by side, CO concentrations from the two methods did not correlate well. The authors attributed this to the asymmetry of the sample ports on the sampler. However, they presented no evidence to support this conclusion.

When the samples were drawn through a common header, the concentrations agreed to within ±1 ppm for at least 90% of the data points for CO concentrations of 1–8 ppm. This indicates that the bag sampler and continuous analyzer do indeed indicate the same CO concentrations for the same air sample. Therefore, the lack of correlation in the earlier experiment may be due to actual differences in the CO concentrations of the different air samples that were analyzed.

The experiment in which two continuous analyzers were attached to the common header showed that CO concentrations along roadways vary widely and at frequencies up to 2 cycles/min. If the CO concentrations show large temporal variations, then, under these conditions, it seems plausible that they would also show large spatial variations, which would give rise to the effect mentioned above.

This could be tested by repeating the first experiment, in which the intakes for the bag samplers and continuous analyzer were placed side by side, with the exception that the continuous analyzer is replaced with another bag sampler. If there is an actual difference of the CO concentrations in the samples measured, there would still be no correlation, even though the same measurement method was used for each sample.

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SIR: The letters by Kuntz, Sperling, and Hoffman center on two distinct points, which must be addressed separately.

The first and most common comment concerned the conclusion that Tedlar bags were unsuitable for use in an air monitoring study. Two of the letters state that, in separate tests conducted in several different laboratories, results were obtained which contradict those of the Texas study. There are a number of possible reasons for this. First and most important is the difference in concentration of the pollutants being measured. As Dr. Kuntz points out, a material may behave quite differently at different concentrations. Moe (2) also noted this effect.

Mr. Sperling mentions a number of other possible factors which could account for the differences. Only two of the unknowns mentioned, bag material and manufacturing techniques, are completely under the manufacturer's control. The material factor was eliminated by a check with the Texas State Department of Highways and Public Transportation, which showed that the bags used in the Texas study were also type 200 SG-40TR. We have talked with DuPont personnel in their films group at Buffalo, N.Y. (telephone number 716-876-4420). They advised us that they recommend only their 200 SG-40TR and 200 SG-10TR films for air sampling work. These two films are their 4- and 1-mil versions of 99% or greater purity PVF. There are 70 to 80 other types of PVF with various dyes, stiffeners, thinners, etc.

Manufacturing techniques are a distinct possibility to consider, meaning that tests should be run on any bags obtained from an unfamiliar manufacturer. All reasonable precautions were taken in the Texas study in regard to conditioning and storage of the bags, as detailed in the article. Ambient air constituents are not under anyone's control. Usually, if the constituents can be characterized, there is no need to collect them.

The contradictory results obtained by other groups highlight the fact that pollutant behavior at ambient levels is a complex subject. Other groups (3, 4) have contacted us indicating that they had confirmed our results. It should be pointed out that having bags which give good results for part of the range of interest are useless for monitoring studies unless the reason for failure and range of failure can be precisely pinpointed. To date this has not been accomplished by

0013-936X/79/0913-0610$01.00/0

any group of which we are aware.

Dr. Hoffman, and to a slight extent Mr. Sperling, addressed the second point, the conclusion that the poor correlation between the samplers and continuous monitors was due to the asymmetry of the sample ports on the sampler. Dr. Hoffman suggests that there are possibly large spatial variations as well as temporal variations in the carbon monoxide concentrations. This was eliminated as a consideration after we completed a phase of testing that had to be deleted from the manuscript sent to *ES&T* to render it short enough for publication. This phase of testing was done to establish the effect of the header materials on carbon monoxide concentration. A pair of continuous monitors was set up, one sampling off a 50-ft long header of the same type material used by the bag sampler and ecolyzer comparison, swept by the same type of vacuum cleaner. The second ecolyzer was set up about 2 ft from the header intake, with no header at all.

Detailed comparisons showed that the header delayed the peaks and valleys by about 20 s and did some slight smoothing, but it had little effect on the averages. In fact, 23 15-min averages showed that, after span correction, the average error was better than the quoted instrument accuracy. This gave us further confidence in the ecolyzers, and made us decide that the bag sampler was indeed disturbing the air flow around it.

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0013-936X/79/0913-0611$01.00/0

ES&T INDUSTRY TRENDS

Clermont Engineering Co., Inc. (Philadelphia, PA) will help Mannington Mills, Inc. (Salem, NJ) to remove plasticizer mist from vinyl chloride-coating line exhaust. Awards are for more than $1 million, to handle 45 000–55 000 scfm of gas flow.

Combustion & Energy Corp. (Runnemede, NJ) has announced a new system to emulsify oil and water into an efficiently combustible mixture. About 5–15% of the mixture is water. The firm says that combustion often approximates that of natural gas.

Rexnord Inc. (Milwaukee, WI) has acquired Dictaphone Corp.'s gas detection business, which makes lines of instruments for measuring toxic and combustible gases which will be marketed under the "Rex" name.

American Air Filter Co., Inc. (Louisville, KY) has an "AAF-Elex" electrostatic precipitator (ESP) handling 306 000 cfm of air for Inland Cement Industries, Ltd. (Canada). Efficiency of removal of more than 78 000 lb/h of dust is rated at 99.99+%.

Research-Cottrell, Inc. (Somerville, NJ) has a $16 million order to rebuild 12 ESP's for TVA at Cumberland, TN. They service two 1300-MW boilers. This is the largest ESP rebuilding order ever let, the firm says.

Environmental Elements Corp. (Baltimore, MD) has a turn-key contract in excess of $5.5 million for two ENELCO® RIGITRODE™ ESP's with Atlantic City (NJ) Electric Co.

Micrometrics Instrument Corp. (Norcross, GA) has sold about $300 000 worth of particle technology and liquid chromatography instruments to the People's Republic of China.

Consolidation Coal Co. has formally petitioned the EPA to relax SO_2 standards from 80 $\mu g/m^3$ to 160 $\mu g/m^3$, which the company says can be done without damaging health.

The National Center for Resource Recovery (Washington, DC) has a Dept. of Energy (DOE) contract for a project to convert office waste paper into storable pellets, and burn the pellets as a supplemental fuel.

Arizona Public Service Co. will study a geothermal electric plant in Mexico under a $30 000 contract with the Electric Power Research Institute (EPRI, Palo Alto, CA).

Lummus GmbH (Germany), a subsidiary of C-E Lummus, will provide engineering designs for pollution abatement programs to the U.S. Army Corps of Engineers, for various U.S. Army installations in West Germany.

LFE Environmental Analysis Laboratories (Richmond, CA) has a $200 000 EPA contract to measure potential air contaminants from geothermal wells.

EG&G, Inc. (Wellesley, MA) is preparing information on solar radiation, weather, hazards to solar systems, and other pertinent matter, for DOE. Publication is expected early next year.

BlueBird Enterprises (Fresno, CA) says that acoustical systems, properly installed and operated, can discourage wildlife from using contaminated ponds, and can save much money over netting systems.

Environmental Control Technology Corp. (Ann Arbor, MI) has a $121 000 EPA contract to validate equivalency of proposed alternative analytical procedures to those currently approved by EPA.

Engineering-Science Companies is working on a combined program of treatability studies, operations assistance, and training for wastewater treatment for Eli Lilly and Co., at Mayagüez, PR

Zurn Industries, Inc. has a letter of intent from Louisville Gas & Electric for a 346 500-gpm natural draft cooling tower.

UOP Inc. (Des Plaines, IL) says that the world's largest reverse osmosis system, which UOP provided, is desalting 3.2 mgd of Red Sea water for drinking water at Jeddah, Saudi Arabia.

Reynolds Aluminum Recycling Co. (Richmond, VA) has raised the price it will pay to the public for beverage cans and other scrap aluminum from 17¢/lb to 20¢/lb.

MacDermid of Bristol (Bristol, CT), maker of WASTESAVER plating chemical recovery systems, is adding 10 000 ft^2 of production space to its facilities.

Oak Ridge National Laboratory (Union Carbide) has been named by DOE's Office of Fusion Energy to be the host site for an Engineering Test Facility Design Center.

Zimpro Inc. has an order for 12 wet air oxidation units to treat 600–700 tpd of sewage sludge at the Newark Bay (NJ) Treatment Plant. It will handle up to 187 200 gph of primary and waste oxygen-activated sludge.

Public Service Electric and Gas Co. (NJ) has decided to cancel a contract to purchase four floating nuclear power plants from Offshore Power Systems (Jacksonville, FL). Reason given was less-than-anticipated growth in peak demand.

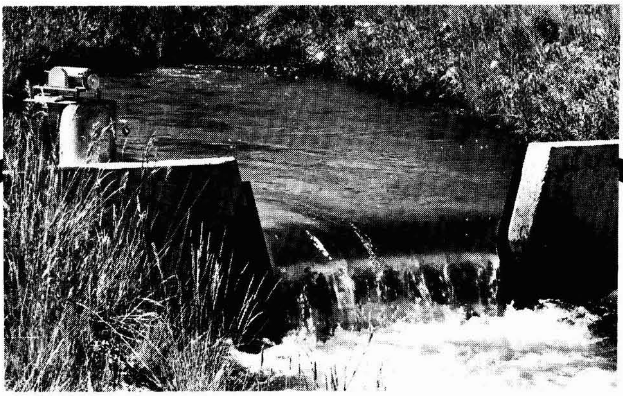
IU Conversion Systems, Inc. (Horsham, PA) will construct a multimillion dollar facility to stabilize SO_2 scrubber sludge for The Cincinnati Gas & Electric Co., to treat 1 million tpy of this sludge with Poz-O-Tec®.

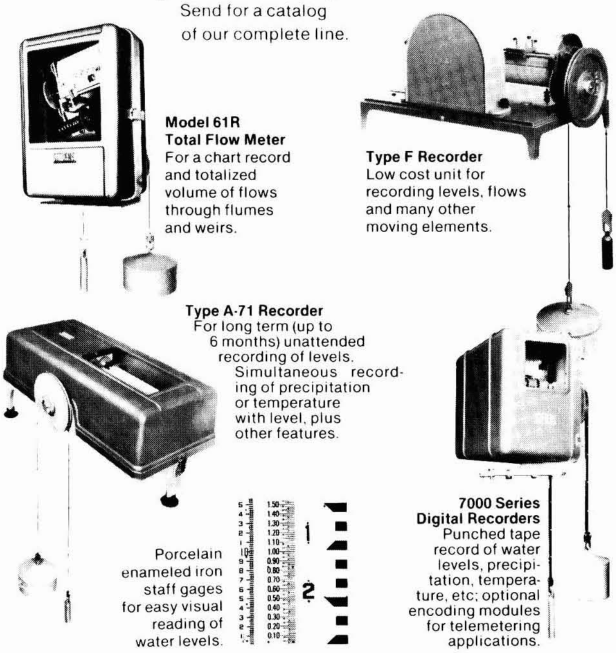
ERT (Concord, MA) has received the American Meteorological Society's annual Award for Outstanding Service to Meteorology by a Corporation. Of ERT's approximately 800 employees, about 90 are meteorologists.

American Air Filter Co., Inc. (Louisville, KY) has a $1 million order for a melt shop ventilation system to control air pollution at Hyudai International, Inc. (Kyunggi-do, Republic of Korea). It will use fabric dust collectors, fume controls, and associated equipment.

Enviro-Systems & Research, Inc. (Roanoke, VA) has a $200 000 contract to supply an SD-10 Fabric Filter Dust Collector to the Federal Bureau of Prisons, to be used at the Federal Correctional Institution (Alderson, WV). It will handle 16 000 acfm.

JI Case Co. (Racine, WI) and **Cummins Engine Co.** have entered into an agreement to study and design a new line of advanced, fuel-efficient diesel engines in the 50–250-hp range.





ES&T PRODUCTS

Viscometer system
The system includes a viscosity sensor, digital electronics, a temperature control dry bath and support stand. The standard range of 0–140 000 cps × g/cm^3 in six decades is activated by push button and has digital reading and recorder output. Nametre **101**

6-channel recorder
This model, Miniservo VI, is a 2-, 4- or 6-pen potentiometric servo recorder that is able to record information from up to six sources on one chart. Esterline Angus Instrument **102**

Automatic SO_3 monitor
The company claims that this is the first monitoring system to be introduced in the U.S. and Canada which chemically and photometrically determines SO_3 content in gas streams on a continuous basis. The Rolfite Co. **103**

Acrylonitrile monitor
Model 555 is a portable analyzer designed for the continuous monitoring of low levels of acrylonitrile in the workplace. The full-scale range is 0–1.5 ppm expandable to 0–0.5 ppm full scale with a detectable limit of 5 ppb. CEA Instruments **104**

Gamma spectroscopy system
It is designed for the qualitative and quantitative analysis of radionuclides in environmental and nuclear power fields. The system includes a graded lead shield chamber, a Germanium detector, signal processing electronics, data acquisition and analysis unit, hard-copy printer and software packages. EG&G Ortec **105**

Differential pressure flowmeter
Combines a laminar-flow element with a graduated manometer for accurate and instantaneous gas-flow measurements, the manufacturer claims. Flows of less than 1 cc/min to above 50 L/min can be read with ±1% full-scale accuracy. Kontes **106**

High-efficiency filter
This high-efficiency particulate air (HEPA) filter has a capacity of 2000 cfm, and 500 fpm face velocity at 1.0-in. water gauge initial pressure drop. American Air Filter **107**

pH transmitter/sensor
This pH monitoring system features a fully isolated 4–20 ma dc output which permits remote indication or recording without common mode problems, the manufacturer claims. The transmitter can be adjusted to full-scale ranges of any two or more pH units. Rexnord Instrument Products **108**

Carbon monoxide monitor
The analyzer/alarm system is able to monitor the concentration in air of carbon monoxide and other toxic gases at up to 16 remote sampling points. The unit is electronically controlled. Becton Dickinson and Company **117**

Portable incubator
This new unit can be used in the field to incubate test cultures to determine total and/or fecal coliform content of water samples by the membrane filter method. Vista Scientific **118**

Slurry/sludge blanket level controller
The instrument detects when solids in a settling tank or clarifier have reached the optimum level for pumping or "alarming" operations. Envirotech **119**

Microsensing electrodes
These electrodes can be used to measure pH and "commonly encountered ions" in volumes as small as 1 μL. The electrodes have a sensor diameter of 380 μ and a tip diameter of less than 50 μ. Lazar Research Laboratories **120**

Conductivity/temperature monitor
The new device measures soil (and water) conductivity, temperature and salinity directly; it offers a means of determining salinity changes caused by seepage and irrigation. Conductivity is corrected to 25 °C. Martek Instruments **121**

Landfill compactor
The machine is designed for small- and medium-sized landfill operations. The 3-35 model provides full-width, single pass compaction, and has such exclusive features as a one-piece belly pan and a spring-assisted, tilt-up hood. Rexnord **122**

Compact pH/temperature meter
The pocket-sized unit automatically compensates for temperature. pH and temperature accuracies are 0.01 pH units over the full 0–14 pH range, and 0.1 degree centigrade from 0–100 degrees. Presto-Tek **123**

Selective ion electrode Na analyzer
The two new units are designed to continuously measure sodium ion concentration in water. Models 300 and 4300 three-decade amplifiers monitor ranges of 0.1–1.0 to 10.0–100.0 ppb, and 0.1–1.0 to 10.0–100.0 ppm. All components and reagent containers are mounted in a single cabinet. Model 4300 includes a 12-in., 24-h circular chart recorder. Calgon **124**

Sulfur in coal/coke determinator
This digital readout "determinator" is designed for the rapid determination of sulfur in coal, coke and oil. The unit uses a controlled combustion method that permits the use of larger sample weights and produces higher sulfur recoveries. LECO **131**

Ultratrace Metal Analysis in Biological Sciences and Environment

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Terence H. Risby, *Editor*
Pennsylvania State University

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Roger W. Bullard, *Editor*
U.S. Fish and Wildlife Service

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Occurrence and Fate in the Environment

ACS Symposium Series No. 82

Fred E. Brinckman, *Editor*
National Bureau of Standards

Jon M. Bellama, *Editor*
University of Maryland

Based on a symposium sponsored by the Division of Inorganic Chemistry of the American Chemical Society

No one in the fields of bioinorganic or water chemistry should be without this valuable collection of up-to-date results and critical reviews by organometallic chemists and microbiologists concerned with the biogenic and abiotic factors governing transformations.

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448 pages (1978) Clothbound $34.00
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Seal-less solar system pumps
In these new pumps for solar heating systems, electric motors rotate magnets around the impeller housing and through the housing walls, and in this way they turn the impeller. The impeller, external magnet holder and impeller housing are molded from polyphenylene sulfide. Hartell Div./Milton Roy **125**

Water quality monitoring system
The user may select any combination of the following parameters to monitor: conductivity, salinity, temperature, depth, dissolved oxygen, pH, turbidity, oxidation-reduction potential and tide measurement. All data channels are transmitted by cable to a remote data display, data recorder or radio telemetry link. InterOcean Systems **126**

Temperature/humidity conditioners
The portable temperature/humidity conditioning systems provide stable and reproducible psychometric conditions for environmental testing and simulation. Vista Scientific **127**

Actuator
The actuator was designed for use in sewage and wastewater applications. It will operate a sluice gate, whose thrust is 200 000 lbs, stroke is 144 in., speed is 60 s, and is fail-safe with no electrical power. M.E.A., Inc. **128**

O_2 flue-gas analyzer
The portable, digital display unit features an electrochemical cell which reads absolute percent oxygen and is not affected by the presence of carbon monoxide or carbon dioxide. The cell requires no maintenance; it is replaced in the field much like a battery, the manufacturer says. Neutronics **132**

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LITERATURE

Microbalance. QCM Brochure describes line of quartz-crystal microbalances for contamination measurement in space and laboratory environments. Applications include pollution fields. Berkeley Controls, Inc. **151**

Flowmeters. Catalog, "Flowmeters," lists line of such instruments, and provides specifications, formulas, and other pertinent information. Matheson Instruments **152**

Filtering. Information tells about stainless steel filter assemblies for in- and out-of-stack use; they apply to EPA Methods 5, 13, and 17. Standard or custom assembly. GII Enterprises, Inc. **153**

Power plant noise. Pamphlet is entitled, "Evaluation of Power Plant Noise Emissions," and tells how the company addresses this problem. TRC **154**

Analyzer. Analyzer uses X-ray absorption, and is portable. Literature describes CSI Model 720. Columbia Scientific Instruments Corp. **155**

Draft control. Form 4079 is a complete information tool for understanding of draft control. Details for solid- and gas-fired plants, including boilers, are included. Field Control Division **156**

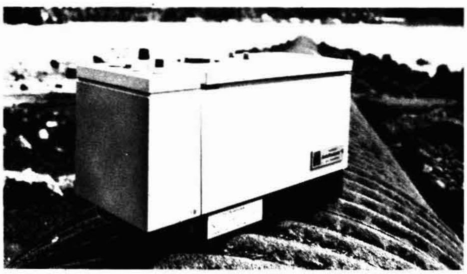
Data acquisition. Brochure describes FIDAC data acquisition and control system which is run in a manner similar to microcomputers, minicomputers, and desk calculators. F.I. Electronics. **157**

Portable mixers. "The LIGHTNIN Catalog Store" lists portable mixers from $^1/_{30}$-hp laboratory models to 3-hp production portables, as well as a full line of accessories. Mixing Equipment Co., Inc. **158**

Plastic labware. New catalog lists plastic ware for many laboratory applications. Could have pollution analysis uses. Cole-Parmer Instrument Co. **159**

Wastewater separation. Bulletin 6001 illustrates how corrugated plate separator removes oil and solids from wastewater by gravity. Wide range of capacities is available for many requirements. ERC/Lancy Division, Dart Environment and Services Co. **160**

Air cleanup. Brochures describe advantages of company's systems for electrostatic precipitation, mechanical collection, and fabric filtration. Written in four languages; applicable to many industries worldwide. Envirotech/Buell **162**



Sulfur analysis. TB-163 describes S-GAS™, a carrier gas for chromatographic analysis of SO_2, hydrogen sulfide, carbon sulfoxide, and other sulfur gases. Matheson **169**

Filtration. General Catalog G-11 is concerned with corrosion-resistant pumps, filtration systems, and purification equipment. Filtration models range 1–10 800 gph; pumps; 1–16 800 gph. Sethco Div., Met-Pro Corp. **176**

Personal monitor. Product Bulletin 78-102 describes the GASBADGE™ for personal monitoring of organic vapors (April issue, p 388). How and why the device works is explained. Abcor Development Corp. **178**

Noise reduction. Leveling mounts, described in catalog, reduce noise, vibration, and shock, and meet OSHA anchorage standards without being bolted to the floor. Tech Products Corp. **179**

Particulates. Bulletin AF-1-110 describes "Astrocel III" high-efficiency particulate air filter. It will handle 2000 cfm at a 500-fpm velocity rating. American Air Filter Co., Inc. **180**

Vacuum filtration. Publication No. 466 describes vacuum filtration manifold for multiple sample filtration for filtrate analysis, and analysis of retained or membrane-bound species. Amicon Corp. **181**

Personal monitor. Data Sheet 08-02-01 illustrates Model C-200 Personal Sampling Pump for atmospheres containing toxic gases and vapors. Flow rate 50–200 mL/min. Mine Safety Appliances Co., Inc. **182**

Instruments. Catalog lists over 9000 items for industrial research, pollution control, agricultural research, and many other areas. Cole-Parmer Instrument Co. **183**

Gas stream separators. Bulletin T-1100 describes HEILEX-EB® liquid entrainment separators and tells how they enhance the effectiveness of entire gas scrubber systems. Dart Environment and Services Co. **184**

FGD waste. Bulletin RC-1800 covers problems and recommended solutions for disposing of stack gas scrubber sludge, and stresses site-specific conditions of FGD (flue gas desulfurization). Research-Cottrell **185**

Deuterium gas (D_2). Form No. 6647 tells about D_2, and describes company's product delivered at minimum purity of 99.7%. Fusion is one important application. Liquid Carbonic **186**

Chlorinators. Bulletin 221 describes improvements in a complete line of gas chlorinators used for municipal and industrial water/wastewater treatment. Chlorinators Inc. **187**

Fabric filters. Brochure WWC-2 describes air pollution control bags for boilers. Long life at elevated temperatures; high reliability for pulse-type collectors; resistance to acid. Wheelabrator-Frye Inc. **188**

Waste heat recovery. Information packet tells how "Econo-Misers" recover waste heat and have about one-year payback periods. They can be retrofitted. Savings are calculable by nomogram. Voss Finned Tube Products, Inc. **189**

Oxygenation. Brochure tells about how the Air-Aqua Induced-Air Aeration System has very high oxygen transfer efficiency with reduced energy requirements, and with no sludge production. Hinde Engineering Co. **190**

Pipeline strainer. Brochure No. 465-ADV introduces new series of automatic, self-cleaning pipeline strainers for municipal, industrial, nuclear plant, and other operations. Zurn Industries, Inc. **191**

Ozone meters. Information is available concerning the CSI Model 1100 ozone meter series, which measure ozone from a few parts per billion to 10 ppm. Negligible zero drift. Designated as reference method by EPA. Columbia Scientific Industries Corp. **192**

Search services. "Directory of ERIC Search Services." While copies last. ERIC® Clearinghouse for Science, Mathematics and Environmental Education, Room 310, 1200 Chambers Road, Columbus, OH 43212 (write direct).

Nuclear science. Catalog lists publications in field—over 800 items. UNIPUB, 345 Park Avenue South, New York, NY 10010 (write direct).

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ES&T BOOKS

Drinking Water Detoxification. M. T. Gillies, Ed. xi + 348 pages. Noyes Data Corp., Mill Rd., at Grand Ave., Park Ridge, NJ 07656. 1978. $48, hard cover.

This book takes a thorough look at proposed, and probably forthcoming EPA drinking water regulations, and comments on them. Trihalomethanes, organics, detoxification processes, granular activated carbon, economics, analysis, and other topics are discussed on a highly up-to-date basis.

Marine Mining of the Continental Shelf. Michael S. Baram et al. xx + 301 pages. Ballinger Publishing Company, 17 Dunster St., Cambridge, MA 02138. 1978. $22.50, hard cover.

More and more, marine mining will be a method of recovering materials that are becoming increasingly scarce on land, or from land whose import channels are threatened. This volume considers legal, technical, and environmental aspects of this type of mining.

Ultratrace Metal Analysis in Biological Sciences and Environment. Terence H. Risby. vii + 263 pages. American Chemical Society, 1155 16th St., N.W., Washington, DC 20036. 1979. $36.50, hard cover.

One concentration of a metal may be essential to an organism or ecosystem, while another may be a disaster. Also, bear in mind that unlike many organics, metals are not biodegradable; nevertheless, long-term exposure could lead to severe problems over a period of time. This book considers these problems, as well as health implications, and roles of infinitesimal amounts of certain specific metals.

Overload. Arthur Hailey. 402 pages. Doubleday & Company, Inc., 245 Park Ave., New York, NY 10017. 1979. $10.95, hard cover.

What would be the environmental and social effects if, for example, a region's electric power were to go out, not for a few hours, but much longer? Could there be darkness, deprivation, and, finally, chaos? Read this novel to get an idea of what could really happen—perhaps very soon!

Disinfection of Wastewater and Water for Reuse. Geo. Clifford White, xi + 387 pages. Van Nostrand Reinhold Co., 135 West 50th St., New York, NY 10020. 1978. $24.50, hard cover.

This book considers up-to-date techniques for wastewater disinfection, and latest standards. New advances in ozone, iodine, chlorine and other halogens, and ultraviolet radiation are clearly outlined. Major hardware and chemical innovations are discussed in depth.

New Processes of Waste Water Treatment and Recovery. G. Mattock, Ed. 415 pages. John Wiley & Sons, Inc., 605 Third Ave., New York, NY 10016. 1978. $60, hard cover.

Some recent advances in wastewater treatment/recovery were made in the U.S., Europe, and Israel in recent years. This book sets forth practical experiences gathered during the course of these advances, and, among other things, looks into gas transfer, sludge processing, and physicochemical technologies. It grows out of a symposium on the topic, held in London, England.

Physics of the Environment. Herbert Inhaber. xii + 225 pages. Ann Arbor Science Publishers Inc., P.O. Box 1425, Ann Arbor, MI 48106. 1978. $16.50, hard cover.

This work looks into physics of water and air pollution, conservation of energy, and use of physical techniques for monitoring. For example, light and optics are dealt with, as well as electric/magnetic methods. Among other topics covered are radioactivity, heat and thermodynamics, and sound.

Inorganic Chemical Industry: Processes, Toxic Effluents and Pollution Control. Marshall Sittig. x + 351 pages. Noyes Data Corp., Mill Rd., at Grand Ave., Park Ridge, NJ 07656. 1978. $42, hard cover.

The list starts with "alumina" and ends with "zinc." It is a long list, and contributes much to pollution. However, control of this pollution has advanced over the last 5–6 years, and the control state-of-the-art is discussed in this book in very great detail.

Toward a Solar Civilization. Robert H. Williams, Ed. ix + 251 pages. The MIT Press, 28 Carleton St., Cambridge, MA 02142. 1978. $12.50, hard cover.

This work portrays solar energy as a very major resource. However, it does also consider the present economic limitations of solar energy, but offers thoughts on how to overcome development obstacles. Electricity, fuels, and third world development are among the numerous topics discussed by the book's contributed papers.

Biological Environmental Impact Studies: Theory and Methods. Diana Valiela Ward. viii + 157 pages. Academic Press Inc., 111 Fifth Avenue, New York, NY 10003. 1978. $14.50, hard cover.

Whatever path environmental impact assessment work may take in the future, some form of biological investigation will almost certainly be a part of it. This book aims at showing how to make this biological aspect of impact assessment as effective as possible. Field surveys, laboratory work, sampling, and experimentation are discussed, and case histories are presented.

Health Aspects of Wastewater Recharge: A State-of-the-Art Review. State of California, State Water Control Board, Department of Water Resources, Department of Health. x + 240 pages. Water Information Center, 7 High St., Huntington, NY 11743. 1978. $22, hard cover.

Can reclaimed wastewater be used to increase domestic water sources? Research to date suggests the technical/economic feasibility of such reuse. But what of human health? This book was prepared in order to point the way to establishing the necessary criteria for satisfying human health requirements.

"EPA's Secret Law"—Opinions of the General Counsel of the U.S. EPA. 2 volumes, total of 1200 pages. Environmental Law Publishing Service, 20675 Bahama Street, Chatsworth, CA 91311. 1979. $150, looseleaf.

These opinions carry formal and informal interpretations of EPA's statutes and regulations. Many carry the force of law. They are organized by topic for ease of reference, and are complete since the EPA began operation in December 1970. Publication was authorized by Joan Bernstein, presently the general counsel of EPA.

ES&T MEETINGS

May 15–17 Philadelphia, Pa.
Fine Particle Society Annual Meeting. Fine Particle Society

Write: Industrial & Scientific Conference Management, Inc., 222 West Adams St., Chicago, Ill. 60606

May 19 Tampa, Fla.
Sixth Annual Conference on Wetlands Restoration and Creation. Hillsborough Community College

Write: Dorothea Cole, Wetlands Conference, Hillsborough Community College, P.O. Box 22127, Tampa. Fla. 33622

May 20–22 West Point, N.Y.
20th Anniversary Meeting of Water Resources Association of the Delaware River Basin. Water Resources Association of the Delaware River Basin

Write: Water Resources Association of the Delaware River Basin, Box 867, Davis Road, Valley Forge, Pa. 19481

May 20–23 St. Louis, Mo.
Coal Convention '79. American Mining Congress

Write: American Mining Congress, 1100 Ring Bldg., Washington, D.C. 20036

May 21–22 Kansas City, Mo.
Fourth Mid-America Conference on Environmental Engineering Design. The University of Iowa, Iowa State University, University of Kansas, and others

Write: Shankha Banerji, Department of Civil Engineering, University of Missouri, Columbia, Mo. 65201

May 21–23 Atlanta, Ga.
ISA Power Instrumentation Symposium. The Instrument Society of America (Atlanta section)

Write: Harold Hendler, Taylor Instrument Company/Division of Sybron Corp., 95 Ames St., Rochester, N.Y. 14601

May 21–24 New York, N.Y.
Symposium on Measurement, Mapping and Management in the Coastal Zone. The American Congress on Surveying and Mapping, Interdivisional Committee on Marine Surveying and Mapping

Write: LCDR John Grubb, USN, DMA Hydrographic/Topographic Center, ATTN: PPII, Washington, D.C. 20315

May 27–June 1 Chicago, Ill.
1979 American Industrial Hygiene Conference. The American Industrial Hygiene Association

Write: American Industrial Hygiene Association, 475 Wolf Ledges Parkway, Akron, Ohio 44311

May 28–June 1 Atlanta, Ga.
1979 International Solar Energy Congress. The International Solar Energy Society

Write: W. A. Beckman, Technical Program Chairman, IES-79, Solar Energy Laboratory, University of Wisconsin-Madison, 1500 Johnson Drive, Madison, Wis. 53706

May 28–June 1 Washington, D.C.
Symposium on Water Quality and Sediment Interrelationships. The Water Quality Committee of the Hydrology Section of the American Geophysical Union

Write: AGU Meetings, 1909 K St., N.W., Washington, D.C. 20006

May 29–31 Williamsburg, Va.
The Effects of Nutrient Enrichment in Estuaries. The U.S. Environmental Protection Agency

Write: Bruce Neilson, Virginia Institute of Marine Science, Gloucester Point, Va. 23062

May 30–31 Grand Forks, N. Dak.
The Tenth Biennial Lignite Symposium. U.S. Department of Energy, the University of North Dakota

Write: Gordon Gronhovd, director, Grand Forks Energy Technology Center, Box 8213, University Station, Grand Forks, N. Dak. 58202

June 4–5 St. Louis, Mo.
Coal Mining Productivity: New Approaches. The Energy Bureau Inc

Write: Robert Nash, executive director, The Energy Bureau Inc., 101 Park Ave., New York, N.Y. 10017

June 4–8 Pittsburgh, Pa.
Analysis of Waters Associated with Alternate Fuel Production. The American Society for Testing and Materials (ASTM)

Write: Jane Wheeler, ASTM, 1916 Race St., Philadelphia, Pa. 19103

June 5–7 Philadelphia, Pa.
Wastewater Equipment Manufacturers Association Industrial Pollution Conference. Wastewater Equipment Manufacturers Association (WWEMA)

Write: George Strudgeon, WWEMA, 7900 Westpark Drive, Suite 304, McLean, Va. 22102

June 7–8 Washington, D.C.
The Fourth National Conference on the Interagency Energy Environment R&D Program. U.S. EPA's Office of Energy Minerals & Industry

Write: Conference Coordinator, Automation Industries, Inc., Vitro Laboratories Div., 4/2109, 14000 Georgia Ave., Silver Spring, Md. 20910

June 11–12 Denver, Colo.
The Third National Conference and Workshops on the Mine Safety and Health Act. The Energy Bureau Inc

Write: Robert Nash, executive director, The Energy Bureau Inc, 101 Park Ave., New York, N.Y. 10017

June 11–13 San Francisco, Calif.
The 19th Annual American Society of Safety Engineers (ASSE) Professional Development Conference. The American Society of Safety Engineers

Occupational health and safety issues will be discussed. *Write:* ASSE, 850 Busse Highway, Park Ridge, Ill. 60068

June 11–15 Sioux Falls, S. Dak.
International Symposium on Satellite Hydrology. The American Water Resources Association

Write: American Water Resources Association, St. Anthony Falls Hydrolic Laboratory, Mississippi River at Third Ave., S.E., Minneapolis, Minn. 55414

June 11–22 Concord, Mass.
Principles of Environmental Management in Developing Countries. ERT International, Inc., a subsidiary of Environmental Research & Technology, Inc.

Write: John Whitman, director, International Environmental Management Institute, ERT International, Inc., 696 Virginia Rd., Concord, Mass. 01742

Courses

May 21–22 Gaithersburg, Md.
Advancing the State of the Art of Thermal Analysis. The National Bureau of Standards and the University of Akron

Fee: $90. *Write:* Kathy Stang, Room B348, Materials Bldg., NBS, Washington, D.C. 20234

(*continued on page 623*)

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Contact: Howard E. Hesketh, Ph.D., PE
Chairman, Search Committee
Department of Thermal & Environmental Engineering
College of Engineering and Technology
Southern Illinois University, Carbondale, IL 62901

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Fee: $315. *Write:* Airtechnical Enterprises, Inc., 29–28 41st Ave., Long Island City, N.Y. 11101

May 21–23 Chevy Chase, Md.
Carcinogenicity–Mutagenicity. The Center for Professional Advancement

Fee: $470. *Write:* The Center for Professional Advancement, P.O. Box H, East Brunswick, N.J. 08816

May 21–23 Chapel Hill, N.C.
Water Supply Engineering: Quality and Treatment. University of North Carolina at Chapel Hill

Fee: $100. *Write:* Judy Beaver, Continuing Education, University of North Carolina at Chapel Hill, School of Public Health 201 H, Chapel Hill, N.C. 27514

May 21–23 Cincinnati, Ohio
1979 Retention and Drainage Short Course. The Papermaking Additives Committee, Technical Association of the Pulp and Paper Industry (TAPPI)

Fee: $235 (members); $270 (nonmembers). *Write:* Jan Bequeath, TAPPI, One Dunwoody Park, Atlanta, Ga. 30338

May 21–25 Cincinnati, Ohio
Analysis of Organic Compounds in Water (Part 2). The Finnigan Institute

Fee: $750. *Write:* Ann Woolley, The Finnigan Institute, 11750 Chesterdale Road, Bldg. No. 5, Cincinnati, Ohio 45246

May 21–25 Alexandria, Va.
Radioactive Waste Management for Nuclear Power Reactors. The American Society of Mechanical Engineers, the University of Virginia

Fee: $500 (ASME members), $550 (non-members). *Write:* ASME, Professional Development Program, 345 East 47th St., New York, N.Y. 10017

May 21–25 Bronx, N.Y.
Biological Waste Treatment. Environmental Engineering and Science Program, Manhattan College.

Fee: $350. *Write:* Kathryn King, program coordinator, Manhattan College, Bronx, N.Y. 10471

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Mathematical Modeling of Natural Systems. Environmental Engineering and Science Program, Manhattan College.

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(*continued on page 624*)

May 22–23 Los Angeles, Calif.
Implementing Resource Recovery Programs. U.S. Environmental Protection Agency

Fee: $75. *Write:* Convention Registration Center, EPA Resource Recovery Seminar, P.O. Box 17413, Dulles International Airport, Washington, D.C. 20041

May 24 Seattle, Wash.
Combustion Practices and Air Pollution Control. The Technical Association of the Pulp and Paper Industry (TAPPI)

Fee: $100 (members), $150 (nonmembers). *Write:* Jan Bequeath, TAPPI, One Dunwoody Park, Atlanta, Ga. 30338

May 24–25 Denver, Colo.
The Role of Desalting Technology in Water Supply, Wastewater Reuse and Industrial Applications. The National Water Supply Improvement Association (NWSIA)

Fee: $25. *Write:* Patricia Burke, NWSIA, 26 Newbury Road, Ipswich, Mass. 01938

May 28–June 1 College Station, Tex.
Stack Sampling Short Course. Texas A&M University

Fee: $350. *Write:* Chemical Engineering Dept., Texas A&M University, College Station, Tex. 77843

June 4–6 New York, N.Y.
Developing and Controlling an Energy Management Program. The New York University

Fee: $670. *Write:* Heidi Kaplan, Dept. 20NR, New York University, Continuing Education Programs, 360 Lexington Ave., New York, N.Y. 10017

June 4–8 Houston, Tex.
Basic Safety Management: Principles and Practices of Safety Management. The International Safety Academy

Fee: $440. *Write:* The International Safety Academy, P.O. Box 19600, 10575 Katy Freeway, Houston, Tex. 77024

Call for Papers

June 1 deadline
Developments in Atomic Plasma Spectrochemical Analyses. The University of Massachusetts

Environmental topics will be discussed. Conference will be held January 6–11, 1980 at San Juan, Puerto Rico. *Write:* Winter Conference 1980, ICP Information Newsletter, Chemistry–GRC Tower I, University of Massachusetts, Amherst, Mass. 01003

June 1 deadline
The Fourth Symposium on Aquatic Toxicology. The American Society for Testing and Materials (ASTM)

Conference will be held October 16–17, 1979 at Chicago, Ill. *Write:* Dean Branson, Dow Chemical USA, 1702 Building, Midland, Mich. 48640

June 1 deadline
The Fourth Annual Symposium on Energy from Biomass and Wastes. The Institute of Gas Technology

Conference will be held January 1980 at a site to be announced. *Write:* Kathy Fisher, Institute of Gas Technology, 3424 South State St., Chicago, Ill. 60616

June 15 deadline
The Standards Engineers Society Annual Conference. The Standards Engineers Society

Conference will be held September 24–26, 1979 at Pittsburgh, Pa. *Write:* D. Cobb, Mobay Chemical Company, Parkway West, Pittsburgh, Pa. 15205

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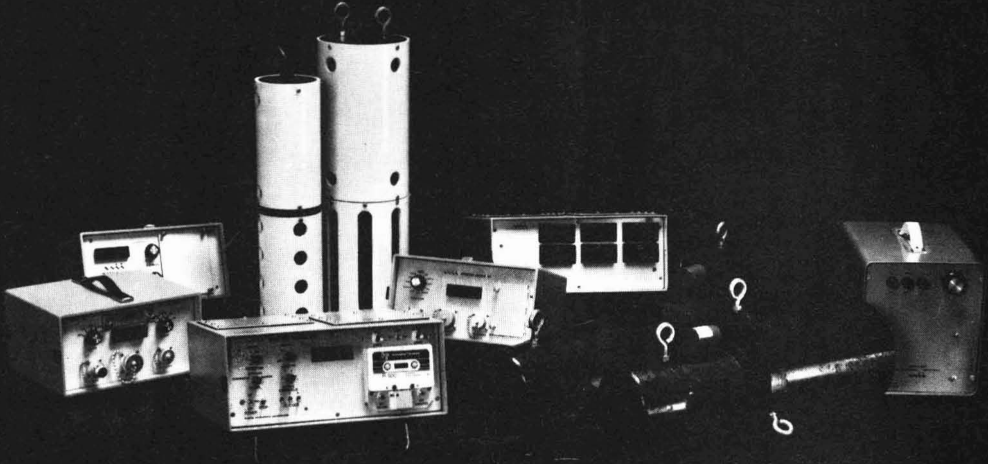

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