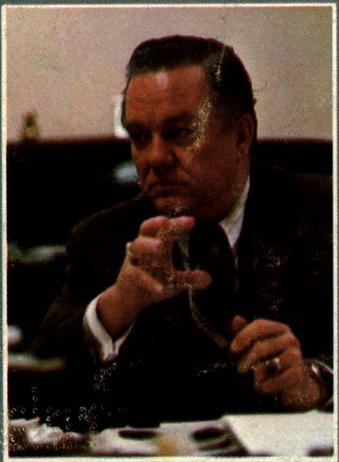
Environmental Science & Technology

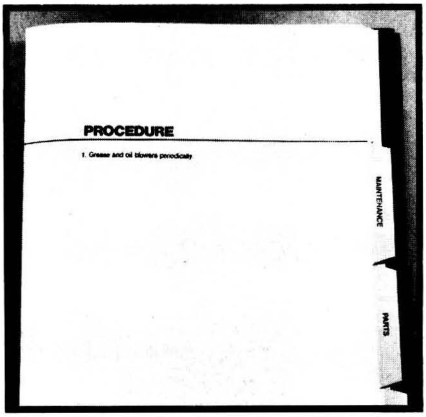
APRIL 1975

Joe Moore on the NCWQ report 297




"One size fits all"
is great for bodysuits, but not
for monitoring SO_2/NO_X.

We tried to write a maintenance manual for Kenics Aerators...



PROCEDURE

1. Grease and oil blowers periodically

And drew a blank.

Because there's virtually nothing we can say. Kenics Aerators are static mixers. No moving parts. No external power in the basin to operate them. Nothing to freeze, clog, or foul-up. They are constructed of high-density polyethylene which is impervious to any type of corrosion. The entire system consists of the static mixer, the air distribution pipe, and the anchor/yoke which stabilizes each unit in position. That's it.

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For more information, call or write:

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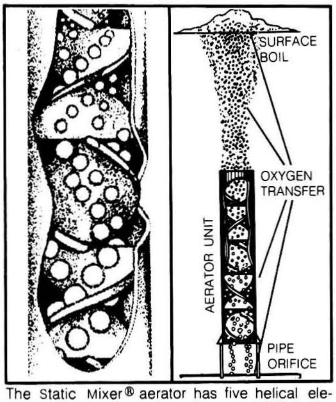

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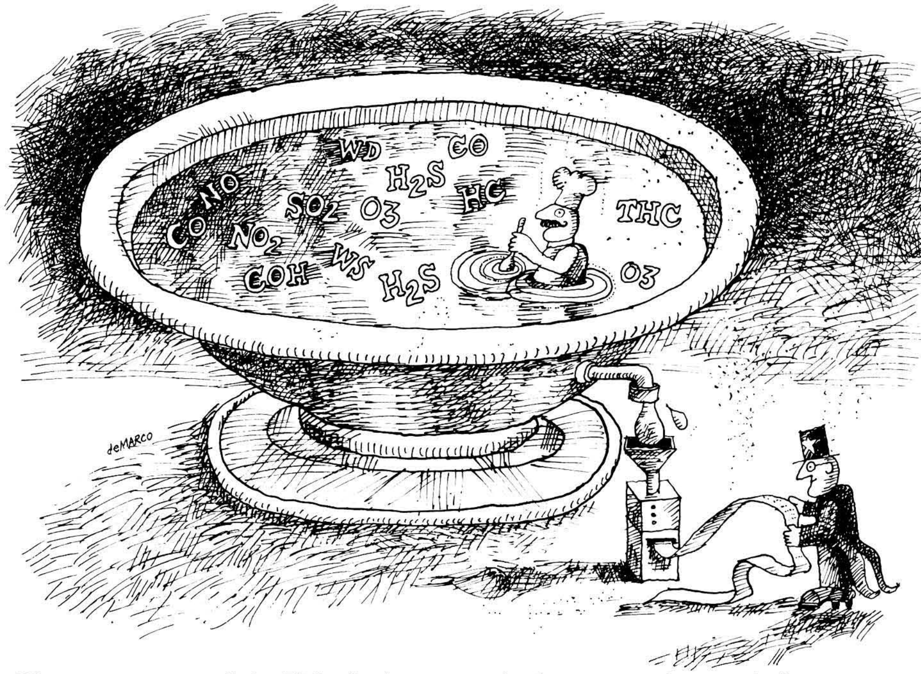
CIRCLE 32 ON READER SERVICE CARD

A Monitor Labs data acquisition system turns alphabet soup into an EPA report.



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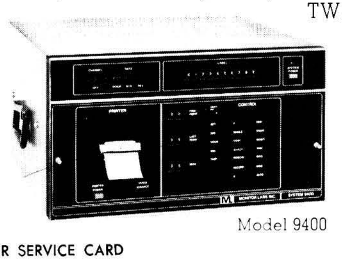

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CIRCLE 28 ON READER SERVICE CARD

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Science & Technology

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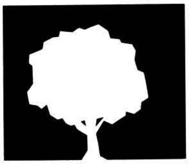

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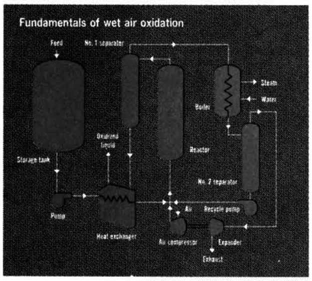

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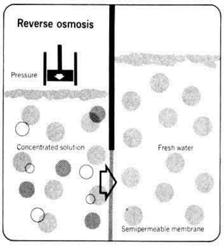

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Current Research

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Those interested in joining the American Chemical Society should write to Admissions Department of Washington Office.

CURRENT RESEARCH

Geochemistries of arsenic, antimony, mercury, and related elements in sediments of Puget Sound 325

E. A. Crecelius,* M. H. Bothner, and Roy Carpenter

Changes in the distributions of arsenic, antimony, and mercury in the sediments of Puget Sound were studied. A copper smelter and a chlor-alkali plant were the major sources of these metals. An arsenic budget revealed the importance of atmospheric input from smokestack emission.

Electrical detection of airborne particulates using surface ionization techniques 334

R. L. Myers and W. L. Fite*

The process of pyrolysis plus surface ionization was examined for detection of aerosols. For sufficiently small particles of similar composition, pulse height is related to particle size. Application to continuous monitoring of particulates is discussed.

Volume resistivity–fly ash composition relationship 336

R. E. Bickelhaupt

Relationships were established between fly ash resistivity and iron concentration, lithium–sodium concentration, temperature, and specimen porosity. Iron affected the magnitude of resistivity inversely, possibly by influencing the number of alkali metal ions capable of migration.

Effect of carbon monoxide on atmospheric photooxidation of nitric oxide–hydrocarbon mixtures 343

W. A. Glasson

Effects of CO on the photooxidation of mixtures of NO with various hydrocarbons, and in a simulated atmospheric hydrocarbon mixture, were studied. CO had effects in the presence of ethylene, isooctane, and mesitylene. It was concluded that CO at levels below 35 ppm had a minimal effect on smog formation.

Dependency of polynuclear aromatic hydrocarbon content on size distribution of atmospheric aerosols 347

R. C. Pierce and Morris Katz*

Ambient aerosols were collected at five sites in Toronto, Ont., using size fractionating cascade impactors. The size distribution of polynuclear aromatic hydrocarbons followed a log-normal relationship, with most PAH-containing particles below 3.0 μm in diameter.

Evaluation of techniques for obtaining least-cost regional strategies for control of SO_2 and suspended particulates 354

G. L. Gipson, Warren Freas, and E. L. Meyer, Jr.*

Methods for determining least-cost regional air pollution control strategies are discussed and evaluated. A heuristic method, using a feasible integer solution and a cost-effectiveness measure, was the most promising technique.

Conversion of marine muds to lightweight construction aggregate 360

D. C. Rhoads,* R. B. Gordon, and J. R. Vaišnys

Muds from harbors and embayments were sintered to produce high-quality construction ceramics. Structural composition and mechanical properties were determined. Environmental consequences of using dredge soil for making bricks are discussed.

NOTES

Treatment of tar sands tailings with fly ash 363

N. N. Bakhshi,* R. G. Gillies, and Pradeep Khare

Fly ash was used to clean tailings generated during the recovery of bitumen from oil sands. Of the several concentrations used, 6 grams of ash to 50 ml of tailings gave the best results.

CORRESPONDENCE

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* To whom correspondence should be addressed.
This issue contains no papers for which there is supplementary material in microform.

Credits: 293, EPA; 295, Fabian Bachrach; 297, 299, John V. Sinnett; 303, 304 (two photos), *ES&T*'s Julian Josephson; 324 (two photos), Mort Stern Photography (Spring Valley, N.Y.)

Cover: John V. Sinnett

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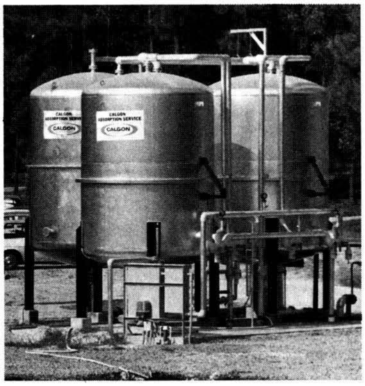

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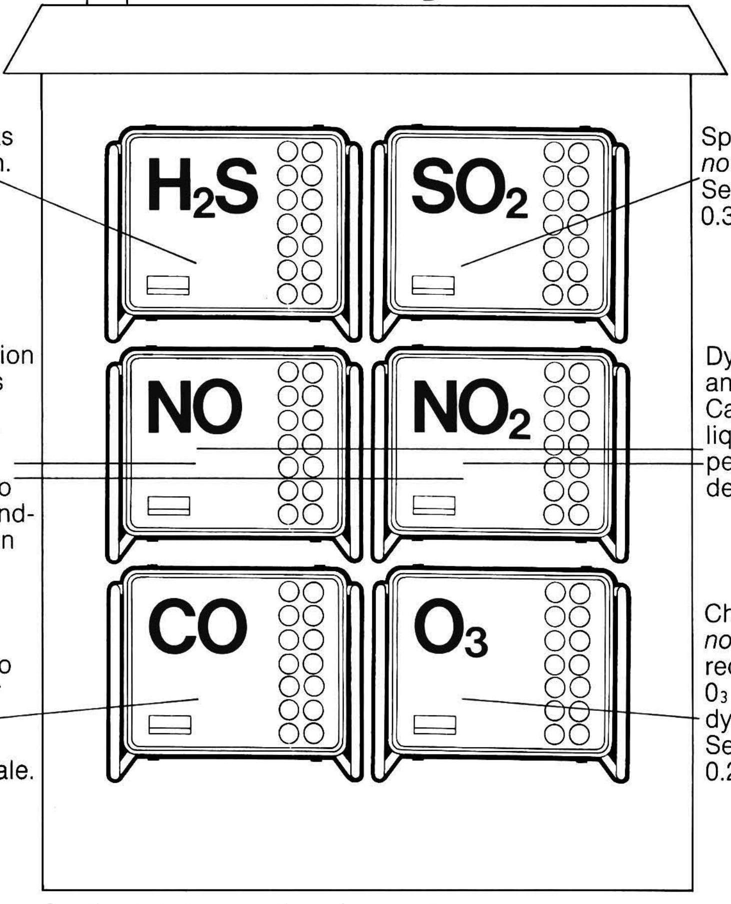
Philips Multi-Component Monitoring System for Air Pollution... unattended operation for 90 days



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CIRCLE 25 ON READER SERVICE CARD

LETTERS

Water analyses

Dear Sir: The Federal Water Pollution Control Act, P.L. 92-500, specifies legally acceptable methods for wastewater analysis. Analysis for cyanide is done according to the method outlined in "Standard Methods for the Examination of Water and Wastewater." Mercuric chloride is used in this method to decompose complex cyanides.

The Illinois Pollution Control Board has established Water Quality Standards that limit mercury to 0.0005 ppm in any effluent; yet, NPDES permit holders are required to submit daily analysis reports on their effluent. Unless the permit holder has an effluent in excess of 250,000 gal a day, he will be in violation of the mercury limit if he runs a single determination.

Does all this mean that in 1985 when EPA demands zero pollution, there will be no more chemical analysis?

Arthur G. Janssen, Environmental Engineer
Illinois Tool Works, Inc.
Chicago, Ill. 60631

Smog, ozone, etc.

Dear Sir: Two items on your Currents page in the January 1975 issue have stimulated me to write this letter. The first reports that smog decreases the amount of ultraviolet (uv) radiation received by the population by as much as 35%. The second refers to the widely publicized speculation that fluorocarbons may catalyze depletion of the ozone layer in the stratosphere resulting in greater penetration of uv to the Earth's surface. I am not trying to suggest that we should keep the smog to protect ourselves from skin cancer after the ozone layer is destroyed. These two items, however, do emphasize the complexity of the chemistry of the atmosphere, and warn against the oversimplifications that have led to scare stories in the newspapers and lawsuits in the courts.

One aspect of the ozone story that I have not seen discussed in either the technical or lay press has to do with what would happen to the excess uv light which would pass through the fluorocarbon-depleted ozone layer. It is well known that oxygen reacts to form ozone when excited by uv light. Would not the ozone that is destroyed in the stratosphere then be regenerated at some lower level in the atmosphere where the oxygen concentration is higher? In other words, I am suggesting that the limiting factor determining the ozone concentration in the upper atmosphere is the amount of uv radiation penetrating it. If some of the ozone is destroyed by some mechanism, allowing more uv to penetrate, then more ozone will be generated at lower levels, but the net amount of uv penetrating to the Earths' surface will not be greatly affected.

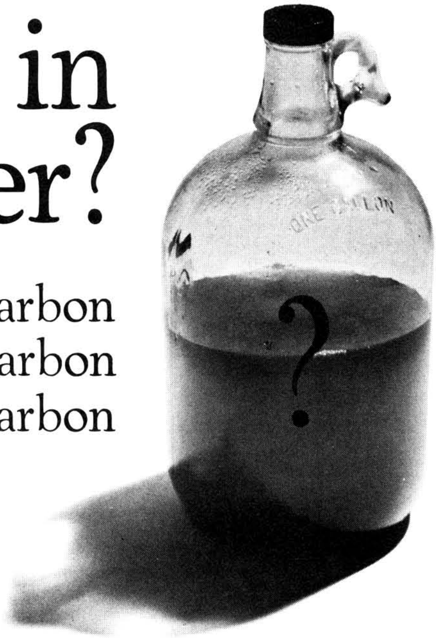
Gerald A. Gordon
Skokie, Ill. 60076

VC monitor—correction

Dear Sir: In the Feb. issue (p 165), it states that our Personnel Monitoring System can measure individual worker exposure to vinyl chloride at "50 ppm" (parts per million). The minimum detectable sensitivity of this system is actually 50 ppb (parts per billion). The sensitivity is a major advantage of our system.

L. F. Millett, Director of Marketing
The Bendix Corp.
Ronceverte, W. Va. 24970

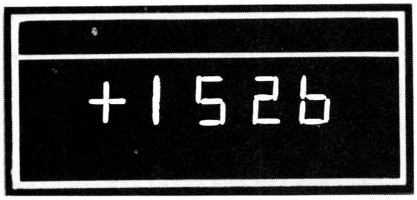
carbon in water?



total organic carbon
volatile organic carbon
total carbon

The Dohrmann® DC-50 organic analyzer

makes *all* of these measurements accurately and rapidly. Based on proven, EPA *approved** methods, it avoids interferences and undesirable pyrolysis reactions that historically have resulted in significant errors.



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ENVIRONMENTAL PROTECTION AGENCY, WATER PROGRAMS, Guidelines Establishing Test Procedures for Analysis of Pollutants. FEDERAL REGISTER Vol. 38, No. 199, Part II, Oct. 16, 1973.

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A slow water year

To date, 1975 has not been a turbulent year for water pollution control activities. It simply does not seem to be a year for any legislative changes in P.L. 92-500. Major controversial difficulties with the Act will probably not be resolved this year; everyone is waiting for the report from the National Commission on Water Quality that is due on the third anniversary of the Act, October 18, 1975.

As a nation, we are not getting on with the water cleanup job. Some deadlines in the Act will not be met. For example, it does not look as though the public is going to have secondary treatment for all municipalities by 1977. With municipalities failing to meet their deadlines, industry spokesmen are beginning to question the compelling reasons for industry to comply with best practicable technology by that same year.

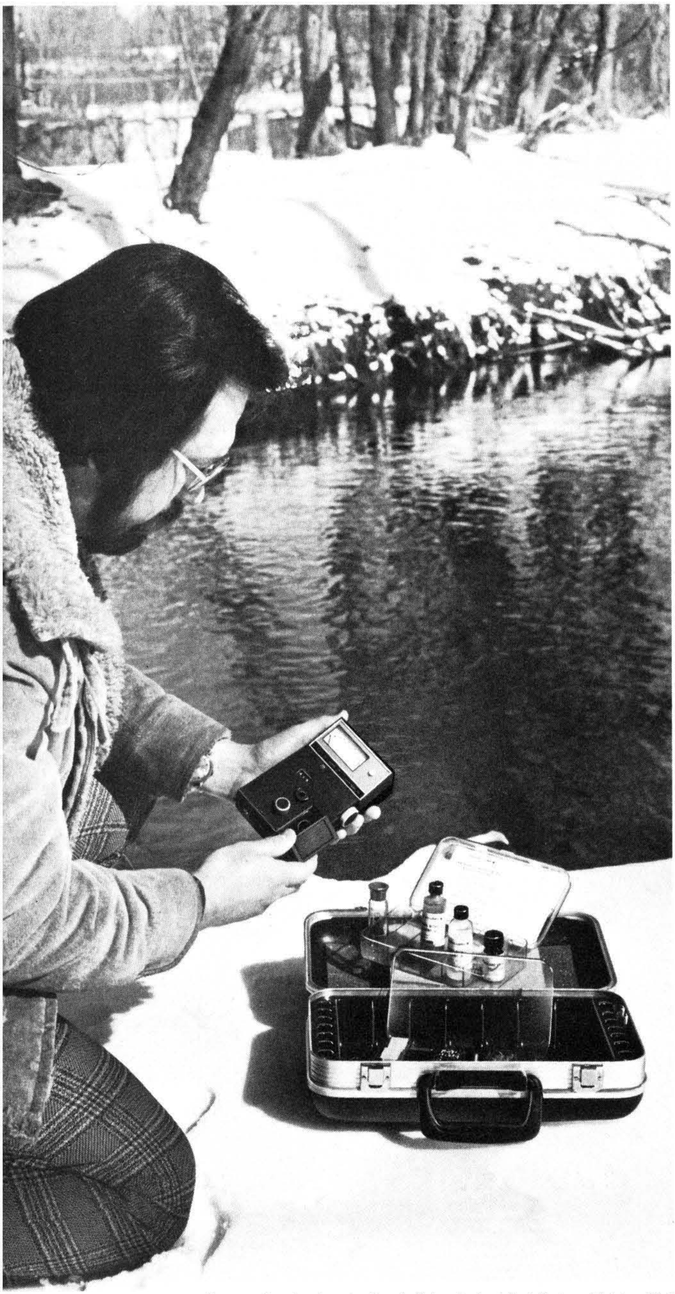
But next year—an election year—the fireworks should begin, if not sooner. After all, one can no longer complain of inadequacy of federal funding. The recent release of the total funds for construction of wastewater treatment facilities is certainly a stimulus for cleanup activity.

Thus, it would seem that 1977 is the year for mid-course correction of P.L. 92-500—five years after enactment of the legislation and five years before its mandated 1983 goals and requirements. By then, also, the water cleanup mandate will have been refocused, redefined, reoriented, retrofitted, and rewritten.

After all, it is a well-known fact that personnel of the U.S. Environmental Protection Agency not only knew about, but endorsed the mandated deadlines in the Water Act of 1972 before it was ever enacted. EPA thought water cleanup was possible, and the Congress did likewise in overriding a Presidental veto. The public hoped that cleanup would follow. We think the public still does, but we could be wrong. Any comments?

Stanton S. Miller

There's no longer any reason to worry about the accuracy of your on-site water quality tests



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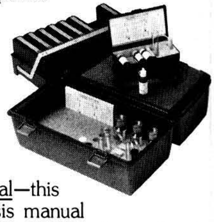

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CURRENTS

INTERNATIONAL

In Sweden, energy from household wastes would not be an alternative to reclamation and reuse, according to a recent report by a group appointed by the Ministry of Agriculture. Recirculating the paper, glass, and metals found in waste would result in lower energy usage in production processes; this energy savings would not be offset by the losses in the incineration value of the waste owing to commodity reuse.

Producing clean-burning hydrogen from water is being tried by use of immobilized chloroplast enzymes which, under the influence of solar light, break water down into hydrogen and oxygen. Prof. Aleksandr M. Ryabchikov, dean of the faculty of geography at Moscow State University, USSR, explained that the hydrogen's danger of explosion would be reduced by adding methanols, and that water is the combustion by-product.

WASHINGTON

An EPA study showed that overland flow is a practical sewage treatment method in rural areas where ample land is available, and above freezing temperatures are prevalent. Overland flow is a process of trickling wastewater over sloping ground to remove nitrogen, phosphorus, suspended solids, and BODs. The process is less expensive than a municipal sewage plant, produces effluents that meet criteria for secondary waste treatment, but requires one acre of land to handle the wastewater for each 200 persons in a community. The method has been used by the food processing industry, but little data exists on its potential for treating other types of wastewater.

At recent EPA hearings on relaxation of the 1977 emission standards imposed under the Clean Air Act of 1970, EPA stated that catalytic converters now used to reduce harmful auto emissions of carbon monoxide and hydrocarbons might emit sulfuric acid mists, and contribute to the problem of sulfate air pollution. Scientific review groups testified that relaxation of sulfur dioxide and particulate emission standards would be inappropriate at this time. In the meantime, the Manufacturers of Emission Controls Association (MECA) has contracted with Energy and Environmental Analysis, Inc., whose President Robert Sansom was formerly assistant administrator of EPA, to analyze EPA's automotive sulfate emissions study.


Sansom and automotive sulfates

A prototype eutrophication study involving EPA, NASA, and the Calif. Institute of Technology that used the ERTS-1 to monitor lake conditions was completed in November 1974. One hundred National Eutrophication Survey (NES)-sampled lakes in Minn., Wis., Mich., and N.Y. were characterized on the basis of six parameters. The Earth Resources Technology Satellite-One imagery was shown to be an effective tool in evaluating the trophic status of surface waters. The NES program identifies lakes with potential or actual aging problems resulting from municipal sewage discharges. The National Aeronautics and Space Administration, the Jet Propulsion Lab. of Cal Tech, and the Eutrophication Survey Branch of EPA were the specific agencies involved.

The SEC will hold public hearings to consider adoption of new corporate disclosure rules relating to environmental and civil rights information. Scheduled to begin this month, the Security and Exchange Commission proceedings are being held at the order of U.S. District Judge Charles Richey, Washington, D.C. The order resulted from a suit brought by the Natural Resources Defense Council (NRDC) and the Center and Project on Corporate Responsibility. The plaintiffs asked the court to review the SEC's rejection of their proposals for broader disclosure rules. Judge Richey held that he could not review the SEC's rejection of these proposals until the Commission held adequate rule-making hearings to determine the extent of "ethical investor" interest in these broader rules.

Design of the first fusion experimental power reactor is being sponsored by EPRI in coordination with ERDA under a $1-million project. The Electric Power Research Institute awarded the contract to General Atomic Co., and it is anticipated that the reactor will be built for operation in the mid-1980's. Some objectives of the study are to demonstrate the production of electrical power from fusion, and to achieve plasma conditions necessary for power-producing reactors. This is only an engineering demonstration of a fusion plant; the construction of a demonstration fusion electric power plant will not occur until the year 2000. The project is part of a broader national fusion research program under the auspices of the Energy Research and Development Agency (ERDA).

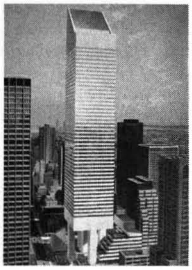
STATES

Nassau and Suffolk Counties plus five towns on Long Island have filed suit against the Department of the Interior, Secretary Rogers Morton, and Curtis Berklund, director of the department's Bureau of Land Management, to block the sale or lease of 10 million acres of offshore lands to oil companies. In papers filed in U.S. Federal Court, Brooklyn, the Long Island officials charged that this use of the outer continental shelf would violate the National Environmental Protection Act, involve Secretary Morton in a conflict of interest, and violate the due process guarantees of the Constitution. No date has been set for hearings on the suit, but the Government has two months in which to file a reply.

The Colorado Department of Health's environmental staff is teaching its wastewater treatment plant operators course to 52 inmates of the state's penal institutions. Otto Havens, an instructor in the Department's Water Quality Control Division, believes that Colorado is the only state to offer such a course to inmates. The inmate-students are scheduled for release within a year.

Montgomery County, Md., running out of landfill sites and barred from incineration of wastes, tried to negotiate a contract with Smith Township, Ohio, to transport 1400 tons of its garbage daily to that state. The company that had proposed to haul the trash to Ohio by rail failed to meet the contract requirements by Montgomery County government's deadline. The deal fell through, and County Executive James Gleason proposed alternatives to the rail-haul plan, including the use of gravel quarries.

MIT is heading a team conducting a design study of a solar energy system atop N.Y. City's Citicorp Center, a 56-story skyscraper under construction. The National Science Foundation awarded Massachusetts Institute of Technology's Energy Laboratory $186,000 for the 12-month study. The initial idea for using solar energy in the Citicorp building emanated from Consolidated Edison Co. of N.Y. The MIT study will determine if this energy form can economically operate a dehumidifier in an air-conditioning unit. The study will also estimate the impact of such systems, if used extensively, on utility operations. Con Edison is providing utility system input data to the study.



N.Y. solar energy design

The new edition of "Profile of Air Pollution Control" for Los Angeles County still lists gasoline-powered motor vehicles as the major source of pollutants. The emissions inventory is compiled by the Air Pollution Control District for Los Angeles County. In a related matter, the California Air Resources Board (ARB) ordered Chrysler Corp. to recall and repair approximately 21,000 cars with defective pollution controls. "This is the largest recall program ever ordered by the State," ARB chairman Tom Quinn explained. Seven hundred pick-up trucks were also found to be defective; 500 have been sold and will be recalled as soon as a repair method is found, the remaining 200 cannot be sold. Chrysler Corp. is cooperating fully with the ARB.

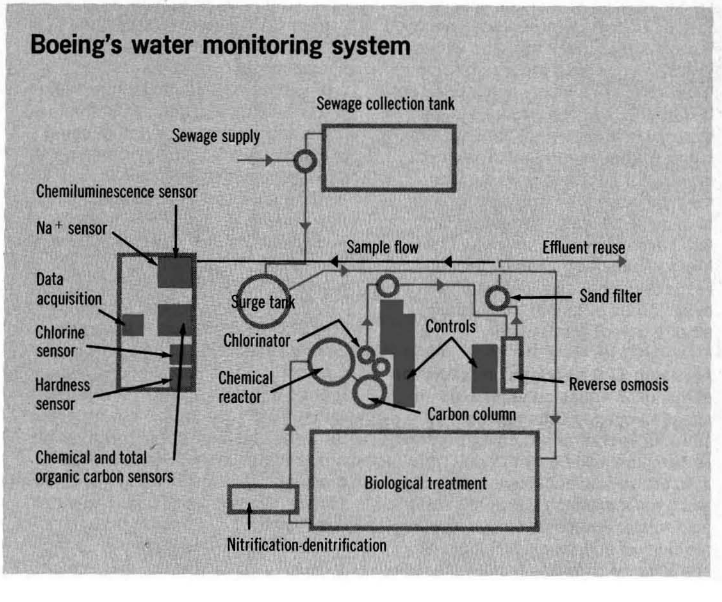
The capacity for deep well disposal of industrial wastes in southwestern Alabama is "unlimited" according to hydrogeologists of the Alabama Geological Survey. Wells installed and operated by Stauffer Chemical, Ciba-Geigy, Inc., U.S. Steel, and Reichhold Chemical, Inc., were monitored for their geologic, geochemical, and hydrologic characteristics. An additional seismic monitoring system was included in the Reichhold well study to assess the possible effects of injection on tectonic activities in this area. The scientists also stressed that depleted oil reservoirs can serve as storage sites.

New York City now has an enforceable law that prohibits smoking in elevators, supermarkets, classrooms lacking designated nonsmoking areas, and other public places. The City Health Department's Bureau for General Operations is enforcing this law, disregarding of which is a misdemeanor carrying fines of up to $1000 and a year in jail. New York joins Arizona, California, Connecticut, Florida, and Nebraska that have similar laws. Massachusetts has pending legislation, and the District of Columbia's statute became enforceable early this year.

MONITORING

Monitoring lead in the atmosphere by the American Society for Testing and Materials (ASTM, Philadelphia, Pa.) D-3112 dithizone method has been validated under Project Threshold. ASTM has made available an abstract of a Battelle Research Report on this validation. Results of extensive field tests at Los Angeles, Calif., Bloomington, Ind., and New York, N.Y., conducted from August 1971 to January 1972, are given, along with confidence levels and other pertinent statistical data. ASTM funded the project, which is in the purview of the society's D-22 Committee.

Real-time wastewater monitoring is the aim of the Modular Integrated Utility System (MIUS), developed by Boeing for NASA (Houston, Tex.). The concept behind the MIUS is the application of aerospace and "conventional" systems technology to upgrade wastewater monitoring. Another objective is to save time normally needed to bring samples to a

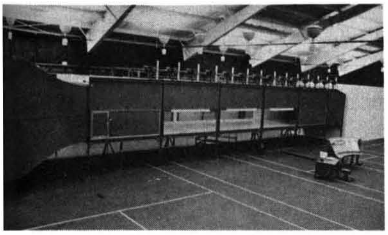


Boeing's water monitoring system

laboratory for analysis. At present, on-line sensors will monitor total organic carbon, dissolved oxygen, turbidity, chloride, ammonium ion, bacterial count, hardness, and chemiluminescence. To come are fecal coliform and bioluminescence sensors. Field tests are scheduled for November to next February.

TECHNOLOGY

A process to recover trace amounts of mercury from industrial wastewater has been developed under a $227,620 grant by the U.S. EPA's Pacific Northwest Environmental Research Laboratory (PNERL, Corvallis, Ore.) to the Georgia-Pacific Corp. (G-P). Because of this process, G-P's Bellingham, Wash., chlor-alkali plant is now saving up to 97% of mercury once considered unrecoverable. Also, up to 99% of the mercury from process sludges can be recovered. Water treatment is effected by sulfide precipitation and sludge treatment by high-temperature roasting. Mercury sells at about $275 per ⅔-gal flask; over 80% of U.S. needs are imported.


Studying air pollutants

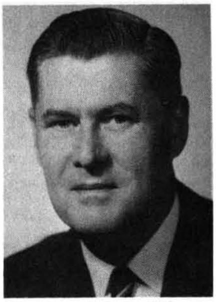
Study of air pollution dispersion received a boost with a new meteorological wind tunnel that the EPA installed at Research Triangle Park, N.C. The tunnel, which is long enough to span three tennis courts, can generate wind velocities of up to 20 mph. Models are placed in a glass-covered area in the tunnel's center where dispersion patterns can be observed. The tunnel can cut time necessary for dispersion studies from years to a few weeks, according to the EPA.

A nonpolluting process for recycling sand and metal will be incorporated into manufacturing operations at Ford Motor Co.'s Cleveland Casting Plant (Cleveland, Ohio). The process, designed by Copeland Systems, Inc., recycles scrap metal for casting operations. It is also expected to help Ford cut use of new sand from 400,000 t/yr to about 50,000 t/yr, since much of the sand, used for casting molds and formerly discarded as solid waste, is returned to the process. Scrap metal chips in the sand will be recycled as an iron value. The system is scheduled to start up early next year.

Elimination of cooling tower blowdown and tower scale prevention are being achieved at St. Joseph's Hospital (Tucson, Ariz.) with a reverse osmosis (RO) system based on Du Pont "Permasep" permeators. The water treatment system provides 15,000 gpd of low-solids water for boiler feed and cooling tower use at a cost for power and chemicals of 15¢/100 gal. Moreover, it reduces total dissolved solids in the hospital's well water from 275 ppm to about 25 ppm. The two cooling towers need only one chemical cleaning per year, and the air conditioning units needed none to date. The system was supplied by Water Services of America, Inc. (Milwaukee, Wis.) in late 1972.

Reclamation of nearly 100% of any type of solvent is possible with a distillation system developed by Interdyne, Inc. (Indianapolis, Ind.). The distillation component operates on a low-pressure, live steam injection principle. The solvent to be recaptured forms a vapor mixture with steam, the mixture is condensed, and the solvent is separated from water. A hybrid convection and/or live steam unit works for water-miscible solvents. A full-time stationary engineer is not needed. Operating costs are less than 3¢/gal, and units from 10–500 gph (up to 10,000 gph on special order) are available.

INDUSTRY


Matthey Bishop's Makin

V. W. Makin, president of Matthey Bishop, Inc., forecast a positive outlook for auto catalyst production at an EPA hearing considering suspension of the 1977 emission control standards. Makin said that raw material stocks are available to support any combination of requirements for 1977 and beyond. He also said that his firm has developed advanced catalyst systems to do the job if other emission control components perform properly. Makin warned, however, that details or required quantities and product mix are needed before May so that scale-up of manufacturing facilities would be possible.

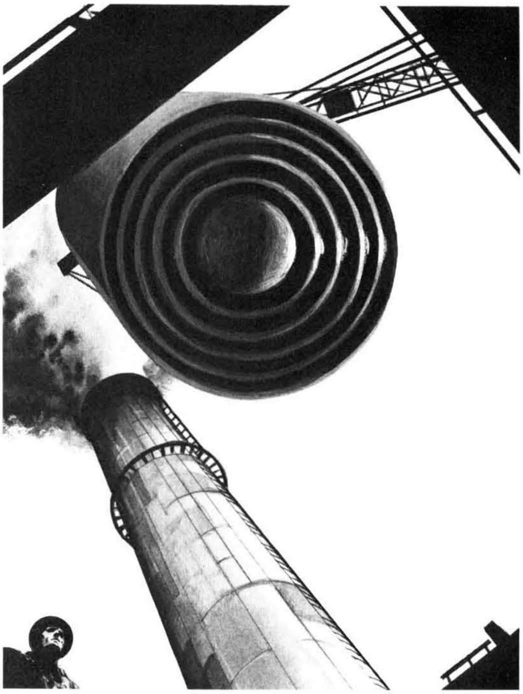
The American National Standards Institute (ANSI, New York, N.Y.) is forming a high-level Environmental Council to promote optimum use of public and private capabilities to develop sound environmental standards. This council will act as an interface between the private sector's standards development organizations and regulatory bodies, rather than be involved in standards development, coordination, and approval. With 12–20 persons from the public and private sectors, the council is an outgrowth of the February 1974 Washington, D.C., meeting on environmental improvement (*ES&T,* May 1974, p 402).

The Aerospace Systems Divison of Bendix Corp. (Ann Arbor, Mich.) is investigating techniques to aid in the surveillance and control of contamination in the Great Lakes by means of Landsat satellites. Under a contract with NASA, Bendix will evaluate the extent of pollution of the Great Lakes by waste nutrients, including salts, oils, and chemicals. The image and mapping products of the Bendix study will go to the EPA and the Michigan and Wisconsin Departments of Natural Resources for purposes of planning and management of the lakes and watershed lands. Cost/benefits of using satellite data will be evaluated.

John Flagg, vice-president-director of research of Universal Oil Products Co. (UOP), announced that UOP has a process to convert one ton of high-sulfur coal—for example, 3.8% sulfur coal from Illinois—to over four bbl of "crude oil." This oil is less than 0.15% sulfur. Flagg said that the "crude" can be further processed to gasoline, jet fuels, and diesel oils by conventional refining methods. UOP has tested its process, which also gives useful gas and light hydrocarbon by-products, on a pilot small-scale development basis, and now plans a demonstration unit.

“HYDRO-PRECIPITROL”

A turning point in the quest for cleaner air.



The “HYDRO-PRECIPITROL” is an integrated wetted-wall electrostatic precipitator designed to abate stack emissions. It is a significant departure from competing systems, thanks to a revolutionary design configuration: Aerodynamic shapes and concentric arrangement of cylindrical elements allow more efficient *vertical* gasflow through a uniform electrical field in a *compact* unit. Here are just some of the results:

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Pulp & Paper: recovery boilers (red & black liquors); hog-fuel boilers.

Glass Industry: furnace stack emissions, hot-end coating (stannic chloride).

Others: meat smokehouse; phosphorous pentoxide; activated carbon dust.

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CIRCLE 10 ON READER SERVICE CARD

INTERVIEW

NCWQ's Moore on record

Will the National Commission on Water Quality be able to file a meaningful report in October 1975 as mandated, considering the fact that it didn't actually get under way until late 1973? We intend to produce a draft report within the statutory deadline, which is October 18, 1975. The Commission is considering holding public hearings that will follow after that date. The intent, now, is to produce the final report for transmission to Congress early in 1976. It is important to remember that 10 of the Commission's 15 members are members of Congress; some were among the original sponsors of P.L. 92-500. They would also sponsor any legislation that would result from the study of this law.

Will the draft report be available to the public? Yes, as soon as it has been cleared by the Commission for distribution, hopefully before the end of the year. I should add that all contract reports will go into the National Technical Information Service as soon as final copies are received.

Is the Commission's report likely to make any recommendations regarding extension of deadlines, or delegation of full responsibility to the states for the conduct of certain provisions of the Act? The Commission's report will have recommendations providing the Commissioners can agree upon recommendations. The Commission could recommend the extension of deadlines and/or changes in the delegation of authority. In both houses of Congress, the Public Works Committees are already discussing the fact that the 1977 deadline for secondary treatment for municipalities will not be reached. There is a discussion of whether that should be statutorily extended. If the deadline for municipalities to achieve secondary treatment is extended, then, is it incumbent upon Congress to extend the deadline for meeting industrial requirements?

Actually, the Commission's focus, as mandated by the Law itself, is on 1983, and it is conceivable that the Commission would recommend changes in the 1983 deadlines and requirements. With regard to the state-local relationship, there is a bill by Congressman James Cleveland (R-N.H.) that would actually assist the funding of state construction grant staffs, and delegate to the states the certification that the construction grant applications meet statutory requirements. I suspect that the Commission's recommendations are more likely to be addressed to the substance of the program between 1977 and 1983 and beyond.

HEALTH ISSUES

Will the Report be responsive to the public's concern for health? We have never focused on the public health effects of water supply as a major thrust of the Commission's charge. The difficulty from a medical viewpoint is getting a credible report that correlates water quality parameters with mortality rates. This is an expertise that we don't have on the staff. We do, however, have an advisory committee from the National Academies of Science and Engineering. The current plan is to include a summary of studies that have been done to produce a state-of-the-art statement. It is important to remember that in the water field the health effects question is different from what it is in the air field. Air is not treated before man breathes it, but water is treated before it gets into the distribution system. It's in the treatment to protect health, such as chlorination, both on the wastewater end of discharges and on the intake side of water supply, that health questions have arisen.

On the question of chlorination, if the secondary treatment requirements for municipalities require postchlorination, which may lead to the formation of hydrocarbons that can be carcinogenic, will that affect your recommendations on secondary treatment? The actual questions furnished to the National Academy related to that very issue. We asked that they review EPA's definition of secondary

Joe Moore, Jr., program director of the National Commission on Water Quality, hails from the hill country of Texas. Prior to his present appointment, Moore was director of the Office of Research, LBJ School of Public Affairs, University of Texas in Austin. In his erudite but still perceptible Texas drawl, Moore discusses the thrust of the Commission's efforts with ES&T's Lois Ember. When the Commission closes shop, Moore would like to return to Austin to teach political science. Whether Washington will let him go is another matter. In previous Washington service, Moore was the second commissioner of the Federal Water Pollution Control Administration, now part of EPA. He was thrice chairman of the Texas Water Pollution Control Board.

treatment, and also the question of disinfection, generally. For example, is disinfection a legitimate part of the definition of secondary treatment? Are there other methods of disinfection in addition to chlorine that could be utilized? Might there be a priority for disinfection? In other words, should disinfection necessarily be required for ocean outfalls? We probably will not add definitively to the knowledge of health effects of water pollution. We will attempt to indicate what has been done thus far, and what might be done in the future.

How will the public be able to participate? The Law as it is now written does not provide for public hearings. In the middle of February, we began a series of 10 regional technical meetings across the U.S. that are explanatory from our viewpoint, and give state, local, and regional governments, industry, trade associations, environmental groups, and the public the opportunity to respond to us and what we are doing. The Commission is now considering holding at least five regional hearings once the draft report is out. These will be held after October 18, 1975, and before the Commission's final recommendations go to Congress.

What happens to the Commission after it files its final report to Congress? I hope it goes out of existence. This is not a Commission, in my view, that should be extended. It is important, however, that there be staff available several months after the Commission goes out of existence who can explain to Congress just exactly what the Commission did. I would hope that we manage to hold together enough key staff people until June of next year.

DEADLINES

In your opinion are the 1977 requirements technologically achievable for municipalities, industry? The 1983 requirements for municipalities, industries? The 1985 goals? I will express an opinion in regard to 1977, but I'll be somewhat more guarded on 1983 and, perhaps, 1985, too. I think it is generally accepted that the 1977 requirements are technologically achievable. I think we can achieve secondary treatment for municipalities, and best practicable control technology currently available, the 1977 requirement for industry. When you add, as Congress did for 1983, the economic achievability test—best available technology economically achievable—I think you have problems. There is no doubt that some of the EPA's Best Available Technology descriptions probably need to be modified. I don't think that it would be unnatural for the Commission to make some recommendations for changes relating to the 1983 requirements because there are probably some of these requirements for which we may not have the technology.

The question of elimination of discharges, the 1985 goal, is somewhat more complicated. I don't think we have the technology, we may never have. This particular goal has provided an opportunity for the argument to be made that the whole Statute has unrealistic goals, some would even want to call them requirements.

The 1985 goal, however, is not defined in the Statute. So we first had to wrestle with the question of whether to take the net or the gross approach to the elimination of pollutants. That is, does the discharger just have to eliminate the pollutants he puts into the intake water, or must he take out of the intake water all of the pollutants that were there, that may have come down to him from upstream? The Commission and the EPA have finally accepted, as a working definition, the net approach. In other words, the polluter removes only the pollutants he adds.

National Commission on Water Quality is charged with . . .

Vice President Nelson Rockefeller, Chairman
Sen. Edmund Muskie (D-Me.), Vice-Chairman
Rep. Robert Jones (D-Ala.), Vice-Chairman

Senate	**House**	**Public**
Jennings Randolph (D-W.Va.)	James Wright, Jr. (D-Tex.)	Edwin Gee
Lloyd Bentsen (D-Tex.)	William Harsha (R-Ohio)	William Gianelli
Howard Baker, Jr. (R-Tenn.)	James Cleveland (R-N.H.)	Raymond Kudukis
James Buckley (C-R-N.Y.)	Harold Johnson (D-Calif.)	S. Ladd Davies

Frederick J. Clarke, Executive Director   Joe G. Moore, Jr., Program Director

Assessing the water cleanup goals and requirements of P.L. 92-500

1977 Requirements	**1983 Requirements**	**1985 Goal**
For municipalities, secondary treatment	For municipalities, best practicable waste technology over the life of the works	Eliminate discharge o pollutants into the navigable waters
For industry, best practicable control technology currently available	For industry, best available technology economically achievable	
	1983 Goal Water quality for protection and propagation of fish, shellfish and wildlife, and recreation in on the water.	

In your opinion, will it be economically feasible to meet the 1977 requirements of the Act for municipalities, industry? The 1983 requirements? The 1985 goals? Well, I think that the question of the achievability of the 1977 industrial requirements, in an economic sense, may hinge upon the whole question of the state of the economy. However, whatever is going to be achieved by 1977 almost has to be under way today, or it won't be on-line by 1977. I think it's obvious that secondary treatment requirements for municipalities will not be achieved by 1977 and, to some degree, the availability of funds at every level of government will impact that achievement whether it's 1977 or 1983. I do feel that the question of achievability of the 1983 requirements is more an economic one than a technological one. I think that the technology is probably there or will be there. Time is important too, by the way. It's probable that whatever is going to be achieved by 1983 will have to be substantially planned, if not under contract, by the time this Commission reports to Congress. If I were to make a guess, I would guess that we would have problems reaching the 1983 requirements.

ENVIRONMENTAL IMPACTS

What do you consider some of the environmental impacts of the Act for 1977? 1983? 1985? I think the environmental benefits are likely to be much more significant for the 1983 requirements than they will be for the 1977 requirements, simply because of the way progress is being made toward secondary treatment, and the fact the industrial treatment technologies are more likely to come between 1977 and 1983, rather than before. One of the major beneficial environmental impacts will be on fish and shellfish.

We also have a series of site-specific studies that attempt to determine what the ecological change would be in the water ecosystem over time, assuming that the requirements are realized, whether they are realized in the years stated or not. In other words, what difference would it make if you achieve the 1977 requirements in 1977, or 1983, or 1985? One of the things we already know about environmental change is that it won't occur within the timeframe of the Statute. Environmental change takes longer than the actual change in individual discharges because of the recovery period.

What do you foresee as some social impacts of the Act for 1977? 1983? 1985? One of the arguments that is always made is that there will be a reduction in employment, particularly in one-company towns, if an industry chose to close rather than meet the environmental requirements. That's one of the effects we will examine. Another is the impacts of not having bodies of water cleaned up.

Social impacts are likely to be very localized. A small percentage change in the national unemployment rate can be shrugged off, but if it's concentrated in one place it can make a great difference. On the other hand, if certain industries meet the requirements of the Act, and if these are localized, then dramatic pluses for social impact can be achieved.

"I think the system of a series of specific deadlines with almost detailed specifications of what is to be done by those dates is a major failing of the Statute."

Joe G. Moore, Jr.

What are some of the financial and institutional problems being considered by the Commission? There has been a general feeling that this Act may have imposed a burden upon the whole institutional structure that it is not designed to accommodate. By institutional structure I'm including governmental and industrial components. For example, are the relationships between the various levels of government and the municipalities, industries, and agricultural dischargers, as permittees, such that they can mutually accommodate the requirements of this Act? Is this Statute so directive in nature that it in effect deprives the states of any responsible role in the implementation of the Act?

The financial problems have to be viewed in two parts. Firstly, are the public monies available for meeting the requirements and goals of the Act? Secondly, is there sufficient capital available for investment by industries? Frankly, I don't think there will be an overall inability to meet capital demands, but I think we may find some difficulty in particular areas.

PROBLEM AREAS

In your opinion, what are the major failings of the 1972 Act? What, if any, midcourse corrections are being contemplated? I think the system of a series of specific deadlines with almost detailed specifications of what is to be done by those dates is a major failing of the Statute.

Probably the attempt to require permits at the federal level rather than specifying that states shall develop permit programs subject to approval at the federal level is another failing. The question is, can the federal agency (EPA) ever get enough personnel to oversee, in detail, as it has attempted to do, the issuance of each individual permit.

It is probable that the technological base of the Statute is not invalid. If you are going to have permits, there must be some standard against which you measure what it is you are going to require individual dischargers to do.

I think it is unlikely that we will ever go back to water quality standards. The Commission is more likely to suggest modifications in the way the effluent limitations are applied to individual discharges, or in the way that the permit program itself is managed, rather than a substantial overhaul of the structure of the permitting procedure.

There are a number of lawsuits against the EPA emanating from its promulgation of industry-wide effluent limitations. Should Congress ensure that applicable local conditions be considered in establishing discharge limitations? I do believe that there is an opportunity for introducing more flexibility into this Statute. The flexibility is likely to come in the subcategorization of industrial discharges, rather than in specific changes in the effluent limitations approach. In other words, rather than abandoning the effluent limitations approach, there will just be more effluent limitation categories.

Do you feel that the constraints of the 1977 secondary treatment requirements for municipal wastes are valid for all municipal facilities? Should exemptions to this requirement be made? The Commission is looking at the questions of whether secondary treatment should be required for discharges to deep ocean waters. That is one that appears to be most questionable. Studies, some of which are already under way, should be done to determine whether or not secondary treatment should be required for discharges to deep ocean waters. Again, you should be aware that I come from a state where secondary treatment was uniformly required beginning in the late 1930's. So I am not very sensitive to the argument that you must make exceptions. I have a great deal of difficulty in saying that you should exempt Memphis from secondary treatment simply because it is discharging into a major river. On the other hand, I might be more sympathetic to Seattle. Downstream water uses do make a difference.

TECHNOLOGY

Are municipal and industrial wastewater treatment areas requiring further research because current technology is not sufficient to protect existing water quality? Well, with regard to secondary treatment in municipalities, I am not sure that more research is needed. I think that when you get to so-called physical-chemical treatment or advanced waste treatment, there undoubtedly is a need for additional research. In the case of industrial technologies, I think it is extremely important that as an industry develops new production processes, it should immediately do an analysis of the waste discharges that are likely to result. That's where I think the focus of industrial technological research should be. In my opinion, at this time, I think there is probably more need for industrial research than municipal.

PAT REPORT
PRACTICAL, AVAILABLE TECHNOLOGY

Wet air oxidation comes of age

Zimpro Inc. has 118 WAO installations on five continents that handle sludges from sewage plants, recover chemicals from paper mills and helps with incineration emissions

Today, wet air oxidation provides some of the best practical available technology to destroy waste substances, recover valuable inorganic materials from the waste stream, and condition sludge solids for easy disposal. And since the oxidation is exothermic, substantial energy recovery is also feasible.

Developed and patented by Zimpro Inc. (Rothschild, Wis.), wet air oxidation (WAO) is based on the discovery that any organic material in aqueous solution or suspension can be oxidized to any desired extent by air, under pressure, at temperatures from 350–700°F. The degree of oxidation (from 0–100%) depends on the temperature and the amount of air supplied. The WAO of some compounds may be effectively catalyzed.

At the Burnie mill of Associated Pulp and Paper Mills Ltd. (APPM-Tasmania, Australia), a WAO system has been processing soda pulping black liquor since 1966. A hemisphere away, on Michigan's Upper Peninsula, a WAO system is being constructed at the Hoerner Waldorf Corp.'s Ontonagon paper mill to recover energy and pulping chemicals and destroy mill sludge. These two plants are the first and the latest industrial members of a family of 118 WAO installations.

Down under experience

At APPM's Australian mill, WAO provides practical and economical recovery of chemicals and energy from the soda pulping of eucalyptus wood, according to APPM's senior research officer, John Morgan. "The WAO unit processes liquor from the production of about 30 long tons of oven-dried pulp per day and returns better than 99% of the pulping chemicals to the pulping operation, with sampling and pump gland leakage being the largest losses," he reports.

"The inorganic chemicals—sodium carbonate and some sodium bicarbonate—remain in the residual solution and can be passed to the recausticizing plant. Energy recovery is in the form of saturated process steam and electric power. The process is sufficiently flexible to allow the proportion of steam and power generated to be varied over wide limits to suit local mill requirements."

Morgan points out that, used in this way, WAO can replace the conventional evaporation and dry incineration approach to heat and chemical recovery in the pulp and paper industry. Evaporation may not be required in the WAO process; in fact, dilution may be required prior to the oxidization reaction.

"The process has operated successfully right from the plant commissioning," Morgan says. "The unit has demonstrated 93-plus% availability. I feel that our working relationship with Zimpro Inc. is good and that our joint development program with them has been conducted successfully during the past eight years the unit has been in operation, even though we are located almost on the other side of the globe."

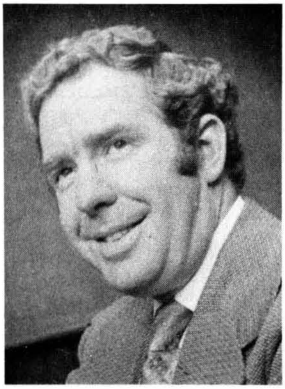
In this country

The Ontonagon mill presently produces 240 tons per day (tpd) of semichemical pulp using a mixture of sodium carbonate–sodium hydroxide in the cooking liquor. In late 1975, capacity will be expanded to 440 tpd, and the present recovery boiler will be replaced by a Zimpro WAO unit. The unit will oxidize the black liquor, returning a sodium carbonate–sodium bicarbonate solution directly to the pulping process. It will also produce steam for process use at the rate of 3.2 lb of steam per pound of black liquor solids. As an extra benefit, the unit will also be able to oxidize about five tpd of activated sludge solids, fed to the unit at a 99% water content from the mill's new secondary wastewater treatment plant.

Another unique application of WAO in the pulp and paper industry is the recovery of filler materials, such as clay and titanium dioxide, from paper manufacturing or de-inking wastes. In a conventional incineration operation, the fillers are recrystallized and can cause abrasion to papermaking machinery when the recovered material is recycled. The low temperatures encountered during WAO, however, produce a recovered organic-free filler that is acceptably bright, without changing the abrasive qualities of the material.

How it works

In the typical WAO process, the feed is pumped to system pressure, mixed with compressed air, and heated by heat exchange with outgoing products. In an enclosed reaction vessel, the mixture is held for a specified length of time and the oxygen in the air reacts with the organic matter in the feed stream. This reaction is accompanied by a rise in temperature. The gas and liquid phases are separated after the reaction. The liquid and solids are passed on for recovery or final disposal; the gas is scrubbed or treated in an afterburner before release to the atmosphere.



APPM's Morgan
"Unit operated well from start-up"

The degree of oxidation can be selected, and can range from 0–100%. At high temperatures (above 600°F) and pressures (above 2000 psig), organic materials can be oxidized almost completely to carbon dioxide, water, and elemental nitrogen, leaving behind inorganic materials and ash suspended or dissolved in the carrying water. At temperatures between 350–600°F and at correspondingly lower pressures (300–2000 psig) partial oxidation takes place.

The latter conditions are popular among municipal sewage treatment systems that use low oxidation to convert difficult-to-dewater sewage sludges to sterile, easily dewatered residues. Such major cities as Toronto, Ont., Canada; Cincinnati and Columbus, Ohio; Davenport and Dubuque, Iowa; Louisville, Ky.; Seoul, Korea; and Port Elizabeth, South Africa, have selected the low-pressure oxidation method of sewage sludge treatment.

Unlike open air burning, the feed in WAO does not need to be dewatered. In fact, water must be present at all times; the system's pressure accomplishes this by preventing water from being converted to steam during heating.

Likewise, WAO eliminates many of the air pollution problems associated with conventional incineration. No smoke or particulate matter is carried to the atmosphere. Since oxidation temperatures are comparatively low, the exhaust gases are free of nitrogen oxides and sulfur oxides, which are retained in the liquid and solid phases. WAO exhausts may, however, contain small amounts of low-molecular-weight organic compounds that can be easily removed by incineration.

The WAO reaction is exothermic, just as in conventional oxidation and, in most cases, sufficient heat is generated to make the process thermally self-sustaining. Under certain conditions, surplus energy is liberated during the reaction, and energy recovery becomes practical. For start-up, and in those cases where energy is not sufficient for self-sustaining operation, additional energy can be added by direct steam injection or by heat exchange between the reactor feed and a heat transfer medium.

Most WAO operations, whether high or low oxidation, are similar. They have an air compressor to supply the air, a pump to deliver the feed material in a continuous flow, a heat exchanger, a reaction vessel, and a boiler or other heat source for start-up. Accessory equipment, such as a heat exchanger washing system, instrumentation, thickening tanks, chemical feed systems, or other equipment, is added as required. Chemical feed is used in industrial or high-oxidation plants where control of pH or hardness is desirable.

Other WAO uses

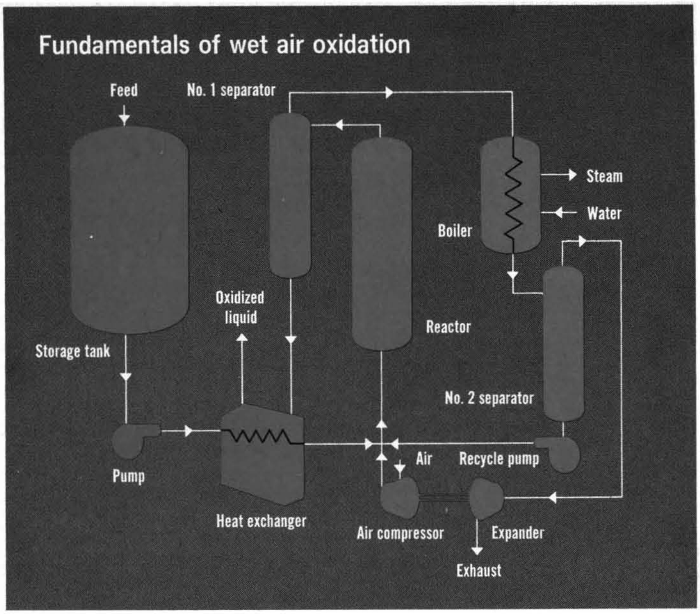
In addition to pulp and paper and municipal waste treatment, Zimpro Inc.'s WAO is being increasingly applied to other pollution and recovery problems.

WAO is being used to detoxify acrylonitrile wastes by destroying cyanide. Recent process developments have made it possible to produce a water-white effluent containing less than 2% of the influent COD. Ammonium sulfate of marketable quality can be recovered from the effluent. Sufficient heat is liberated during the oxidation not only to make the process thermally self-sustaining, but also to concentrate the ammonium sulfate by evaporation. To date, four acrylonitrile waste plants have been built.

WAO will also be used by the U.S. Navy to safely destroy, without air pollution, off-specification and outdated propellants, explosives, and munitions. Such materials have been disposed of in the past by open-pit burning. In WAO, however, a slurry of ground explosives is oxidized with air; the residue is a small volume of inert ash and salts. The Naval Ordnance Station at Indian Head, Md., will be the site of the first such installation.

The WAO process is also applicable to the regeneration of powdered activated carbon. Zimpro Inc. is marketing such systems in combination with waste treatment plants, or as individual wastewater reclamation units. In this application, spent powdered activated carbon is processed through a WAO unit where adsorbed and associated impurities are destroyed, and about 95% of the carbon is regenerated for reuse.

In the past, high-oxidation plants often have been characterized by relatively high capital costs and low operating costs. Where inexpensive fuel and electric power have been available, the economics of the situation might not have justified the capital investment needed for the high-temperature, high-pressure, high-oxidation equipment. Recently, however, the energy squeeze and increasing fuel and power costs have changed the economics of the situation so that high oxidation plants once again appear to be attractive for the municipal, as well as the industrial, market.


Fundamentals of wet air oxidation

Status of wet air oxidation installations

World region	Number of plants	Typical waste treated
United States and Canada	68	Municipal sewage sludge Pulp and paper wastes Various industrial wastes
Far East and Australia	40	Municipal sewage sludge and night soil Acrylonitrile waste liquors Pulp and paper wastes Food processing wastes Petrochemical wastes
Europe	8	Municipal sewage sludge
Africa	2	Municipal sewage sludge and night soil

Source: Zimpro Inc.,

OUTLOOK

The toxic substances regulations industry may be facing

Analysis. *New rules may require more microdeterminations*

As life in the 20th century becomes more involved, so do factors in product selection and use. The most recent complexities that have evolved in product selection criteria are environmental, ecological, toxicological, and safety (E/E/T/S) considerations, in addition to price-benefit ratio, reliability and maintainability, warranties, technical documentation, and the like.

E/E/T/S parameters will have to be exhaustively accounted qualitatively and quantitatively through the whole cycle of manufacture, distribution, use, and disposal of a product, George Dominguez reminded the recent Symposium on Toxic Substances Control (Washington, D.C.) in his keynote address. Dominguez is the general manager of EN-CAS Systems (Greensboro, N.C.), a Ciba-Geigy company. The symposium was convened by the Synthetic Organic Chemical Manufacturers Association (SOCMA) and the Council of Chemical Associations (CCA), and concerned itself principally with occupational safety and health matters.

New ethics

Thomas Carmody, Union Carbide's vice-president and general manager of Safety, Health, and Affairs Related to the Environment (SHARE, *ES&T*, August 1974, p 695), told the symposium that however regulations may ultimately turn out, pollution abatement and occupational safety and health have become ethics of industrial practice. Moreover, he feels that new and much more stringent toxic substances control proposals with respect to E/E/T/S could pass the 94th Congress. Indeed, the main "hang-up" in the enactment of such proposals is the present state of the U.S. economy.

To help manufacturing companies cope with E/E/T/S, the Ciba-Geigy Corp. founded EN-CAS (Environment Concerns and Safety) Systems. Officially founded last May, it commenced operations in October, and has a staff of 22 professionals. Ciba-Geigy, the parent company, is headquartered in Basel, Switzerland; its first forerunner was started there by Johann Rudolf Geigy in 1758. In 1974, Ciba-Geigy, mainly in chemicals and pharmaceuticals, had 77,000 employes in 46 countries, and sales of more than $2.5 billion. Its five U.S. divisions and operations employed approximately 7000 (about 800 at Greensboro) and racked up $900 million in sales.

EN-CAS Systems manager Dominguez told *ES&T* that his company's uniqueness lies in its capabilities to provide a customer with full consulting, monitoring, analysis, and systems design services for handling problems of air and water pollution, solid waste management, and occupational safety/health. These services also cover potentially carcinogenic, mutagenic, and teratogenic substances. In other words, if engaged to do so, the company could address all aspects of E/E/T/S from the beginning of a client's product manufacture to ultimate disposal of the product. As Dominguez put it, EN-CAS Systems could be said to offer turn-key services in analyzing all customer needs, and providing postanalysis recommendations as to how the customer could most rationally proceed. However, the company does not fabricate hardware.

Confidentiality

EN-CAS Systems does all of its business in the U.S., and, at present, tries to key its services to the textile and pulp and paper industries, as well as other customer industries with which its staff members are familiar. This type of familiarity with a customer's processes and technology could make an EN-CAS representative privy to that customer's trade secrets; for this reason, among others, the customer usually insists upon a strict confidentiality agreement.

Another reason for customer insistence upon confidentiality may be this: That outside knowledge of the fact that a client company has a pollution or occupational safety/health problem would be, at best, a source of considerable embarrassment to that company. At worst, the client could conceivably find itself harrassed by federal, state, and local government inquiries and public agitation. Moreover, if an occupational safety/health matter were in question, labor and insurance troubles might also crop up.

For these principal reasons, EN-CAS Systems declines to list its customers and the values of its con-

Environment, ecology, toxicity, and safety will have to be accounted for qualitatively and quantitatively from product manufacture to ultimate disposal. Advising how this must be done could prove to be a good business

tracts. Dominguez did tell *ES&T,* however, that all of its business is industrial; however, the prospect of doing government or municipal business is not ruled out.

Some EN-CAS projects

One on-going project is the development of sophisticated methodology for the complete analysis of carcinogens, heavy metals, toxic organic chemicals, and other hazardous materials in air and process chemical samples for work related to Occupational Safety and Health Administration (OSHA) requirements. In this effort, it serves a number of customers.

In an analytical survey, it showed a textile manufacturer that about 50% of the water being discarded was actually of good enough quality to be recycled straight back into his steam lines and dyeing process. The client company was able, therefore, to save dollars on water and sewer charges, as well as on energy.

Another job involves dye carrier analysis with respect to dyes and processes for polyester fabrics. The object is to alleviate odor problems in work areas and in the outside air. Here again, the company also would, if called upon, not only run a complete analysis, but also suggest alternatives so that the customer could best meet his production needs and environmental/OSHA regulations. Other air projects, handled on the same basis, could involve vinyl chloride, highly carcinogenic bis-chloromethyl ether (BCME), and other toxic substances.

Dominguez said that his company has acquired "first-class" laboratory and field equipment, and expertise in order to perform analyses, sometimes down to hundreds of parts per trillion (pptr) as fast as possible. Speed is sometimes of the essence, since cases in which a customer needs hurry-up help with an environmental or OSHA problem do occur. The company can also obtain technical support from other components of the parent company when the need arises.

Parallel efforts

In addition to Union Carbide's SHARE program and the total service concept of EN-CAS Systems, there will be expanded efforts in research and testing activities in occupational and environmental health by Du Pont's Haskell Laboratory for Toxicology and Industrial Medicine (Newark, Del.). A 70% expansion of the Haskell Lab, which now has a staff of about 100 scientists and technicians, should be completed early next year.

John Zapp, Jr., Haskell Lab director, told the symposium that he foresees increased capabilities for

- screening substances for carcinogenic properties
- testing industrial effluent toxicity on aquatic life
- evaluating combustion by-products
- improving a toxicology information storage/retrieval system serving the company and the public
- identifying and eliminating potential occupational health hazards for employees.

Haskell Lab provides Du Pont's research laboratories with information on the toxicity and handling of chemicals, and influences new manufacturing unit design to assure maximum safety standards. The labs also assist in package labeling to aid consumers in using products safely.

As environmental, occupational safety/health, product safety, and eventually, toxic substances regulations play an ever-increasing role in the manufacturing process, more organizations, in business to assist manufacturers with economical compliance, will probably come into being. Some, like Kahl Associates (Washington, D.C.), may offer a total services concept in dealing with the actual government regulatory mechanism. Others would provide a full spectrum of technical assistance in these matters.


EN-CAS manager Dominguez
"Exhaustive accounting of E/E/T/S"

Premarket screening

Perhaps Rep. Bob Eckhardt (D-Tex.) defined the crux of the toxic substances and environmental issues by enumerating two competing objectives at a dinner speech at the symposium:

- assurance that no substance harmful to the people or the environment would slip into the spectrum of chemical products put on the market, but on the other hand
- protection of the interests of the chemical manufacturers who seek to bring useful new products to the market without undue bureaucratic delay.

To provide protection against potentially harmful materials, Congress is once again looking at premarket screening. The Senate's concept is to require screening for all new substances and all uses of existing products, except those which EPA deems do not pose "an unreasonable threat." The House calls for screening of substances and uses more specifically "identified as posing a substantial danger." The Senate-House differences have been a major impediment to passage of a toxic substances law. The Administration, on the other hand, does not view premarket screening with favor.

Given the present mood of the 94th Congress, there are good chances for passage of some sort of toxic substances law. If these provisions materialize, service-oriented organizations such as EN-CAS Systems, Kahl Associates, and other existing or new ones will be called upon to help manufacturers meet the challenges of marketing new products, and yet protect the environment, employees, and the consuming public most effectively and economically, pursuant to existing and forthcoming regulations. JJ

Clean water at cooling towers

Can water pollution control needs be met without detriment to cooling tower performance? Some approaches were discussed at a CTI forum

Take a trip to the new power plant in your area. There, you may see immense cooling towers, similar to two at Chalk Point, Md., 400 ft high, 350 ft in base diameter, and 162 ft in throat (top) diameter, built by the Marley Co. The first of these cooling towers, brought on stream last October, services the 660 MW Unit No. 3 oil-fired generator of Potomac Electric Power Co. (PEPCO), and, incidentally, is the first in the U.S. to use brackish water.

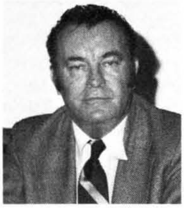
These cooling towers, and others of different sizes, configurations, and applications, are coming into increasing use as water pollution regulations, especially those dealing with thermal pollution, become ever more stringent. In 1974, for example, cooling towers accounted for $200 million worth of business with about 98% for new construction and thermal pollution abatement; for this year, estimates of at least $240 million are given by the Cooling Tower Institute (CTI, Houston, Tex.), which has over 110 members. Compliance with present and forthcoming water regulations and its effect on cooling tower business and technology were the principal themes of the Institute's 25th annual meeting, held in Houston in February, and attended by 285 people from the U.S., Brazil, Canada, France, and Japan.

Water regulations

In the view of J. Robert DeMonbrun of Union Carbide Corp. (Oak Ridge, Tenn.), CTI's immediate past president, the new water regulations will require cooling tower suppliers to be cognizant of needs for preventing chemical pollution of water. In his keynote speech, DeMonbrun said that CTI will maintain the necessary liaison with regulatory agencies in order to provide information necessary to suppliers and users for compliance with these regulations. An example of typical regulations, in this case for steam electric power generating point sources, can be found in the *Federal Register,* Vol. 39, No. 196, October 8, 1974; effluent limitations for cooling tower blowdown are included.

The stringent new effluent limitations will certainly present challenges to devise new techniques to combat the four major cooling tower problems—corrosion, scaling, deposition fouling, and microbiological attack. For example, when blowdown is discharged, pH will be limited to 6.0–9.0, and no polychlorinated biphenyl compounds will be discharged. Moreover, free available chlorine in blowdown will be sharply curtailed, generally to 0.5 ppm, maximum, and 0.2 ppm, average. Thus, choices of anticorrosion, antiscaling, and biocidal compounds may be limited; the more so, since chlorine availability could prove to be a "sometime thing."

CTI past-president DeMonbrun
"Prevent chemical water pollution"



CCT president John Hubenthal
New president of Institute

Among corrosion inhibitors, the most effective and least expensive so far are toxic chromate/zinc and chromate/zinc/phosphate. Rules under P.L. 92-500, however, will drastically reduce the amount of chromate, zinc, and phosphate allowable in cooling tower blowdown, especially under best available technology economically achievable (BATEA, 1983) regulations. Limits for other corrosion inhibitors will be established on a case-by-case basis. Moreover, for new sources, corrosion inhibitor discharge apparently will be a "no-no."

Recovery possibilities

Despite regulations, in some cases, conversion to a nonchromate corrosion inhibitor may not be feasible because of given system conditions. However, the rules do not say that chromate cannot be used; they only limit or ban chromate discharge. The possibility to recover and reuse chromate could thus arouse interest on the part of cooling tower operators. Another reason for interest in chromate or chromium recovery and reuse is the paucity of chromium ore in the U.S. and Canada, as Robert Kunin of the Rohm and Haas Co. reminded the CTI meeting.

Kunin said that to remove chromate for possible recovery, ion-exchange resins must withstand the high oxidative potential of chromate-bearing solutions. He discussed the Rohm & Haas Amberlite resins which he said meet this requirement, and pointed out that 1 ft^3 of these resins will treat 15,000–30,000 gal of average blowdown before breakthrough is realized. Recovery of over 99% chromate has been demonstrated in the field, according to Kunin.

A similar approach to chromate recovery, by means of a weakly basic anion exchange resin, was discussed by Koichi Yabe of Kurita Water Industries Ltd. (Yokohama, Japan). The resin selectively removes chromate and allows its subsequent reuse, and has been used mainly for cooling tower blowdown treatment to meet a 1971 Japanese requirement that chromate discharge be less than 0.5 ppm. A cation resin then permits substantial zinc removal.

The system has been tried operationally in Japan with chemical, electric power, and resin replacement costs which Yabe pegged at $0.067/1000 gal. Cost of sodium chromate recovered is put at $0.285/lb. Five towers in Japan are using the Kurita ion-exchange process with regenerable Lowatit resins imported from West Germany.

Another chromate removal technique involves electrochemical methods. Joseph Duffey, president of Andco Environmental Processes, Inc., told the meeting that by these methods, chrome can be kept below 0.05 ppm with operating costs, exclusive of labor, of 5–10¢/1000 gal, depending upon chromate concentration. Labor, mainly for an acid wash procedure, is less than one-half man-hour/day. An arrangement of steel electrodes removes the chrome and the bulk of zinc ions as well. Andco has several commercial units in service.

Some options

In the game of makeup water treatment and blowdown disposal, there might be some anticorrosion options, and A. F. Brunn of Du Pont's Gulf Regional Office (Beaumont, Tex.) mentioned a few. One possibility was a "zero blowdown" system; another was chromate/zinc removal by ion exchange, or precipitation and solids disposal; and a third was blowdown impoundment and evaporation. While all three options are technically feasible, and indeed in use, Brunn pointed out that Du Pont evaluated the first two methods as being justified only where benefits would outweigh the high capital and operational costs involved. The third method was described as being applicable to hot dry areas where space for large impounding ponds was no object.

Other options, which Du Pont seems to find more attractive, would involve using corrosion inhibitors as replacements or substitutes for chromate/zinc, or, better for the long term, designing the system so that corrosion would not occur. The first concept would involve finding and directly adding an environmentally acceptable replacement for chromate/zinc, or using a substitute and incorporating some corrosion protection and allowance for fouling into the design. The "noncorrosion" option, for which Brunn expresses preference, would call for the provision of additional heat transfer surface for unknowns.

It might be recalled that disposal of replacements of substitutes for chromate/zinc is treated about as stringently by regulations as is chromate/zinc, especially under BATEA and new source rules. Thus, the noncorrosion option seems more palatable. Indeed, last year, Du Pont started a 50,000-gpm noncorrosion cooling system. With pH adjustment, suspended solids and microbiological control, and slightly higher than normal fouling factors designed into the heat exchangers "as insurance," the system has "performed as anticipated," according to Brunn.

Some CTI members[a]

Constructors

Ceramic Cooling Tower Co.
Ecodyne Cooling Products
Lilie-Hoffman Cooling Towers, Inc.
Zurn Industries, Cooling Tower Div.

Chemical and material suppliers

American Cyanamid Co.
Andco Environmental Processes, Inc.
Betz Laboratories, Inc.
Bio-Lab, Inc.
Calgon Corp.
California Redwood Association
Ciba-Geigy Corp.
Diamond Shamrock Corp.
Nalco Chemical Co.
Olin Water Services
Petrolite Corp., Tretolite Div.
Zimmite Corp.

Maintenance

Robert Burger Associates
United Tower Maintenance, Inc.

Specifiers

Bechtel Power Corp.
Fluor Engineers & Constructors

Users

Carolina Power & Light Co.
Celanese Chemical Co., Corpus Christi, Tex.
Dow Chemical Co., Texas Div.
  Dow Badische
  Dow Chemical Co., Houston Center
  Dow Chemical Co., Louisiana Div.
  Dow Chemical Co., Midland Div.
Exxon Co., U.S.A. (Baytown, Tex.)
Goodyear Atomic Corp.
Monsanto Co.
Shell Oil Co.
Southwestern Public Service Co.
Universal Oil Products Co.

International

Abonos Colombianos, S.A. (Colombia)
Ishikawajima-Harima (Japan)
Kurita Water Industries, Ltd. (Japan)
SCAM (Italy)
Takasago Thermal Engineering Co., Ltd. (Japan)

[a] List is not exhaustive.

Yet another option involves complete reuse of cooling tower blowdown. M. I. Perry of S & B Engineers (Houston) said that his company carried out pilot tests of a well-known lime-softening technique to upgrade blowdown for reuse as makeup water. He enumerated the advantages of this approach as being uncomplicated; less expensive than ion exchange, dialysis, osmosis, and evaporation; less consumptive of fresh water and chromate; and permitting use of chrome inhibitators. Perry estimated a total uniform cost of about $0.86/1000 gal of recycle for a 625-gpm softening unit.

Debugging

One of the cooling tower problems is attack by microorganisms and the formation of slime, which can interfere with heat transfer. For this reason, it is necessary to add biocides to the makeup water, as well as corrosion inhibitors and substances to control pH and prevent fouling and scaling. The biocide most preferred has been chlorine. However, free chlorine discharge in blowdown is under federal regulation; and in the system itself, if there is any leakage, chlorine can oxidize materials. Moreover, chlorine demands increase if SO_2, ammonia, hydrogen sulfide, olefins, or similar contaminants find their way into the tower from the surrounding atmosphere or from process leaks.

John Chatfield of Exxon Chemical Co. (Baytown, Tex.) told the meeting that automatic chlorination, regulated by oxidation-reduction potential (ORP) sensing, used in wastewater chlorination and at paper mills, for example, is one approach to chlorine use. The normal shock dosage is 1 lb of chlorine for each 1 million lb of water pumped. If leaks or similar defects plague the system, however, an interim alternative is a nonoxidizing biocide.

In any case, biocides, even those other than chlorine, must be compatible with other chemicals used in makeup water. Their discharge is also coming under federal regulations. To comply with these regulations, a biocide might:

- have a natural decay mechanism
- be able to be detoxified before discharge
- be destroyed in a plant's waste treatment system.

Clearing the air

Possible air effects from cooling tower drift (droplets escaping through its throat) may be a problem. For instance, in the case of the Chalk Point towers that use brackish water, a group consisting of Environmental Systems Corp. (Knoxville, Tenn.), the University of Maryland, and state authorities will monitor fogging, downwind icing, and effects on vegetation from deposition of salts originating from brackish water drift.

Thus, with regard to technology and P.L. 92-500 (and perhaps air and noise pollution abatement) compliance, suppliers, users, and the CTI and its members face hefty challenges in the years ahead. However, John Hubenthal, president of Ceramic Cooling Tower Co. (CCT, Fort Worth, Tex.) and CTI's new president, expresses strong confidence that the Institute and the industry in general will be able to meet these challenges, especially with respect to thermal performance, and take them in stride. JJ

Capabilities of equipment makers

Recent survey of the WWEMA association reveals that its 275 member companies are geared for growth that now appears imminent with release of construction funds

The release of funds in the wastewater construction field is welcome news to equipment manufacturers. A Supreme Court decision (Feb. 18) said, in effect, that the Administration could not withhold allocation of the authorized contract authority level in P.L. 92-500. At the end of calendar year 1974, a total of $9 billion had been allotted to the states. Based on the high court decision, the remaining $9-billion amount was allotted to the states in February. In effect, "the total authorization of $18 billion has been allotted to the states," says Harold Cahill, director of municipal construction division of the EPA.

The semantics on allocation and obligations must be clarified. Allocations make funds available to a state for obligation. Obligations are the actual making of the contract.

Cahill explains, "Since $4 billion had been obligated directly to projects as of January 31, 1975, in the course of time, another $14 billion in new projects will be undertaken."

In the more recent past, the WWEMA (Water and Wastewater Equipment Manufacturers Association) member companies have been in many cases left high and dry because of a strain on cash flow. But recent changes in EPA construction program policies now should correct certain earlier deficiencies and improve the flow of funds to support the substantial growth contemplated without straining the financial market and at the lowest cost to the federal government.

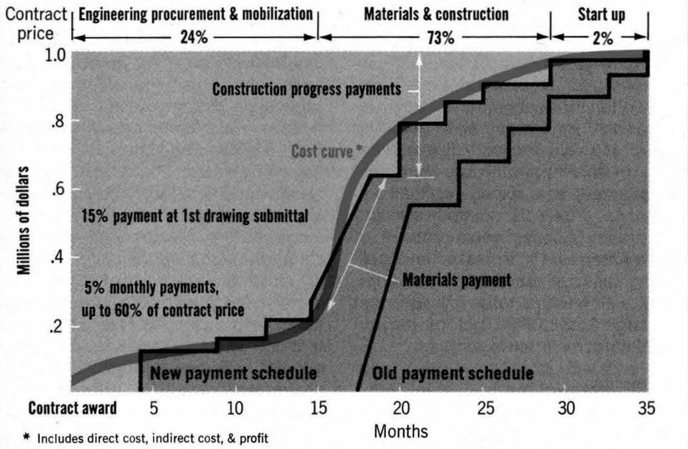
Equipment sales generated by these companies totaled $350 million in calendar year 1974. What these companies provide are the various pieces of equipment used in the water supply and wastewater treatment fields. This month WWEMA moved its offices to McLean, Va.; previous headquarters for this trade association were in Newark, N.J.

Manufacturers capabilities

In April 1974, WWEMA conducted a first survey of its member companies and did a follow-up questionnaire last November. This January, the results of the WWEMA capabilities survey were presented to professional staff members of the Senate Public Works Subcommittee on Environmental Pollution and of the House Public Works Committee.

The survey, for example, revealed that the main causes why equipment companies were not meeting normal delivery schedules were due to both a lack of raw materials and a lack of equipment components. In the November results, 49% of the respondents expected difficulty in meeting delivery schedules when they were questioned on their ability to meet delivery schedules in fiscal year 1975. Earlier, in the April results, the response was 33%. Perhaps, this reassurance is highlighted considering that the total equipment potential sales increase from $260 million in fiscal year 1974 to $500 million in fiscal year 1975 and $700 million in fiscal year 1976, as reported in the WWEMA survey.

Payment schedule



* Includes direct cost, indirect cost, & profit

However, Cahill points out that total equipment in an actual wastewater treatment plant can be as much as 50% of the total plant cost. An example is seen in an advanced waste treatment (awt) plant with physical-chemical treatment as opposed to a plant with the conventional activated sludge treatment process.

Nevertheless, it does take time to manufacture these items. The lead time required to obtain certain components ranged from 13 weeks for compressors to 37 weeks for gear reducers. The survey ranked components in order of decreasing critical need (see box) and assessed the lead time required for delivery of each item.

Some other interesting aspects of the survey revealed that no company reported it was operating at more than 76% production capacity. It went on to point out that if an unlimited supply of critically needed components were available, the new production levels for these companies would range from 72–119%.

Other reassuring data are available. For example, when respondents were asked if companies were able to increase production of equipment items, the majority of them responded that they could double their level of production within 10 months. Specifically, on this point, 70% of the respondents said yes; 30% said no.

Progress payments

Although no change in the water law, P.L. 92-500, was needed to correct certain operating difficulties encountered by equipment manufacturers, according to the survey consensus, the companies did point out that certain changes were needed in the

Critical equipment and associated lead times[a]

Component	Lead time in weeks
Castings	30
Motors	34
Fabricated steel	20
Gear reducers	37
Pumps	28
Stainless steel	22
Instruments and controls	23
Plastic supplier	15
Electrical components	25
Blowers	20
Valves	20
Pipe fittings	15
Transformers	30
Compressors	13

[a] Ranked in order of most critically needed item. Source: WWEMA.

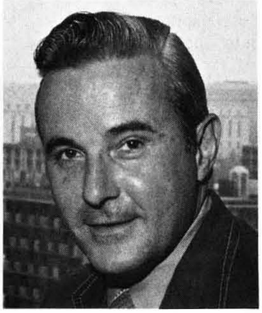
EPA construction program guidelines. Although certain changes have already taken place, considerable time is needed before they are firmly established and well understood.

The changes in the guidelines modify two procedures—progress payments on equipment and reduced retainage—items deemed inequitable, at least in the opinion of equipment companies. In the past, the equipment manufacturers did not, for example, receive any of their payment for equipment on a project until after the equipment had been delivered to the construction site. Delivery times averaged 9–18 months after the start of work on the order. What was previously happening was that the wastewater treatment construction industry contractors were borrowing funds at high interest rates because of delayed payment for work performed and passing these interest costs through in their bids.

The new changes in EPA construction program policies were announced by EPA administrator, Russell Train, at a public meeting on November 7 in Washington, D.C., as part of a major push to eliminate bottlenecks and step up the level of the construction grants program. Seminars were held in the 10 EPA regions.

"The importance of payment charges was the key item discussed by the manufacturers in these meetings," says Frank Sebastian, WWEMA's second vice-president who spearheaded the survey and served as liaison with the EPA. "Without EPA's initiative to provide this financial relief it would have been impossible to respond to the demands for more wastewater treatment equipment."

Cahill elaborates, "EPA has taken the initiative in revising its construction payment policies to improve essential cash flow in the program while at the same time moving to minimize any inflationary impact of the 'pass-through' costs necessitated by the higher cost of working capital for the industry. Hopefully, the improved fiscal posture will enable the manufacturers of needed equipment to expand more rapidly production capacity to meet the growing demand of this vital national water cleanup program."



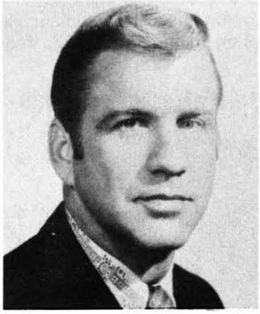
EPA's Cahill
"Preventing 'pass-through' costs"

The good news under the revised guideline for equipment manufacturers is that now they will receive 15% of the payment for equipment from the EPA when the equipment drawings are submitted, and 5% each month as the manufacturing of equipment proceeds. In other words, their costs will be recovered as the work proceeds; their payment accumulates each month as the construction proceeds.

"These payments will be for specifically manufactured items designated in the bidding documents for the construction contract," Cahill explains. "These payments normally will be only for those items that require more than nine months to design and fabricate. An interesting point in this procedure is the requirement that the supplier secure these payments with a surety document to protect the owner's risk pending delivery."

Reduced retainage

The other significant point achieved by the change in EPA policy deals with the retention of payments to the construction contractors and includes provisions for prompt payment to subcontractors including the equipment suppliers. In the past, 10% of the periodic payment was withheld for as much as a year or two until literally every nut and bolt was tightened. With the change, no longer is the 10% withheld for the lifetime of the project. Now, when the construction is 50% complete, the retainage is reduced to 5%, but this percentage now can be substituted by letter of credit or a security bond. In this way, the equipment manufacturer is debt-free and can be self-funding on a 100% basis.



WWEMA's Scheer
Heads new office in McLean, Va.

Research

Contrary to popular belief, the WWEMA group feel that they have funded the larger share of municipal and wastewater treatment technology development. As a group, WWEMA estimated that 5.44% of its members' sales (presumably the $350 million in 1974) was spent on R&D directed to clean water standards and goals.

SSM

FEATURE

Pesticide residues and field workers

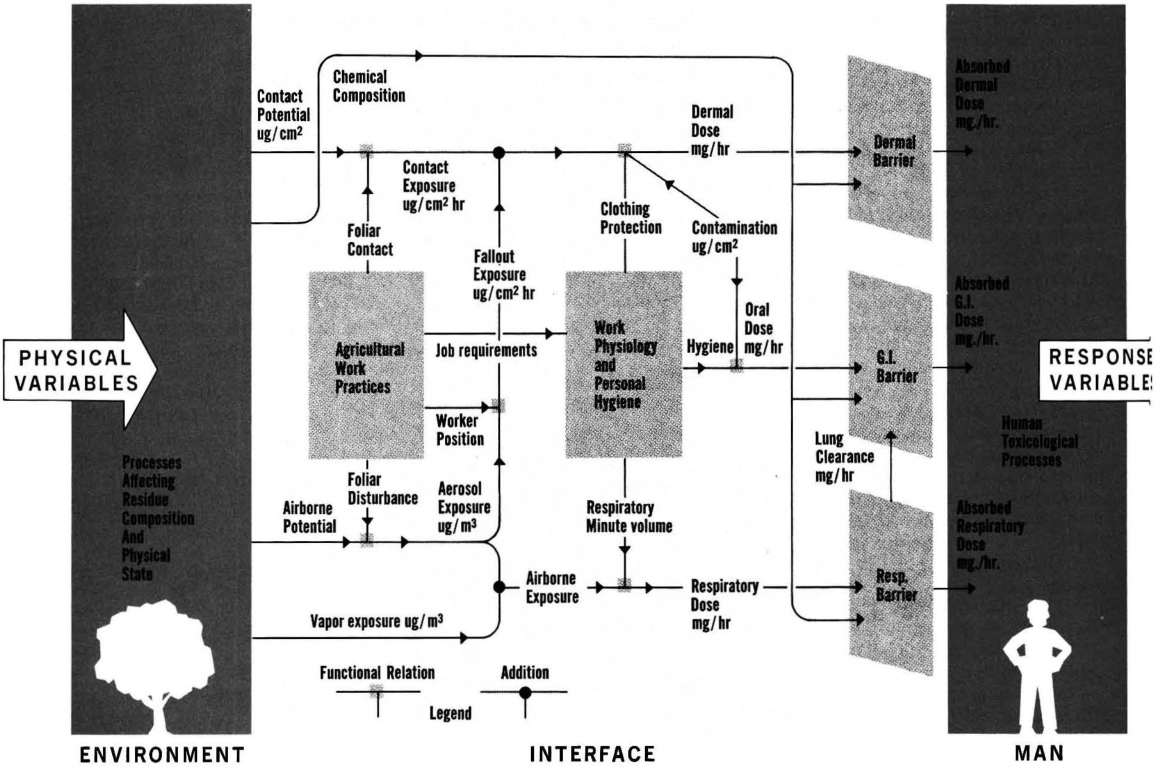
Spraying of crops with organophosphorus chemicals may be good for the plants but not so good for the pickers

Robert C. Spear
David L. Jenkins
Thomas H. Milby
University of California, Berkeley,
Berkeley, Calif. 94720

At about 10:00 a.m. on September 17, 1970, several of a crew of 35 workers who had been harvesting oranges in a grove near McFarland, Calif., complained of feeling ill. By 2:00 p.m., 12 of the crew had been admitted to a nearby hospital and treated for cramps, vomiting, and pinpoint pupils—symptoms consistent with organophosphorus (OP) pesticide intoxication. Laboratory tests confirmed that most of this initial group and others of the crew who had subsequently sought medical attention showed depressed levels of red blood cell cholinesterase, which is a specific indicator of OP exposure. Field investigations revealed that 34 days before the crew commenced work, this grove had been treated with 9 lb/acre of ethyl parathion. Analysis for pesticides on the leaf surfaces confirmed the presence of parathion and dioxathion, the latter having been applied four months previously.

In many respects, the McFarland incident is typical of the recorded episodes of intoxication resulting from exposure to residues of the OP pesticides. Parathion, in particular, was first implicated in 1949 in California, which has historically been the center of the reported cases of residue-related illnesses. Much of what can be learned of the California experience from the records of the state departments of agriculture and public health is summarized in Table 1. In a number of these reported cases, the exposure of the crew before it entered the field or grove where illness occurred is unknown. In others, data confirming the medical diagnosis of pesticide poisoning are often minimal, and data regarding pesticide applica-

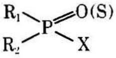
Factors affecting residue intoxication



tion are frequently sketchy at best. Nonetheless, there is now no doubt that for days or even weeks following application, agricultural workers can and have become ill from exposure to foliar residues of toxic chemicals.

Background

In 1936, Gerhard Schrader began work on the OP compounds, and in 1937 patented the general formula for contact insecticides:



Although reported incidents of worker poisoning from exposure to OP pesticide residues have been relatively rare, there has never been any doubt that the concentrated pesticides are highly toxic.

In man, the toxic effects of the OP insecticides are due largely to their ability to inhibit the enzyme cholinesterase. Cholinesterases hydrolyze acetylcholine, the chemical messenger released by nerve impulses at various critical points in the body. The inhibition of cholinesterase results in an accumulation of acetylcholine responsible for the toxic effects. Initial symptoms of OP intoxication include headache, nausea, vomiting, sweating, diarrhea, and abdominal pain. In moderate to severe poisoning, symptoms may progress from dyspnea and salivation to loss of muscular control, convulsions, shock, coma, and death.

Treatment of OP poisoning ranges from simple removal from exposure for very mild cases to provision of very rigorous supportive and antidotal measures in severe cases. In moderate to severe cases, weakness of the muscles of respiration may necessitate the use of artificial respiration which, together with the induction of vomiting in cases of ingestion or cleansing of the skin in cases of spillage, is a primary first-aid measure. Fortunately, atropine, supplemented in severe cases by pralidoxime chloride, provides the physician with effective antidotal measures.

Because OP's are readily absorbed through the skin, as well as by ingestion and inhalation, they present a particular hazard to agricultural workers who engage in mixing, loading, and applying the concentrated materials. Virtually all occupationally related cases of either severe intoxication or death from OP exposure have occurred among this group; the causative factors and means of control are relatively well defined, although difficult to administer and enforce.

The poisoning which follows exposure to OP residues on foliage presents quite a different picture in terms of both causation and control:

- There are potentially a greater number of workers exposed to residues than to the concentrated pesticides.
- A large proportion of these workers move with the harvest and, consequently, are not candidates for the traditional forms of occupational health surveillance that are becoming more common for workers who apply pesticides.
- Frequently, the worker will not be aware of the presence of a residue or of its significance.
- Exposure to these pesticide residues is by no means synonomous with intoxication.

TABLE 1

Incidence of multiple systematic illness from exposure to OP-pesticides for agricultural workers in California, 1949–1974

Date	Location	No. ill	Probable no. exposed	Crop and activity[a]	Pesticide implicated	AIA[b]	Entry time[c]	Previous applications	
								Spray used	Interval[d]
7/8/49	**Marysville**	20–25	56	Pears	**Parathion**	2.50	12	—	—
6/27/51	**Delano**	16	24	Grapes	**Parathion**	1.87	33	—	—
8/27/52	**Riverside**	11	30	Oranges	**Parathion**	2.00	16	—	19
7/6/53	**Riverside**	7	—	Oranges	**Parathion**	—	17	—	—
7/ /53	**Riverside**	—	—	Citrus	**Parathion**	—	34	—	—
7/ /53	**Bryn Mawr**	—	—	Citrus	**Parathion**	—	33	—	—
/ /59	**Whole State**	275	—	Citrus	**Parathion**	—	—	—	—
10/5/61	**Terra Bella**	10	—	Lemons	**Parathion**	3.00	17	Parathion	97
8/9/63	**Hughson**	94	—	Peaches	**Parathion**	2.00	14–38	Parathion	36–110
6/29/66	**Terra Bella**	9	15	Oranges	**Parathion**	1.87	15	—	—
7/8/66	**Porterville**	6	11	Oranges	**Parathion**	1.33	32	—	—
7/21/66	**Lindsay**	3	30	Oranges	**Parathion**	2.00	13	—	—
8/2/66	**Navelencia**	11	22	Oranges	**Parathion–malathion**	13.5p	28	—	—
8/11/66	**Terra Bella**	9	28	Oranges	**Parathion–ethion**	3.75p	46	—	—
9/2–23/67	**Hughson**	24	—	Peaches	**Azinphosmethyl** **ethion**	1.5a 2.0e	38–47	Dicofol TEPP	38–47 15–30
9/14–16/67	**Ballico**	3	—	Peaches	**Azinphosmethyl**	1.5	66	Dicofol	38
5/5/70	**Porterville**	3	30	Lemons (prune)	**Dioxathion** **naled**	6d 1n	1	—	—
5/25/70	**Lindsay**	2	22	Oranges	**Parathion–ethion**	7.5p 6.75e	14	Parathion	17
5/27–28/70	**Terra Bella**	8–11	—	Oranges	**Azinphosmethyl** **ethion**	12a 4e	8 11	Azinphosmethyl	10–12
9/14–17/70	**McFarland**	35	35	Oranges	**Parathion**	9.00	34–37	Dioxathion	120
10/1/70	**Orosi**	11	55	Oranges	**Parathion** **malathion**	3p	31	Azinphosmethyl	180
8/16–24/71	**Orange Cove**	8	9	Olives (prune)	**Parathion**	6.00	31	—	—
5/6/72	**Lindcove**	3	—	Oranges	**Parathion**	2.5	21	—	—
9/15/72	**Exeter**	9	22	Oranges	**Parathion**	5.00	12	—	—
9/9/72	**Huron**	4	31	Lettuce (weed)	**Parathion**	2.50	1	Parathion	4–25
8/30/73	**Fowler**	27	32	Grapes	**?**	—	41	—	—

[a] Unless otherwise indicated in "Crop" column, workers are engaged in picking operation. [b] Active ingredient per acre expressed in lb. [c] Days postapplication. [d] Days prior to most recent application.

If one considers the amounts of OP pesticide applied to crops in the U.S. since their introduction, the number of reported multiple illness incidents attributed to OP residue exposure is small. However, the relative infrequency of reported incidents does not reflect the degree of concern held by many occupational health specialists who recognize that occupationally related OP illnesses are underreported among the agricultural workforce because of administrative weaknesses in reporting systems, and the self-limiting nature of the illness itself—removal from exposure results in improvement.

For example, at dose rates somewhat less than those which must have occurred in the McFarland incident, the symptoms would be quite similar to those of influenza or mild heat exhaustion. Suffering such effects, the worker is likely to go home to rest thereby terminating the exposure. The symptoms would be likely to abate in 24–48 hr allowing a return to work and possible further exposure and illness.

Regulatory aspects

Because the possibility of chronic low-level exposure and its debilitating effect on exposed workers is difficult to either confirm or discount, considerable controversy exists over the necessity of imposing regulations designed to limit the exposure of agricultural workers to OP residues. The first such regulation was imposed by California in 1971. It specified that a certain time interval must elapse between the application of pesticide and the entry of workers into a field or grove for work that involved substantial foliar contact.

This regulation proved quite effective and, for the most part, was accepted with little serious objection from purveyors and users of pesticides.

In early 1972, the federal government created a task group whose charge was to:

- assemble and interpret all available information regarding the extent and severity of this occupational health problem in the U.S.
- prepare a report which would identify significant areas in which relevant information was not available
- make recommendations for the development of standard research protocols to determine safe reentry intervals for the protection of agricultural and forest workers and
- suggest interim reentry standards, where possible, based upon existing knowledge.

The report of the Task Group was transmitted to the chairman of the Federal Working Group on Pest Management in July, 1974. The Task Group found that the lack of technical data and the lack of occupational illness reporting mechanisms in agriculture combined to make it impossible to formulate interim national reentry standards.

Further, in view of the marked regional variations in weather conditions, application practices and, perhaps,

Orange grove. Parathion residue on leaf (*left*); worker re-enters grove after appropriate interval

FIGURE 2

Phosalone dislodgeable foliar residues

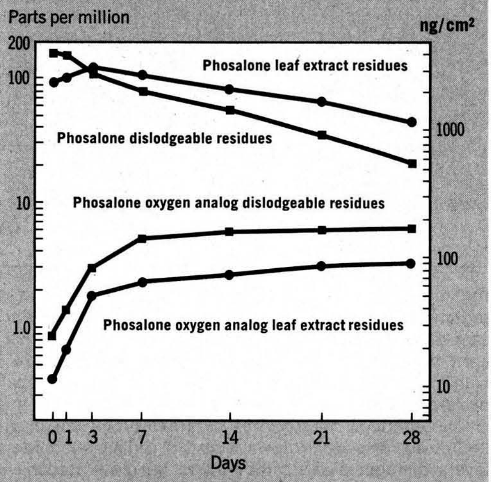
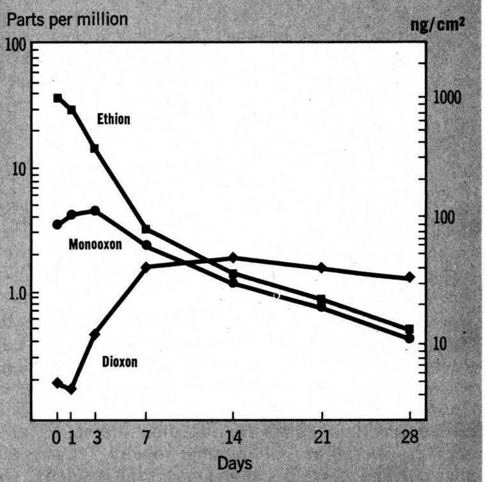


FIGURE 3

Ethion foliar residues



exposure mechanisms that existed throughout the country, the Group recommended that for the immediate future, innovative and flexible research would be of greater merit than standardized testing. The Task Group formulated guidelines for such work, particularly as it concerned applicability to field situations and studies involving human subjects.

Most recently, because of their role in pesticide registration and regulation, the Environmental Protection Agency (EPA) has published reentry regulations (*Federal Register*, May 10, 1974) which do not state a fixed reentry interval except for a list of "highly toxic" pesticides that had individual reentry intervals ranging from 24–48 hr.

The problems inherent in establishing reentry intervals on a national scale are immediately apparent when one recalls that parathion, which received a 48-hr reentry interval from the EPA, was the pesticide implicated in the poisoning incident at McFarland, Calif., where the workers entered the field 34 *days* after application! Recognizing this kind of regional variation, the EPA, in its regulations, provided for authorized state regulatory agencies to set and enforce their own more restrictive standards when they deemed it necessary.

Foliar residues

With the increasing interest of federal agencies in the problem of occupationally related residue intoxication, there has been an intensification of research aimed at defining the extent of the problem and elucidating the mechanisms of exposure and intoxication. The conceptual scheme in Figure 1 is useful in considering the various segments of the problem. It depicts the three essential components of the process: environmental factors, factors defining the exposure mechanism, and toxicological processes.

A large body of information exists on the toxicology of the organophosphates, only meager quantitative data on the exposure mechanism, and very little data on the nature, composition and persistence of foliar residues. The lack of foliar residue data stems from the fact that interest has been directed toward the edible portion of the commodity rather than to the foliage. Also only recently have methods been developed to quantify "dislodgeable" foliar residues clearly more related to exposure potential than are foliar residues determined from leaf extracts, the method previously used. Although the relationship between foliar residues and the biochemical response of workers has not yet been clearly established, it seems safe to state that the development of dislodgeable residue data is the first step in the determination of the degree of hazard. The only substantial amounts of dislodgeable residue decay data that currently exist are for dioxathion on citrus foliage and for ethion and phosalone on grape foliage. Figure 2, taken from a study of the latter, shows that significant differences exist between the composition and decay of dislodgeable residues and leaf extract residues.

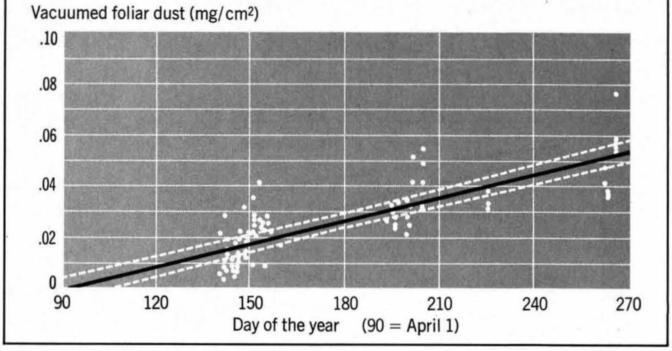
In the study of ethion and phosalone on grape foliage the finding of appreciable amounts of the oxygen analogs of both of these materials on the leaves (Figures 2 and 3) is of great toxicological significance. These oxygen analogs are direct cholinesterase inhibitors, and are generally more toxic than the parent compounds. For example, paraoxon, the oxygen analog of parathion, is absorbed through the skin about five times as fast as parathion and is about ten times as potent as a cholinesterase inhibitor. In recent studies, scientists have detected significant fractions of the oxygen analogs in the residues on various crops:

- In North Carolina, paraoxon was detected at above trace levels on tobacco foliage.
- In California, appreciable residues of paraoxon have been determined in surface soils of parathion-treated groves.
- In central California, our group has found significant levels of paraoxon in the foliar residue following applications of ethyl parathion in orange groves.

If the oxons are confirmed to be important to clinical intoxication and cholinesterase depressions, it will be mandatory to identify the environmental and application variables that favor oxon production and persistence, as well as to examine the persistence of the parent compounds.

FIGURE 4

Seasonal buildup of dust on the foliage of orange trees



Environmental factors

A great deal of field research has been conducted on pesticides and their multitude of formulations, but the thrust of this work is mainly aimed at determining how environmental conditions affect the efficacy of the chemical or its formulation as a pest control agent. Only a relatively small number of such studies attempt to take into account the effect of weather-related factors on the physical and chemical makeup of the residues. On the other hand, the environmental fate of pesticides has been the subject of numerous *in vitro* laboratory investigations, especially in the area of photodecomposition. Unfortunately, no claim can be made that *in vitro* work actually simulates what befalls the residue in the field.

Although field data on the effects of weathering on the physical and chemical makeup of dislodgeable foliar residues is very difficult to obtain, research in this area needs to be expanded since there are indications that weather-related factors may be important in determining residue composition, persistence, and toxicity.

Comparison of central California, central Florida, and the Rio Grande Valley of Texas, three of the major citrus growing areas in the nation, may well illustrate this importance. While central California is virtually without rain from June to September and humidity is low throughout the late spring and summer months, the other two regions rarely experience dry spells of even a month's duration. It is interesting that reported incidents of residue intoxication are among the highest in the nation in central California while the other two regions had little experience with this problem.

It should not be inferred, however, that weather is the only difference among these regions. For example, in Florida, parathion was never used in the amounts of 8–10 lb of active ingredient per acre, poundages which are common for control of California red scale and in recent years its usage has virtually disappeared.

Exposure mechanisms

Probably the most common speculation among investigators has concerned the role of foliar dust in the exposure process. Early work by Quinby and Lemmon indicated that in all of the poisoning incidents they examined, the crop foliage was at least chest high, which they felt might imply that "workers are poisoned only when dusted or bathed in the dilute residues." The data in Table 1 indicate that, with one exception, the multiple illness incidents in California have occurred in crops with foliage at least chest high.

Our recent work in the central valley of California has also implicated foliar dust as an exposure vehicle. Using personal air samplers on a small number of professional pickers, we found mean airborne dust levels of 13.5 mg/m^3 in grapes, 28.6 mg/m^3 in peaches and 40.2 mg/m^3 in orange groves. The geometric mean particle size of these dusts ranges from 1.8–3.1 μm. It is significant that while the majority of these particles are well within respirable range, it appears that the potential respiratory dose of pesticide carried on such dusts is quite small. Although the sources of these dusts are currently undefined, it is well known that this region has quite high levels of fugitive dusts thought to be generated by agricultural activities during the hot, dry summer months. Figure 4 demonstrates the season-long buildup of dust on the foliage of orange trees in Tulare county. Interestingly, the zero dust intercept of the regression line occurs nine days after the last significant rainfall.

At present, there is little published information on the interaction of foliar dust particles and the pesticide decay process. It has been suggested that soil type may play an important role in oxon production and/or persistence. We have found in our work in central California an indication that the ratio of paraoxon to parathion on the dust is a function of particle size—higher ratios are associated with smaller particles. These data seem to have important implications with regard to the penetration of the pesticide-laden dust through the clothing of the worker.

Human exposure research

The residue intoxication problem is typical of many in environmental toxicology. It is much easier to quantify the important variables associated with the environmental factors and the toxicological processes than it is to relate them through a well-defined exposure mechanism.

Some factors important to the exposure process, such as work practices, clothing, sweat rate, vary from crop to crop and from one region of the country to another. Work rate also is an important variable in the exposure process, although the dose rate may not be particularly sensitive to work rate at levels typical of mature professional pickers.

A more extensive list of factors potentially important to the exposure process can be compiled. The almost total lack of data makes any attempt to assess their relative importance speculative at best. As a result of the multitude of complicating factors in exposure, research in this area has tended toward direct experimentation involving the exposure of volunteer workers under controlled and closely supervised conditions. The objectives of such research fall into two distinct categories: to establish or verify the adequacy of a reentry interval for worker protection; and to study the mechanisms of the exposure process. Human exposure studies designed to develop data for setting reentry times are addressed in detail in the Federal Task Group report, and are recommended as the most efficient way to immediately develop data for worker protection. The ethical issues surrounding this type of research are extensively considered there and, in the final analysis, such research is justified on the grounds that it is preferable to expose small numbers of volunteers under controlled and medically supervised conditions than to expose an entire workforce under uncontrolled and unsupervised conditions.

In general terms, both the reentry interval type of experiment and the exposure mechanism research experiment are similarly designed. Both involve:

- treatment of one or more plots with pesticide
- measurement of foliar residues
- subsequent entry of a workforce of 6–20 men who carry out the cultural practice under study
- repetitive assessment of blood cholinesterase for all workers and comparison with their pre-exposure baselines
- collection of urine samples for the analysis of the urinary metabolites of the OP pesticide
- termination of the experiment if adverse cholinesterase response occurs among the workers.

Specific details of the experimental design are particularly important as they relate to the medical and ethical issues of protecting the participants. The Task Group report provides guidelines covering these critical issues.

At present, about a dozen human exposure studies have been conducted in the U.S., almost all of them having been directed toward setting reentry times. Few have been published in the technical literature. One of the greatest difficulties in assessing the results of these studies is concerned with the degree to which their results can be extrapolated from one environment to another. Here again the questions are those of physical availability of the residues, and the details of the exposure mechanisms. For this reason the Task Group guidelines heavily emphasized the collection of exposure and environmental related data in parallel with dislodgeable pesticide residue data and human response data. This collection of parallel data should allow informed extrapolations to be made as the exposure mechanisms become better understood.

In recognition of the importance of gaining a detailed understanding of the exposure mechanisms mediating the transport of residue from the environment to the worker, the National Institute for Occupational Safety and Health has supported the research at Berkeley for the past several years. We have now conducted two human exposure studies in parathion-treated orange groves. These studies focused on elucidating the exposure mechanism in this pesticide–crop combination that has been historically associated with work-related OP residue intoxication. From these studies we can conclude that:

- Paraoxon is the principal toxic constituent of the weathered residue.
- The absorbed dose is almost entirely dermal.
- The fallout mechanism of Figure 1 is probably of greater importance than direct foliar contact. Of complementary importance has been the finding that the remarkable paraoxon levels seen in both of our human exposure studies are not unusual, but appear to be quite typical of the levels seen in orange groves that have received similar applications of ethyl parathion throughout the central region of California.

Prospects

We are developing a relatively good understanding of the environmental and application conditions that can lead to residue intoxication in parathion-treated orange groves in central California. Other investigators appear to possess a similar assessment capability for certain pesticides applied to crops such as tobacco, cotton, and apples in various regions of the country. When data from these sources are synthesized and comparable information is developed for grapes and peaches, the general features of the exposure mechanisms relevant to residue intoxication among the crops of historical interest should be considerably clarified.

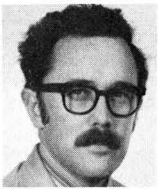
The next major task will be to determine the influence of particular pesticides on the exposure process and on the ultimate hazard. For example, it is already known that conversion from the parent compound to the oxygen analog varies in time and in degree for different pesticides. Both the existing epidemiological information, and the ongoing surveillance of worker groups should provide valuable clues in this regard as well as needed data on the extent of this occupational health problem. In the interim, regulatory agencies, assisted by the scientific community, are left with the difficult task of making the best of scanty data in the development of strategies for the protection of the agricultural workforce.

Additional reading

"Occupational Exposure to Pesticides," Report to the Federal Working Group on Pest Management from the Task Group on Occupational Exposure to Pesticides, January 1974. Only a limited number of copies of this report are available. Requests should be addressed to: Federal Working Group on Pesticide Management, Code WH 566, Room E 431, 401 M St., S.W., Washington, D. C. 20460.

Milby, Thomas H., Ottoboni, Fred, Mitchell, Howard W., "Parathion Residue Poisoning Among Orchard Workers," J.A.M.A. **189**, 351-6 (1964).

Quinby, Griffith E., Lemmon, Allen B., "Parathion Residues as a Cause of Poisoning in Crop Workers," J.A.M.A. **166**, 740-6 (1958).



Robert C. Spear *is an assistant professor in the Department of Biomedical and Environmental Health Sciences, University of California at Berkeley. His principal interest is in occupational health problems in agriculture and the construction industry.*

David L. Jenkins *is an associate professor in the Department of Civil Engineering, College of Engineering, University of California at Berkeley, and director of the Sanitary Engineering Research Laboratory. His major research interests are in the areas of chemistry of waters, wastewater treatment, and environmental chemistry.*

Thomas H. Milby *is a consultant in Occupational Medicine, and an adjunct associate professor in Environmental Health Sciences, School of Public Health, University of California at Berkeley.*

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FEATURE

Taking a physical phenomenon—osmosis; reversing it, and coming up with a water purification process for tomorrow's water supply

Reverse osmosis makes high quality water now

Seymour S. Kremen
UOP, Roga Division, San Diego, Calif. 92101

As the nation's population surpasses 200 million and its affluence grows even more rapidly, the demands on our natural resources have created critical problems. Not the least of these problems is supplying the needed electric energy. Already the impact of the energy crisis is being felt. Society's only apparent alternative to brownouts or some kind of power rationing seems to be the construction of electric power plants, nuclear or otherwise, which are viewed by environmentalists with considerable alarm.

Less well publicized, but inevitable, is a shortage of good quality water. The demands of industry and agriculture, as well as 200 million private citizens, will generate demands for water that will completely obsolete the present distribution system before the end of this decade. How is the problem solved—by continuing to compromise the environment by building more dams, laying thousands of miles of pipelines, constructing massive interbasin water transfer systems? Is there a better and, even perchance, a less costly way?

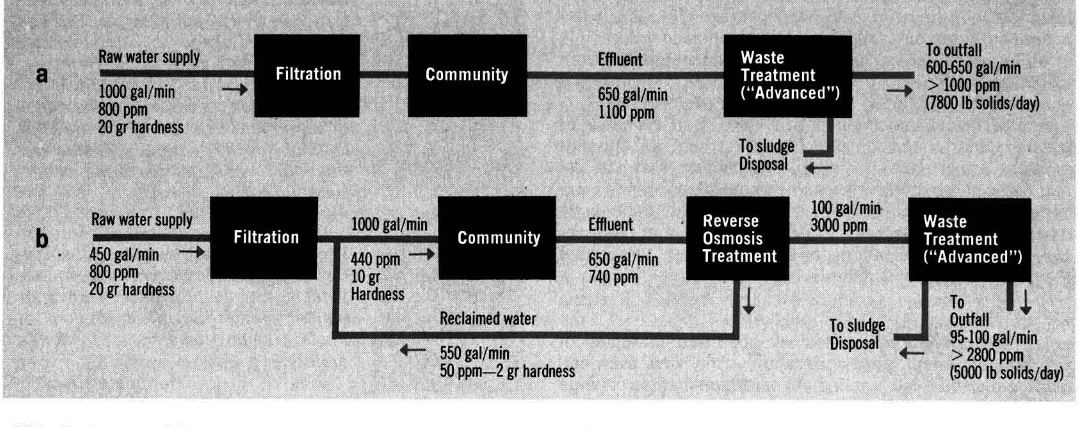
Perhaps there is. Already there are enormous supplies of water in and around our cities that are not being used. A sizable percentage of the U.S. population lives within 100 mi of the oceans, yet the ocean is presently almost totally unavailable as a useful source of water. In every municipality, vast quantities of water are dumped into rivers, lakes, and sewers daily—sometimes polluting, but always lost as a source of potable water.

Reverse osmosis

The magnitude of the future supply problem, coupled with the enormous potential of seawater and wastewater as sources of this needed water, have prodded an old industry into rapid expansion with application of new and improved technology. This industry, the water purification industry, has been working feverishly to develop practical methods to tap these water sources. It may have found a solution by applying the long-known physical principle of osmosis. From this, it has developed a system known as reverse osmosis (RO) that already is purifying tens of millions of gallons of water every day.

To understand how reverse osmosis works, it is first necessary to review the natural process of osmosis. What happens in the osmotic process is illustrated in Figure 1. If pure water (without any dissolved solids) is placed on one side of a hypothetical ideal semipermeable membrane, and a salt solution is placed on the other, then pure water will tend to flow through the membrane and dilute the salt solution on the other side. As this flow continues, there will be a reduced height on the pure

Conventional (a) versus reverse osmosis (b) water reclamation system



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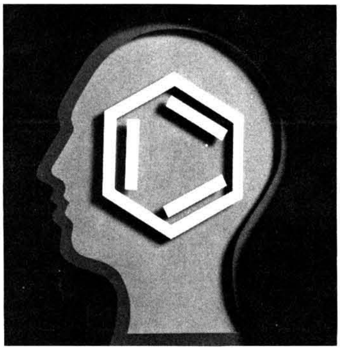

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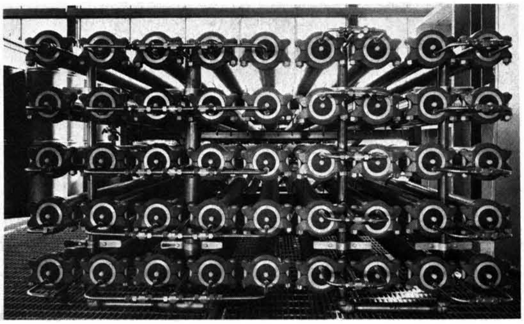


RO system. *Such equipment is purifying millions of gallons of water every day*

water side, and an increased height on the salt water side, now somewhat diluted. At some point of dilution and difference in column heights (head), the flow will stop. The pressure represented by this differential head is the numerical equivalent of the osmotic pressure of the diluted salt solution when equilibrium is approached. While it may seem simple, osmosis is the major mechanism by which plant and animal cells exchange nourishment and waste products across their cell walls (membranes).

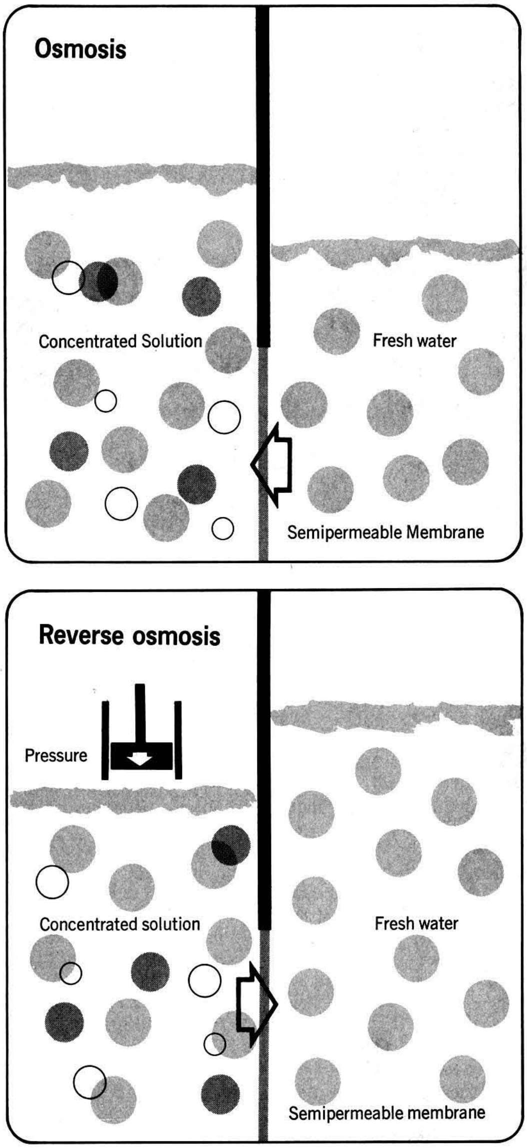
About 20 years ago research, with the important practical goals based on reversing this common natural process, began. As shown, also in Figure 1, if a mechanical pressure is applied to the saline solution, water will be forced through the membrane and, ideally, all of the salt will remain behind in concentrated form. This process requires a membrane that freely allows the passage of water, while essentially preventing the passage of salt. It also requires a pressure greater at all times than the osmotic pressure of the salt solution, which increases as concentration increases.

This concept marked the birth of reverse osmosis, but much developmental work ensued before RO became the practical water purification process it is today. Private firms, the Office of Saline Water, and the Federal Water Quality Administration (predecessor to the Environmental Protection Agency) invested heavily in the development of this new process. Membranes had to be developed; practical packaging methods and configurations had to be perfected; and systems with the proper plumbing, pumps, controls, and tankage had to be designed and tested.

By the late sixties, the reverse osmosis process had been developed sufficiently for industrial plants throughout the world to begin using them. Some of these plants, outfitted with fixed-price RO equipment that is fully warranted as to performance and cost, use more than a million gallons per day of purified water. Industrial giants in the semiconductor field now use this equipment as a part of their operations. Basically, the process has been used as a means of demineralizing a feed water while concurrently clarifying and removing other unwanted components.

As would be expected, much of the initial utilization has been in industries where purified water, available on a plentiful, reliable, and relatively low-cost basis, is a major contributor to a high-value product, such as semiconductors and other sophisticated, sensitive electronic components. This also applies to large power plants using very high-pressure steam. Reverse osmosis is also used as an antipollution method of treating industrial wastewaters, and for advanced treatment of sanitary wastes.

Figure 1.



Concurrent with these initial industrial applications, development and refinement of reverse osmosis continued—both to improve the industrial process itself, and to find a way economically to purify local water sources to provide large quantities of drinking water. Then, in 1969, a system was developed that transformed brackish water into pure drinking water for a seaside community.

Purifying water sources

The effectiveness of a reverse osmosis system in purifying brackish water is shown in Figure 2. The results shown summarize data from the operation of a 350,000 gal/day RO plant in the Florida resort community of Ocean Reef; the water supply is very brackish well water, the result of seawater intrusion. The plant, put on-line in 1971, has since been uprated to 30,000 gal/day. It produces a soft, clear water of low salinity that is consistent with U.S. Public Health Service recommended standards for drinking water.

The system is not limited just to seaside communities. Colorado River water, a substantial part of the water supply of southern California, has a total dissolved solids content only slightly below 800 parts per million (ppm). Since it also has a hardness of approximately 340 ppm, reverse osmosis offers a practical alternative to the softening and filtration now needed to make it usable for most municipal and industrial purposes.

Figure 2

Typical reverse osmosis plant cleans up brackish water

	Parts per million		
	Feed	Final product	USPHS standards
Calcium	200	12	...
Magnesium	175	4	...
Sodium	1725	90	...
Potassium	94	7	...
Bicarbonate	201	31	...
Sulfate	677	0	250
Chloride	3060	155	250
Silica	12	2	...
Alkalinity, $CaCO_3$	165	25	...
Hardness, $CaCO_3$	1222	50	...
Dissolved solids	6144	301	500

For the purification of brackish waters (ultimately, for potable purposes, any water where the total dissolved solids concentration is more than 500 ppm) by reverse osmosis, present costs are already competitive with pipeline water available or soon to be available from massive interbasin transfer systems. Both capital cost recovery and operating costs, including the relatively low energy utilization, are featured in reverse osmosis. This has important implications in terms of increased ability to use, enhance, or protect local underground water supplies that have grown unacceptably brackish with increased use and overdrafts, aggravated in many instances by seawater intrusions.

Even more important are the capabilities to reclaim large quantities of municipal and industrial wastewater and to concentrate the solids for simplified disposal. Concentration usually contributes to a practical solution to the disposal problem since the value of the reclaimed water offsets the cost of RO. Moreover, the concentration of the waste solids leads to further economies in liquid waste treatment processes. Since most of these waste streams are relatively dilute, the treatment used today to remove often minute quantities of offensive materials is disproportionately expensive and inefficient.

The quality of water that the Roga Division of UOP has produced by reverse osmosis treatment of a clarified municipal primary effluent in a pilot plant operation in Pomona, Calif., is shown in Figure 3. The quality of the reclaimed water is of particular interest since, in many respects, it is superior to the raw water supply used at that municipality. The economic value to a community of purified raw waters or reclaimed wastewaters is not inconsiderable. The costs for using poor quality water—high in hardness, alkalinity, turbidity, silica—are substantial to the residential and commercial user. For one thing, hard water often dictates the use of detergents and phosphates that place an environmental burden on a community; the use of purified water greatly reduces the need for these items.

Figure 3

Quality of water resulting from treatment of clarified primary effluent

	Feed concn, mg/liter, range	Product concn, mg/liter, range	Reduction, %[a]
Calcium	54–114	<0.1–1.2	>99.6
Magnesium	13.3–26	<0.1–0.3	>99.3
Sodium	92–188	6.3–17	92.5
Potassium	17.2–29	0.7–2.6	91.5
Ammonia-N[b]	37.5–57	2.8–7.5	90.2
Chloride	209–378	14–44	90.4
Sulfate	256–388	Nil–3	>99.8
Phosphate	0.27–3.1	<0.1–0.08	>99.4
Total COD	24–109	15.7–33.4	65.7
COD, after aeration	—	6–12	85.7
Turbidity, JTU	7.6 (typical)	None detected	100
TDS[c]	757–1170	49–92	93.3

[a] Based on feed to reverse osmosis unit only. Total process reduction based on raw sewage is significantly higher for several species.
[b] N as NO_3^-. No significant amounts in either feed or product.
[c] Total dissolved solids.

The question of unrestricted reuse of reclaimed wastewaters for drinking water requires careful examination. However, RO membranes are practically a complete barrier to viruses, bacteria, and many other entities that must be kept out of a potable supply. Beyond this, the purity and clarity of the water resulting from RO treatment are such that it readily lends itself to the subsequent use of proved precautionary disinfection procedures. The process development on reclaiming wastewaters has advanced to the stage where programs are

Table 1

Representative costs of spiral-wound reverse osmosis operation

	Treatment cost, ¢/1000 gal, mgd[a]		
Cost component	1	10	100
Capital recovery, 8%, 25 yr	14.9	10.9	8.2
Power, 1.5 ¢/kWh	9.5	9.5	9.5
Chemicals	2.5	2.4	2.4
Operation and maintenance	5.0	1.8	0.6
Membrane replacement			
2-yr life	23.4	14.6	10.5
3-yr life	15.6	9.74	7.0
Total operating cost			
2-yr life	55.3	39.2	31.2
3-yr life	47.5	34.34	27.7
Capital cost, millions of dollars	**0.50**	**3.83**	**28.75**

	Unit size, mgd		
	1	10	100
Labor, 1000 $	10	30	50
Material, 1000 $	6.2	30	150
Total, 1000 $	16.2	60	200
¢/1000 gal	5.0	1.8	0.6

[a] Million gallons per day.

under way to monitor the effectiveness of disinfection measures and treatment under sustained conditions.

How reverse osmosis could be employed to improve current (conventional) waste treatment methods, and simultaneously reduce the required net quantity of raw water, imported or locally available, is shown. Reverse osmosis truly represents an advanced waste treatment system with minimal adverse environmental effects. With RO, 55% of the water can be reused—in this example, more than three quarters of a million gallons every day!

The economics

At this point it is appropriate to consider the economics of reverse osmosis treatment, both as a means of water purification from a brackish source and as part of a municipal waste effluent treatment sequence. In the latter instance, the water thus produced would meet present and prospective stream discharge standards, or be suitable for reuse in many situations. These costs for the waste treatment sequence do *not* include any credits for the reused water; these credits would be very significant if the water were to be used for industrial purposes where treatments such as softening, coagulation, and filtration are often needed when a virgin municipal source is used.

In Table 1, the capital and operating costs that are currently being quoted and warranted are listed for reverse osmosis brackish water purification plants of various sizes. These plants will convert up to 90% of the feed volume to purified water; this water quality represents a total dissolved solids (TDS) reduction of 90–95%, with the additional features of near zero hardness and turbidity. Generally speaking the water cost, including capital recovery, is in the range of $0.29–0.31/1000 gal, which closely approaches conventional combinations of pipelines, reservoirs, and treatments. The rapidly advancing technology and the increasing volume of manufacturing reverse osmosis equipment provide assurance that the downward cost trend will continue.

In Table 2, a number of municipal waste treatment sequences are shown with respective costs at various size levels and indicated degrees of removal of a particularly important contaminant. Whenever there are requirements for relatively high levels of removal, including some TDS removal, the combinations embodying RO become attractive as to cost, and in some respects are essential to achieve the high levels of removal that are beginning to be required.

Seawater desalination

Presently, distillation is by far the predominant method used in desalting seawater. Its use, however, is limited because of cost and, to a significant degree, reliability problems. The corrosive nature of seawater and its scaling tendencies at high-boiling temperatures play havoc with the distillation equipment. In meeting the forthcoming water crisis, reverse osmosis is an exciting technique for the desalination of seawater. The major promise of reverse osmosis for seawater desalination lies in the fact that it does not require a phase change (liquid-vapor-liquid) as distillation does. Thus, it largely avoids the scaling problems, and its energy requirements are sharply lower. Again, this is extremely valuable both in terms of cost and conservation.

The distillation system has an energy requirement of approximately 1,000,000 Btu per 1000 gal of purified water produced (see Figure 4). The reverse osmosis system, which uses conventional electrically driven pumps, has an energy requirement of less than 30% of that required for distillation. This can be further reduced, with concomitant reduction of capital cost, by the use of steam-driven pumps to power the RO system. Both technologies will use fuel more efficiently in the future, but the inherent lower energy requirements of RO should re-

Table 2

Estimated total operating costs of several municipal waste treatment combinations

	Treatment cost, ¢/1000 gal, mgd[a]			Estimated total contaminant removal, %			
Combination of treatment processes	**1**	**10**	**100**	**COD* or BOD$_5$****	**Phosphorus**	**Nitrogen**	**TDS[b]**
Primary + activated sludge (including sludge disposal)	64	20.3	11.5	85**	...	...	...
Primary + activated sludge + activated carbon	113.9	37.7	23.2	97*	...	...	...
Primary + activated sludge + activated carbon + lime treatment + separate nitrification + chlorination	154.5	59.75	35.42	97*	98	85	...
Primary + activated sludge + activated carbon + ion exchange + chlorination		67.7 (700 mg/l)		98*	99	76 (NH_3—N)	
		84.8 (1000 mg/l)				86 (NO_3—N)	86
		102.7 (1500 mg/l)					
Primary + activated sludge + dual media filtration + reverse osmosis	122.2	59.6	41.4	99+*	99.7+	95 (NH_3—N) 75 (NO_3—N)	95
Primary + activated sludge + activated carbon + reverse osmosis	161.4	72.2	50.9	99+*	99.7+	95 (NH_3—N) 75 (NO_3—N)	95
Chemically clarified raw sewage + activated carbon + reverse osmosis (product aeration)	113.35	72.6	58.0	95+*	99.7+	90 (NH_3—N) 75 (NO_3—N)	95
Chemically clarified raw sewage + dual media filtration + reverse osmosis (product aeration)	86.55	64.8	51.8	95+*	99.7+	90 (NH_3—N) 75 (NO_3—N)	95

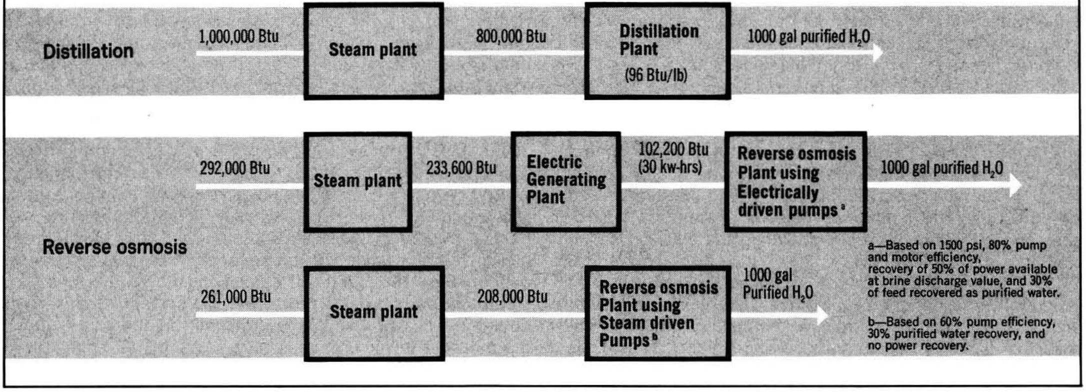
[a] Million gallons per day. [b] Total dissolved solids.

Some of today's reverse osmosis installations

	Product water capacity, gpd	Use
NATIONAL		
Texas semiconductor manufacturer	1,130,000	Electronic wash water
Florida semiconductor manufacturer	260,000	Electronic wash water
California semiconductor manufacturer	300,000	Electronic wash water
Florida resort community	930,000	Potable water
Florida resort community	75,000	Potable water
Utah military base	30,000	Potable water
Arizona resort community	320,000	Sewage reclamation
California resort community	250,000	Sewage reclamation
California demonstration plant	150,000	Sewage reclamation
New Mexico fertilizer plant	430,000	Boiler feedwater
Pennsylvania power plant	300,000	Boiler feedwater
Texas power plant	110,000	Boiler feedwater
INTERNATIONAL		
Japan industrial complex	4,650,000	Boiler feedwater
Mexico electronics plant	144,000	Electronic work water
Bahamas resort	240,000	Potable water
France industrial complex	105,669	Surface water
Spain industrial complex	1,320,000	Boiler feedwater
Yugoslavian ranch	158,400	Horticulture

Figure 4.

Energy costs of converting seawater to potable water



a—Based on 1500 psi, 80% pump and motor efficiency, recovery of 50% of power available at brine discharge value, and 30% of feed recovered as purified water.

b—Based on 60% pump efficiency, 30% purified water recovery, and no power recovery.

main in the same general proportion to those required for distillation. Reverse osmosis can also offer lower operating costs, because of low (ambient) temperature operation, and relative freedom from scaling.

Environmental payoff

Reverse osmosis appears to offer a way of obtaining the needed water in the generations ahead without the "inevitable" deterioration of the environment. With practical seawater desalination, it is not unreasonable to envision a reversal of current water supply movement. We could even transport large quantities of purified water of ocean origin to inland areas, given reliable and sufficiently low-cost methods of desalination. More development is needed. The relatively high salinity (35,000 ppm) and correspondingly high osmotic pressure of seawater require high-pressure membranes, pumps, and collateral components. The development of seawater desalination through RO will be an important element in preserving and augmenting our fresh water.

Similarly, and perhaps more urgent, reverse osmosis can reduce the drain on the remaining water sources by allowing practical recycling of used water. When advanced municipal waste treatment and concomitant water reclamation systems are installed, our cities can cut their raw water needs in half, at least. At the very least, this means a lot fewer dams; a lot less wilderness scarred by the laying of pipes and the building of pumping stations; and, perhaps, an end to those ecologically threatening interbasin water transfers.

Acknowledgment is hereby made to the Office of Saline Water (U.S. Department of the Interior) and the Environmental Protection Agency for their support of various aspects of the work reported and discussed herein.

Seymour S. Kremen *is currently manager of Applied Development, ROGA Division, Universal Oil Products in San Diego, Calif. Since 1967, Dr. Kremen has concentrated his technical and administrative efforts on the development of water and waste treatment processes that use reverse osmosis membranes. He is the author of a number of articles and holds several patents in the field.*

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PRICE/PERFORMANCE
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OBSOLESCENCE
EI
C_4H_6
VCM
$Fe(CO)_5$
$C_2H_2Cl_2$
bisCME
PH_3

FEATURE

NPDES permits and water analyses

Robert B. Pojasek
QLM Laboratories, Inc., Nyack, N.Y. 10960

The Federal Water Pollution Control Act, as amended by P.L. 92-500, prohibits any individual from discharging pollutants into a waterway from a point source, unless the discharge is authorized by a permit issued by either the U.S. Environmental Protection Agency or by an EPA approved state agency. Under Section 401 of the Act, the affected facility must submit an application for such a permit.

A substantial monitoring program may be necessary to provide the information required in the permit. For example, the applicant is required to summarize its wastewater characteristics. The presence or absence of a wastewater constituent must be based upon analyses performed or on the knowledge of the chemical constituents associated with the activities and/or processes causing the discharge. Constituents found solely in the intake water and not part of any plant process, for which no previous analysis has been performed, do not require additional analyses to determine their presence in the effluent.

A description of the intake and discharge water is also required. For each of the parameters listed in the application, concentrations representative of the discharge during the previous 12 months of operation or representative of the best engineering estimates for proposed discharges must be given. The following analytical details must support the information described above:

- sample type
- number of analyses
- analytical methods
- daily average
- frequency of sampling
- minimum-maximum concentration ranges.

Permit process

Typically, the application is filed with the state, who must within 30 days refer it to the Regional EPA permit section for review. Previous monitoring data are used in the review to understand the characteristics of the receiving waters in the vicinity of the discharge. This picture of water quality, together with the water quality standards and the effluent limitation guidelines, will determine whether the industry may be required to inaugurate in the area of effluent treatability studies or optimization of its selected treatment process.

Furthermore, the permit must comply with the provisions of Sections 301, 302, 306, and 307 of the Act. During the review, and within 90 days of application, the state drafts a proposed permit including limitations, compliance schedules, and state monitoring requirements. Thirty days prior to issuance of the permit, the permit forms are made available to the public. At this point, a hearing in the geographical area of the point source may be requested. Only after public inspection and approval of the EPA Regional Administrator will a permit be issued under Section 402 of the Act. This procedure has been given the title, "National Pollutant Discharge Elimination System" (NPDES), and the permits are called NPDES permits. When the states have the authority to issue permits, they are termed SPDES permits. Regulations for the operation of this program are published in the *Federal Register* under Title 40 of the "Code of Federal Regulations," Part 125.

The NPDES permit controls the type and amount of effluent that can be released from each point source. Target dates for reducing the amount of discharge in accordance with the aims of the Act are arranged in specific steps. Receipt of the permit legally binds the industry to obey the conditions outlined under the threat of a severe criminal penalty.

EPA approved analytical methods

Certainly, one of the most important considerations in this permit-granting process is the analytical methodology employed by the applicant or the environmental consulting firm that has been retained by the applicant. Because the importance of monitoring was recognized, Section 304(g) of the Act established a mechanism for promulgating test procedure guidelines: "The Administrator shall, within 180 days from the date of enactment of this title, promulgate guidelines establishing test procedures for the analysis of pollutants that shall include the factors which must be provided in any certification pursuant to section 401 of this Act or permit application pursuant to section 402 of this Act." In the *Federal Register* of October 16, 1973, the Administrator assumed the power of specifying what the EPA felt to be acceptable analytical methods.

These methods, which become part of Title 40 of the "Code of Federal Regulations" Part 136, are entitled, "Guidelines Establishing Test Procedures for the Analysis of Pollutants." Seventy-one parameters are included on this list (Table 1). The EPA guidance was strictly to interpret the wording of Section 304(g) and to require that all sampling and analytical methods used to meet the monitoring requirements shall conform to these guidelines except in cases where a formal variance has been granted. In the few instances where these guidelines do not list a pollutant required to be monitored by the permit, sampling and analytical methods used to meet the monitoring requirements should conform to the latest edition of the references (see Table).

Confusion and differences

While the intent of EPA is apparently clear from the wording of the promulgation, there is still a certain

Performing the proper analysis for 71 water pollutants by the approved method is specified in a number of regulations

EPA variance procedures

- Applicant must provide the name and address of the responsible person or firm making the discharge (if not applicant), the applicant ID number of the existing or pending permit, issuing agency, type of permit for which the alternate test procedure is requested, and the discharge serial number.
- Applicant must identify the pollutant or parameter for which approval of an alternate testing procedure is being requested.
- Applicant must provide justification for using testing procedure other than those specified in Table 1.
- Applicant must provide a detailed description of the proposed alternate test procedure, together with references to published studies of the applicability of the alternate test procedure to the effluents in question.

amount of confusion concerning the interpretation of these guidelines. There is a school of thought that feels that "Standard Methods" should always be used even though EPA failed to cite them in several cases and gave alternative references in the other cases. A second school of thought feels that this promulgation was only meant to be a guideline and that a competent analytical chemist may use any method that can be adequately justified. The EPA, however, has stated that alternative procedures must be formally approved in a rigidly defined variance procedure.

Compounding this confusion is the fact that in the standard "Application for Permit to Discharge Wastewater," the NPDES form, a different set of analytical methods is presented in some cases. EPA assumes the applicant is aware of the changes which have been published in the *Federal Register* article (footnote d in Table 1).

A comparison of the two lists show major differences for selenium and bromide. Many of the page references for the other parameters also differ. When a method has been used in the permit application which has since been superseded, the EPA permit review will generally caution the applicant to revise the analytical method for all future point source monitoring. There are a number of problems involved in the universal application of these criteria. These problems can be appreciated by examining the manner in which a competent environmental chemist might select an analytical method in the absence of semirigid restrictions.

Analytical method selection

In the selection of methods, full use should be made of authoritative and widely accepted references. In addition to the citations listed (in Table 1), two other sources are widely used in water pollution laboratories, they are: "Methods for Collection and Analysis of Water Samples for Dissolved Minerals and Gases: Techniques of Water-Resources Investigations of the U.S. Geological Survey," 1973, Book 5, Chapter A1, by Eugene Brown, M. W. Skougstad, and M. J. Fishman, and "A Practical Handbook of Seawater Analysis," 1972, Bulletin 167, Second edition, Fisheries Research Board of Canada, by J. D. H. Strickland and T. R. Parsons. In addition to these references, many equipment vendors provide excellent reviews or manuals of tested environmental applications of their instrumentation. Before using any novel method, the careful analyst will check it against a more widely used method for comparability purposes.

For a given parameter, several methods may be available. The actual selection of a test procedure would probably vary with the application. A prime consideration here is the detection limit required. For example, if one is measuring trace metals in natural waters, atomic absorption spectrophotometry may be adequate. However, to use the same procedure for ultrapure waters or even seawater, may require considerable sample pretreatment or concentration to obtain meaningful results. In this latter case, neutron activation analysis might be more desirable because of the generally lower detection limits, if the equipment were readily available.

The precision and accuracy of the method within the concentration range of interest are also important. For example, it may be important to detect small changes in the concentration of a parameter at very low levels. Certainly some particular method may do this better than another, while yielding equivalent or poorer sensitivity in a more normal concentration range.

Because of the inherent instability of some chemical parameters, the analyst is often faced with having to analyze the parameter in the field. The method must also be directly applicable to the working conditions (electrical sources, shelter, and the like) at the sample site. Often considerations may be given to continuous monitoring of the parameter(s). However, even while there may be a number of parameters which can be reliably determined in this manner, many consulting firms are continuing to sample (by composite or grab) and analyze most of the parameters in the laboratory. The initial capital outlay for the on-site apparatus, along with the lack of a sufficient range of parameters available for permit applications, make such an equipment purchase difficult to justify economically.

Many of the factors discussed above may be tempered in importance by a cost evaluation and the assessment of available manpower. These economic considerations are also important in the choice of a method. This fact is reflected in the EPA criteria. However, good chemical judgment should always be the primary consideration. By setting restrictive guidelines, the EPA has granted only one way in which the competent environmental chemist can select a method not included on the list, and that is by following an established procedure.

EPA criteria for NPDES methods

- Methods must measure constituents with a precision and accuracy sufficient to meet data needs in the presence of interferences normally encountered in polluted waters. This would provide comparable data throughout the country.
- Methods must utilize skills and equipment normally available in a typical water pollution control laboratory.
- Methods must be sufficiently tested in many laboratories to establish their validity.
- Methods must be sufficiently rapid to permit routine use for the examination of large numbers of samples.

Variance procedure

Any person wishing to use alternative methods for the parameters listed in Table 1, when filing for an NPDES permit, must go through the variance procedures outlined in Title 40 of the "Code of Federal Regulations," Parts 136.4 and 136.5. Until printed applications forms are made available, the following information must be sent in triplicate to the Director of the approved agency in the State where the discharge occurs.

Within 30 days of receipt of this application, the Director must forward this information together with his recommendations to the Regional Administrator. Where the Director recommends rejection of the application for scientific and technical reasons, which he provides, the Regional Administrator shall deny the application and shall forward a copy of the rejected application and his decision to the Director of the State Permit Program and to the Director of the Methods Development and Quality Assurance Research Laboratory (National Environmental Research Center, Cincinnati, Ohio or any MDQAL branch). Before any application for an alternate test procedure is approved, a copy should be forwarded to the Director of the MDQAL for review and recommendations.

Within 120 days of submission of the application for an alternate test procedure, the Regional Administrator shall notify the applicant and the appropriate State agency of approval or rejection, or shall specify the additional information required to determine whether to approve the proposed test procedure. Prior to the expiration of this period, a recommendation providing the scientific and technical basis for acceptance or rejection will be forwarded to the Regional Administrator by the Director of the MDQAL. A copy of all approval and rejection notifications will be forwarded to the Director, MDQAL, for the purposes of national coordination.

Section 101(f) of the Act states, "It is the national policy that to the maximum extent possible the procedures utilized for implementing this Act shall encourage the drastic minimization of paperwork . . .". The variance procedures described above are quite costly to environmental consultants both in time and money. An alternate approach, which would allow direct contact between the analyst on the project and the technical experts in the EPA laboratories, would help alleviate some of the ad-

TABLE 1

Comparison of analytical methods for water pollutants under permits (page numbers in references)

Water pollutants	Standard methods[a] Approved[d]	Standard methods[a] NPDES[e]	ASTM[b] Approved	ASTM[b] NPDES	EPA methods[c] Approved	EPA methods[c] NPDES
Alkalinity, as $CaCO_3$	370	370	143	143	6	6, 8
BOD 5-day	489	489	—	618	—	15
Chemical oxygen demand (COD)	495	495	219	219	17	17
Total solids	535	535	—	—	280	280
Total dissolved, filterable	—	—	—	—	275	275
Total suspended, nonfilterable	537	537	—	—	278	278
Total volatile solids	536	536	—	—	282	282
Settleable matter (residue)	—	539	—	—	—	—
Ammonia, as N	—	—	—	—	134, 141	134, 141
Kjeldahl nitrogen, as N	469	469	—	—	149, 157	149, 157
Nitrate, as N	458, 461	461	124	124	170, 175, 185	185, 170, 175
Total phosphorus, as P	526, 532	526	42	—	235, 246, 259	246, 235, 259
Acidity, as $CaCO_3$	—	370	148	143	—	5
Total organic carbon (TOC)	257	257	702	702	221	221
Hardness-total as $CaCO_3$	179	179	170	169	76, 78	76, 78
Nitrite, as N	—	468	—	228	185, 195	195
Total metal content						
Aluminum	210	57	—	—	98	98
Antimony	—	—	—	—	—	83
Arsenic	65, 62	62	—	—	13	13, 99
Barium	210	66	—	—	—	83
Beryllium	67, 210	67	—	—	—	83
Boron	69	69	—	—	—	83
Cadmium	210, 422	422	692	692	101	101
Calcium	84	84	692	692	102	102
Chromium VI	429	—	—	—	94	—
Chromium—total	210, 426	426	692, 403	692	104	104
Cobalt	—	—	692	692	—	83
Copper	210, 430	430	692, 410	692	106	106
Iron	210, 433	433	692, 152	692	108	108
Lead	210, 436	436	692	692	110	110
Magnesium	210, 416, 201	416	692	692	112	112
Manganese	210	—	692	692	114	114
Mercury	—	—	—	—	—	121
Molybdenum	—	—	—	—	—	83
Nickel	443	443	692	692	—	83
Potassium	283, 285	285, 283	326	326	115	115
Selenium	—	296	—	—	—	271

ninistrative delays and misunderstandings that may be resent in the current procedure. Such a restrictive approach may unnecessarily retard many future advances n analytical chemistry from reaching those analysts who nay require such techniques for specific applications. In ome of the stricter regions, it is difficult to justify small nodifications in procedure because of the reluctance of he Regional staff to set a precedent for program modifications.

ther concerns

A noteworthy aspect in the promulgation of analytical nethodology is the expressed desire of EPA not to intere with the rapidly advancing state-of-the-art in the deign of industrial sampling programs. Monitoring is a deeloping field with nearly continual changes. By the publiation of a technology transfer manual entitled, "Industrial Wastewater Sampling" (1973), the EPA hoped to rovide guidance to industry and consultants alike who re directly involved in planning, executing, or continuing program of industrial waste monitoring. This document bstracts a number of analytical standards and texts and presents them in the form of a general informational guide. It should allow the user to determine effectively the applicability of a large variety of samplers, instruments, and techniques that might be considered for solving unique industrial wastewater sampling problems or for simply satisfying provisions of the NPDES Permit.

Another item which the EPA has begun to stress with renewed spirit in its NPDES Permits and other programs (for example, "Water Quality and Pollutant Source Monitoring, Title 40" of "Code of Federal Regulations" Part 35) is the importance of analytical quality control. It is extremely important for consulting firms, who are responsible for the court-defensibility of the data generated on behalf of their industrial and municipal clients, to carefully practice and document quality control procedures. In the EPA publication entitled "Handbook for Analytical Quality Control in Water and Wastewater Laboratories" (1972), information is presented to allow the user to inaugurate or reinforce a program of analytical quality control which emphasizes early recognition, prevention, and correction of factors leading to breakdowns in the validity of environmental data.

	Standard methods[a]		ASTM[b]		EPA methods[c]	
Water pollutants	Approved[d]	NPDES[e]	Approved	NPDES	Approved	NPDES
Sodium	317	317	326	326	118	118
Thallium	—	—	—	—	—	83
Tin	—	—	—	—	—	83
Titanium	—	—	—	—	—	83
Vanadium	157	—	—	—	—	—
Zinc	210, 444	444, 211	692	692	120	120
Chemical parameters						
Organic nitrogen, as N	468	468	—	—	149	149
o-Phosphate, as P	532	532	42	42	235, 246, 259	235, 246, 259
Sulfate, as SO_4	331, 334	334	51, 52	52	286, 288	286, 288
Sulfide, as S	551	551	—	—	294	294
Sulfite, as SO_3	337	337	261	261	—	—
Bromide	—	75	216	214	—	—
Chloride	96, 97	97	23, 21	21	29, 31	29, 31
Cyanide	397	404	556	556	41	41
Fluoride	171, 174	171	191	191	64	64, 66, 72
Chlorine	382	107	223	—	—	—
Oil and grease	254	254	—	—	—	—
Phenols	502	502	445	445	232	232
Surfactants	339	559	619	619	131	131
Algicides	—	—	—	—	—	—
Benzidine	—	—	—	—	—	—
Chlorinated organic (except pesticides)	—	—	—	—	—	—
Pesticides	—	—	—	—	—	—
Physical and biological parameters						
Color Pt-Co units	160, 392	160	—	—	38	38
Specific conductance	323	323	163	163	284	284
Turbidity Jackson units	350	577	467	467	308	308
Fecal streptococci bacteria	689, 690	688	—	—	—	—
Coliform bacteria, fecal	669, 684	669, 684	—	—	—	—
Coliform bacteria, total	664, 679	664, 679	—	—	—	—
Radioactive parameters						
Alpha total	598	598	509	509	—	—
Alpha-counting error	598	598	512	512	—	—
Beta total	598	598	478	473	—	—
Beta-counting error	598	598	478	478	—	—
Radium total	611, 617	—	674	—	—	—

[a] "Standard Methods for the Examination of Water and Wastewaters," 13th ed., 1971, American Public Health Association, New York, N. Y. 10019. [b] "ASTM Standards, Part 23, Water; Atmospheric Analysis," 1972, American Society for Testing and Materials, Philadelphia, Pa. 19103. [c] "Methods for Chemical Analysis of Water and Wastes," April 1971, Environmental Protection Agency, Water Quality Office, Analytical Quality Control Laboratory, NERC, 1014 Broadway, Cincinnati, Ohio 45268. This reference has been recently revised (EPA-625-16-74-003) to be more consistent with the Federal Register promulgation. [d] Fed. Regist., **38** (199), 28758–60 (Oct. 16, 1973). [e] Application for Permit to Discharge Wastewater, EPA Form 7550-23A (July 1973).

COD digestion. *Lab assistant checks on progress of wastewater analyses of samples containing a chemical-oxygen-demand pollutant*

In many draft permits, the EPA is requiring laboratories to routinely utilize and document intralaboratory analytical quality control procedures. These include a combination of techniques, such as spiked sample recovery, replicate sample analyses, and reference sample analyses. In addition, the permittee must calibrate and perform maintenance procedures on all monitoring and analytical instrumentation at sufficiently frequent intervals to ensure the accuracy of the measurements. All this quality control information must be documented and made available at the request of the Regional Administrator to demonstrate that the laboratory has a viable quality control program.

The quality control program must not be confined to the analytical laboratory. At QLM Laboratories, Inc., we have established an active quality program not only in our analytical field and laboratory programs, but also in our biological field and laboratory programs. An all-inclusive quality program is necessary in every environmental laboratory, because the data is only as good as the manner in which the sample is obtained, the way it is transported, and the methodology used to analyze it.

Observations

At one time, environmental monitoring was exclusively within the domains of sanitary engineering, limnology, soil science, environmental health, and oceanography. Only recently has environmental chemistry been recognized by some as a legitimate division of chemistry, even though studies involving the chemistry of man's environment are as old as the fields listed above. While there may be made reasons for the delay in acceptance, it is apparent that the fundamental chemical approach and the use of sophisticated chemical instrumentation are now an integral part of environmental studies.

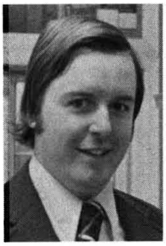
The EPA has provided excellent guidance for the rapidly developing field of environmental chemistry with the issuance of its publications on quality control and industrial wastewater sampling. By carefully revising and continually updating these important documents, EPA will continue to provide environmental chemists with the direction they need to further advance the state-of-the-art.

On the other hand, the promulgation of semirigid guidelines for analytical test procedures provided the emerging discipline with a major hurdle. It would have been more constructive to issue the NPDES list in Table 1 as guidelines only. Certainly, justification would have to be provided for the use of any procedures which do not appear on the list. A competent environmental chemist could provide such a justification. This consideration would promote professionalism in the field of environmental chemistry which, in turn, would provide greater assurance in the quality of environmental data. Restrictive guidelines in themselves will enhance the quality of the data but they will contribute little to the increased quality to the profession generating this data.

An alternative approach to the current situation would be for EPA to revise the current variance procedures. This is particularly important to avoid the indiscriminate application of pretreatment techniques (for example, required fluoride distillation or metal digestions for all samples regardless of source). In cases where pretreatment has been shown to be unnecessary, a considerable savings could be made by omitting this step.

It was the original intent of EPA to undertake an annual revision of the guidelines. In addition, a series of amendments (for example, pH, flow, fluoride ion selective electrode, and the like) has been proposed within the agency. These important considerations have been delayed due to the temporary shift in agency priorities to energy matters. Publication of the amendments in proposed form should be forthcoming in the *Federal Register* but the annual revision has been pushed into the future.

With the flourish of rules, regulations, and guidelines being issued by the EPA regarding water pollution assessment and control, it is essential that both industry and its environmental consultants remain informed of the changes. A considerable effort is required to keep abreast of these changes and to assess their impact on their operations. Every opportunity should be afforded the public to respond to proposed promulgations in order to protect their interests and to provide the EPA with the information it needs to evaluate its program.



Robert B. Pojasek *is the senior staff chemist for Lawler, Matusky and Skelly Engineers (formerly Quirk, Lawler and Matusky Engineers) in Tappan, N.Y., and director of quality control in its Environmental Measurements Division (QLM Laboratories, Inc.). Dr. Pojasek's primary interests include the environmental cycling of heavy metals and the active promotion of chemistry in environmental investigations and litigation.*

Geochemistries of Arsenic, Antimony, Mercury, and Related Elements in Sediments of Puget Sound

Eric A. Crecelius,*,[1] Michael H. Bothner,[2] and Roy Carpenter

Department of Oceanography, University of Washington, Seattle, Wash. 98195

■ The natural distributions of arsenic, antimony mercury, chromium, cobalt, iron, aluminum, and carbon in the surface sediments of Puget Sound are perturbed by two major anthropogenic sources of trace metals: a copper smelter near Tacoma, Wash., that discharges large amounts of arsenic and antimony, and a chlor-alkali plant in Bellingham, Wash., which, in the recent past, discharged significant amounts of mercury. Arsenic and antimony inputs from the smelter over the past 80 years are evident in sediment cores whose accumulation rates have been determined by the lead-210 technique. An arsenic budget for Puget Sound reveals the importance of atmospheric input resulting from smokestack emissions of the smelter. Chemical extraction studies of sediments showed that more than 82% of the mercury was associated with easily oxidizable organic matter, whereas about 50% of both arsenic and antimony was associated with extractable iron and aluminum compounds.

Puget Sound, an estuary in northwestern Washington State, has both relatively remote areas that are apparently still uncontaminated and other areas which receive significant amounts of industrial and domestic wastes containing high concentrations of trace metals. We could find no data in the literature on distribution or biogeochemistry of arsenic, mercury, antimony, or other trace metals in Puget Sound. The purpose of this study was to determine the distributions of arsenic, antimony, mercury, chromium, and cobalt in the surface sediments and arsenic in sediment cores from Puget Sound, and to relate these distributions to sources, transport paths, and geochemical reactions these metals may undergo. We also determined the concentrations of iron, aluminum, and carbon in the sediments to aid in interpreting the sources and reactions of the trace metals. An arsenic budget was calculated to compare the importance of removal to the sediments and discharge to the Strait of Juan de Fuca as sinks for arsenic entering Puget Sound.

The largest natural sources of trace metals to Puget Sound are particulate and dissolved phases in seawater entering from the Strait of Juan de Fuca and in river water which enters at various locations around the Sound. Three rivers north of Seattle (Skagit, Stillaguamish, and Snohomish) supply over 75% of the fresh water to the Sound.

The major anthropogenic source of arsenic and antimony to Puget Sound is a large copper smelter located near Tacoma. This smelter, which has been in operation since 1890, produces as a by-product almost all the arsenic trioxide sold in the United States. The smelter releases arsenic and antimony into the environment in three ways: (1) as stack dust into the air, 2×10^5 kg/yr of As_2O_3 and 2×10^4 kg/yr of antimony oxides; (2) as dissolved arsenic and antimony species in liquid effluent discharged directly into Puget Sound, $2–7 \times 10^4$ kg As/yr and 2×10^3 kg Sb/yr; (3) as crystalline slag particles dumped directly into the Sound, 1.5×10^6 kg As/yr and 1.5×10^6 kg Sb/yr. (These figures are estimates compiled by Crecelius (*1*), using data from regulatory agencies.)

One of the most significant industrial sources of mercury to Puget Sound has been a mercury cell chlor-alkali plant in Bellingham, which discharged an estimated 4.5–9 kg mercury/day to Bellingham Bay between 1965 and 1970. Since 1970 the discharge has been reduced to about 0.1 kg/day (2).

Another source of arsenic, antimony, mercury, and other trace metals to Puget Sound is the effluent from sewage treatment plants. The largest treatment plant is the METRO plant at West Point in northwest Seattle that processes most of the domestic and industrial sewage of Seattle and discharges it at a 200-meter depth into Puget Sound. Based on METRO effluent data, this discharge introduced into Puget Sound 800 kg of arsenic, 250 kg of antimony, and 420 kg of mercury per year prior to 1973.

Collection and Analytical Procedures

Sediments were collected with a special coring apparatus that has a hydrostatically slowed rate of penetration into the sediments (3). Under normal conditions this apparatus collects cores of sediment without disturbing the water–sediment interface. The surface sediment (0–2 cm) was subsampled from cores and frozen until analysis. A few samples were collected with a conventional gravity corer or with a Van Veen grab. All samples were collected during the period 1970–72.

Arsenic, antimony, iron, chromium, cobalt, and aluminum were determined by nondestructive neutron activation techniques. The sediment samples were oven dried at 80°C for 48 hr, cooled, and 0.5–1.0 gram were weighed and sealed in 2/5 dram of polyethylene vials. Samples and suitable standards were irradiated for 1–2 hr in a thermal neutron flux of 10^{12} n cm^{-2} sec^{-1} at the University of Washington Nuclear Reactor. After cooling for 3–6 days, the samples were counted for 0.5–4 hr on a Ge(Li) diode detector with an energy-resolving capability of 2.56 keV FWHM at 1333 kev. The following gamma-ray peaks were used for the determinations: ^{76}As 559, ^{122}Sb 564, ^{59}Fe 1099, ^{51}Cr 320, and ^{60}Co 1333 kev. Analyses of both wet

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[1] Present address, Battelle Northwest, Richland, Wash. 99352.

[2] Present address, Office of Marine Geology, U.S. Geological Survey, Woods Hole, Mass. 02543.

Table I. Location, Water Depth, Grain Size and Concentration of Eight

N lat.	W long.	Depth, m	Sediment size[a]	As	Sb	Hg	Cr	Co	Fe	Al	C
				Ppm					%		
Bellingham Bay											
48°45.2′	122°33.7′	10	Mud	9.7	0.83	0.80					1.50
48°44.9′	122°29.3′	10	Mud			100					4.70
48°44.7′	122°30.1′	7	Mud	11.0	0.92	10.7					3.00
48°44.3′	122°30.8′	16	Mud	15.4	1.11	0.807	199	18	5.15	7.42	3.30
48°43.6′	122°30.8′	18	Mud	13.5	1.43	4.0					2.70
48°41.3′	122°33.5′	28	Mud			0.35					2.40
48°38.3′	122°34.0′	112	Mud			0.10					1.90
48°38.1′	122°31.6′	12	Mud			0.20					1.40
48°35.6′	122°33.6′	49	Mud			0.10					1.20
Strait of Juan de Fuca and Northern Puget Sound											
48°23.2′[b]	123°10.5′	120	Sand	6.3	0.45	0.033	98	11	3.07	6.35	0.72
48°20.5′[b]	122°32.1′	30	(2.4) Sand	5.8	0.40	0.010	55	8.7	2.40	7.68	0.55
48°17.8′[b]	122°29.2′	25	(3.4) Sand	4.7	0.35	0.017	127	12	3.06	7.19	0.13
48°14.0′[b]	122°36.3′	23	Mud	15.7	0.79	0.098	107	15	3.84	6.51	2.32
48°9.6′[b]	122°59.5′	75	Sand	5.5	0.38	0.049	82	9.5	2.62	6.64	0.90
48°8.7′[b]	122°24.2′	116	(8.9) Mud	15.5	0.97	0.110	179	21	4.46	7.35	1.65
48°8.6′	122°32.8′	90	(9.4) Mud	12.6	0.92	0.063				6.46	2.22
48°7.5′[b]	123°24.6′	14	Mud	9.6	0.64	0.051	77	11	2.93	5.69	4.69
48°5.6′[b]	122°46.6′	20	Mud	8.6	0.67	0.098	87	13	3.54	6.95	0.96
48°0.8′	122°38.0′	120	(1.8) Sand	3.2	0.43	0.009					1.55
47°55.4′[b]	122°20.8′	186	(9.2) Mud	16.1	1.13	0.146	88	17	3.61	6.85	2.39
Hood Canal											
47°54.5′[b]	122°37.9′	85	(3.4) Sand	4.3	0.33	0.027	123	9.2	2.49	6.30	0.36
47°41.0′[b]	122°45.8′	83	(8.2) Mud	9.7	0.63	0.042	92	15	3.62	6.77	1.98
47°40.4′[b]	122°52.5′	138	(8.4) Mud	11	0.72	0.085	88	16	3.88	6.25	2.37
47°28.7′[b]	123°3.9′	155	(9.3) Mud	12	1.16	0.022	80	25	4.26	4.75	2.51
47°23.6′[b]	122°56.1′	25	(8.5) Mud	17	0.61	0.073	108	20	3.39	4.81	4.04
47°22.5′[b]	123°7.8′	100	(8.3) Mud	16	0.68	0.046	126	30	6.33	5.90	2.42
Central Puget Sound and Seattle Area											
47°50.0′	122°26.7′	185	(5.0) Sand	7.0	0.47	0.069					1.21
47°43.2′	122°26.7′	200	Mud	9.8	0.82	0.186					1.83
47°43.2′	122°26.7′	200	Mud	11.7	0.86		106	15	3.92	6.12	1.98
47°40.7′	122°26.8′	135	Mud	11.0	0.93	0.111				6.00	0.88
47°40.1′	122°26.0′	60	Sand	6.0	0.57					4.16	0.52
47°39.7′	122°27.1′	112	Sand	5.0	0.95					6.39	0.49
47°39.3′	122°26.3′	30	Sand	4.4	1.15					6.37	0.45
47°39.0′	122°26.9′	200	Mud	14	2.4	0.254				5.96	2.81
47°39.0′	122°26.9′	200	Mud	14	1.8					6.64	2.52
47°36.0′	122°22.0′	75	Mud	14	3.34	0.392				6.54	1.42
47°35.1′	122°21.6′	16	Mud	19	12	0.522	70	13	3.82	7.10	1.21
47°33.8′	122°28.8′	100	Mud	15	3.2	0.111	139	15	2.64	6.36	0.99
47°33.1′	122°37.8′	16	Mud	20	3.9	0.303	104	15	3.10	6.52	3.02
47°32.6′	122°25.8′	205	Mud	11	3.8	0.331				5.84	2.69
47°28.4′	122°24.8′	200	(8.8) Mud	29	3.6	0.338				6.38	2.92
47°25.3′	122°22.9′	203	Mud	35	3.5	0.390	67		4.20	6.13	2.99

and dried sediments indicated that loss of arsenic and antimony during oven drying under these conditions was less than 2%. Aluminum was determined by irradiating the same samples used for the other neutron activation analyses for 1 min along with standard rocks in a thermal neutron flux of 5 × 10^{10} n cm^{-2} sec^{-1}. After cooling for 2-3 min the samples were counted for 1 min on a Ge(Li) diode detector. The ^{28}Al gamma-ray peak of 1777 kev was used for the determination. The possibility of an error caused by the ^{28}Si (n, p) reaction forming ^{28}Al was checked and found to be insignificant for the activation conditions and samples used.

Water samples were also analyzed for arsenic by neutron activation analysis after the arsenic was preconcen-

Elements in Puget Sound Surface Sediments (0–2 cm) on Dry Weight Basis

N lat.	W long.	Depth, m	Sediment size[a]	As	Sb	Hg	Cr	Co	Fe	Al	C
				Ppm					%		
Tacoma Area											
47°23.8′	122°26.6′	7	Mud	50	3.2	0.441	110	14	3.06	6.09	3.12
47°23.8′	122°26.6′	7	Mud	49	3.2	0.511	126		3.17	6.14	2.36
47°22.9′	122°28.1′	14	Mud	54	3.6				3.60	6.77	2.63
47°22.5′	122°21.6′	200	Mud	12.3	2.92					5.99	2.56
47°22.4′[b]	122°28.4′	14	Sand	7.5	0.68	0.101	147	5.1	1.75	5.50	0.45
47°21.9′	122°32.0′	95	Sand	8.3	2.2						0.95
47°21.9′	122°32.0′	95	Sand	8.1	2.2				1.80		0.89
47°21.5′	122°25.2′	175	Mud	24	2.7		81	15	3.72	7.01	2.45
47°20.7′	122°23.9′	180	Mud	17.4	3.3					6.58	2.55
47°20.7′	122°32.5′	85	Sand	7.0	2.4		77	10	1.60		1.66
47°20.2′	122°28.5′	55	Sand	7.5	0.80		101	7.5	2.00		0.29
47°20.2′	122°28.5′	55	Sand	7.8	1.00		86	7.3	2.10	5.33	0.33
47°19.8′	122°26.4′	190	Mud	11.3	4.6					7.89	2.15
47°19.6′	122°30.8′	105	Sand	3.2	1.76		126	8.0	2.00	5.37	0.66
47°19.6′	122°31.4′	88	Sand	4.8	2.3						0.12
47°19.3′	122°32.2′	62	Sand	4.2	1.50			12	3.40		0.19
47°19.2′	122°27.8′	180	Mud	14.2	2.31		68	14	3.47	7.27	3.65
47°19.1′	122°31.4′	100	Sand	27	20						0.48
47°18.9′	122°30.9′	130	Sand	36	24		163	12	2.60	6.06	0.37
47°18.8′	122°30.3′	157	Sand	5.4	1.74					8.30	0.48
47°18.7′	122°30.4′	148	Sand	292	293						0.39
47°18.6′	122°30.1′	89	Sand	1,253	874		153		5.80	5.85	0.55
47°18.5′	122°30.8′	65	Sand	980	570	0.370				6.04	0.28
47°18.5′	122°30.5′	53	Sand	10,000	12,500						0.20
47°18.4′	122°29.8′	120	Sand	14.6	4.6		154	12	2.90	6.31	0.55
47°18.3′	122°30.2′	55	Sand	9,196	5,811					3.72	
47°18.2′	122°28.6′	172	Mud	10.3	2.68					6.83	
47°18.1′	122°29.3′	150	Mud	17.6	6.8		86	9.7		6.00	0.60
47°18.1′	122°29.8′	45	Sand	107	45						0.57
47°17.8′	122°29.4′	32	Mud	37	13.7		43	9.0	2.00	6.34	0.59
47°17.6′	122°27.7′	170	Mud	12.2	2.4						1.97
47°17.2′[b]	122°26.2′	125	Mud	13.7	1.4	0.154	52	12	3.40	7.88	1.77
47°17.1′	122°28.4′	32	Mud	15.5	5.23		103	8.0	2.23	5.68	0.38
47°16.5′	122°27.1′	45	Mud	50	10		57	9.8	3.10	6.09	14.2
Southern Puget Sound											
47°18.4′[b]	122°42.6′	78	Mud	15.7	1.82	0.114	80	14	3.64	6.98	2.95
47°18.1′[b]	122°49.2′	32	Mud	14.7	1.28	0.121	77	17	3.72	6.32	2.69
47°18.1′[b]	122°49.2′	32	Mud	18.5	1.51	0.117	87	16	2.49	7.51	
47°12.9′	122°37.3′	140	Sand	39	12	0.158	135	16	3.10		1.58
47°11.4′	122°37.3′	180	Sand	7.0	0.90	0.025			1.90	5.34	0.31
47°11.6′	122°49.2′	60	Mud	12.7	1.69	0.150	79	14	3.45	7.76	
47°8.4′[b]	122°45.3′	70	Sand	4.0	0.59	0.023	60	17	4.16	7.88	0.57
47°8.3′[b]	122°54.7′	12	Mud	16.5	1.67	0.186	81	15	3.35	6.45	3.30
47°6.1′[b]	122°54.7′	10	Mud	16.8	1.40	0.234	78	16	3.61	7.16	2.89
47°6.1′[b]	122°42.1′	1	Sand	2.9	0.28	0.015	58	14	3.61	8.06	0.43

[a] Mean grain size in phi notation and/or sediment type. [b] "Noncontaminated" sample, used in statistical analysis.

trated by quantitative coprecipitation with ferric hydroxide, according to the procedure described in Robertson and Carpenter (*4*).

The concentrations of mercury in the sediments were determined by flameless atomic absorption using a wet chemical technique described by Cranston and Buckley (*5*). Most of the samples were dried at 80°C for 48 hr before analysis. The potential loss of mercury by drying, as pointed out by Iskandar et al. (*6*), was checked on sediments from Puget Sound by comparing results on aliquots run wet and dry. No loss of mercury was observed in either oxidizing or reducing sediments.

To check the precision and accuracy of the flameless AA method, well-homogenized samples of sediment were analyzed both by flameless AA and nondestructive neutron activation of samples sealed in quartz vials. The precision of replicate analyses is better than 8% and the accuracy is within 14%, assuming the analysis, by neutron activation in quartz vials, gives the true value. Further details and justification of the mercury techniques are reported elsewhere (*7*).

We have checked our procedures for the trace metal determinations by analyzing standard reference materials, including USGS rock standards, NBS orchard leaves and tuna meal, and EPA solutions and sediments. Our results on these reference materials are within 10% of the certified or recommended values. Two separate sediment samples were collected at a number of sampling sites and analyzed to give an estimate of the precision of replicate samples. The pooled estimate of standard deviations for analysis of replicate samples is less than 10% for each of the elements.

Total carbon was determined on oven-dried sediment (80°C for 48 hr) with a Leco carbon analyzer. Analyses before and after acidification with HCl were used to separate contributions from organic matter and from $CaCO_3$. The analytical uncertainty (one standard deviation about the mean) for replicate sediment analyses was 10%.

Standard sieve and pipet techniques (*8*) were used for grain size analysis, and Inman (*9*) statistical parameters were calculated by computer (*10*). Sediment samples for which we made no size analyses were grouped into three size classes (mud, sand, and gravel) by using sediment distribution charts compiled by Wang (*11*) and our own visual observations. Samples containing a majority of material larger than 62 μm and less than 2 mm were classed as sand.

Some preliminary chemical extraction procedures were conducted on both contaminated and uncontaminated sediments to obtain some idea of how the trace metals are bound in the sediments. Hydrogen peroxide was used to oxidize organic matter (*12*). Amorphous iron and aluminum compounds were removed by both an oxalate technique (*13*) and a citrate–dithionite–bicarbonate (CDB) extraction procedure (*12*).

Sediment accumulation rates over the last 100 years were determined for several cores by E. S. Twiss, using the lead-210 technique introduced by Koide et al. (*14*). The lead-210 activities were determined by measuring the activity of the "granddaughter" polonium-210 and using in-growth curves to calculate the lead-210 activities. The sediment samples were wet ashed and the ^{210}Po was spontaneously plated, together with ^{208}Po tracer for yield determination, onto silver disks. The two Po isotopes were then measured by alpha spectroscopy.

Results and Discussion

The concentrations of the eight elements analyzed in the surface sediments and supporting information on location, water depth, and sediment type are listed in Table I. All the sediments were oxidizing except the few from within half a km of the Bellingham chlor-alkali plant. The distributions of arsenic and mercury in surface Puget Sound sediments are summarized in Figures 1 and 2. Figure 3 gives some arsenic profiles in sediment cores.

As an aid to the interpretation of these data, a correlation coefficient matrix was constructed, and R-mode and Q-mode factor analyses were applied to 23 selected "noncontaminated" samples. These "noncontaminated" samples contained arsenic, antimony, and mercury concentrations of not more than twice the concentrations we measured at depths in cores from Puget Sound (arsenic <20 ppm, antimony <2 ppm, and mercury <0.25 ppm dry weight). This selection of "noncontaminated" samples was necessary to prevent a few highly contaminated samples from dominating the results and thus giving little in-

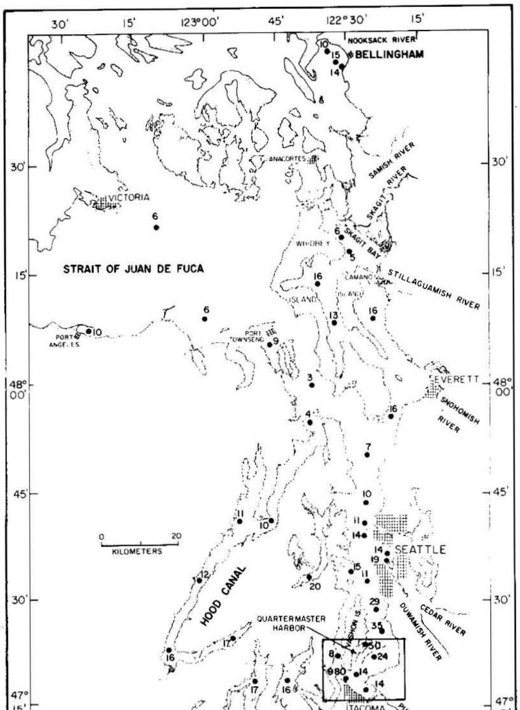

Figure 1. Concentration of arsenic (ppm dry weight) in the surface sediments (0–2 cm) of Puget Sound.

The boxed area contains more samples than could be plotted on the figure (see Table I)

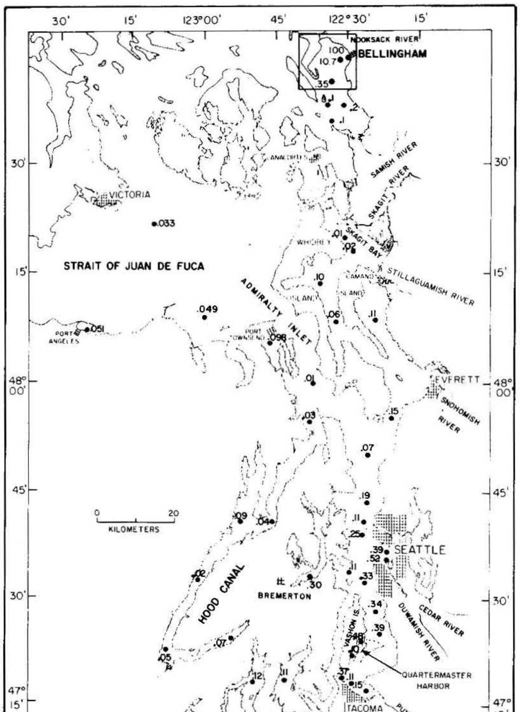

Figure 2. Concentration of mercury (ppm dry weight) in the surface sediments (0–2 cm) of Puget Sound

The boxed area contains more samples than could be plotted on the figure (Table I). Samples in the boxed area were collected between 1970–71 and have been observed to decrease with time since the discharge of mercury was essentially stopped in 1970 (*7*)

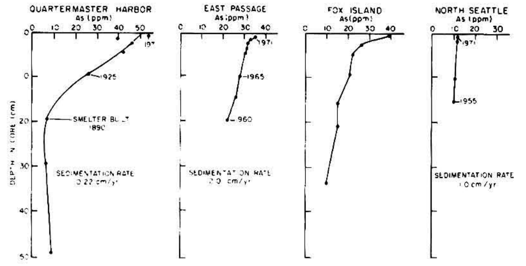

Figure 3. Concentration of arsenic (ppm dry weight) in sediment cores from Puget Sound
Sedimentation rates were determined by lead-210 technique

formation about the natural processes affecting the trace metals. Both the raw data and the logarithm (base *e*) of the raw data were used, with very similar results.

The calculated linear correlation coefficients for the eight elements and grain size are shown in Table II. All 23 "noncontaminated" samples were used to calculate the coefficients of the eight elements. For the grain-size coefficients only 10 of the 23 samples were used, resulting in a lower confidence level for these coefficients. The grain size data are mean diameter in mm, so a negative correlation coefficient between grain size and an element indicates that the element is more abundant in finer grained sediments.

The R-mode varimax factor loadings of the chemical analyses of the 23 "noncontaminated" samples showed that 95% of the variance of each of the elements is explained by four factors. Factor 1 is characterized by high positive loadings for arsenic, antimony, and mercury and a moderately positive loading for carbon. This factor reflects the high correlation among arsenic, antimony, mercury, carbon, and grain size which indicates that the finer grained sediments are richer in organic matter and also in these trace metals. Factor 2 is essentially an iron-cobalt factor, with minor loadings for carbon and arsenic. The correlation coefficient matrix also suggests the relationship among iron, cobalt, grain size, and carbon. Factor 3 is a chromium factor. Chromium correlates poorly with all the other variables measured for unknown reasons. Factor 4 is an aluminum factor with a moderate negative carbon loading. The negative correlation between aluminum and carbon and the positive correlation of aluminum with grain size are surprising and will be discussed later.

Q-mode factor analysis on the 23 "noncontaminated" samples showed that two factors explained 89% of the variance in the data. Those samples with high factor 1 loadings, which account for 77% of the variance, were fine-grained silty clays. Those samples with high factor 2 loadings, accounting for 12% of the variance, were coarser-grained sandy samples. Thus the Q-mode factor analysis is another indication of the importance of sediment grain size to the distribution of eight of the elements analyzed in Puget Sound sediments.

Arsenic and Antimony

The concentrations of arsenic in "noncontaminated" Puget Sound surface sediments and at depths in cores range from 3–15 ppm dry weight (Figures 1 and 3). The concentrations of antimony in these same samples range from 0.3–1.0 ppm. These concentrations are similar to those reported for fine-grained sedimentary rocks and deep sea sediments (*15–17*).

The arsenic and antimony distributions in the surface sediments of Puget Sound (Figure 1) indicate that the Tacoma copper smelter is the only major antropogenic source of these two metals in the region. Within 8–15 km of the Tacoma smelter, arsenic and antimony concentrations rise to 2–3 times background values. Sediments within 1 km of the smelter contain significant amounts of slag from the smelter, and thus contain up to 10,000 ppm of arsenic and antimony. Our laboratory leaching tests of the slag and our electron microprobe analyses of the slag particles collected in sediment samples near the slag pile both show that the slag is chemically and physically very stable in seawater.

Arsenic and antimony from the copper smelter are distributed by both wind and water. The arsenic and antimony accumulating in the muds of Quartermaster Harbor (at the southeastern end of Vashon Island, Figure 1) and in the muds east of Vashon Island are the result of wind-transported stack dust. The tidal current patterns do not transport slag material in that direction and extremely high concentrations of arsenic (400 ppm) and antimony (100 ppm) have been measured in the Vashon Island soils near Quartermaster Harbor, indicating arsenic and antimony are blown into and settle out in this area (*18*). During most of the year winds blow out of the southwest, and the smelter plume is directed toward the Vashon area. The smelter stack dust has arsenic to antimony ratios of about 10:1, while the slag has ratios of about 1:1. The ratio in sediments of Quartermaster Harbor is between 5:1 and 10:1, which also suggests that slag is not the major source of the arsenic and antimony in this area.

The low arsenic and antimony contents of the sediments between the smelter and Vashon Island (not near the slag pile) are the result of moderate tidal currents of

Table II. Correlation Coefficients Matrix
23 "noncontaminated" sediment samples[a]

	As	Sb	Hg	Fe	Al	Cr	Co	C	Mean[a] grain size
As	1.00	0.84[b]	0.77[b]	0.43[c]	−0.34	0.19	0.50[c]	0.85[b]	−0.92[b]
Sb		1.00	0.78[b]	0.34	−0.10	−0.09	0.37	0.72[b]	−0.91[b]
Hg			1.00	0.13	−0.07	0.16	0.12	0.63[c]	−0.76[c]
Fe				1.00	0.05	0.00	0.94[b]	0.45[c]	−0.77[c]
Al					1.00	−0.39	−0.15	−0.39	0.46
Cr						1.00	0.04	−0.11	−0.20
Co							1.00	0.53[c]	−0.86[b]
C								1.00	−0.89[b]
Mean[a] grain size									1.00

[a] 10 samples used for grain size correlations, 23 samples for all other correlations. [b] significant at $p = 0.001$ level. [c] significant at $p = 0.01$ level.

2–3 km/hr, preventing any slag or atmospheric dust material from accumulating in the bottom sediment. The tidal currents in this area near the smelter move predominantly from east to west, thus transporting suspended slag or dust either north along the west side of Vashon Island or south through the narrow channel west of Tacoma called The Narrows. In the central region of the Tacoma Harbor any contribution of arsenic and antimony from the smelter and other industrial sources are diluted to near background concentrations by the large sediment load of the Puyallup River which enters the east side of the Tacoma Harbor. The high arsenic (39 ppm) and antimony (12 ppm) levels observed in the sandy sediments off the east end of Fox Island (directly west of Tacoma) are due to slag particles transported through The Narrows (west of Tacoma) by strong tidal currents of up to 10 km/hr.

The concentrations of arsenic and antimony in sediments near the large METRO sewage outfall in Seattle indicate the sewage discharge has no noticeable effect on the distributions of these two metals in the sediments of this area. Such sewage effluents are often high in arsenic, which may come from detergents, herbicides, and various industrial discharges. The strong tidal mixing in the area of the METRO discharge mixes and dilutes the arsenic so effectively that elevated concentrations in nearby sediments do not occur.

Sediment cores taken in Quartermaster Harbor, near Fox Island, and in East Passage (east of Vashon Island) show relatively high arsenic concentrations in the surface sediments that decreased with depth in the cores to the usual background concentrations of about 10 ppm (Figure 3). The carbon content and grain size were similar throughout these cores. These arsenic profiles (and similar profiles for antimony) strongly suggest a recent additional input of arsenic and antimony to these areas and that the sediments are a sink for at least a portion of the arsenic and antimony released by the smelter. For comparison, a core from Puget Sound northwest of Seattle, from an area believed out of the influence of the smelter, shows background concentrations at all depths in the core.

The sedimentation rate has been determined for the cores from Quartermaster Harbor, East Passage, and North Seattle by the lead-210 dating technique. In the core from Quartermaster Harbor, the age or depth at which arsenic reaches background levels is the time when the Tacoma smelter begins operations (Figure 3). The sedimentation rate in East Passage is four times greater than the rate in Quartermaster Harbor, and our core was too short to reach background arsenic contents. The higher sedimentation rate in East Passage is due to the turbid Puyallup River which flows into Puget Sound at Tacoma.

It is clear from these cores that at least a portion of the arsenic introduced to Puget Sound by the Tacoma smelter has accumulated in bottom sediments. To understand the geochemical budget of arsenic in Puget Sound, we determined the fraction of arsenic from various natural and anthropogenic sources removed by sedimentation and the fraction removed in the surface waters flowing out of Puget Sound through Admiralty Inlet into the Strait of Juan de Fuca. (About 98% of the seawater entering Puget Sound enters at depth through Admiralty Inlet, and correspondingly 98% of the outflowing less saline waters leave in the surface water of Admiralty Inlet.) We have estimated the relative importance of arsenic removal via sedimentation vs. removal in outflowing surface waters of Admiralty Inlet in two ways. First, we have compared the arsenic content of the suspended matter of rivers entering Puget Sound with the arsenic content of the bottom sediments of Puget Sound. Second, we have estimated all the major inputs of arsenic and the removal in surface waters flowing out of Admiralty Inlet, and, by difference, we estimated the relative importance of the sedimentation term for arsenic. Each approach is discussed further below. Both approaches lead to the conclusion that the sediments are much less important as a sink for arsenic than discharge to the Strait of Juan de Fuca.

We have determined on a seasonal basis the concentrations of arsenic and antimony in the suspended sediments of the major rivers entering Puget Sound (Table III). The concentrations of arsenic in the river-borne particulates vary greatly (3–74 ppm dry weight) with river discharge, grain size, and organic content of the particulates. They are usually much higher during periods of low discharge, generally when grain size is at a minimum and organic content is at a maximum. However, the mean concentrations of arsenic (18 ppm) and antimony (1.5 ppm) in the suspended river sediments approximate those of the "noncontaminated" Puget Sound muds. These similarities in river-suspended sediments and Puget Sound muds indicate that the majority of the arsenic and antimony in Puget Sound sediments is supplied by the river particulates, and that uptake or release of these metals as the river particulates enter the Sound can be of only minor importance.

In contrast, DeGroot (*19*) suggested that 70% of the arsenic bound to the Rhine River suspended matter was released as the particles enter seawater. There are a number of possible explanations for the differences between our results and DeGroot's. The nature of the inorganic and organic load in the relatively uncontaminated Puget Sound rivers and the highly contaminated Rhine could account for the differences. The Rhine contains 5.6 ppb of total arsenic, two thirds in particulate phases, while the Puget Sound rivers contain 0.9 ppb of total arsenic and only one third in particulate phases. Part of the disagreement

Table III. Concentration of Arsenic and Antimony in Suspended Matter (Dry Weight Basis) from Rivers Entering Puget Sound

River[a]	Date	As, ppm	Sb, ppm
Skagit	6/13/72	21	1.4
	6/13/72	18	1.6
	6/13/72	18	1.3
	9/15/72	34	1.1
	12/28/72	20	1.6
	12/28/72	16	1.5
	7/16/73	15	1.4
Stillaguamish	6/13/72	17	1.3
	9/15/72	48	2.0
	7/16/73	30	2.2
Snohomish	6/13/72	22	1.5
	6/13/72	28	1.7
	9/15/72	74	2.9
	7/16/73	31	1.1
Duwamish	6/15/72	40	3.6
	9/16/72	27	2.1
	12/29/72	15	1.3
	12/29/72	15	1.0
	7/16/73	31	4.2
Puyallup	6/15/72	5.2	0.58
	9/16/72	6.3	0.33
	12/29/72	7.5	0.99
	12/29/72	7.3	0.50
	7/17/73	2.6	0.20
Nisqually	6/15/72	9.2	0.61
	9/16/72	4.5	0.21
	7/16/73	12	0.61
Dosewallips	9/16/72	7.4	1.1
Duckabush	9/16/72	6.8	2.6

[a] Samples were collected within 15 km of the river mouth.

could also be due to the different sampling methods of the two studies. We have collected suspended sediments from the rivers and surface sediments from the Sound, while DeGroot has collected bottom sediments from both the rivers and the coastal zone and then normalized their results to represent sediments of a certain size distribution assumed to be in suspension.

In setting up an estimate of fluxes of arsenic through Puget Sound, we have considered inputs from the incoming seawater, river water, atmospheric precipitation, the Tacoma smelter liquid effluent, and sewage and industrial discharges of Seattle. Besides sedimentation, the only removal process to be estimated is the discharge of surface waters through Admiralty Inlet.

We have measured an average of 1.51 ± 0.15 ppb (± one standard deviation) of arsenic in nine samples of deep seawaters flowing into Puget Sound at depth through Admiralty Inlet. The volume of seawater entering here is about 3.8×10^{11} m^3/yr, so the total arsenic input from the incoming seawaters is about $5.8 \pm 0.6 \times 10^8$ g/yr. We have analyzed 16 samples of the major rivers entering the Sound over an 18-month period and find they average 0.9 ± 0.4 ppb of total arsenic; approximately one third of the arsenic is in particulate phases ($>0.45\mu$ size). When we consider the average arsenic concentration for each river and its flow rate, the river influx of total arsenic is $3 \pm 1 \times 10^7$ g As/yr.

We have found that 24 samples of unfiltered rain and snow collected in Seattle during the past year averaged 17 ± 8 ppb of As. Since samples collected from the coast of Washington west of the Olympic mountains contained only 0.4 ± 0.2 ppb of As, the effects of the atmospheric arsenic emissions from the Tacoma smelter are clearly evident in the precipitation samples collected 35 km downwind in Seattle. The arsenic content of precipitation will thus be higher in the southern part of the Sound nearer Tacoma and less further north of Seattle, and we can only estimate an average arsenic content of precipitation at the present time. The average content measured in Seattle is likely to be an upper limit for precipitation falling over the entire Sound, and it gives $7.7 \pm 3.6 \times 10^7$ g As/yr input, using 1 m/yr of precipitation (*20*). Daily analyses of the liquid effluent discharged directly to the surface waters by the Tacoma smelter show this input amounts to $4.0 \pm 1.0 \times 10^7$ g As/yr. Other known arsenic inputs are from Seattle's METRO sewage treatment plant and from the use of arsenite solutions in treating ship drydocks in Seattle Harbor. Our estimates of these inputs are 7×10^5 g As/yr from the sewage plant and 9×10^5 g As/yr from the drydock operations, both clearly negligible when compared to the other inputs. We have measured an average of 1.48 ± 0.12 ppb of total arsenic in five samples of surface seawaters flowing out Admiralty Inlet, which, combined with the volume of outflowing waters, gives $6.3 \pm 0.6 \times 10^8$ g As/yr leaving through this Inlet.

The sum of the inputs of arsenic to Puget Sound total $7.3 \pm 0.7 \times 10^8$ g As/yr, and the outflowing waters remove $6.3 \pm 0.6 \times 10^8$ g As/yr. This crude budget indicates $1.0 \pm 0.9 \times 10^8$ g As/yr or 14% of the arsenic input to the Sound is removed to the sediments. Because of the large errors associated with this calculation, the percentage of the arsenic input removed to the Sound sediments could range from 0–30%.

We attribute this relatively low importance of the sedimentation term for arsenic removal from waters of Puget Sound to both physical and chemical oceanographic factors. The vigorous exchange of waters through Admiralty Inlet, driven mainly by strong tidal currents, replaces the waters of Puget Sound approximately twice a year, and thus allows limited time for reactions between dissolved and solid phases before their removal from the Sound. The chemical form of the arsenic dissolved in the rivers and seawaters of Puget Sound will also play a major role in its reactivity, and we are just beginning to obtain such information. Thermodynamically, most of the arsenic should be present as the arsenate anion, and there is some evidence in other areas that this is the major form of arsenic in seawaters (*21*). However, the major input from the Tacoma smelter effluent is rich in arsenite, and its rate of oxidation under the natural conditions of Puget Sound is not known. Arsenic speciation studies of coastal waters of Florida indicate that methylarsonic acid and dimethylarsonic acid may also be present in such coastal waters (*22*).

Our analyses of seven samples of Puget Sound seawaters show that the particulate arsenic is less than 10% of the total arsenic in the water. Further explanation of the small reactivity of dissolved arsenic with the sedimentary phases in the time available before flushing out through Admiralty Inlet will have to await our determinations of the speciation of arsenic in the waters and studies of sorption reactions of the dominant species with Puget Sound particulate matter. It is already clear, however, that uptake by particulate phases are much less important for arsenic than they are for other metals such as mercury and lead.

The correlation coefficient matrix indicated a strong relationship between arsenic, antimony, carbon, and fine grain size. Arsenic and antimony are expected to have some similarities in geochemical behavior as are other elements from the same group in the periodic table. Other workers have shown a similar relationship between arsenic, organic matter, and fine-grained sediments from the Black Sea (*23*). Similarly, shales containing organic matter, sulfides, and iron oxides tend to be high in arsenic and antimony (*15, 16*). However, because fine-grained sediments and shales are naturally rich in both organic matter and either sulfides or amorphous hydrous iron oxides, it is important to supplement the statistical relationships with chemical leaching studies to determine which phases of the fine-grained sediments contain the arsenic and antimony.

To better define the relationship between arsenic, antimony, organic matter, amorphous iron, and amorphous aluminum compounds in the sediments, we conducted a number of sediment extraction or "selective leaching" experiments. Less than 10% of the total arsenic and antimony in two contaminated and two "noncontaminated" sediments was removed by hydrogen peroxide treatment, indicating that most of the arsenic and antimony must be bound to the sediments in some manner other than to the readily oxidizable organic matter.

Several investigators have shown that soils high in reactive amorphous iron and aluminum compounds absorb large amounts of arsenic (*24, 25*). Oxalate and citrate–dithionite–bicarbonate (CDB) extractions have been used to determine the amount of arsenic bound to iron and aluminum in soils, and we applied these same procedures to Puget Sound sediments.

Oxalate extracted 66% of the total arsenic and 48% of the total antimony from three "noncontaminated" Puget Sound sediments. The CDB extracted 34% of the total arsenic and 31% of the antimony. Thus, in these "noncontaminated" muds of Puget Sound, the majority of the arsenic and half the antimony appear to be bound to the extractable iron and aluminum compounds. Similar extractions of two contaminated sediments near the smelter indicated that less than 20% of the arsenic and antimony is bound to extractable iron and aluminum compounds and that most of the arsenic and antimony is present in a rather chemically stable form, probably the slag particles.

Mercury

The concentrations of mercury in surface sediments south of Bellingham Bay varies between 0.01 and 0.5 ppm dry weight (Figure 2). Values between 0.01 and 0.1 ppm are found in areas away from industrial activities (such as Hood Canal, the Strait of Juan de Fuca, and Skagit Bay) and in areas where sediments are coarse due to strong tidal currents (Admiralty Inlet). These values are similar to background concentrations in sedimentary rocks unrelated to mineralization and unaffected by man's use of mercury (*26*). Sediments from deeper parts of Puget Sound south of Seattle, from protected embayments, and samples from harbor areas receiving domestic and industrial wastes have higher concentrations of mercury (Figure 2). The values of about 0.3 ppm south of Seattle may reflect a source of mercury from the major METRO sewage outfall, where digested sludge with about 10 ppm mercury dry weight (*27*) was discharged between July 1966 and December 1972 to bottom waters which have a net flow to the south.

The highest mercury concentrations south of Bellingham Bay were observed in Quartermaster Harbor on Vashon Island and at the mouth of the Duwamish River in Seattle (about 0.5 ppm of Hg). The high values in Quartermaster Harbor are consistent with the earlier suggestion that airborne smelt in stack dust having high concentrations of arsenic and mercury is transported to this area. Two samples of stack dust collected at different points contained 29 and 2750 ppm of mercury. At the Duwamish River mouth the higher mercury values reflect waste inputs from a number of industries.

As expected, the highest concentrations of mercury in Puget Sound sediments were found in Bellingham Bay in the vicinity of waste outfall from a mercury cell chlor-alkali plant (Figure 2). The relatively high mercury discharge (an estimated 4.5–9 kg/day) between 1965–70 resulted in elevated mercury concentrations in surface sediments within 7 km of the plant. In 1970 the concentrations were maximum at about 100 ppm within 100 meters of the plant outfall and decreased to background levels at distances greater than 9 km.

The accumulation of mercury in sediments of Bellingham Bay and in other areas such as Minimata Bay, Japan (*28*), and the Saint Clair River in Michigan (*29*) indicates that sediments can serve as a sink for some of the industrially discharged mercury. However, we have found that the sediments of Bellingham Bay are not a permanent sink for the mercury discharged between 1965–1970. Our analyses of sediment cores collected periodically from 1970–1973 at the same stations show that the mercury concentrations in the oxidizing sediments are decreasing with time since the high discharge of mercury was stopped in 1970. The rate of mercury loss appears to follow first-order kinetics with a "half-life" of about 1.3 years in sediments that are generally oxidizing and that had initial mercury concentrations of 2–10 ppm. The details of the changes of mercury with time in the sediments are presented elsewhere (*30*). The high mercury concentrations in Bellingham Bay sediments in Figure 2 are for samples collected between 1970–71.

A number of other workers have reported a correlation between organic matter and mercury in sediments (*31, 32*). Proteins with R—SH groups and the "humic acid" fraction of organic matter in sediments contain especially favorable binding sites for mercury. However, the mercury-total carbon correlation for surface sediments of Puget Sound is only fair (Table II). When the samples were corrected for the generally small amounts of carbonate carbon, the mercury-organic carbon relationship was not improved.

The chemical extraction experiments carried out on contaminated and "noncontaminated" sediments indicated that more than 82% of the mercury in the sediments is leachable with hydrogen peroxide. Since the sediments were not reducing, it is reasonable to assume that this mercury is bound to organic matter rather than to authigenic sulfides. Mercury removed by 10% NaCl solution, or by CDB which removed ferromanganese oxides, was less than 8% of the total mercury.

The good correlation of mercury with decreasing grain size (Table II) has also been observed by Cranston and Buckley (*5*), who argued that the relationship reflected increased surface area of the finer-grained particles. Our study shows also that a strong covariant relationship exists between carbon and decreasing grain size. Based on the chemical extraction experiments, it would appear that the organic matter rather than surface area seems to be a more important factor in controlling the mercury contents of the sediments. This contrasts with the behavior of arsenic, which seemed to be related more to the surface area (grain size) and Fe/Al oxides than to organic matter. The good correlation between arsenic, antimony, and mercury (Table II) is most likely just a reflection of the strong correlation between fine-grained sediment and carbon.

Chromium, Cobalt, Iron, and Aluminum

No elevated chromium or cobalt concentrations were observed that can be attributed to inputs of man. The chromium concentrations ranged 40–200 ppm dry weight, with a mean of 90 ppm. The cobalt concentrations ranged 5–30 ppm, with a mean of 15 ppm. These concentrations are similar to those determined for other nearshore sediments (*33*) and for shales (*17, 34*).

No strong relationships between chromium and the other elements or grain size were observed in the statistical analyses. Cobalt is strongly correlated with iron and with grain size in these sediments. The correlation with iron is almost certainly due both to the association of some of the cobalt with the detrital iron-rich minerals and to the extraction of cobalt from seawater by ferric hydroxides and oxyhydroxides.

Total iron in the sediments ranged from 2–6%, with a mean of 3.5%. No obvious geographic trends were evident, and unusually high values were not found even in the Seattle Harbor near a steel mill and shipyards.

The aluminum concentrations in the surface sediments varied from 4–8%, mean of 6.4%. We have measured the same range of aluminum concentrations in the suspended sediments of the major rivers entering Puget Sound, suggesting that aluminum is chemically inert following its introduction to the Sound, and hence is a good indicator of the detrital component of the sediment.

We expected the finer-grained sediments to be richer in aluminum than the coarser sediments, but this was not observed to be the case. The correlation between aluminum and grain size is positive (Table II), indicating the finer-grained sediments are lower in aluminum. This occurs because the coarser sediments are rich in feldspars, while the finer sediments contain more clays that have less aluminum than the feldspars. White (*35*) reported a similar relationship for Washington shelf sediments near the Columbia River.

Conclusions

The distributions of arsenic and antimony in surface sediments of Puget Sound shows natural levels of 3-15 ppm of arsenic and 0.3-1.0 ppm of antimony. Contaminated surface sediment contained up to 10,000 ppm of arsenic and antimony in the vicinity of a copper smelter near Tacoma. The output of arsenic and antimony from this smelter is distributed by both wind and water. The arsenic inputs from this smelter over the past 80 years are visible in sediment cores whose accumulation rates have been determined by lead-210 techniques.

Chemical extraction experiments indicate that more than half of the arsenic and antimony in "noncontaminated" sediments is bound to extractable iron and aluminum compounds. However, in contaminated samples from near the smelter most of the arsenic and antimony are nonextractable and appear bound in rather stable chemical forms. Less than 10% of the arsenic and antimony from both contaminated and "noncontaminated" sediments are associated with easily oxidizable organic matter.

An arsenic budget for Puget Sound indicates that the sediments accumulate less than 30% of the arsenic entering the Sound, and that discharge to the Strait of Juan de Fuca is the major sink for arsenic entering the Sound. The budget also reveals the importance of atmospheric input of arsenic resulting from smokestack emission of the smelter.

The natural mercury concentrations in Puget Sound surface sediments ranged 0.01-0.1 ppm. The maximum values were observed in Bellingham Bay (between 1970-71) near chlor-alkali plant which prior to 1971 discharged significant amounts of mercury to the bay. In contrast to arsenic, chemical extraction experiments indicated that more than 80% of the mercury in both contaminated and "noncontaminated" sediments is associated with easily oxidizable organic matter. Mercury in easily exchangeable positions and that associated with ferromanganese oxides was less than 8% of the total mercury.

In "noncontaminated" sediments, arsenic, antimony, mercury, carbon, and grain size have a good correlation with each other. The association of higher carbon with finer-grained sediments may account for the apparent covariant relationship between arsenic, which is associated with amorphous iron and aluminum oxides, and mercury, which is primarily associated with organic matter.

No elevated chromium, cobalt, iron, and aluminum concentrations were observed that can be attributed to inputs by man.

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Electrical Detection of Airborne Particulates Using Surface Ionization Techniques

Richard L. Myers and Wade L. Fite*
Department of Physics, University of Pittsburgh, Pittsburgh, Pa. 15260

■ A variety of individual aerosol particles can be detected by causing them to impinge onto a heated metal surface where they pyrolyze and transfer surface-ionizable constituents to the surface within times of 10^{-6}–10^{-2} sec, depending on the filament temperature. These surface-ionizable constituents then become ionized and are released from the surface as a burst of ions. For particles of similar composition, the number of ions per pulse is related to the particle size. This technique has been studied and has been applied to the continuous monitoring of submicron urban particulate matter.

Sodium and potassium are the sixth and seventh most abundant elements in the earth's crust and are common impurities in virtually all substances. The atoms of these metals are converted to ions upon striking a heated surface having a sufficiently high work function (*1*). Detection of these ions is commonly used in molecular beam research.

When an aerosol particle less than 10 μ in diameter strikes a heated surface, the time required to heat up to the surface temperature is calculated to be of the order of 0.1–10 μsec, depending on the composition of the particle and its contact with the surface. If in the process of heating, the particle melts, sublimes, decomposes through the breaking of chemical bonds or otherwise pyrolyzes, and if the particle contains sodium, potassium, or other surface-ionizable atoms or molecules, either as a prime constituent or as an impurity, these atoms are released, come into contact with the surface and become surface ionized. The effect is to release a burst of ions that, upon detection, indicates the arrival of a particle at the surface.

This report summarizes some results of investigations about the basic process of pyrolysis plus surface ionization for particulate detection and describes some results of using the technique for particulate detection in urban air.

Fundamental Studies

The apparatus used to study the basic phenomena, shown in Figure 1, consists of a differentially pumped high-vacuum system into which the aerosol to be tested is admitted through a pinhole. Once inside the vacuum system, the particles travel in a straight line to a heated filament. Any ions formed at the filament are focused into a quadrupole mass filter, the output of which is sent into an ion multiplier. The amplified signals are then analyzed electronically for pulse height, shape, and count rate. In each case, the integrating time of the pulse-counting circuitry was kept longer than the duration of the real ion pulses coming from the filament. Under this condition, the measured pulse height is proportional to the total charge delivered by the real ion pulse, while the measured rise time is equal to the duration of the ion pulse. In the following discussions, the "pulse duration" refers to the duration of the real ion pulse, as measured by the rise time of the electronic pulse.

Under the experimental conditions, background ion currents consisting primarily of K^+ (80%) and Na^+ (10%) with a large number of hydrocarbon and metal ions making up the rest of the spectrum, were observed. These ions are formed at the surface by surface ionization of impurities in the surface material and in the residual gas in the vacuum. In the present application of surface ionization, it is not the currents which are troublesome, but rather the fluctuations in the currents which appear to the circuitry as pulses similar to those generated by particulates. Using a filament producing a steady current of 10^6 ions/sec, and a circuit time constant of 20 μsec, the authors found that to limit these background pulses to a count rate of 1/sec requires setting the pulse height discriminator to 700 ions per pulse. Setting the discrimination level to 1000 ions per pulse virtually eliminated the background pulses.

Background pulses of 1000 ions eliminated by discrimination in the circuitry are to be contrasted with pulses from real particles of interest. For example, carbonyl iron powder particles with diameters from 2-4 μ (passed through a vertical elutriator to eliminate clumps) upon striking a heated (1400°C) oxidized tungsten surface, produced pulses of up to 3×10^6 ions per pulse. The ions observed were about 70% K^+, 20% Na^+, with cesium and lithium constituting the remaining 10%. Coal dust, after passing through a 6-stage Anderson impactor specified to remove over 90% of particles larger than 1 μ produced high count rates of pulses in excess of 6×10^6 ions composed about equally of Na^+ and K^+. Cigarette smoke particles, after having been filtered through a 0.2-μ (pore size) millipore filter, produced pulses of mostly K^+ of up to 10^5 ions. Rubidium was conspicuously absent from the major components of the spectrum. It was observed that as the temperature was increased from 900-1400°C the pulse durations decreased from about 10^{-3} to about 10^{-5} sec. Also there is a filament temperature between about 1000° and 1200°C where the pulse height is maximum. Whether the decrease of pulse height at higher temperatures is caused by some change in the work function of the

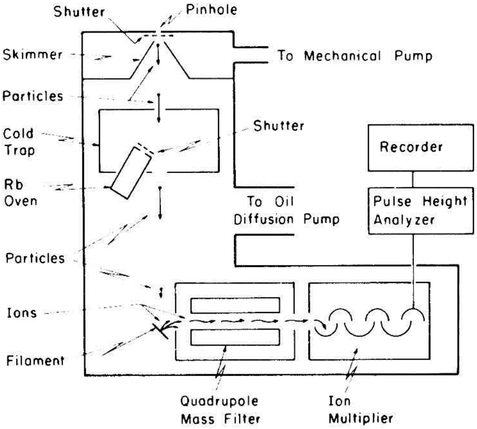

Figure 1. Schematic of basic apparatus for detecting particles using technique of pyrolysis followed by surface ionization

surface or by some specific pyrolysis problem, such as the tendency for a particle to be driven from a very hot surface before pyrolysis is completed, is not known. That such "reflection" of particles, particularly those with diameters in excess of a few microns, does occur is suggested by the observation of the ratios of pulse height to particle size. The relationship which holds for particles less than 1 μ in diameter weakens as the size is increased and the pulse heights become almost independent of particle size above about 10 μ. Thus, although we have found no upper limit on particle size for *detectability*, the method does seem to be limited with regard to *sizing* of particles on the basis of pulse height to a range below a few microns in diameter.

Test particles believed to be less than 0.1 μ in diameter were generated by spraying dilute solutions of alkali and alkali earth salts into dry air and allowing the droplets to evaporate. The principal conclusions reached were that (1) the optimum temperature for the development of a pulse depends on the ionization potential and vapor pressure of the element being ionized, with the required temperature being higher for Na^+ than for K^+, and (2) the efficiency with which alkali atoms within a particle are ionized is of the order of 10% of the efficiency with which the same atoms from an atomic beam are surface ionized. Evidently, for sufficiently small particles, the surface ionizable impurities are fairly efficiently transferred to the hot surface during the pyrolysis process. These observations are in general agreement with the independent research carried out by other investigators (*2*).

Coal dust, iron powder, cigarette smoke and certain other particles were also detectable by the formation of negative ion pulses at the heated surface. In this case the surface used was a thoria-coated iridium filament with the low (2.7 eV) work function conducive to the formation of negative ions. Particles containing appreciable amounts of halogen atoms, NO_3, or CN radical were found to produce pulses of the corresponding ions. In the case of all the naturally occurring particles detected by means of negative ions, the predominant ion formed has been Cl^-. The pulses formed displayed shorter pulse durations and considerably smaller amplitudes than corresponding alkali metal pulses. For example, when the aerosol used was a suspension of CsCl crystals (formed by spraying an aqeuous solution of CsCl into dry air), the pulse duration for the Cl^- pulse was about 3 μsec, as compared to 10 μsec for the Cs^+ pulse, and the amplitude of the Cs^+ pulse was about 10 times greater than the amplitude of the Cl^- pulse. On the other hand, the background signal of negative ions is considerably smaller than the positive ion signals, so that the use of negative ion detection is not without merit.

To increase detectability and extend the range of the method into centimicron particle detection, the introduction of specific impurities onto the particle's surface has been used. A rubidium oven shown in Figure 1 was inserted into the vacuum chamber in such a way that, prior to striking the filament, the particles were made to traverse a crossed beam of rubidium atoms that adhere to the surface of each particle and render it detectable. Rubidium was chosen for this technique because it is absent from the background species, it has the second lowest ionization potential among the elements, and its vapor pressure makes it possible both to produce an intense beam at easily obtained temperatures and to trap that beam once it has crossed the interaction area. Filtered (<0.3 μ) cigarette smoke particles, which were detectable by means of their K^+ ion pulses, but which contain little or no natural Rb, easily produced measurable pulses of Rb^+ upon being subjected to the Rb crossed beam. The pulse heights and noise levels indicate that particles down to a few hundred Angstroms may be detectable.

Applications

When the apparatus was opened to ordinary laboratory air, as opposed to filtered air, a significant increase in the number of positive pulses/sec was noted, indicating that the device shown in Figure 1 is capable of monitoring the level of alkali-containing particles present in ordinary urban air.

A simplified apparatus shown in Figure 2 was constructed, in which the aerosol is drawn through a capillary tube into a region maintained at a vacuum of 1–10 torr. It can be shown that under these conditions particles with diameters larger than about 50 Å will impact with nearly 100% efficiency onto any obstruction. The filaments used here were made of platinum, iridium, and rhodium, and were maintained at temperatures near 1100°C. The ions were collected onto an electrode which was biased several hundred volts negative with respect to the filament. The collector electrode was ac coupled to a pulse-analyzing circuit which rejected background noise and recorded the average number per second of pulses above the noise level. The geometry (the capillary-to-filament distance and the filament thickness and length) was chosen such as to give a pulse count rate of about 100 counts/sec from unfiltered air at a pollution level of about 100 $\mu g/m^3$ as reported by the Allegheny County Air Pollution Control authorities—a moderately clear day in Pittsburgh.

When such air was examined it was found that the

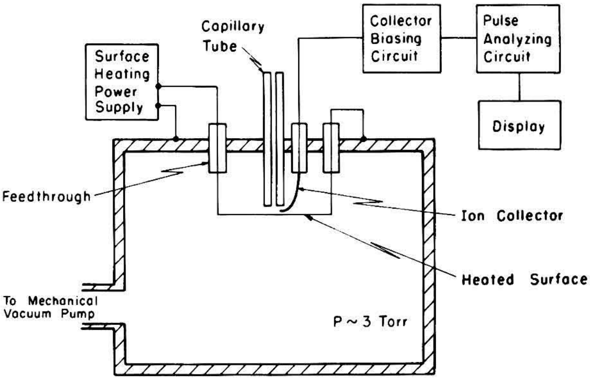

Figure 2. Simplified apparatus for continuous air monitoring

count rate, upon passage of the air through a Nuclepore membrane filter with a pore radius of 1 μ was 30% of the rate using unfiltered air. Calculated transmission for this filter exceeds 30% only for particles in the 0.02–0.1 μ radius range with the maximum size transmitted being about 1 μ. The largest pulses observed had charges of about 4×10^{-12} C, or about 2.5×10^7 ions. This is about 10% of the product of the surface ionization efficiency of free alkali atoms times the number of such atoms at a concentration of 1% (i.e., comparable to the alkali impurity level in coal, soil, and common minerals) in a 1.0-μ particle with a mass density of 1 g/cm^3.

The device described above has been used for 24-hr air sampling in the Oakland section of Pittsburgh. In this case, the particles being sampled were submicron (the air was passed through a 1-μ Nuclepore filter) and, to be detected, were required to contain an appreciable amount of alkali metals (the level of the pulse height discriminator was set high). Under these circumstances, large increases in nighttime particulate level were detected nearly every night, including weekends. The contribution from rush hour traffic was found to be small, perhaps because the sampling device was located in a light traffic area upwind from the main streets, and the percentage of Na and K in particulate auto exhaust is small compared to the percentage in fuel oil emission particulates (*3*) and in coal ash (*4*). The second of these considerations has been somewhat substantiated by the observation that when the level of the pulse-height discriminator is set sufficiently high that the instrument does not respond to auto exhaust (1973 Capri, regular gasoline), the instrument is still highly responsive to submicron (filtered by a 1-μ pore size Nuclepore filter) particles in the smoke from a burning bed of coal.

While gasoline tends to have a low content of alkali metals, it does contain a high content of halides, mostly in the form of additives. By reversing the polarity of the potentials applied to the apparatus, the instrument was made to detect gasoline combustion particulates by negative surface ionization.

Further details of the instrumentation used in these studies are being prepared for publication elsewhere.

Summary

The process of pyrolysis plus surface ionization has been used with many aerosols and seems to respond to every type of particle, provides immediate response to the presence of aerosols, and seems to work best for particles in the submicron range. For sufficiently small particles, pulse height appears to be related to the particle size in a sufficiently simple manner to permit the technique's being used for particle sizing. As a means of detecting particles separated by size by other means, the technique appears quite general. The detection of both positive and negative ions concurrently apparently provides information relative to the source of particulate matter in the atmosphere, and does so in real time.

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Volume Resistivity–Fly Ash Composition Relationship

Roy E. Bickelhaupt
Southern Research Institute, 2000 Ninth Ave. South, Birmingham, Ala. 35205

■ This research was undertaken to establish a relationship between electrical resistivity and chemical composition for fly ash. Commercially produced ashes having a wide variation in chemical composition were used. The ashes were characterized and made into sintered-disk specimens for resistivity and chemical transference experiments. Characterization revealed that the ashes were principally spherically shaped, glassy particles. The results confirmed that volume conduction was controlled by an ionic mechanism in which the alkali metal ions, mainly sodium, served as charge carriers. It was observed that the iron concentration of the ash affected the magnitude of resistivity in an inverse manner. Chemical transference and other ancillary experiments suggested that the presence of iron influenced the number of alkali metal ions capable of migration. Relationships were established between resistivity and specimen porosity, temperature, lithium–sodium concentration, and iron concentration. These relationships were combined to give an expression with which one can predict volume resistivity.

Approximately 30 million tons of fly ash are produced annually in the United States by burning fossil fuels. Electrical resistivity is one of the critical parameters influencing the design and successful operation of electrostatic precipitation devices used to collect the ash. Therefore, a study of this ash property was undertaken.

Although the study involves the entire normal resistivity–temperature range (100–400°C), this paper is restricted to the region in which volume conduction is of primary importance—i.e., $> \sim 225°C$. Volume conduction denotes the transport of electrical charge through the individual fly ash particulates and the multiplicity of contacts. Above 225°C, resistivity is principally governed by the following factors: the amount and chemical constitution of the various microconstituents making up the fly ash, the degree of continuity of the ash layer, the temperature, and the voltage gradient across the ash layer.

It has been previously concluded (*1*) that the volume conduction mechanism is ionic in a manner analogous to that of glass and that the alkali metals, principally sodium, are the charge carriers. This conclusion was reached from the evidence of the proportionality between mass transfer and the quantity of electricity conducted and by the chemical identification of the migrating elements. For fly ashes of limited compositional range, it was shown that resistivity was inversely proportional to the concentration of lithium and sodium.

The research reported herein was designed to verify the preceding statements, expand the scope to include a greater number of ashes so that a wide range of ash composition might be evaluated, and develop an expression capable of a reasonable prediction of volume resistivity based on ash chemistry, temperature, and ash layer porosity. The ability to predict this property would be advantageous with respect to the design and operation of electrostatic precipitators and the forecasting of resistivities for coals located in unopened fields.

Twenty-eight fly ashes representing a broad range of chemical composition were utilized in this research. Ash characterization, resistivity-temperature, specimen porosity, and chemical transference data were acquired. After normalization to a constant temperature and specimen porosity, the resistivity data were interpreted in terms of ash composition. Transference data were used to understand the conduction mechanism and justify the resistivity-ash chemistry relationships.

Procedures

Ash Characterization. All the ashes were subjected to chemical analysis for the determination of the major elements present and loss on ignition. Flame atomic absorption and emission spectrophotometry, colorimetric, and turbidimetric techniques were employed. The chemical analyses were reported as oxides in weight percent. For use in this research, the weight percent values, exclusive of loss on ignition, were totaled and normalized to 100%. The weight percentages were then converted to molecular fractions from which the molecular percent oxides and atomic percent cations could be determined.

Many of the ashes were characterized by methods such as: optical and electron microscopy, X-ray diffraction, electron microprobe analyzer, helium pycnometer, and Bahco size analyzer. In all cases, commercially produced equipment and either manufacturer's suggested procedures or otherwise standard techniques were employed.

Resistivity and Transference Experiments. Procedures used to conduct these experiments have been recorded in detail elsewhere (*2*). The following comments will briefly describe the techniques.

By use of methods common to ceramic technology, self-supporting disks were made from each ash by pressing and sintering. Noble metal electrodes were affixed to the opposing disk faces. With the specimen clamped between noble metal contacts, resistivity was determined by measuring current flow under a dc potential of about 500 V/cm. Current data were taken approximately every 30°C as the specimen cooled from about 450° to 200°C. Resistivity was calculated from the measured current, known voltage, and specimen and electrode geometry.

Specimens used in the transference experiments were prepared as stated above. In this case, three disk specimens were positioned in axial alignment with disk faces contiguous. Electrodes were affixed only on those faces in contact with the positive and negative contactors and leads. After the furnace had equilibrated at about 600°C, the dc voltage (1000 V/cm) was applied and the current-time relationship was recorded for approximately 200 hr.

The current-time plot was graphically integrated and converted to coulombs of electricity. This measured quantity of electricity, the measured weight change of the specimens, and pre- and post-test chemical analyses were used to illustrate a mass transfer and to qualitatively identify the charge carriers.

Results and Discussion

Ash Characterization. The 28 commercially produced fly ashes used were about equally divided with respect to having been produced from coals of the eastern and western parts of the country. Several ashes from each geographic section were selected for characterization based on variations in chemical analyses.

Optical and electron microscopy revealed that the ash particles were principally spherical in shape over the entire size spectrum and that each ash possessed a wide variation in color and ability to transmit light. A wide variation in helium pycnometer density, 2.1 to 3.0 g/cc, was found for as-received ashes. This variation can be related to such items as ash chemistry, amounts of unburned carbon, and cenospheres. Although the mass-median diameter varied from about 7–20 μ, little significance can be implied, because the source history of the ashes was not known in all cases.

The heterogeneity of fly ash is obvious when microscopically examined. One can note unburned carbon particles, the predominance of the spherically shaped material, a few particles having crystalline morphology, and bits of extraneous debris. If the spherical particles are examined by electron microprobe analysis, it is found that chemical heterogeneity can persist in particles of micron size.

X-ray diffraction patterns for the 12 ashes examined in this manner produced a pair of weak halos in the low two-theta region with a number of diffraction peaks superimposed on a somewhat noisy background radiation. As one might expect, these patterns were not of the quality and clarity produced by a mixture of two or three relatively pure, totally crystalline compounds. For the western ashes, the peaks were produced by the compounds: quartz, mullite, a calcium silicate, and, in some cases, calcium sulfate. Compounds identified for eastern ashes included: quartz, mullite, an iron oxide, and an iron-alumina-silicate. Based on the origin, the typical chemical analyses and the thermal history of fly ash, the identified compounds were expected.

However, it was interesting that the intensities of the diffraction peaks were quite low. In each pattern the peak for the principal line for quartz (SiO_2) was one of the most intense lines. With the use of this line, two of the ashes were subjected to quantitative analysis for quartz content by the internal standard, X-ray diffraction technique. It was learned that both of these contained less than 4 wt % of this compound. From this it can be inferred that even the most prevalent crystalline compound in the fly ash represented a rather minor portion of the overall ash composition, and it would seem that the total crystalline material might be typically about 10 wt %. Knowledge of the ash chemistry, the low percentage of crystalline compounds detected, the general character of the X-ray patterns, and the thermal history of fly ash suggests that the major portion of the ash is an amorphous substance. Assuming that 80% of a loss on ignition value is due to unburned carbon, two of the 28 ashes had 5–8% carbon, while the remainder contained less than 5%. When all the above factors are considered, one concludes that the major microconstituent in the fly ash is a glassy solid.

A typical fly ash used in this research can be described as a collection of heterogeneous particles that are principally spherical in shape and submicron to 1 mm in size

Table I. Chemical Analyses of Fly Ashes

Ash no.	Expressed in weight percent as oxides											
	Li_2O	Na_2O	K_2O	MgO	CaO	Fe_2O_3	Al_2O_3	SiO_2	TiO_2	P_2O_5	SO_3[a]	LOI
1	0.04	0.09	0.30	5.40	21.50	4.30	22.80	40.15	1.30	0.34	1.70	0.33
2	0.01	0.24	0.89	3.30	23.50	5.53	21.20	40.50	2.13	0.54	1.83	0.20
3	0.01	0.25	0.89	1.88	11.10	3.71	23.60	55.60	1.56	0.14	0.32	0.74
4	0.01	0.34	0.77	1.60	11.60	3.60	25.30	56.80	0.83	0.17	0.17	0.60
5	0.01	0.32	0.90	1.80	12.70	3.90	25.80	55.00	0.89	0.17	0.32	0.65
6	0.01	0.53	1.10	1.70	12.20	4.20	25.10	55.10	0.83	0.18	0.24	0.60
7	0.02	1.30	0.72	2.50	8.60	4.65	18.20	59.00	2.20	0.19	1.05	0.45
8	0.02	1.07	0.70	2.23	8.30	4.66	17.70	61.00	1.53	0.16	0.77	0.50
9	0.02	1.77	1.13	1.93	6.36	4.61	24.60	53.70	1.49	1.06	0.79	1.49
10	0.01	3.10	0.80	0.90	10.40	3.40	28.20	52.00	0.88	0.18	0.26	0.45
11	0.01	2.10	1.00	0.99	12.30	4.60	26.50	52.00	0.93	0.21	0.36	0.40
12	0.01	2.40	1.00	0.93	13.60	4.80	26.20	49.20	0.93	0.24	0.46	0.45
13	0.02	0.38	2.36	2.59	11.41	6.03	19.64	55.29	0.95	0.60	0.58	0.35
14	0.01	1.47	0.68	1.73	7.33	5.33	23.10	53.10	4.17	0.90	1.11	0.44
15	0.01	1.84	0.20	12.75	31.00	11.20	14.80	22.00	0.60	0.39	4.80	0.41
16	0.05	0.48	2.75	0.88	0.87	5.50	27.80	50.45	1.85	0.23	0.70	7.70
17	0.04	0.49	3.12	1.09	2.48	13.24	26.40	50.70	1.62	0.28	0.57	1.00
18	0.05	0.32	2.30	0.98	4.60	23.70	21.20	42.70	1.40	0.34	0.69	5.50
19	0.02	0.23	2.80	0.86	2.20	23.00	21.00	47.70	1.80	0.52	1.30	2.10
20	0.02	0.51	2.80	0.93	0.26	17.90	21.90	51.00	1.40	0.33	0.96	1.80
21	0.01	0.35	2.36	1.66	3.72	16.10	17.80	43.30	1.27	0.36	0.64	10.30
22	0.04	0.33	3.88	1.57	0.77	10.01	27.50	51.40	1.79	0.32	0.37	1.50
23	0.03	0.38	3.34	1.29	1.04	9.70	25.90	49.90	1.98	0.32	0.42	4.40
24	0.07	0.40	3.10	1.20	1.40	8.80	29.00	52.40	1.70	0.40	0.29	3.20
25	0.05	0.16	2.60	0.93	0.87	8.40	31.00	55.10	2.30	0.36	0.23	1.40
26	0.04	0.51	3.80	1.30	0.68	4.90	30.20	53.00	2.00	0.17	0.36	2.50
27	0.05	1.55	2.80	1.15	2.50	3.85	25.00	56.75	1.55	0.28	1.12	1.70
28	0.06	0.42	3.70	1.30	1.10	9.90	30.30	52.40	1.70	0.51	0.45	1.30

[a] Total sulfur.

with a mass-median diameter of 15 μ, having a helium pycnometer density of 2.4 g/cc, and containing 80-90% glassy solids with the balance being unburned carbon and crystalline compounds.

All the ashes used in this research were chemically analyzed for the major elements. These data expressed in weight percent as oxides are shown in Table I. For reference, ashes 1-15 came from western coals, while ashes 16-28 were produced from eastern coals. The ashes were produced mainly from bituminous and sub-bituminous coals but also from lignite, anthracite, and coal prepared for metallurgical use. It is believed that the ash compositional ranges were sufficiently broad to meet the research objectives.

Resistivity Data. Resistivity data were obtained in the temperature range of 200-450°C. Typical results are shown graphically in Figure 1 with resistivity plotted on a log-scale ordinate vs. the reciprocal of absolute temperature. For a given temperature, about a three order of magnitude range in resistivity was encountered for the 28 ashes evaluated.

The linear curves in Figure 1 indicate the data can be interpreted in terms on an Arrhenius equation, in logarithmic form,

$$\log \rho = \log \rho_0 + [(\theta/k) \log e](1/T) \qquad (1)$$

where

ρ = resistivity
ρ_0 = a complex material parameter including the number of mobile charge carriers
θ = experimental activation energy
k = Boltzmann's constant
T = absolute temperature

The experimental activation energy (θ) is proportional to the slope of the curves and is between 1.0 and 1.1 eV for all the ashes. This suggests that a similar conduction mechanism prevails for each ash. An average value of 1.03 eV was used to establish an equation for predicting resistivity from ash chemistry and temperature. To develop the relationship between resistivity and certain chemical parameters, the resistivity at the reciprocal temperature of $1000/T = 1.6$ was used.

Intuitively, one would expect the volume conduction process to be influenced by the amount of specimen porosity. This was found to be true. When resistivity was

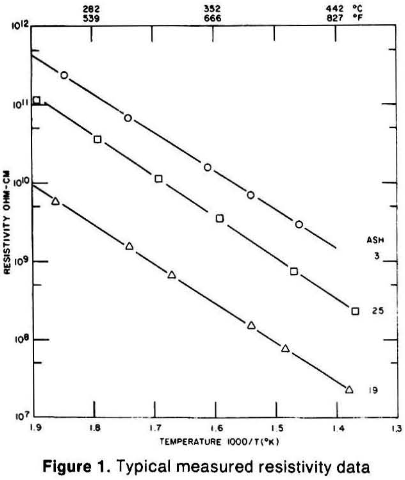

Figure 1. Typical measured resistivity data

determined for several ashes fabricated to two levels of porosity, the higher porosity produced greater resistivity. Dalmon and Tidy (*3*), as well as others, have also observed this effect.

An empirical expression was developed to correct the measured resistivity values to a constant porosity. By use of the initial approximations of the curves relating resistivity to the critical chemical concentrations, the measured resistivity value for each ash was normalized to a constant chemical concentration. The normalized resistivity value for each ash was then plotted against the porosity of the respective ash specimen. The percent specimen porosity was calculated from the measured bulk volume and the determined helium pycnometer volume as follows:

$$\%P = \frac{V_{\text{bulk}} - V_{\text{He Pyc}}}{V_{\text{bulk}}} \times 100 \tag{2}$$

The plot of chemically normalized resistivity data vs. porosity was subjected to a linear regression analysis from which the following relationship was generated:

$$\log \rho_c = \log \rho_m + S(P_c - P_m) \tag{3}$$

where

ρ_c = resistivity corrected to porosity P_c
ρ_m = resistivity measured at porosity P_m
S = $\Delta \log \rho / \Delta \% P = 0.04$

Porosity for the 28 test specimens ranged from 31–50%. For subsequent use, the measured resistivity data taken at $1000/T(°\text{K}) = 1.6$ from curves such as those shown in Figure 1 were corrected to a constant porosity of 40%. This level of porosity was selected because it represented the average porosity and necessitated a minimum correction.

Resistivity–Ash Chemistry Correlation. The resistivity data were initially examined by testing for the inverse proportionality between resistivity and the combined concentrations of lithium and sodium. The measured resistivity at $1000/T(°\text{K}) = 1.6$ was corrected to 40% porosity using Equation 3 and plotted on log-log paper vs. the atomic percentage of lithium plus sodium for the respective ash. Using underlined ash designation numbers for the eastern ashes, the results are shown in Figure 2. Although the data produce the expected negative slope, the amount of scatter does not suggest a very good correlation. To verify the results of Reference *1*, a linear regression analysis was made using only those data points representing western ashes containing <1.0 atomic percent iron. These data points were selected to conform with the chemistry of the ashes used in the earlier work. The curve constructed in Figure 2 with a slope of −1.84 is the result of the regression analysis. The coefficient of correlation between the calculated curve and the data points used was 0.98, and the slope was within 5% of that previously determined with similar ashes.

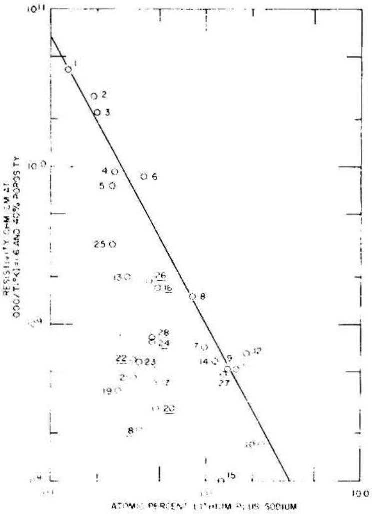

Figure 2. Relationship between resistivity and lithium plus sodium concentration

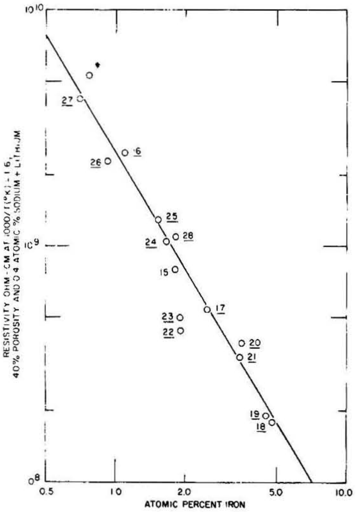

Figure 3. Relationship between resistivity and iron concentration

These results substantiate the conclusion that resistivity is inversely proportional to the concentration of lithium and sodium for ashes of generally similar composition. It is also apparent from these data that some other factor influences the resistivity. A large number of the data points lie below the constructed curve in Figure 2. Inspection of the resistivity and chemical analysis data suggests that the iron concentration affects resistivity.

The effect of iron was evaluated by examining the ash resistivities normalized to a constant lithium–sodium concentration as a function of iron concentration. Resistivity values for all ashes having an iron concentration >1.0 atom % were graphically normalized to 0.4 atom % sodium plus lithium by drawing a line through the specific data point parallel to the constructed curve in Figure 2 and reading the resistivity at the point where this line intersected the 0.4% ordinate. Figure 3 shows the data acquired in this manner plotted against atomic percent iron on a log-log scale. The data point marked (*) represents the average resistivity and iron concentration for all the western ashes containing <1.0 atom % iron. A linear regression analysis of all the data points except 22 and 23 yielded the line constructed in Figure 3. This line has a slope of −1.65 and a coefficient of correlation with the data points used of 0.99. Figure 3 suggests that the volume resistivity of fly ash is also a function of iron concentration and empirically explains the scatter of data shown in Figure 2. The similarity of the magnitude of the slopes of the curves in Figures 2 and 3 shows that resistivity is only slightly less sensitive to iron concentration than it is to lithium–sodium concentration.

When one normalizes the resistivity data to constant temperature, porosity, and concentrations of iron, lithium and sodium, the 28 ashes have a constant resistivity value ±25%. Inspection of the resistivity and chemical analysis data does not suggest an additional factor with which one might explain the ±25% deviation in resistivity. It is possible that this variation is due to unknown physical and chemical inequities associated with the inherent character of the material being studied or results from inadvertent experimental error.

Previously it has been stated that the role of lithium and sodium in the volume conduction of fly ash was one of supplying mobile charge carriers to the glassy portion of the ash. One therefore would expect the resistivity to be inversely proportional to the concentration of these elements. Now it has been observed that iron concentration has a similar relationship to resistivity. Both from the fundamental viewpoint as well as the pragmatic with respect to ash conditioning and the prediction of resistivity data, it was desirable to explore the role of iron.

Role of Iron. Background. Several investigators have mentioned the effect of iron with regard to fly ash resistivity. Shale et al. (*4*) experienced little difference in resistivity between two ashes having significantly different levels of iron. However, in this comparison, the ash having the lower iron content contained about twice as much Na_2O as the other ash. This, coupled with the absence of information regarding lithium content and specimen porosity, makes comment impossible. A regression analysis (*5*) of ash resistivity vs. iron concentration for 38 low-sulfur western coals suggested that resistivity increases with increased iron concentration. The coefficient of correlation for these data was too low to consider the data meaningful. Without normalization of data for other parameters of influence, the effect of iron can be masked.

Dalmon and Raask (*6*) observed a decrease in resistivity of accessory coal minerals that contained iron and sodium and were subjected to fusion at high temperatures. Utilizing synthetic coal slags, Frederikse and Hosler (*7*) showed a large decrease in resistivity with increase in iron content at a given elevated temperature and oxygen partial pressure. They attribute the lower resistivity of these slags to electronic conduction.

In general, iron content is held to a minimum in commercial glasses and other ceramics designed to have electrical insulative properties since this element decreases resistivity. Little work has been done with reference to small quantities of iron in glass since the element also has a great effect on optical character. Morey (*8*) mentions some early research that showed an initial increase followed by a dramatic decrease in surface resistivity as the iron content was increased in a simple sodium silicate glass. Considerable literature (*9–11*) is available showing the effect of iron in producing semiconducting glasses. The low resistivity is associated with electronic conduction. These glasses, however, are oxide glasses containing no silica, chalcogenide glasses, or inverted silicate glasses that are unlike the glass one would probably find in fly ash.

From the foregoing, it would seem there is mixed evidence regarding the effect of iron on fly ash resistivity. With respect to silicate glasses, the decrease in resistivity with increase in or introduction of iron is associated with electronic conduction in invert glasses.

Several hypotheses can be advanced that would explain the relationship illustrated in Figure 3. First, higher iron concentration reduces the fusion temperature of an ash and therefore, for a sintered disk-type resistivity specimen, could promote enhanced particle to particle bonding. Second, with sufficient concentration and in a particular state of oxidation, the iron could add an electronic component to the conduction process thereby lowering resistivity. Third, the iron may affect the amorphous phase of the fly ash so that the effective concentration, the mobility, or the type of alkali metal serving as a charge carrier was affected. The following observations and experiments are discussed in an attempt to clarify the role of iron in the volume conduction process for fly ash.

Transference Experiments. Transference experiments were conducted on four ashes (Nos. 19, 20, 22 and 26) to evaluate certain facets of the aforementioned hypotheses. These ashes contained a relatively uniform concentration of alkali metals and represented the total range of iron concentration encountered. The experimental conditions and the character of the materials investigated preclude the extraction of unequivocal data. These limitations were discussed in Reference *1*. The data are used only for the qualitative understanding of the conduction process.

Gravimetric data for the transference experiments are shown in Figure 4. In this figure, the mass transferred out of the ash disk adjacent to the positive electrode toward the negative electrode is plotted against the quantity of electricity passed during the experiment. The lines labeled with the names of alkali metals represent Faraday's law. For example, if conduction were entirely ionic and potassium were the only charge carrier, one would expect a weight loss of about 50 mg for the passage of 120 C of electricity.

The open circles represent the experimental data points. The data for ashes 3 and 10 were acquired at an earlier date for ashes of the lowest iron level. Figure 4 strongly suggests that the electricity passed is accounted for by a mass transfer and that sodium is the principal charge carrier. The only other way in which the data points could occur near the sodium line would be due to some fortuitous situation whereby charge carriers both heavier and lighter than sodium ions participated to yield an average weight change equivalent to that of sodium.

The above is not meant to imply that sodium was the exclusive carrier. The migration of lithium was obvious; however, quantitatively this represents a small contribution. Also, the migration of potassium can be detected with the support of microprobe analysis; however, it, too, amounts to a small quantitative contribution. Since the amount of potassium migrating is extremely small in comparison to the relatively large concentration of this element in the ash, it is excluded from resistivity-ash chemistry correlations.

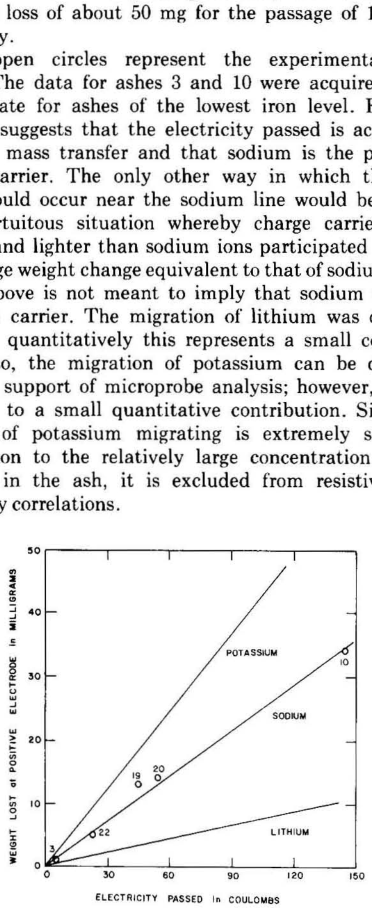

Figure 4. Gravimetric data for transference experiments

Table II. Transference Experiments, Chemical Analyses of Specimens in Weight Percent

Ash	Oxide	Disk contiguous to positive electrode	Baseline composition	Disk contiguous to negative electrode
19	Li_2O	0.013	0.019	0.027
	Na_2O	—	0.29	0.53
	K_2O	2.9	3.1	3.2
	Fe_2O_3	21.1	21.6	21.0
20	Li_2O	—	0.024	0.041
	Na_2O	—	0.45	0.80
	K_2O	—	2.9	2.9
	Fe_2O_3	—	16.8	16.6
22	Li_2O	0.03	0.04	0.05
	Na_2O	0.29	0.39	0.48
	K_2O	3.8	4.1	4.0
	Fe_2O_3	10.0	10.2	10.2
26	Li_2O	0.030	0.04	0.049
	Na_2O	0.40	0.48	0.56
	K_2O	3.9	3.9	4.0
	Fe_2O_3	4.8	4.9	4.9

In Table II, the results of the chemical analyses for the transference experiments are given. The data show a trend similar to that experienced previously for transference tests on low iron specimens and that these data complement or support the gravimetric data expressed in Figure 4. For ashes containing from 5–22% wt % iron, only the migration of sodium and lithium from the positive to the negative electrode can be unquestionably observed. The small variations in potassium and iron concentrations in Table II are thought to be within the data error for the technique of analysis and the selection of random samples. From this information, it was concluded that the iron does not act as an ionic carrier, and its presence in increased amounts does not induce an increased participation by potassium.

In carefully examining the data in Table II, it was observed that the percentage of lithium and sodium that had migrated, relative to the amounts initially present, increased with increasing iron concentration. For a constant amount of electricity passed in each test, the percent increase in sodium and lithium content at the negative electrode over that contained initially by the ash was computed as "relative effectiveness." It is suggested that this dimensionless parameter represents the ratio of mobile to total lithium and sodium ions. These values plotted against the iron concentrations for the four ashes studied gave the result shown in Figure 5. The increase in the "relative effectiveness" with increasing iron concentration suggests that the role of iron is indirect in that it seemingly enhances the participation of lithium and sodium in the conduction process. A possible explanation is that an increasing iron concentration alters the amorphous structure of the glassy ash allowing the migration of a greater percentage of the total available metal ions.

Miscellaneous Observations and Ancillary Experiments. Although the transference experiments suggest that the role of iron is not related to an electronic contribution to the conduction process, this point was additionally considered. It has been observed that the experimental activation energy for conduction has varied little among ashes. If the high-iron ashes imparted an electronic contribution to the total conduction process, one might expect a change in activation energy. Also, it has been noted that the current decreases with time for a given voltage potential using blocking electrodes. If there were an electronic conduction mechanism, the polarization effect should not be apparent.

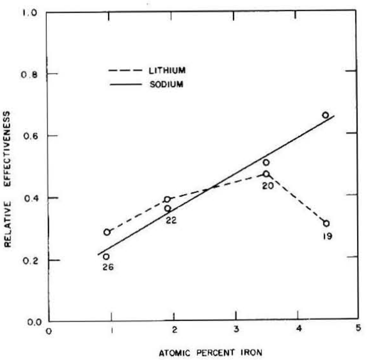

Figure 5. Relative effectiveness of lithium and sodium as charge carriers as a function of iron concentration

Two additional experiments were run regarding the potential electronic contribution of iron. First, ash 22 was repeatedly passed through a magnetic separator prior to fabricating a resistivity specimen. The iron concentration was reduced by 50% without significantly altering the resistivity. It is believed that the iron removed was that fraction which most likely would have provided an electronic contribution, while that which remained was principally diluted in the glassy ash. The observation that the removal of the magnetic fraction did not increase the resistivity indicates the absence of electronic conduction. Second, solid electrolyte experiments (*12*) were conducted on sintered specimens of ashes 10 and 19 using a calcium stabilized zirconia as a standard. Both ashes produced sufficient emf so that the consideration of an electronic contribution to the overall conduction process for the ashes could be dismissed.

Ashes containing high-iron concentrations might develop better particle to particle contacts, thereby lowering the resistivity of sintered disk specimens. To examine this point, ashes having high- and low-iron concentrations were used to measure resistivity in the temperature range of 200–450°C using the ASME PTC 28 apparatus (*13*). These tests utilizing loose ash produced resistivities identical to their respective sintered disk counterparts when the sintered disk data were corrected to the same porosity as the PTC 28 specimens. These observations indicate the sinterability of the various ashes does not bias the resistivity data when sintered disk specimens are prepared at a high level of porosity without specimen shrinkage.

Summary. An unequivocal interpretation of the role of iron in the fly ash conduction process is not available. However, it is reasonably certain that the pronounced influence of the iron concentration shown in Figure 3 is neither related to an electronic contribution to the conduction process nor is it an aberration due to the particle to particle bonding in the sintered disk resistivity specimen. The evidence obtained indicates that the presence of increased iron concentration does not alter the previously identified mechanism for volume conduction—i.e., the ionic migration of the alkali metals. It is conceivable that the iron concentration associated with the principal fraction of the ash, the glassy phase, alters the structure of the glass so that a greater number of the total alkali metal ions present are capable of migration. Although no direct proof of this rationalization is available, the concept is compatible with the findings: only obvious evidence of lithium and sodium migration has been found, no electronic component to the conduction process has been shown, and very little variation in conduction activation energy has been observed.

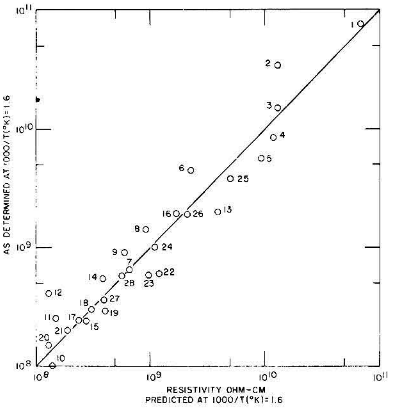

Figure 6. Correlation between as determined and predicted resistivities

Prediction of Volume Resistivity

Several factors including ash chemistry, amount of unburned carbon, temperature, field strength, and porosity control the magnitude of volume resistivity. The type of specimens used in this research precluded the consideration of the influence of unburned carbon. However, almost all of the ashes used contained less than 5% carbon in the as-received condition. Shale (*4*) has indicated that the effect on fly ash resistivity is minor when the carbon content is under 8%. The effect of field strength has not been considered. Although it has been observed that resistivity decreases with increasing field strength, sufficient high-temperature data are not available to accurately relate volume resistivity to field strength. Therefore, the expression for predicting volume resistivity given below is related to a nominal field strength of 500 V/cm, the value used in this research.

Equations for the constructed lines in Figures 2 and 3 were determined to express resistivity as a function of the lithium-sodium content and the iron content, respectively. The Arrhenius expression, Equation 1, was used to introduce the effect of temperature. By use of a series of substitutions, detailed elsewhere (*2*), the following expression was developed to predict volume resistivity as a function of temperature and the atomic percentages of lithium, sodium and iron:

$$\log \rho = [0.3601 - 1.65(\log a/o\ \text{Fe}) - 1.84(\log a/o\ \text{Li} + \text{Na})] + 5.193 \times 10^{3}\ {}^{\circ}\text{K} \times (1/T)^{\circ}\text{K}^{-1} \quad (4)$$

Equation 4 yields a predicted volume resistivity for an ash specimen porosity of 40%. If the value of log ρ given in Equation 4 is substituted into Equation 3 for log ρ_m and P_m assigned the value of 40%, the predicted resistivity can be calculated for other porosities.

A computer program has been written to utilize these expressions to predict volume resistivity for ashes containing low amounts of carbon at a field strength of 500 V/cm. The program accepts the chemical analysis of the ash in weight percent as oxides and calculates resistivity for three temperatures and five levels of porosity. By use of this program, the resistivities of the 28 ashes employed in this research were calculated based on the chemical analyses shown in Table I, the measured porosity of each test specimen, and a temperature of 625°K (~666°F). Figure 6 shows the correlation between the predicted values and the measured values taken from curves such as those shown in Figure 1. For an initial attempt to predict volume resistivity, the correlation seems reasonably good.

Whether predicted volume resistivity values will duplicate or at least correlate with field measurements or laboratory values utilizing other experimental techniques remains to be determined. It would seem that at present the predicted resistivity values might be useful on a relative basis for comparing ashes from various coal suppliers.

Conclusions

The characterization of ashes representing a wide variety of coals suggests that 80-90% of the fly ash is a glassy solid. It has been rationalized that volume conduction takes place through a continuous matrix of these glassy particles.

It has been verified that volume conduction is an ionic mechanism involving the alkali metal ions, principally sodium, as charge carriers. Experimental data show an inverse proportionality between resistivity and iron concentration for a given level of lithium and sodium. In the absence of an electronic contribution to the conduction process, it has been suggested that the iron concentration associated with the glassy solids alters the structure of this phase to permit a greater percentage of the total number of sodium and lithium ions to migrate.

An expression has been developed to predict volume resistivity for fly ashes produced from the efficient burning of coals as a function of ash chemistry, temperature and porosity for one level of field strength.

Acknowledgments

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Effect of Carbon Monoxide on Atmospheric Photooxidation of Nitric Oxide–Hydrocarbon Mixtures

William A. Glasson

Environmental Science Department, General Motors Research Laboratories, Warren, Mich. 48090

■ This study was undertaken to assess the importance of CO in photochemical smog formation. The effect of CO concentrations up to 424 ppm on the photooxidation of an ethylene–NO mixture was studied in a long-path infrared cell. The NO_2 rate, O_3 rate, and O_3 yield increased with CO concentration, while ethylene oxidation was unaffected. The effect of CO on the photooxidation of mixtures of NO with various hydrocarbons was also studied. Of the six hydrocarbons studied, CO had effects in the presence of ethylene, isooctane, and mesitylene. The effect of CO concentration on the photooxidation of a simulated atmospheric hydrocarbon mixture was studied. The results were consistent with the conclusion that the effect of CO, at ≤ 35 ppm, on photochemical smog formation would be minimal.

Recent investigations have implicated the involvement of carbon monoxide in the chain-photooxidation of nitric oxide (*1*) and in the photooxidation of nitric oxide–hydrocarbon mixtures (*1–5*). These investigations concentrated on specific aspects of the photooxidation process—e.g., such items as nitric oxide oxidation and oxidant formation. To further characterize the effect of carbon monoxide on the overall photochemical smog formation process, irradiations of various hydrocarbon–nitric oxide–carbon monoxide systems were studied. Three series of experiments were performed. In the first series, the photooxidation of fixed concentrations of ethylene and nitric oxide in air was studied as a function of carbon monoxide concentration. In the second series, the irradiation of fixed concentrations of hydrocarbon, nitric oxide, and nitrogen dioxide in air was studied, with and without carbon monoxide, using mesitylene, 1,3-butadiene, propylene, *m*-xylene, and isooctane. In the third series, the photooxidation of a hydrocarbon mixture was studied as a function of the carbon monoxide concentration. The composition of the mixture was chosen to simulate that of a typical Los Angeles atmospheric sample.

Experimental

Apparatus. Analyses were performed with a 3-meter base-path, multiple-reflection cell used in conjunction with a modified Perkin-Elmer Model 21 infrared spectrophotometer. Analyses were made with a path length of 120 meters. Irradiation was supplied by a number of black-light fluorescent bulbs mounted in the long-path cell which also served as the reaction vessel. Details of the cell and the irradiation system are given elsewhere (*6*).

Chemicals. Ethylene, propylene, 1,3-butadiene, ethane, propane, *n*-butane, benzene, and toluene were Phillips Research grade materials. Mesitylene, isooctane, and *m*-xylene were API standard samples. Nitric oxide (Matheson) was purified by passage through a bed of Ascarite followed by repeated bulb-to-bulb distillations. Nitrogen dioxide was prepared, as needed, by the thermal oxidation of nitric oxide (*7*). Carbon monoxide (Matheson, CP) was purified by passage through a charcoal bed. The presence of iron pentacarbonyl in carbon monoxide cylinders has been shown to be a potential problem because of its high photolytic activity (*5*). Infrared analysis of carbon monoxide–nitrogen mixtures indicated no $Fe(CO)_5$ within the limits of detection (2 ppb). Airco nitrogen and oxygen were used without further purification.

Procedure. The experimental procedures for NO, NO_2, and hydrocarbons have been described (*8*). Carbon monoxide was added to the long-path cell from a vacuum system. The following conditions were used for all experiments in this study: 155 mm Hg oxygen; 605 mm Hg nitrogen; and temperature of (26 ± 1)°C. The nitrogen-oxygen mixtures used in this study contained no more than 100 ppm water, according to the manufacturer's specifications.

The hydrocarbon mixtures were prepared by adding known amounts of gas and liquid mixtures to the long-path cell. The gas mixture, prepared manometrically and stored on the vacuum line, contained ethane, propane, *n*-butane, ethylene, and propylene. The liquid mixture, prepared volumetrically and stored at 0°C, contained benzene, toluene, and *m*-xylene. The liquid mixture was added to the cell by injecting the sample into a stainless steel, electrically heated manifold, then opening the manifold to the cell, and flushing the sample into the cell with nitrogen.

The light intensity, measured by photolyzing low concentrations of nitrogen dioxide in nitrogen, is expressed as the first-order rate constant for photolysis, k_D. The light intensity for all of the experiments was $k_D = 0.28\ \text{min}^{-1}$.

The formation of nitrogen dioxide was followed by measuring the absorption at 6.15 μm. A portion of the spectrum containing this wavelength was scanned repeatedly throughout the nitric oxide oxidation period. Water vapor absorption was monitored at 6.4 or 6.8 μm, and the absorption at 6.15 μm corrected for any changes in the water absorption at that wavelength. The nitrogen dioxide formation rate is expressed as the average rate to the half time ($t_{1/2}$)—i.e.,

$$\text{Average } NO_2 \text{ formation rate} = \frac{(NO)_0}{2t_{1/2}} \qquad (1)$$

where $(NO)_0$ is the initial nitric oxide concentration and $t_{1/2}$ is the time necessary to convert one half of this concentration to nitrogen dioxide. The rate is given in the units ppb (v/v) per min (ppb min^{-1}).

After the peak nitrogen dioxide concentration had been attained, wider spectral ranges were monitored for reactant disappearance and product formation data. Products and reactants measured and the wavelengths used were: ethylene, 10.6 μm; propylene, 11.0 μm; 1,3-butadiene, 11.0 μm; *m*-xylene, 13.0 μm; mesitylene, 12.0 μm; PAN, 8.6 μm; ozone, 9.5 μm; formaldehyde, 3.6 μm; and acrolein, 8.7 μm.

Results and Discussion

Effect of CO Concentration on Ethylene–NO Photooxidation. The effect of CO on photochemical smog formation was initially evaluated with the ethylene–NO system. Photooxidations of 2.0 ppm ethylene and 1.0 ppm

Table I. Effect of CO Concentration on Photooxidation of C_2H_4–NO Mixtures[a]

Initial concn			Product results			
C_2H_4, ppm	NO, ppm	CO, ppm	NO_2 rate,[b] ppb min^{-1}	C_2H_4 reacted,[c] (%)	Yield, ppm[c] O_3	Yield, ppm[c] HCHO
2.05	1.02	0.0	4.6	32	0.06	0.68
2.01	1.01	46	5.3	35	0.19	0.68
2.01	1.01	92	6.8	35	0.26	0.68
2.01	1.01	183	7.9	36	0.48	0.72
2.01	1.01	424	10.2	31	0.60	0.64

[a] The experimental conditions were: 155 mm Hg oxygen, 605 mm Hg nitrogen, $k_D = 0.28\ min^{-1}$, and temperature = 26°C. [b] Average rate of NO_2 formation (see Experimental Section for definition). [c] After 300 min of irradiation.

NO, in air, were carried out at CO concentrations from 0-424 ppm. The NO_2 formation rate, ethylene conversion, and ozone and formaldehyde yields, after 300 min irradiation, were measured. The results are given in Table I.

The addition of CO significantly increased the NO_2 rate and the O_3 yield. Dodge and Bufalini (2) recently found that CO increases the NO_2 rate, but that the O_3 yield was unaffected by the addition of up to 2000 ppm of CO. The O_3 yield data, from Table I, are plotted as a function of the initial CO concentration in Figure 1. The O_3 yield increases as the CO concentration increases at the lower CO concentrations but at the higher CO concentrations, the O_3 yield appears to be leveling off. This observation can be correlated with the increased NO_2 rate and hence the resulting decrease in the time necessary to attain the maximum NO_2 concentration.

These experiments were all terminated after 300 min irradiation, at which time the maximum O_3 yield had not been attained. An increased NO_2 rate results in a decreased time to reach the maximum NO_2 concentration and hence permits more time for the development of ozone. Thus, an increase in the NO_2 rate due to carbon monoxide addition will result in increased O_3 yields. This explanation is similar to one suggested by Westberg and co-workers (5) for their work on the isobutene-NO-CO system. The apparent leveling off of the O_3 yield at high CO concentrations is indicative of the attainment of the O_3 yield, which would have been reached, if the reaction had been allowed to proceed for a sufficiently long time.

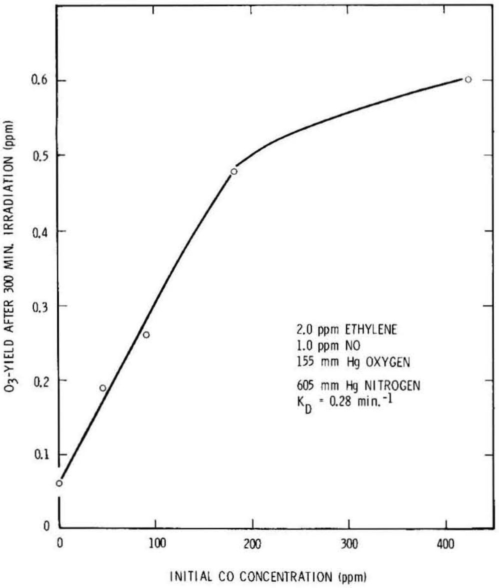

Figure 1. Effect of CO on ozone yield from ethylene-NO photooxidation

To verify this point, the photooxidation of 2.0 ppm of ethylene, 1.0 ppm of nitric oxide, and 0 ppm of carbon monoxide in air was followed for an irradiation period of 570 min. At the end of this time, 0.61 ppm of ozone had been formed. Reference to Figure 1 shows that this O_3 yield is in good agreement with that obtained in 300 min from the corresponding system containing 424 ppm of carbon monoxide. This agreement may be somewhat fortuitous in that small losses of O_3 would be expected in the run without CO due to the lengthy irradiation period.

The photooxidation of ethylene was unaffected by the addition of CO, as evidenced by the ethylene reacted and the formaldehyde yield after 300 min irradiation, as shown in Table I. It is difficult to explain both increased O_3 yields and unaffected ethylene conversion since ozone and ethylene should react readily at the concentrations present in these systems (*9*, *10*). In this regard, Westberg et al. (*5*) have reported that CO increases the NO_2 rate, O_3 yield, and isobutene oxidation in the isobutene-NO-CO system.

To explore ethylene photooxidation more deeply, pseudo first-order plots of ln (C_2H_4) vs. time were constructed for the experiments given in Table I. A typical plot is given in Figure 2. These plots show an initial period of little or no reaction followed by a period of faster reaction characterized by constant slope. The latter period began about the time that the maximum NO_2 concentration was attained and continued to the end of the experiment. These slopes are given in Table II along with calculated values of $-d \ln (C_2H_4)/dt$ for the O_3-ethylene reaction obtained by using the rate constant of Altshuller (*11*) and taking the average O_3 concentration, over the reaction period of interest, as one half of the concentrations given in Table I. The contribution of the oxygen atom-ethylene reaction has been ignored since it is negligible relative to

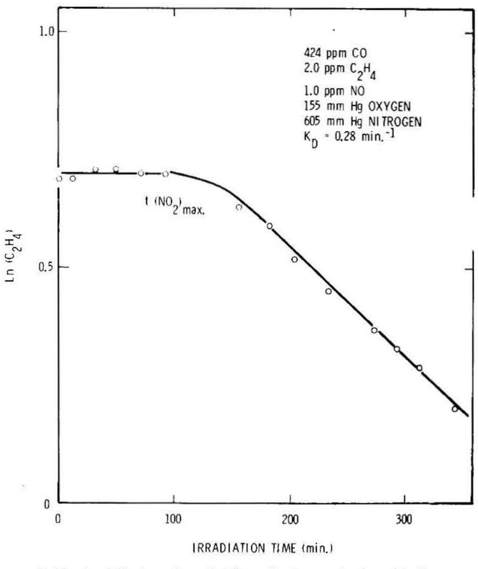

Figure 2. Typical first-order plot for ethylene photooxidation

Table II. Effect of CO Concentration on Ethylene Photooxidation[a]

CO, ppm	$-d \ln (C_2H_4)/dt$,[b] $\text{min}^{-1} \times 10^3$	$k(O_3)$ av,[c] $\text{min}^{-1} \times 10^3$
0	2.0	0.1
46	2.3	0.4
92	2.3	0.5
183	2.3	0.9
424	2.3	1.2

[a] 2.0 ppm ethylene, 1.0 ppm NO, 155 mm Hg oxygen, 605 mm Hg nitrogen, $k_D = 0.28$ min^{-1}, and temperature = 26°C. [b] The slope of a plot of ln (C_2H_4) vs. time, measured after ozone formation had begun. [c] The rate constant employed is that of Altshuller (11). O_3 av is taken as one-half of the values given in Table I.

that of the O_3–ethylene reaction for the reaction period of interest. The values of $-d \ln (C_2H_4)/dt$ given in Table II show very little effect of added CO and are consistently larger than the calculated values for the O_3–ethylene reaction. As the O_3 concentration increased, the calculated values approached the measured values. At the highest O_3 concentration measured (0.6 ppm), the two values were identical. These results can be interpreted in terms of the involvement of an unknown species (possibly hydroxyl radicals) in ethylene photooxidation. Since $-d \ln (C_2H_4)/dt$ remained constant over the wide range of CO concentration employed in this study, while the O_3 concentration increased, the concentration of the unknown species must have decreased. If the unknown species is the hydroxyl radical, its concentration varied from (7 to 3) $\times 10^{-7}$ ppm for 0–424 ppm CO, using the rate constant of Morris and Niki (*12*) for the hydroxyl radical–ethylene reaction.

The effect of CO on ethylene photooxidation appears to be twofold. First, CO increases ethylene photooxidation by allowing an increased O_3 yield by means of increasing the NO_2 rate. Secondly, CO apparently decreases ethylene photooxidation by decreasing the concentration of an unknown species. Thus, the net result of CO addition on ethylene photooxidation is no change.

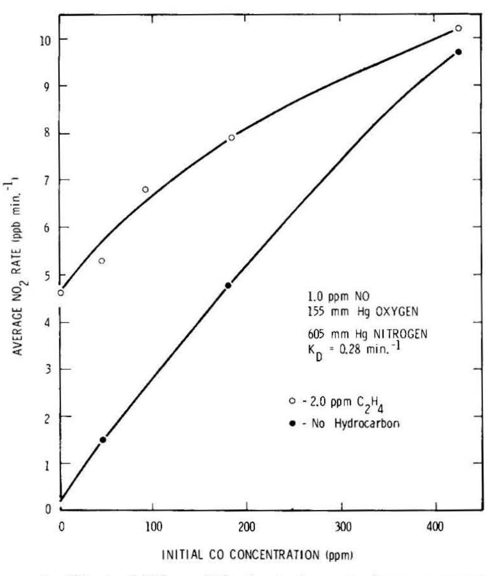

Figure 3. Effect of CO on NO_2 formation rate in presence and absence of ethylene

To more fully understand the effect of CO on the NO_2 formation rate, a series of experiments was performed to study the effect of CO on NO oxidation in the absence of added hydrocarbon. The CO concentrations covered the same range as given in Table I. The results are plotted in Figure 3 along with the comparative data from Table I. The intercept is the NO_2 rate calculated for the thermal oxidation of 1.0 ppm NO using the rate constant of Glasson and Tuesday (*8*).

The rate of NO_2 formation at the highest CO concentration is practically independent of the presence of ethylene. This observation is supported by the effect of CO on the extent of ethylene conversion occurring prior to the attainment of the maximum NO_2 concentration. With no added CO, 27% of the ethylene was oxidized during the NO oxidation period, while in the presence of 424 ppm of CO, no ethylene conversion was observed during this reaction period. These facts suggest that the addition of CO to the ethylene-NO system affords a reaction path that does not require the presence of the hydrocarbon. The chain reaction suggested by Heicklen and co-workers (*13*), Reactions 2–4, provides an explanation for this observation.

$$OH\cdot + CO \longrightarrow CO_2 + H\cdot \quad (2)$$

$$H\cdot + O_2 + M \longrightarrow HO_2\cdot + M \quad (3)$$

$$HO_2\cdot + NO \longrightarrow NO_2 + OH\cdot \quad (4)$$

Thus, as the CO concentration increases, Reactions 2–4 become increasingly dominant. The data given in Figure 3 indicate that the rates of NO_2 formation in the presence of CO but the absence of hydrocarbon are not additive with the rate of NO_2 formation in the absence of CO but in the presence of ethylene. This implies that CO is retarding the reaction instrumental in NO_2 formation without CO. This reaction is probably that of an hydroxyl radical with ethylene to produce the reactive intermediates ultimately responsible for oxidation of NO. The role of CO in this system would be: (1) to provide an alternate reaction pathway (Reactions 2–4) for NO oxidation and (2) to inhibit the "normal" ethylene–NO reaction mechanism by competing with ethylene for hydroxyl radicals. At 425 ppm of CO and 2.0 ppm of ethylene, the rate of the reaction of hydroxyl radicals with CO (*14*) and with ethylene (*12*) are in the ratio of 17:1. Thus, at this CO concentration, the relative independence of the NO_2 rate on the concentration of ethylene can be adequately explained.

Effect of CO on Photooxidation of Various Hydrocarbon–NO Systems. To determine the generality of the CO effects observed in the ethylene–NO system, the effect of CO on the photooxidations, in air, of 2.0 ppm of various hydrocarbons with 0.95 ppm of NO and 0.05 ppm of NO_2 were investigated. Two runs were performed per hydrocarbon, one with 50 ppm of CO and the other with zero CO. The NO_2 formation rate, hydrocarbon conversion, and product yields are given in Table III for the hydrocarbons studied. Hydrocarbon conversion and product yields are given for irradiation periods which vary from hydrocarbon to hydrocarbon, depending on the reactivity of the specific hydrocarbon. Hydrocarbon conversion and product yields are not given for isooctane because of the lack of unique infrared absorption for isooctane and the length of time necessary to reach the maximum NO_2 concentration (about 7 hr).

The addition of 50 ppm of CO affected the photooxidation of NO only in the presence of isooctane and mesitylene. The PAN yield, in the presence of mesitylene, was increased by CO, but the magnitude of the increase is close to the combined experimental error (±0.04 ppm) of

Table III. Effect of CO on Photooxidation of Hydrocarbon–NO Mixtures[a]

		Product results			
				Yields, ppm	
Hydrocarbon	CO, ppm	NO_2 rate, ppb min^{-1}	HC reacted,[b] %	O_3	Other[c]
Mesitylene	50	20	36	0.32	0.14
	0	15	36	0.32	0.09
1,3-Butadiene	50	17	83	0.47	0.69
	0	17	87	0.56	0.83
m-Xylene	50	12	29	0.32	0.07
	0	12	36	0.32	0.07
Propylene	50	11	85	0.63	0.19
	0	10	80	0.63	0.20
Isooctane	50	3.0	—	—	—
	0	2.2	—	—	—

[a] All runs were perfomed with 2.0 ppm of hydrocarbon, 0.95 ppm of NO, and 0.05 ppm of NO_2. The other conditions were 155 mm Hg oxygen, 605 mm Hg nitrogen, $k_D = 0.28$ min.$^{-1}$, and temperature = 26°C. [b] Hydrocarbon reacted and yields were measured at the following irradiation times: mesitylene, 70 min; 1,3-butadiene, 100 min; m-xylene, 90 min; propylene, 90 min; and isooctane, 420 min. [c] The other products were acrolein for 1,3-butadiene and PAN for all other hydrocarbons.

the two measurements. The hydrocarbon conversion and O_3 yield results indicate no change within the experimental error, due to CO addition. The acrolein yield from 1,3-butadiene photooxidation is unaffected by CO within the experimental error (±0.2 ppm). These results indicate very little, if any, effect of CO on hydrocarbon photooxidation in these systems.

In this regard, the results of a recent study (*2*) can be compared to the results of the present study. Addition of 75 ppm of CO had no effect on the oxidation of mesitylene or NO and led to a small decrease in the O_3 yield. Whereas the results of the present study are in qualitative agreement with the observations on mesitylene oxidation and O_3 yield, the NO oxidation results are not in agreement.

The NO results of the present study appear to be anomalous for reasons given below. Dodge and Bufalini found that addition of up to 2000 ppm of CO increased the oxidation of NO and 1-butene and the O_3 yield. Comparing these results to the propylene results of the current investigation demonstrates qualitative agreement on NO and HC oxidation but disagreement on O_3 yield. It is the author's opinion that the differences in these observations are probably due to the substantially higher reactant concentrations used in Dodge and Bufalini's work. Dodge and Bufalini also studied the pentane–NO system and found increased NO oxidation in the presence of added CO. The isooctane results in Table III also show increased NO oxidation in the presence of CO.

The NO_2 rate results, with the exception of those for mesitylene, imply an effect of CO only with the lower reactivity hydrocarbons. As others (*1, 5*) have pointed out, the CO effects reported in photooxidation systems are suggestive of the presence of hydroxyl radicals in these systems. The effect of hydrocarbon reactivity on the magnitude of CO effects, as demonstrated in the present work, suggests that hydroxyl radicals are more important in systems containing the less reactive hydrocarbons.

The effect of hydrocarbon reactivity on the CO effect can be at least qualitatively explained by the relative rate constants for reaction of hydroxyl radicals with the appropriate hydrocarbons and CO. The rate constants (relative to propylene) for ethylene and a mixture of xylene isomers are 0.1 and 1.1 (*12*) while those for isooctane and CO are 0.069 (*15*) and 0.008, respectively. At a CO concentration of 50 ppm, CO cannot compete effectively with 2.0 ppm of propylene or the xylenes for hydroxyl radicals, but CO can compete for hydroxyl radicals in the presence of 2.0 ppm of ethylene or isooctane. Thus, no CO effect was observed with propylene and *m*-xylene, and moderate effects were observed with ethylene and isooctane. The rate constant for the mesitylene–hydroxyl radical reaction has not been reported but is probably similar to that for the xylenes, in light of the reactivity of the hydroxyl radical. Therefore, it is difficult to rationalize the magnitude of the CO effect found with mesitylene, on the basis of competition for hydroxyl radicals between CO and mesitylene.

Effect of CO on Photooxidation of Hydrocarbon Mixture. The effect of carbon monoxide on photochemical smog formation was studied by investigating the photooxidation of a hydrocarbon mixture as a function of the initial carbon monoxide concentration. The composition of the hydrocarbon mixture was chosen to simulate that of a typical early morning Los Angeles atmospheric sample (*16*). The mixture contained 52% paraffins, 20% olefins, and 28% aromatics. The nitrogen dioxide formation rate and ozone yield after 500 min of irradiation were measured at carbon monoxide concentrations of 0, 25, and 50 ppm. The results are given in Table IV.

The nitrogen dioxide formation rate was increased by carbon monoxide addition. The ozone yield was unaffected by the addition of 25 ppm of carbon monoxide within the experimental error, but was increased by the addition of 50 ppm. The effect of carbon monoxide on the nitrogen dioxide formation rate is consistent with the largely paraffinic nature of the mixture and the carbon monoxide effects noted with isooctane (Table III). The effect of carbon monoxide concentration on the ozone yield is more complex. At low carbon monoxide concentrations, no effect was observed. As discussed earlier, the ozone yield in the ethylene–nitric oxide system increased with increasing carbon monoxide concentration due to the increased time available for ozone formation. In the hydrocarbon mixture experiments, the amount of time available for ozone formation increased by only 10 min by adding 25 ppm of carbon monoxide; whereas, addition of 50 ppm of carbon monoxide increased this time by 50 min. The ozone yields at 500 min probably reflect this increased amount of time available for ozone formation. This conclusion is consistent with the conclusion of Dodge and Bufalini.

Effect of Carbon Monoxide on Photochemical Smog Formation. Data from a recent report (*17*) can be used to estimate average carbon monoxide concentration for the Los Angeles atmosphere. The data, covering the period from June through November of 1970, were obtained at the downtown Los Angeles station and are given as the daily maximum hourly average values. Maximum hourly average values are not truly representative of atmospheric concentrations in so far as the time scale of atmospheric photochemistry is concerned. However, such values do serve as an upper limit to atmospheric concentrations.

Table IV. Effect of Carbon Monoxide Concentration on Photooxidation of Hydrocarbon Mixture[a]

CO, ppm	NO_2 rate, ppb min^{-1}	O_3 yield,[b] ppm
0	4.3	0.29
25	5.6	0.25
50	6.3	0.40

[a] The experimental conditions were: 1.96 ppm of total hydrocarbon; 0.97 ppm of nitric oxide; 0.05 ppm of nitrogen dioxide; 155 mm Hg oxygen; 605 mm Hg nitrogen; $k_D = 0.41$ min^{-1}; and temperature = 26°C. The composition of the hydrocarbon mixture was: 0.48 ppm of ethane; 0.23 ppm of propane; 0.31 ppm of *n*-butane; 0.30 ppm of ethylene; 0.09 ppm of propylene; 0.12 ppm of benzene; 0.30 ppm of toluene; and 0.13 ppm of *m*-xylene. [b] Measured after 500 min of irradiation.

Statistical analysis of the Los Angeles data indicate that the geometric mean carbon monoxide concentration (*18*) was 10 ppm with 90% confidence limits of 4–25 ppm. The largest daily maximum hourly average CO concentration reported was 37 ppm.

Assuming that the hydrocarbon mixture used in this investigation (Table IV) is representative of the Los Angeles atmosphere, the effect of reducing the carbon monoxide concentration from the geometric mean given above to zero, by whatever means, would be small. The NO_2 formation rate would be reduced about 14% while the ozone yield would be unaffected. Thus, based on the data of this investigation, the effect of carbon monoxide on photochemical smog formation would be negligible, in accord with the conclusion of Dodge and Bufalini.

Acknowledgment

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Dependency of Polynuclear Aromatic Hydrocarbon Content on Size Distribution of Atmospheric Aerosols

Ronald C. Pierce and Morris Katz*

Centre for Research on Environmental Quality, T-115 Steacie Science Building,
York University, 4700 Keele St., Toronto, Ont. M3J 2R3, Canada

■ An examination was made of the dependency of polynuclear aromatic hydrocarbon (PAH) content on the particle size distribution of atmospheric suspended particulate matter. Ambient aerosols were collected in specific time periods during 1972 and 1973 using size-fractionating cascade impactors (Anderson "Hi-Vol" samplers) at five sites in Toronto, Ont. Collected particulate matter was extracted with benzene in a Soxhlet apparatus. Eight PAH's and two oxygenated arenes were separated by thin-layer chromatography and identified and analyzed by absorption and fluorescence spectrophotometry. The efficiency and accuracy of the procedures involved were studied. The size distribution of PAH-containing particulates followed approximately a log-normal relationship for suburban and rural sampling sites with the majority of PAH content associated with particles below 3.0 μm diameter. Significant variations were discovered in PAH content between downtown-urban, urban, suburban, and rural areas. PAH concentration in submicron particles increased during the winter months.

Polynuclear aromatic hydrocarbons (PAH) and related polycyclic arenes are known to be widely distributed in the atmospheric environment. Some of these compounds are carcinogenic for experimental animals and have been associated with the incidence of various types of cancer in man.

Since the majority of PAH compounds are adsorbed on particulate matter, the great increase in the potential carcinogenic effect of such compounds as benzo(*a*)pyrene by incorporation with substantially inert particulate matter of small size is believed to be brought about by transport through the upper respiratory tract into the bronchioles and alveoli of the lungs (*1*).

At present, progress in control of air pollution by atmospheric particulate matter is evaluated by calculating the total weight of material collected by standard high-volume sampling techniques (*2*). However, it is important to realize that the total weight of particulate collected is a cumulative total of the fractional contribution of all particulate sizes composing the heterogeneous, polydisperse aerosol that is present in the atmosphere. Because the content of PAH's and other suspected carcinogens has been determined almost exclusively on the basis of separation and analysis of organic matter obtained from the above type of sampling system, no assessment of the PAH content with respect to size of particles in an aerosol can be made.

Technological advances toward increased burning efficiency of fossil fuels and on control techniques of particulate and gaseous emissions from stack effluents and transportation sources will lead to a decrease in the amount of large, nonrespirable particle emissions but may also lead to an increase in the number of particles in the respirable size range. Respirable particles may be defined as those particles with aerodynamic diameter below 5.0 μm that are deposited in the human respiratory tract (*3*). Hence, from an inhalation health aspect, it is important to determine the amount of potential carcinogenic material associated with the particles in an aerosol that may be inhaled and deposited in the respiratory tract.

Particle size distributions of various trace inorganic materials have been measured by Lee et al. (*4*), Natusch et al. (*5*), and Gladney et al. (*6*). There is presently little information on the particle size or mass distribution of PAH in an aerosol. In one study (*7*), more than 75% of the weight of selected PAH's was associated with aerosol particles less than 2.5 μm in diameter. However, Thomas (*8*) has shown that the amount of benzo(*a*)pyrene per unit weight of soot obtained from the combustion of various fuels was constant for all particle sizes. In this paper, the size distributions of chrysene, benz(*a*)anthracene, benzo(*a*)pyrene, benzo(*k*)fluoranthene, perylene, benzo(*ghi*)perylene, anthanthrene, coronene, 7-H-benzo(*de*)-anthracen-7-one, and phenalen-1-one are examined in relation to sampling location and seasonal variations.

Experimental

Sample Collection. Suspended particulate matter was collected at five locations in the Toronto, Ont., area. The locations may be described as follows: (1) York University, a northern suburban-rural area, (2) Evans Ave., a southwestern suburban area, (3) south of the Toronto International Airport, a rural area near the MacDonald-Cartier Freeway, (4) Bathurst St., a northern suburban area, and (5) College St., a downtown urban area.

Aerosol samples were collected during 1972 and 1973 by five-stage Anderson Hi-Vol cascade impactors. The first four stages of the sampler comprise the fractionating head, while the fifth stage is a backup filter positioned between the fractionating head and a standard Hi-Vol air sampler [for a more detailed description of the sampler, see Burton et al. (*9*)]. At a flow rate of 20 cfm (566 l/min) the sampler fractionates suspended particulate matter into five aerodynamic size ranges according to the calculated 50% cutoff diameters given in Table I. Calibration with a synthetic aerosol and field evaluation of this sampler has recently been carried out (*9*).

The fractionators were carefully assembled with fiber glass collection media (pH 6.5) and installed on the Hi-Vol samplers. Originally, fiber glass collection media at pH 11.0 were used. However, sulfate production in the presence of sulphur dioxide increased the weight of collected particulates to yield invalid samples (*9*). The flow rates were adjusted with variable voltage transformers and measured with oil manometers. Sampling time varied between 24 and 48 hr, depending on the atmospheric particulate loading of the sampling location. Before and after each sampling period, the filters were conditioned at constant relative humidity (50 ± 2%) and temperature (22 ± 2°C) for 24 hr and weighed to obtain the total weight collected particulate matter. The particulate-laden filte were placed in a Soxhlet extractor, and the organic matt was extracted with 250 ml of spectrograde benzene for hr. The organic matter was filtered and reduced to a vo ume of 50 ml by flash evaporation at a temperature belo 40°C. The remaining benzene was carefully evaporat under a stream of dry nitrogen at room temperature. T residue was dissolved in a known amount of benzene ai stored in the cold and dark until analysis was performed.

Table I. Aerodynamic Size Range of Suspended Particulate Matter Collected with Anderson Hi-Vol Cascade Impactor

Stage no.	Size range, μm
1	≥7.0
2	3.3–7.0
3	2.0–3.3
4	1.1–2.0
5[a]	≤1.1

[a] Stage 5 is the backup filter (8 × 10 in. glass fiber).

Analytical Technique. The standard PAH's were pu fied through recrystallization and thin-layer chromatogr phy on cellulose acetate where necessary. All solvents er ployed were of spectrograde quality. Estimations of PA content in organic matter, in airborne particulates, and volume of air sampled were carried out with the aid of i ternal standards and calibration curves for each cor pound investigated.

Isolation of the PAH's contained in the organic matt was accomplished through the use of neutral aluminu oxide thin-layer plates (20 × 20 × 0.1 cm) as the statio ary phase with a mixture of pentane: ether (19:1, v/v) the mobile phase by the ascending method of develo ment in a sandwich chamber (Brinkmann, Model 116 minimum volume chamber that saturates rapidly). Favo able results were obtained with this type of chamber sin the necessity of letting the chamber equilibrate for 1½ hr prior to development was eliminated. Also, better res lution of PAH's was achieved for a shorter time of deve opment.

Aliquots of the various extracts were added 1.5 cm fro the bottom of the thin-layer plate. Pure samples of PAH were added to the origin of the same plate to be used internal standards. After the solvent was allowed to rise a height of 15 cm in the chamber, the developed chr matogram was dried and viewed under a long-wave ultr violet light source. The fluorescent areas of internal sta dards and corresponding areas of the PAH's isolated fro the organic matter were marked and the absorbent, co taining standard and unknown, was removed from t plate. The desired PAH's were eluted with 20–30 ml of h spectrograde dichloromethane. The solvent was th evaporated under dry nitrogen at room temperature ar the residue taken up in a specific volume of spectrogra toluene.

Luminescence measurements were carried out at roo temperature on a Farrand MkI spectrofluoromet equipped with a high intensity Xenon arc lamp, grati monochromators for wavelength selection in both excit tion and emission spectra, a RCA 1P28 photomultipli tube and a Heath strip chart recorder. Wavelength resol tion was achieved with the aid of slits varying in wid from 1–20 nm. Both excitation and emission spectra we recorded at a scanning speed of 75 nm/min.

In sufficiently dilute solutions and in the absence of i terfering substances, fluorescence emission intensity is linear function of concentration. For all analytic wor calibration curves were determined in conditions exact the same as those encountered in the analysis. Beer's la was obeyed for PAH concentrations below 10 ^{5} mol, Samples of PAH were efficiently degassed by displaci dissolved oxygen with dry nitrogen prior to luminescen analysis.

Determination of the benzo(*a*)pyrene [BaP] and be zo(*k*)fluoranthene [BkF] content present in both the i ternal standards and organic matter was accomplish using the method of Dubois and Monkman (*10*). Oth members of the benzopyrene series –i.e., benzo(*e*)pyren benzo(*b*)fluoranthene, benzo(*j*)fluoranthene, and benzo(

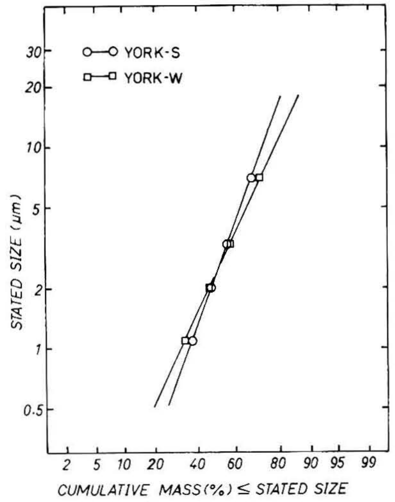

Figure 1. Least squares plot of average cumulative mass of suspended particulate matter for York site (summer—S, winter—W, 1972)

hi)fluoranthene, did not interfere with the luminescence measurements of BaP and BkF.

Two ring carbonyls, 7-H-benz(*de*)anthracene-7-one and phenalen-1-one were extracted from samples of atmospheric particulate matter using benzene (93 ± 4%) and isolated by thin-layer chromatography (91 ± 2%) with aluminum oxide and pentane:chloroform (3:2, v/v). Luminescence measurements were carried out at room temperature in concentrated sulfuric acid.

Results and Discussion

Sample Collection. The common technique for representing the particle-weight distribution of an aerosol calls for a determination of the relationship between the cumulative mass of the collected particulate matter and the size of that particulate matter (*11*). This is accomplished by plotting the logarithm of the effective cutoff diameter (ECD) for each stage on the ordinate as a function of the cumulative mass, expressed as a percent, less than or equal to the ECD at each stage on the abscissa. In practice, log-probability paper is used.

Since the particle sizes of most suspended particulate matter follow approximately a normal logarithmic distribution, the mass median diameter (MMD) is found at the 50% mass cumulative point. The geometric standard deviation (σg), which is roughly equivalent to the slope of the distribution curve, provides an indication of the particle dispersion on the range of particle sizes in an aerosol. The value is estimated from the ratio of the 84% value of particle size to the 50% value of the particle size. Figure 1 is a least squares plot of the average cumulative mass of suspended particulate matter in relation to particle size for the York sampling station. Data indicated that the suspended particulate matter was well described by a log-normal function as indicated by the linearity of the calculated size distribution.The size distribution curves were also used to determine the percentage of particulate mass, less than or equal to a selected size. The actual concentration of particles less than or equal to a selected diameter was determined from the product of the percentage of the cumulative mass for that fraction and the total aerosol concentration.

Data presented in Table II include the total mass concentration, MMD, σg, and the percentage of particles in the respirable size range for the five sampling sites in Toronto, Ont., including sampling periods representative of both winter and summer seasons. Unfortunately, no winter samples for the Evans or MacDonald Cartier stations were available. The geometric mean values for each station, together with the geometric standard deviations, were calculated using standard techniques. In this case, the geometric standard deviation represents the spread of the values over the number of samples analyzed and, hence, gives an indication of the degree of variability for different sampling periods. The mean mass concentration varied from a low of 67 $\mu g/m^3$ in the relatively clean air of the rural-suburban areas to a high of 108 $\mu g/m^3$ in suburban-metro areas. However, the mass concentration for all stations displayed a significant fluctuation from the mean values. The MMD's and σg's appear to be dependent upon the sampling location and time of year. In most cases, at least 50% of the aerosol mass was associated with particles less than or equal to 3.0 μm.

Analytical Technique. Sensitivity and Accuracy. All quantitative data were secured with the aid of internal standards under reproducible conditions (internal standard is defined as a compound that is subjected to exactly the same treatment as the unknown compound being investigated). The efficiency of extraction of enriched par-

Table II. Data Obtained with Anderson Impactors at Five Different Sites in Toronto, Ont.

Geometric mean ± geometric standard deviation

Sampling station	Sampling period	No. of samples	Mass concn, $\mu g/m^3$	MMD, μm	σg	Concn, ≤ 1.0 μm, %	Concn, ≤ 3.0 μm, %
York	24/06/72–28/07/72	10	78.0 ± 25.8	2.3 ± 0.6	10.8 ± 1.5	34.2 ± 2.0	54.1 ± 1.8
York	31/01/72–31/03/72	15	67.2 ± 18.3	2.4 ± 0.4	6.2 ± 1.1	31.0 ± 1.6	54.5 ± 2.0
Evans	22/05/73–29/05/73	6	92.8 ± 23.1	3.1 ± 0.5	6.8 ± 1.1	26.0 ± 2.1	51.2 ± 2.0
MacDonald-Cartier	14/05/73–20/05/73	12	68.7 ± 37.5	2.7 ± 0.7	7.9 ± 2.4	32.0 ± 1.4	51.0 ± 2.0
Bathurst	30/06/73–24/07/73	4	108.1 ± 17.3	1.5 ± 0.5	20.1 ± 2.5	40.7 ± 0.9	57.2 ± 1.3
Bathurst	15/12/73–29/01/74	3	107.4 ± 25.9	4.3 ± 0.2	9.4 ± 0.5	28.2 ± 0.5	44.2 ± 0.7
College	30/06/73–24/07/73	4	105.4 ± 23.7	1.8 ± 1.2	16.1 ± 4.5	36.2 ± 1.0	54.7 ± 2.6
College	15/12/73–27/02/74	5	78.8 ± 22.8	3.4 ± 0.4	13.5 ± 0.4	30.2 ± 0.7	46.3 ± 0.9

ticulate matter and recovery of PAH's by Soxhlet extraction with benzene ranged from 95–100% with a relative standard deviation of ±3%. Reduction in the volume of organic matter using flash evaporation with subsequent drying using a stream of dry nitrogen at room temperature did not lead to any loss of PAH content through either evaporation or decomposition. Recoveries of standard PAH's using alumina thin-layer chromatography varied from 94–98% with a relative standard deviation of ±2 to ±4%. The spectroscopic procedure itself appeared to be highly sensitive and accurate. The lower limit of detection and measurement of a standard BaP solution of 2.0 ng/ml was achieved with a deviation of less than 1%. The limiting factor in the analysis of PAH appeared to be the efficiency and reproducibility of the extraction and separation procedures used prior to luminescence analysis. Corrections of up to 5 ± 3% for extraction and 6 ± 4% for separation, elution, and analysis were applied for estimation of PAH content. Because of the very small concentration of PAH's in the atmosphere, it was not possible to analyze individual samples. Particulate samples, corresponding to a specific stage of the Anderson sampler and hence size fraction of aerosol collected, were combined and extracted as a group. As a result, average values of PAH concentration were obtained for aerosol samples collected over a period of several particulate sampling periods and, thus, any variation in PAH content within the specified sampling period could not be determined. However, monthly and seasonal variations were obtained. All data reported below were averaged over multiple determinations and have been corrected for the losses reported above.

PAH-Size Distribution. Data on the PAH-size distribution of three representative PAH's, expressed in relation to μg PAH/g particulate and in relation to ng PAH/1000 m^3 air, are presented in Tables III and IV, respectively. The values reported are averages of multiple determinations on the same sample and, in this case, the standard deviations reported represent the degree of reproducibility of the analysis procedure.

By comparing Tables III and IV, it is observed that the MMD values are different for the same aerosol sample. However, it must be remembered that the values are based on two different parameters—data in Table III are obtained with respect to weight of particulate matter collected whereas data in Table IV are obtained with respect to volume of air sampled. During atmospheric sampling, the volume of air passing through each stage of the sampling device is the same, but the amount of particulate matter collected on each stage will be different. Hence, the amount of PAH appears to be different depending upon the frame of reference that is chosen. Most data on concentration of toxic trace species are expressed as a mass per volume of air sampled.

The PAH content with respect to particle size of the suspended particulate matter followed approximately a log-normal distribution for three of the five sampling sites—i.e., York, Evans, and MacDonald Cartier. However, the distribution curves were significantly nonlinear for the Bathurst and College sampling stations. The total PAH concentration tended to be highest in the urban areas, while the rural-suburban areas exhibited the lowest concentration. In general, the MMD values for the PAH-containing aerosols were larger at the York station than at the Evans or MacDonald-Cartier stations, indicating a relatively smaller amount of PAH's in the respirable size range. This is supported by the fact that only 6–14% of the PAH content at York was associated with particles of diameter ≤1.0 μm, whereas 40–60% PAH content for the same particle size was found at the other two stations. All geometric standard deviations (σg) were small, denoting a narrow distribution of PAH content in the particle size investigated.

The lack of linearity in the PAH-size distribution curves for both the Bathurst and College sampling sites indicated that the PAH content was significantly influenced by the presence of specific emission sources different from those present at the other sampling sites. The percent mass of BaP for each stage of the Anderson sampler with respect to volume of air sampled (i.e., size frac-

Table III. Data on PAH Content with Respect to Weight of Particulate Matter Collected at Five Different Sites in Toronto, Ont.

(μg PAH/g particulate)

Sampling station	Sampling period	Compound	Total[a] concn	MMD, μm	σg	Concn, ≤1.0 μm, %	Concn, ≤3.0 μm, %
York	24/06/72–28/07/72	BaP	12.6	2.4	2.2	14	62
		BkF	11.2	2.7	1.9	6	56
		Per	7.4	2.8	1.9	8	56
York	31/01/72–31/03/72	BaP	17.1	1.6	2.5	30	76
		BaF	17.4	1.8	2.4	22	72
		Per	10.1	1.6	2.6	28	78
Evans	22/05/73–29/05/73	BaP	11.2	1.4	3.3	40	70
		BkF	13.4	1.4	4.1	40	71
		Per	4.6	1.8	2.7	29	68
MacDonald-Cartier	14/05/73–20/05/73	BaP	4.8	0.9	5.1	56	78
		BkF	5.2	0.8	5.4	58	79
		Per	1.9	1.0	4.9	54	74
Bathurst	30/06/73–24/07/73	BaP	39.8				
		BkF	41.7				
		Per	14.3				
Bathurst	15/12/73–29/01/74	Bap	41.0				
		BkF	46.2				
		Per	15.6				
College	30/06/73–24/07/73	BaP	24.9				
		BkF	24.0				
		Per	11.8				
College	15/12/73–27/02/74	BaP	65.0				
		BkF	64.4				
		Per	37.2				

[a] Reproducibility of PAH concentration is ±6% for BaP, ±5% for BKF and Per.

Table IV. Data on PAH Content with Respect to Volume of Air Sampled at Five Different Sites in Toronto, Ont.
(Ng/1000 m^3 air)

Sampling station	Sampling period	Compound	Total[a] concn	MMD, μm	σg	Concn, ≤1.0 μm, %	Concn, ≤3.0 μm, %
York	24/06/72– 28/07/72	BaP	127.1	2.6	2.6	15	56
		BkF	115.8	2.9	2.8	14	54
		Per	72.1	2.7	2.7	15	54
York	31/01/72– 31/03/72	BaP	238.2	1.2	4.2	46	76
		BkF	250.8	1.1	3.8	47	78
		Per	135.6	1.2	3.5	42	78
Evans	22/05/73– 29/05/73	BaP	216.8	1.0	5.3	46	70
		BkF	263.7	0.9	6.2	52	72
		Per	69.5	1.1	6.1	46	68
MacDonald-Cartier	14/05/73– 20/05/73	BaP	112.7	0.3	11.7	70	82
		BkF	125.6	0.3	12.0	72	84
		Per	34.6	0.5	10.9	68	80
Bathurst	30/06/73– 24/07/73	BaP	831.3				
		BkF	907.9				
		Per	148.2				
Bathurst	15/12/73– 29/01/74	BaP	850.2				
		BkF	961.7				
		Per	172.4				
College	30/06/73– 24/07/73	BaP	389.6				
		BkF	389.6				
		Per	174.8				
College	15/12/73– 27/02/74	BaP	716.5				
		BkF	767.8				
		Per	305.9				

[a] Reproducibility of PAH concentration is ±6% for BaP, ±5% for BkF and Per.

tion of BaP-containing particulate matter) for all five sampling locations is presented in Figure 2.

Significantly different variations in the benzo(*a*)pyrene content were recorded for different sampling sites. The York site had a maximal amount of BaP for stage 3 (2.0–3.3 μm) whereas the Evans and MacDonald-Cartier sites exhibited the greatest concentration of BaP for stage 5 (≤1.1 μm) during the summer sampling period. However, during the winter sampling period at York, the BaP content significantly increased for particle sizes below 1.0 μm. This indicates that, during the winter period, PAH content was associated primarily with smaller particles than during the summer period. The same relationship holds for several other PAH's analyzed at this station.

The College St. station, in general, showed the same BaP distribution for both winter and summer samples, although the PAH concentration for particles collected during winter was very much higher than the PAH content for the summer. Also, during the winter period, most of the PAH content was associated with particles less than 1.0 μm and greater than 7.0 μm. At least 50% of the BaP content was found in particles of diameter greater than 7.0 μm at the Bathurst location during the summer sampling period, while only approximately 25% was found in particles of size less than 1.0 μm. However, during the winter sampling period this distribution was essentially reversed—i.e., 50% of the BaP mass was associated with particles less than 1.0 μm and only 25% associated with particles greater than 7.0 μm. It is interesting to note that although the PAH content increased significantly for the winter season at most sampling locations, the PAH content at the Bathurst site remained essentially constant.

For all of the test sites, approximately 85–90% of the total PAH content with respect to volume of air sampled was associated with particles less than 5.0 μm diameter for the winter sampling period, while 70–85% was associated with the same size fraction for the summer sampling period. These values are essentially in agreement with the values reported by DeMaio and Corn (*7*) for aerosol samples collected in Pittsburgh but are slightly lower than the concentrations reported by Kertész-Sáringer et al. (*12*) for the same size of particles collected in Budapest. It is evident that the dependency of PAH content on size and, perhaps, on the type of particle found in the aerosol, varies significantly with sampling locations, season, and relevant emission sources.

Seasonal Effects on PAH-Size Distribution. It is generally accepted that the gross concentration of PAH's is lower in the summer months than the winter months (*13*). To determine any seasonal effects on the PAH-size distribution, samples of organic matter, representative of summer and winter suspended particulate levels at the York station, were quantitatively measured for the presence of the following PAH's: chrysene, benz(*a*)anthracene, benzo(*a*)pyrene, benzo(*k*)fluoranthene, perylene, benzo(*ghi*)perylene, anthanthrene, and coronene. Size distribution curves for each compound followed approximately a normal logarithmic distribution with significant differences between the summer and winter sampling periods. Com-

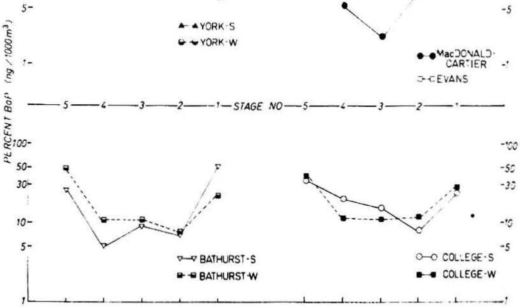

Figure 2. Percent mass of benzo(*a*)pyrene in relation to stage number for the five sampling sites

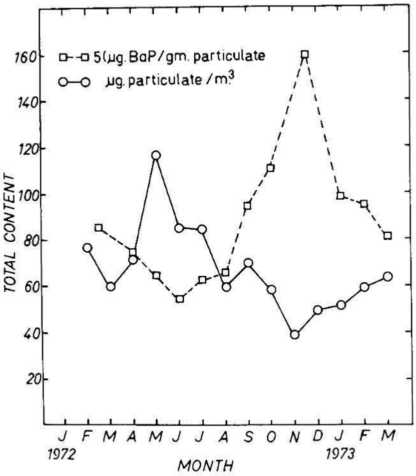

Figure 3. Monthly change in total concentration of particulate matter and total benzo(a)pyrene content (X5)

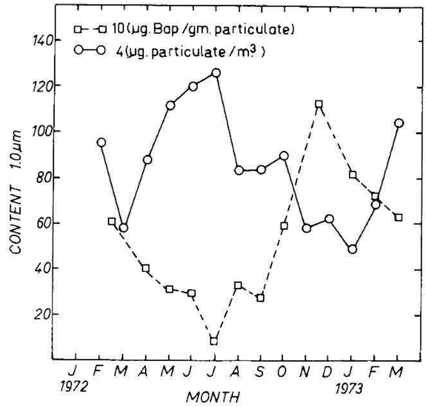

Figure 4. Monthly change in submicron concentration of particulate matter (X4) and submicron benzo(a)pyrene content (X10)

parison of the total PAH content, MMD, σg, and respirable PAH content in relation to weight of particulate matter for both sampling periods is given in Table V.

The total PAH content for the summer period ranged from anthanthrene with the lowest concentration of approximately 2 µg/g particulate to benzo(*ghi*)perylene with the highest concentration of 20 µg/g particulate. Chrysene, benzo(*a*)pyrene, and benzo(*k*)fluoranthene had approximately the same concentration as did coronene and perylene. The total concentration of PAH's were higher for the winter period by a factor of 65–75%.

The MMD's of all PAH's were lower in the winter than in the summer, indicating that the PAH's were associated with a smaller range of particles of relatively large average diameter in summer but with a larger size range of particles of relatively small average diameter in winter. This conclusion is borne out by the fact that the MMD's for PAH's in summer are larger than the MMD's for PAH's in winter, while the σg's for PAH's in winter are larger than the σg's for PAH's in summer (Tables III, IV, V).

During the summer period, 6–23% of the total PAH content was found in particulates with diameter ≤1.0 µm, while particles of diameter ≤3.0 µm contained 56–70% of the total PAH content. Hence, during the colder winter months the PAH content increased substantially for the smaller respirable particles found in the suspended particulate matter.

Comparison of the monthly particulate matter concentration in the air with the amount of PAH associated with that particulate matter indicated a more marked change in the content of PAH than in the amount of airborne particulates. A one-year study of the amount of three representative PAH's: benzo(*a*)pyrene, benzo(*k*)fluoranthene, and perylene, was carried out for the particulate matter collected at the York sampling station and is presented in Figures 3 and 4 (data shown for BaP only). The amount of

Table V. Seasonal Effects on PAH-Size Distribution at York Site, Toronto, Ont.

(µg PAH/g particulate)

Compound	R_B	Sampling period[a]	Total concn	MMD, µm	σg	Concn, ≤1.0 µm, %	Concn, ≤3.0 µm, %
Chrysene	1.19	S	11.6 ± 0.5	2.7	1.9	7	56
		W	17.5 ± 0.8	1.6	2.9	33	72
Benz(*a*)anthracene	1.09	S	11.3 ± 0.5	2.4	2.1	12	62
		W	22.2 ± 0.4	1.6	3.2	36	70
Benzo(*a*)pyrene	1.00	S	12.6 ± 0.7	2.4	2.2	14	62
		W	17.1 ± 0.9	1.5	2.9	35	74
Benzo(*k*)fluoranthene	0.99	S	11.2 ± 0.5	2.7	1.9	6	56
		W	17.4 ± 0.8	1.4	3.1	38	74
Perylene	0.95	S	7.4 ± 0.3	2.8	1.9	8	56
		W	10.1 ± 0.5	1.6	2.3	30	76
Benzo(*ghi*)perylene	0.85	S	20.2 ± 1.0	2.0	2.3	23	69
		W	31.1 ± 1.5	1.2	3.3	43	78
Coronene	0.40	S	8.2 ± 0.5	2.5	2.0	9	59
		W	12.3 ± 0.7	1.4	3.1	37	74
Anthanthrene	0.78	S	1.8 ± 0.1	2.4	2.2	14	61
		W	2.6 ± 0.1	1.3	3.0	40	78
Benzanthrone	0.67	S	30.5 ± 1.8	2.6	2.1	9	56
		W	39.1 ± 2.3	1.6	3.3	35	70
Perinaphthanone	0.37	S	26.5 ± 1.6	3.0	1.9	4	50
		W	15.9 ± 1.0	2.0	2.6	22	66

[a] S, York (24/06/72–28/07/72). W, York (31/01/72–31/03/72).
R_B, distance traveled by compound with respect to benzo(*a*)pyrene.

Table VI. Ratio of Benzo(*k*)fluoranthene and Perylene to Benzo(*a*)pyrene Found in Particulate Samples Collected at York Site

	Total content		Content ≤1.0 μm	
Month	BkF/BaP	Per/BaP	BkF/BaP	Per/BaP
1972 F-M	1.02	0.59	1.14	0.53
A	1.01	0.37	1.09	0.43
M	0.88	0.20	1.06	0.16
J	0.93	0.23	1.14	0.18
J	1.13	0.67	1.01	0.47
A	0.82	0.37	0.67	0.34
S	1.59	0.36	1.78	0.38
O	1.16	0.37	1.21	0.39
N-D	0.93	0.43	1.00	0.27
1973 J	0.99	0.46	1.18	0.37
F	1.00	0.52	1.16	0.38
M	1.01	0.62	1.10	0.47

BkF and Per may be calculated by multiplying the concentration of BaP found in Figures 3 and 4 by the appropriate ratios found in Table VI for each sampling period.

Figure 3 indicates that the total amount of particulate matter in the air (i.e., sum of all size fractions) was highest during the early summer and then decreased to a minimal value during the winter. However, the total content of benzo(*a*)pyrene with respect to weight of particulate matter followed the opposite pattern. The highest value for the total benzo(*a*)pyrene content was recorded for the early winter period while the lowest value was recorded for the early summer period. Hence, it is apparent that the increase in benzo(*a*)pyrene content during the early winter months was not due to an increased amount of particulate matter but, instead, to an increased amount of benzo(*a*)pyrene adsorbed in the particulate matter.

Essentially the same pattern was observed for submicron particles in the sampled aerosols as indicated in Figure 4. An increase in the particulate concentration of particles ≤1.0 μm was observed during the early summer months with a decrease in the early winter months. Maximal values for the benzo(*a*)pyrene content associated with particles ≤1.0 μm diameter were recorded during early winter while minimal values were recorded during early summer. In this case, there is a more dramatic increase in the PAH content of submicron particles between summer and winter as opposed to the total PAH content. The percent mass of the various PAH's in the respirable size range calculated from the size distribution data was higher during the winter than the summer, as indicated in Table V. As a result, the MMD's were lower for this time period.

Size Distribution of Heterocyclic Arenes. There are some indications that PAH's are degraded in the atmosphere by photooxidation, by reaction with atmospheric oxidants, and by reaction with sulfur oxides (*14*). Reactions may be particularly facile when the compounds are adsorbed on particulate matter, such as soot, with the likely reactions of hydrocarbons being the production of oxygenated compounds. Such oxygenated derivatives as 7-H-benz(*de*)anthracen-7-one (benzanthrone) and phenalen-1-one (perinaphthanone) are found in urban air and the oxygenated fraction of air extracts seem to be carcinogenic (*15*). Concentrations of both compounds were determined and appear in Table V. Size distribution curves followed approximately the same pattern as did the curves for PAH—i.e., a normal logarithmic distribution. The MMD for each compound decreased for the winter period while the σg increased. The content of these two oxygenated arenes also significantly increased in respirable particles during the winter.

Conclusion

The content of polynuclear aromatic hydrocarbons has been examined in relation to the size of suspended particulate matter found in the air of five different locations in Toronto, Ont. The polycyclics investigated were found to be highly dependent upon the size of the atmospheric aerosol with the greatest concentration being the respirable size range. Studies have also shown that the content of heteroaromatics is also size dependent. Seasonal variations in the PAH content were also found to be quite size dependent.

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Evaluation of Techniques for Obtaining Least-Cost Regional Strategies for Control of SO_2 and Suspended Particulates

Gerald L. Gipson, Warren Freas, Edwin L. Meyer, Jr.*
Environmental Protection Agency, Research Triangle Park, N.C. 27711

■ The cost of implementing an air pollution control strategy is an important criterion to be considered when assessing the effectiveness of a particular strategy. One means which can be used to evaluate a given control strategy is to compare its cost with the least-cost regional strategy for attaining national ambient air quality standards. The problem of determining the least-cost regional strategy for meeting yearly standards within bounds posed by fuel availability and the availability of control devices is formulated as an integer programming problem. Several methods of solving this problem are discussed and evaluated in terms of their reliability in approaching the theoretical least-cost solution, computer requirements, and ease of operation. Data from three different types of cities are used to evaluate eight techniques for obtaining least-cost solutions. A heuristic method that uses a feasible integer solution obtained by rounding off the linear programming solution as a starting basis and a cost-effectiveness measure to compare the starting basis with other feasible integer solutions is concluded to be the most promising technique for approximating the least-cost solution.

Need for Least-Cost Pollutant Strategy Models. The Implementation Planning Program (IPP) and related models have been used to evaluate the adequacy of State Implementation Plan (SIP) regulations for attaining National Ambient Air Quality Standards (NAAQS) and to estimate the associated costs. (The Implementation Planning Program, developed by TRW Systems Group, is a mathematical model that determines the impact of various air pollution control strategies on air quality levels and costs of air pollution control.) The effect of SIP's is assessed by combining source-receptor relationships with cost estimates associated with the use of pollutant control devices necessitated by emission regulations. If we assume the standards can be met with existing technology, it would be desirable to do so in an economical way. By use of IPP alone, the only means for selecting relatively economical strategies for meeting standards is to examine each of the many available control alternatives. This approach is very unwieldy and expensive. As a result, considerable effort has been devoted by the Office of Air Quality Planning and Standards, EPA to develop rational techniques to determine the regional least-cost strategy for meeting NAAQS. By comparing the costs associated with the SIP with those estimated for the least-cost strategy, a better assessment of the SIP's cost-effectiveness can be made.

Formulation of Least-Cost Models. The problem of selecting the least-cost regional "mix" of emission controls that will meet NAAQS and be consistent with fuel availability constraints was originally formulated by Consad Research Corp. as an integer programming problem.

Objective function: Minimize $C =$

$$\sum_{n=1}^{N} \sum_{s=1}^{S(n)} C(n,s)X(n,s) \qquad (1)$$

Subject to the following constraints:

$$\sum_{n=1}^{N} \sum_{s=1}^{S(n)} A(n,s,k,m)x(n,s) \leq B'(k,m) \qquad k = 1,\ldots,K;\quad m = 1,\ldots,M \qquad (2)$$

$$\sum_{s=1}^{S(n)} \sum_{n=1}^{N} F(n,s,j)x(n,s) \leq F'(j) \qquad j = 1,\ldots,J \qquad (3)$$

$$\sum_{s=1}^{S(n)} x(n,s) = 1 \qquad n = 1,\ldots,N \qquad (4)$$

$$x(n,s) = 0, \text{or } 1 \qquad (5)$$

where

$C(n,s)$ = cost associated with control of the nth source in the sth control state. (The imposition of a given control device on a source represents a distinct control state for that source. One such control state would be the imposition of *no* control device—maintenance of the status quo for a source)

$x(n,s)$ = 0 or 1; where "1" indicates that state "s" is being used for source n

$A(n,s,k,m)$ = concentration of pollutant k at receptor m resulting from source n in the sth control state

$B'(k,m)$ = air quality constraint at receptor m for pollutant k

$F(n,s,j)$ = fuel of type j needed by source n under control state s

$F'(j)$ = total regional amount of fuel type j available

The integer programming formulation was selected to simulate the actual practice of applying discrete control measures to individual sources of emissions. This simulation was made more realistic by including fuel constraints reflecting the limited availability of some fuel types. In addition, the nonlinear costs of removing pollutants from each one of many sources can be incorporated into an integer programming formulation. These nonlinearities result from such as the control costs being functions of the type of control measure employed, the characteristics of the source, the amount of pollutant removed, and regional cost factors. The reason these nonlinear costs can be treated by an integer programming approach is that a specific cost is assigned to each individual control measure–source combination.

The role of the constraints in the above formulation can be illustrated by a very simple example. Suppose there is a region in which there is only one source of SO_2. Further, suppose there are three available control alternatives:

A. Maintain the status quo
B. Switch to a low-sulfur fuel
C. Use a dry limestone injection flue gas cleaning process

In Figure 1a, alternative A is represented by $X_1 = 0$, $X_2 = 0$, $X_3 = 1$. Similarly, alternatives B and C are represented by coordinates (0, 1, 0) and (1, 0, 0), respectively. Plane ABC represents the range of acceptable strategies specified by Equation 4. However, suppose constraints imposed

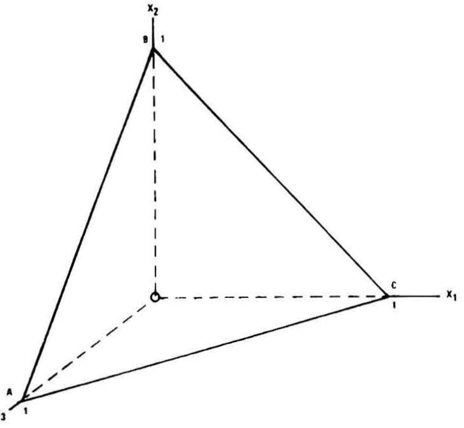

Figure 1a. Range of feasible strategies for one source with three control states

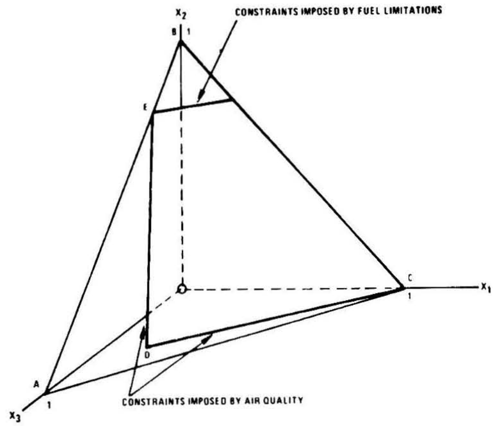

Figure 1b. Range of feasible strategies with added air quality and fuel constraints

by air quality and fuel requirements (Equations 2 and 3) further limit the range of acceptable strategies, as shown in Figure 1b. Now the acceptable range is defined by plane DEFC. Finally, Equation 5 requires that each X coordinate be either "1" or "0". This constraint means that point C in Figure 1b is the only acceptable solution. Hence, in this example, the only feasible control technique would be to apply the dry limestone injection flue gas cleaning device. The difficulty in obtaining a solution to the formulation expressed by Equations 1–5 is, of course, greatly magnified when there are a number of sources and feasible control devices.

The Problem

Although techniques for obtaining optimum (least-cost) solutions for problems expressed as linear programming formulations are well developed, the integer requirements of the above formulation make solutions by linear programming techniques inadequate. The problem can best be envisioned in two dimensions by picturing the range of feasible solutions to a linear programming problem as being defined by a closed box as shown in Figure 2. The sides of the box are determined by the constraints to the problem. Linear programming theory dictates that the optimum solution to the problem will occur at one of the corners of the box, in this case point (1). The way an integer programming problem must be formulated however, point (1) would not be a feasible solution, because the requirement that all variables in the solution be integers is not met. Only those solutions composed solely of whole numbers (dots in the diagram) are acceptable. The problem of attaining a least-cost integer solution then becomes one of determining which dot in the solution space has the least cost associated with it. An acceptable solution to the integer programming problem can be obtained by altering constraints in such a way that dots occur on the corners (i.e., so that the conventional linear programming solution happens to be all integers) or by devising a systematic way of examining the individual dots within the solution space.

Purpose

In these investigations, a number of techniques have been examined to determine their utility in arriving at the least-cost integer solution for implementing a regional control strategy. The purpose of this paper is to discuss the observed utility of each of these techniques in reaching least-cost solutions and to make recommendations accordingly. The techniques examined can be categorized in 4 ways: linear programming (LP) related methods, an integer programming (IP) method, heuristic programming techniques, and combination LP-heuristic techniques.

Discussion

Definition of Terms. A basis is a unique mix of source-device combinations. If a particular mix does not satisfy Equations 2–5 in the integer programming problem formulated, the basis is said to be infeasible; however, if each of the constraints is met, the basis is a feasible solution to the problem (e.g., one of the dots in Figure 2). In general, only one feasible basis represents the optimal solution. This basis is the one which minimizes the cost of meeting ambient air quality standards and is referred to as the least-cost solution.

Description of Techniques. Linear Programming-Related Methods. The problem, as formulated by Equations 1–5, was modified to obtain an LP solution using a commercially available linear programming package (Mathematical Programming System, IBM). The restrictions de-

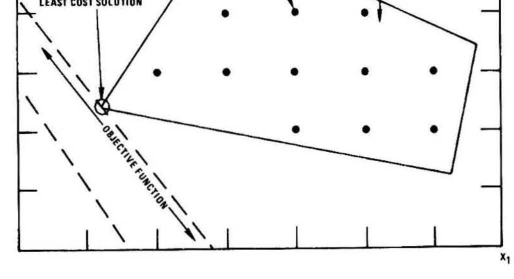

Figure 2. Illustration of two-dimensional integer programming problem

Table I. Summary of Problem Statistics

	Number of variables/number of rows		
AQCR	Control of SO_x only	Control of particulate matter only	Simultaneous control of SO_2 and particulate matter
Louisville	1422/191	1422/191	1422/200
Buffalo	2000/351	2000/351	2000/360
New York	4421/688	4421/688	4421/697

scribed in Equation 5 were disregarded, which allowed the individual $x\ (n,s)$ to be zero or any positive number less than or equal to one (i.e., noninteger solutions were allowed). A feasible solution to the original problem was then obtained by "rounding-off" each noninteger value of $x\ (n,s)$ to either 0 or 1 in such a manner as to ensure that none of the air quality or fuel constraints imposed by the right hand sides of Equations 2 and 3 were exceeded.

Integer Programming Solutions. The true optimal solution to the problem described by Equations 1–5, was obtained using a commercial integer programming package (IBM's MPSX with Mixed Integer Programming option). The system utilizes a branch-and-bound technique for determining optimal solutions to integer programming problems. The technique first solves the problem as an ordinary linear programming problem and then forces the noninteger values in one of two directions (toward higher or lower integers). A number of subsequent "paths" may have to be explored to assure that the least-cost integer solution is obtained. The size of the branch-and-bound problem was greatly reduced by setting an upper limit to the objective function. Thus, if a path led to a value of the objective function exceeding the imposed upper limit, it could be rejected without further examination of its subsequent paths. The upper limit of the objective function used was determined by one of the heuristic methods described below.

Heuristic Algorithms. A heuristic algorithm was developed by CONSAD Research Corp. in an attempt to solve the problem formulated in Equations 1–5. The solution technique is initiated by selecting the basis which yields the minimum regional cost (an infeasible basis since either air quality or fuel constraints, or both, are violated). The other source-control state combinations are then examined for entry into the basis. For each of these combinations, called activities, a cost-effectiveness ranking procedure is performed as follows. First, the present basis is inserted into the left-hand sides of Equations 2 and 3 to determine the air quality concentrations and fuel usage levels associated with that particular source-control state mix. Then, considering only those equations which are infeasible (i.e., those equations for which the values of the left-hand exceeds the right-hand side), the most infeasible constraint is selected by choosing the equation with the highest ratio of the difference between the left-hand and right-hand sides to the right-hand side. Every source-control state combination that would cause an increase in the pollution or fuel usage level of the left-hand side when substituted in that most infeasible constraint equation is eliminated from consideration for entry to the basis. For each of the remaining candidate activities, a cost-effectiveness index is calculated as follows:

$$I(n,s) = \frac{\Delta C(n,s)}{\sum_{p=1}^{P} \left(\frac{\Delta A(n,s,k,m)}{B'(k,m)} + \frac{\Delta F(n,s,j)}{F'(j)} \right)} \qquad (6)$$

where

$I(n,s)$ = cost-effectiveness index for the sth control state the nth source

$\Delta C(n,s)$ = incremental change in the cost incurred by the application of the sth control state to source n

$\Delta A(n,s,k,m)$ = incremental change in concentration of the kth pollutant at receptor m resulting from applying the sth control state to source n

$\Delta F(n,s,j)$ = incremental change in the usage of fuel j resulting from the application to control state s to source n

$B'(k,m)$ = air quality constraint for the kth pollutant at receptor m

$F'(j)$ = jth fuel constraint

P = the number of receptors at which the maximum allowable concentration is exceeded for each pollutant, plus the number of cases in which the available fuel amounts are exceeded

Since a small index indicates a large cost-effectiveness, the activity with the smallest index is chosen to enter the basis. This process is repeated until a feasible solution is obtained. DCIM 1 and DCIM 2 are algorithms similar to that described above with some minor changes. In DCIM 1, the only difference is that the fuel constraints are satis-

Table II. Louisville AQCR Results

Technique	Objective function, 10^6 \$	Percent difference from LP objective function
Simultaneous control of SO_x and particulates		
1. LP-related techniques		
LP solution	7.530	—
LP round-off solution	9.678	28.5
2. IP Technique		
MIP system	7.807	3.7
3. Heuristic techniques		
DCIM 1	14.082	87.0
DCIM 2	8.600	14.2
4. LP + heuristic techniques		
LP + DCIM 1	NS[a]	NA
LP + DCIM 2	7.938	5.4
LP round-off + heuristic	7.856	4.3
Control of SO_x only		
1. LP related techniques		
LP solution	4.984	—
LP round-off solution	6.030	21.0
2. IP Technique		
MIP system	5.404	8.4
3. Heuristic techniques		
DCIM 1	5.410	8.5
DCIM 2	5.405	8.4
4. LP + heuristic techniques		
LP + DCIM 1	5.562	11.6
LP + DCIM 2	5.562	11.6
LP round-off + heuristic	5.562	11.6
Control of Particulates Only		
1. LP related techniques		
LP solution	0.1286	—
LP round-off solution	0.1311	1.9
2. IP technique		
MIP system	0.1288	0.2
3. Heuristic techniques		
DCIM 1	0.1290	0.3
DCIM 2	0.1290	0.3
4. LP + heuristic techniques		
LP + DCIM 1	0.1290	0.3
LP + DCIM 2	0.1290	0.3
LP roundoff + heuristic	0.1290	0.3

[a] Technique did not converge to a solution.

fied before considering the air quality constraints. Once the fuel constraints are satisfied, any candidate source-control state combination that will cause the fuel constraints to be violated is not allowed to enter the basis. Unlike DCIM 1, DCIM 2 considers all constraints simultaneously. However, any candidate activity that causes a reduction in SO_x, TSP, or fuel usage levels while simultaneously causing an increase in the left-hand side of one or more of the constraint equations is not allowed entry to the basis unless this increase does not cause the right-hand side of a constraint equation to be exceeded.

Combination LP-Heuristic Techniques. These techniques use the results of the linear program as a starting point for the two heuristic algorithms. In the LP plus heuristic technique, the LP solution is modified in such a manner that it can be used with the heuristic techniques. An examination of the LP solution is made for noninteger values of each $x(n,s)$. The sources associated with each of the noninteger $x(n,s)$ are then assumed to be in the original control state. This new adjusted basis, which is infeasible, is used as the initial basis by the heuristic algorithms. The second technique—LP round-off plus heuristic—utilizes the rounded-off LP solution described previously. The basis of this solution is used as the starting point for a heuristic algorithm which examines the possibility of relaxing the control states of each source. If any improvement in cost can be made without causing the air quality fuel constraints to be violated, the algorithm will determine the new solution. It should be noted that in the first technique, an infeasible solution was used as a starting point for a heuristic algorithm, whereas in the second type, a feasible solution was used as the initial basis.

Method of Evaluation. To test the efficiency of these techniques, they were used to obtain least-cost strategies for three different cities—Louisville, New York City, and Buffalo. These three cities provide examples of the different types of urban areas likely to be modeled. Louisville represents a medium-sized urban area; New York typifies the large, densely populated, metropolitan region; and Buffalo provides an example of a heavily industrialized area. In each of these areas, least-cost strategy solutions were sought for the following three situations: control of particulate matter only, control of SO_x only, and control of SO_x and particulate matter simultaneously.

Initially the air quality constraints were set at the primary national ambient annual air quality standards for SO_x and particulates. However, in some cases, these standards had to be relaxed in order to obtain feasible solutions. (The inability to obtain feasible solutions using the NAAQS is believed to be attributable, at least in part, to shortcomings within IPP. IPP was used to generate the control measure-source combinations along with the associated costs and pollutant removal efficiencies. Because IPP is not capable of simulating the application of in-tandem control devices—e.g., combination SO_x and particulate devices—and because 1967 state-of-the-art control technology is incorporated within IPP, the resultant control alternatives are limited. Efforts are currently proceeding to correct both of these deficiencies, as well as to update the costs associated with each control alternative to current levels.) In addition to the air quality constraints, one fuel limitation which restricted the use of natural gas to base state levels was imposed. Table I summarizes the size of the problems formulated for each city.

Basis for Evaluation. Four criteria were used in evaluating the different techniques: (1) closeness of the solution to the optimal solution, (2) reliability of the technique in obtaining a feasible solution, (3) comparison of computer requirements, and (4) ease of operations.

Table III. Buffalo AQCR Results

Technique	Objective function 10^6 \$	Percent difference from LP objective function
Simultaneous Control of SO_x and Particulates		
1. LP related techniques		
LP solution	7.334	—
LP round-off solution	8.111	10.6
2. IP Technique		
MIP system	NA[a]	NA
3. Heuristic techniques		
DCIM 1	NS[b]	NA
DCIM 2	NS[c]	NA
4. LP + heuristic techniques		
LP + DCIM 1	NS[b]	NA
LP + DCIM 2	NS[c]	NA
LP round-off + heuristic	7.680	4.7
Control of SO_x Only		
1. LP-related techniques		
LP solution	2.932	—
LP round-off solution	3.575	21.9
2. IP technique		
MIP system	NA[a]	NA
3. Heuristic techniques		
DCIM 1	3.021	3.0
DCIM 2	3.021	3.0
4. LP + heuristic techniques		
LP + DCIM 1	3.266	11.4
LP + DCIM 2	3.266	11.4
LP round-off + heuristic	3.162	8.0
Control of Particulates Only		
1. LP-related techniques		
LP solution	2.517	—
LP round-off solution	2.535	0.7
2. IP technique		
MIP system	NA[a]	NA
3. Heuristic techniques		
DCIM 1	2.531	0.6
DCIM 2	2.531	0.6
4. LP + heuristic techniques		
LP + DCIM 1	2.620	4.1
LP + DCIM 2	2.620	4.1
LP round-off + heuristic	2.526	0.4

[a] The IP technique was not used. [b] Technique did not converge to a solution. [c] Technique indicated no feasible solution existed.

Closeness to True Optimum. When comparing a particular solution with the optimal solution, major emphasis was placed on the nearness of the objective function (the regional cost of control) to the value of the LP objective function. If an objective function obtained by any of the techniques was less than 20% greater than the value of the LP objective function, it was considered to be sufficiently close to satisfy the first criterion. The inexactness of cost, device efficiency, and emission data and the approximate nature of predicted relationships between emissions and air quality were used to justify divergences as large as 20%. Since the objective function associated with the optimal integer solution must be greater than or equal to the LP objection function, any solution within 20% of the LP objective function, must necessarily be within 20% of the integer solution's objective function. Little attention was focused on the nature of the activities [i.e., each individual $x(n,s)$] associated with each of the solutions obtained using the different techniques.

Reliability. By using all these techniques to obtain "least-cost" solutions for the three control cases in each AQCR, a good test of the reliability of each method was acquired. Two facets of reliability were considered: reliability in consistently obtaining feasible solutions, and reliability in obtaining feasible solutions with objective functions sufficiently close to the optimal values.

Computer Requirements. Also of importance in evaluating each algorithm was the computer size and time necessary to solve the problem. An effective algorithm which does not require excessive storage space or execution time was desired.

Ease of Operation. Even though all the algorithms tested are complex, some were easier to use than others. Each technique was evaluated for ease of operation and relative complexity. This criterion was not weighted as heavily as the previously mentioned ones.

Results

Tables II–IV show the individual regional costs of control obtained using these techniques for each of the previously prescribed control cases in Louisville, Buffalo, and New York City, respectively. An overall summary of the reliability and computer requirements of each method is shown in Table V.

Table IV. New York AQCR Results

Technique	Objective function $10^6\,\$$	Percent difference from LP objective function
Simultaneous SO_x and Particulate Control		
1. LP-related techniques		
LP solution	53.253	—
LP round-off solution	55.105	3.5
2. IP technique		
MIP system	NA[a]	NA
3. Heuristic techniques		
DCIM 1	NS[b]	NA
DCIM 2	NS[c]	NA
4. LP + heuristic techniques		
LP + DCIM 1	NS[b]	NA
LP + DCIM 2	NS[c]	NA
LP round-off + heuristic	54.360	2.1
Control of SO_x Only		
1. LP-related techniques		
LP solution	38.270	—
LP round-off solution	39.222	2.5
2. IP technique		
MIP system	NA[a]	NA
3. Heuristic techniques		
DCIM 1	39.108	2.2
DCIM 2	39.108	2.2
4. LP + heuristic techniques		
LP + DCIM 1	39.846	4.1
LP + DCIM 2	39.846	4.1
LP round-off + heuristic	39.129	2.2
	Objective function $10^6\,\$$[d]	Percent difference from LP objective function[e]
Control of Particulates Only		
1. LP-related techniques		
LP solution	−15.199	—
LP round-off solution	−15.184	0.1
2. IP technique		
MIP system	NA[a]	NA
3. Heuristic techniques		
DCIM 1	−15.076	0.8
DCIM 2	−15.076	0.8
4. LP + heuristic techniques		
LP + DCIM 1	−15.094	0.7
LP + DCIM 2	−15.094	0.7
LP round-off + heuristic	−15.101	0.6

[a] The IP technique was not used. [b] The technique did not converge to a solution. [c] The technique indicated no feasible solution existed. [d] The negative costs are the results of no SO_x constraints. Most fuel combustion sources in the NY-NJ-Conn. AQCR were burning relatively expensive low-sulfur oils in the base control state. The least-cost solution indicated that burning higher sulfur oils would be more cost effective since no increase in particulate emissions would occur and the amount of SO_x emitted is irrelevant when considering the control of particulates only. [e] Absolute percent difference.

LP-Related Techniques. Solutions were obtained in every case using the LP-related techniques. In one case, the round-off technique yielded a solution that was 28% greater than the LP objective function; consequently, criterion 1 was not met.

Integer Programming Technique. Actual least-cost solutions were obtained for each control case in the Louisville AQCR by using the integer programming package. The computer time necessary to find the optimal solutions was quite large, not only in central processing unit (CPU) time, but also in input/output time and total residence time. Because of this, the limited availability of the interger programming package, and the fact that the problems for Louisville were considerably smaller than any of the others considered, the integer programming package was not used to obtain solutions for any of the control cases in the other two AQCR's.

Heuristic Techniques. The heuristic algorithms failed to obtain solutions for the case of multipollutant constraints (i.e., simultaneous SO_x and particulate constraints on allowable concentrations) for the Buffalo and New York AQCR's. In these cases, DCIM 1 did not converge to a feasible solution, whereas DCIM 2 indicated that there was no feasible solution. In the one case of multipollutant constraints for which solutions were obtained (i.e., Louisville), DCIM 1 found a solution whose objective function differed from that of the LP by more than 85%.

Combination LP-Heuristic Techniques. Approximately the same results acquired using the heuristic algorithms were obtained by using the infeasible LP basis as a starting point for the heuristic algorithms. Just as previously described, the technique failed to obtain solutions for the case of multipollutant constraints in the Buffalo and New York AQCR's. However, when the feasible "LP round-off" basis was used as the starting point for the heuristic algorithm, solutions were obtained that met criterion 1 in every case (i.e., the objective function less than 20% greater than the LP objective function). The maximum difference between the objective functions was approximately 12%.

Conclusions

Ideally, the algorithm to be used to obtain a solution to the integer programming problem defined in Equations 1–5 would determine the true optimal solution. The only technique tested that guarantees an optimal solution (if one exists) is the integer programming method. Unfortunately, the computer requirements associated with obtaining this solution appear excessive—especially for large problems. The only other techniques that provided feasible solutions consistently were the LP round-off method and the LP round-off plus heuristic method. Since the latter method satisfied criteria 1 and 2 in every case and, in fact, always obtained lower regional costs than the LP round-off technique, it is considered the most viable of these two techniques. In addition, the computer requirements for this technique are far less than those of the integer programming method. For the cases in which the solutions obtained by the LP round-off plus heuristic technique were compared with true optimal solutions, the greatest difference in objective functions was less than 3%. Since the LP round-off plus heuristic technique is not severely complex and yields results superior to those obtained by the other heuristic algorithms, it is planned to

Table V. Summary of Results

	Solutions obtained for every case?	Largest percent difference	Average percent difference	Average computer time, min [a]	Largest amount of computer time required, min[a]
1. LP-related techniques					
LP	Yes	—	—	0.8	2.6
LP round-off		28.5	9.4	0.8	2.6
2. IP technique					
MIP	Yes[b]	NA	NA	2.0[c]	14.0[c]
3. Heuristic techniques					
DCIM 1	No	87.0	14.6	1.0	7.7
DCIM 2	No	14.2	4.2	1.5	11.0
4. LP + heuristic techniques					
LP + DCIM 1	No	11.6	5.4	1.1	3.1
LP.+ DCIM 2	No	11.6	5.4	1.1	3.1
LP round-off + heuristic	Yes	11.6	3.8	3.1	3.1

[a] Central processing unit (CPU) time. [b] Technique applied to Louisville AQCR only. [c] The I/o and residency times were extremely large.

utilize this technique as the primary method for arriving at regional least-cost solutions, with the integer programming method serving as a backup technique.

Having an effective method of determining least-cost regional control strategies for attaining NAAQS permits better analysis of economic considerations in developing and testing emission control regulations. Direct costs of control strategies designed to implement emission regulations can be compared with least-cost solutions. Such comparisons would enable users to assess the potential for revising regulations so as to reduce the direct cost of implementation, and perhaps provide insight into how such reductions might be achieved equitably. The methodology described herein could be applied to problems with further linear constraints requiring equitable treatment of similar sources once these problems are properly formulated. Other areas of potential applicability include estimating the least cost associated with direct implementation of SIP revisions and changes in NAAQS. Immediate plans include providing the model with the capability of estimating the lowest cost of implementation associated with meeting short-term standards for SO_2 and TSP, and providing an easy-to-use programmed product for general use.

Nomenclature

$A(n,s,k,m)$ = Concentration of pollutant k at receptor m caused by source n which is using control state s

$B'(k,m)$ = Allowable concentration of pollutant k at receptor m

$C(n,s)$ = Direct cost of controlling emissions from source n associated with using control state s

$F(n,s,j)$ = The amount of fuel type j needed by source n exercising control state s

$F'(j)$ = Amount of fuel type j which is available to the region

$I(n,s)$ = Cost-effectiveness index associated with using the sth control state on source n to meet air quality constraints at receptors where the constraints are exceeded. This parameter is proportional to the change in direct cost of implementation divided by changes in air quality and fuel requirements

P = This parameter is used as an indicator of the number of air quality and fuel constraints not being met by a given regional control strategy

$x(n,s)$ = This parameter is used as an indicator of whether or not source n is using control state s. If $x(n,s) = 1$, control state s is being used by source n. If $x(n,s) = 0$, control state s is not being used

$\Delta A(n,s,k,m)$ = Change in the concentrations of pollutant k at receptor m which results from applying control state s to source n

$\Delta C(n,s)$ = Change in direct cost of implementation incurred by application of control state s to source n

$\Delta F(n,s,j)$ = Change in the usage of fuel j resulting from the application of control state s by source n

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Conversion of Marine Muds to Lightweight Construction Aggregate

Donald C. Rhoads,* Robert B. Gordon, and J. Rimas Vaišnys
Department of Geology and Geophysics, Yale University, New Haven, Conn. 06520

■ Fine-grained mud recovered from harbors and embayments along the northeast coast of the U.S. was sintered to produce ceramic materials at temperature of about 1050°C and firing times of 8 hr. High-quality construction ceramics were produced from sediments containing 87–99% silicate minerals with 80% (by wt) of the sediment less than 62 μ in size (coarse silt). Shell carbonate was less than 10% and volatile organics 2–3% (by wt). Only 3% of the initial NaCl is retained after firing. Mechanical properties of fired test bricks show compressive strengths of 5200–16,500 psi with strength to weight ratios of 3700–6200 (psi)/(g/cm^3). The strength-to-weight ratio of aggregate produced from sintered mud (6700) is comparable, or superior, to commercially used lightweight expanded shale aggregates. The firing process may be expected to release mercury, cadmium, and lead into the gas phase if they are present in the mud. Other metallic contaminants will enter the glass phase of the material and therefore become relatively inert when exposed to the leaching effects of percolating water.

Material A was collected from a silt–clay deposit which extends over an area of over 400 km^2 in central Cape Cod Bay, Mass. (41° 55′ N and 70° 15′ W) at a depth of 37 meters. The mineralogic analysis of this sediment is given in Table I.

Material B is from silt–clay deposit in Buzzards Bay, at a depth of 16 meters located 40° 34′ N and 70° 41′ W. This deposit extends over an area of at least 160 km^2. A mineralogic analysis of this sediment is given in Table II.

Material C was obtained from intertidal muds on the Long Wharf tidal flat on the west side of New Haven Harbor, Conn. Several samples were also collected from silt–clay deposits in central Long Island Sound for studies of compressive strength of fired material with differing content of sand and shell.

Methods

Samples were obtained with a 0.1 m^2 bucket-type grab or with 4.6-cm diameter gravity cores. Water content was determined by weighing core samples before and after drying at 130°C. No corrections were made for salts precipitated during the drying process. Water content of samples prepared for extrusion prior to firing were adjusted from values $\geq 60\%$ by weight to 10–30% by partial drying at 130°C. Muds in the range 10–30% are plastic and can be extruded into desired shapes.

Grain size of the sediment was determined both by wet or dry sieving. The coarse silt and finer fraction was separated from the sand fraction on a 62-μ Tyler test screen.

Mineralogic analyses of samples from Cape Code Bay are given by Hough (*1*) and analyses of muds from Buzzards Bay by Moore (*2*). Because shell carbonate and organic content of specific samples may vary widely, we did not rely on published analyses for these components. The quantity of calcium carbonate in the samples was estimated by comparing sample weights before and after dissolution with 5% HCl. Sediment organic content was determined with a Leco carbon analyzer.

To determine the strength properties of the sintered silt, test bars were prepared by extruding silt into 6 cm long by 2-cm diameter cylinders. These cylinders were then dried and fired. After firing, the ends of each cylinder were ground flat and parallel with a diamond wheel.

The bulk density of the finished bars was calculated from the mass and dimensions. Compressive strength was determined with a hydraulic ram and a test fixture fitted with hardened steel end platens. These platens were maintained parallel to within 0.001 in. over their diameter throughout the tests. The hydraulic ram was calibrated against a standard Instron compression load cell. In each test, pressure was increased gradually until the bar failed. The strength, S, was calculated from the greatest load sustained and the initial cross-sectional area. From two to five bars of each material were tested; the variation of strength between tests was in all cases less than 10%.

Crushing strengths of sintered silt in the form of aggregate were measured in a 7.6-cm diameter steel cylinder fitted with free-sliding, hardened pistons. Force was applied with a 100-ton capacity hydraulic press. Tests were made on sintered silt A broken to roughly equiaxial particles. The size range of this aggregate was >1.19 mm – <4.76 mm (U.S. Sieve Series nos. 16 and 4). Sixty percent (by wt) of the particles were greater than 2.38 mm and 40% less than 2.38 mm (sieve no. 8). The cylinder was filled with aggregate to a depth of about 13 cm. Results are expressed in terms of the bulk density (d) and the crushing strengths for 2.5 cm (S_1) and 5 cm (S_2) of compaction.

Processing

Successful sintering is achieved with feed material containing from 87–99% silicate component; this was comprised of 10–55% quartz, 10–50% feldspar, and 20–60% clay. Minor amounts of other silicates, such as hornblende, may also be present. The term clay means silicate minerals belonging to the phyllosilicate group. Sinter with the best properties is made from feed containing over 50% illite and chlorite with lesser amounts of other clay minerals.

The sequence of steps involved in sintering marine silt follows:

1. Reduce, if necessary, the water content by air or squeeze drying to the plastic range (10–30% water).
2. Form the sediment into the desired shape by extrusion or other means.
3. Remove the remaining water content by heating to a temperature between 90° and 150°C.
4. Fire the dry sediment in an oxidizing atmosphere at a temperature of about 1050°C.

Depending on physical shape and water content of the starting material and the nature of the desired finished product, Step 1 or 2 may not be required. The temperature range for drying, Step 3, is chosen so that all of the pore water in the feed material will be driven off without destroying organic matter present. If sinter having a high strength-to-weight ratio is a desired product, it is advan-

Table I. Mineralogic Analysis of Cape Cod Bay Material A

[Silicate data (*1*)]

	Wt %[a]
Silicate component	90
Quartz	30
Feldspar	18
Clay	45
Hornblende	2
Shell $CaCO_3$	4
Organics	1–2

[a] Over 80% of this sediment by weight is finer than 62 μ.

Table II. Mineralogic Analysis of Buzzards Bay Material B

[Silicate data (*2*)]

	Wt %[a]
Silicate component	92
Quartz	37
Feldspar	23
Clay	40
Shell $CaCO_3$	6.5
Organics	1.5

[a] Over 80% of this sediment by weight is finer than 62 μ.

tageous to retain organic matter until the final firing stage; gas released by its decomposition will then, by forming pores rather than continuous voids, reduce density of the final product. Time required for drying at room temperature depends on size of the pieces being processed. For equiaxial pieces of about 10 cm, this time is about 10 hr.

Oxidizing conditions required for final firing are most easily obtained by heating dried sediment in a kiln or furnace which is open to the atmosphere. All of our samples were fired in a commercial brick kiln. A typical firing schedule for pieces of approximately 10 cm mean radius is 8 hr heating, 4 hr at the firing temperature, and 8 hr cooling. Time at the firing temperature may be reduced if the temperature is increased, but heating and cooling times may not be decreased if strong, solid blocks of sinter are desired: Rapid heating and cooling produce thermal stresses which crack or break the fired blocks.

These processing operations are equally adaptable to continuous or batch procedures. Waste heat from the sintering kiln could be utilized in the drying operations of Steps 1 and 3.

Results

By subjecting our sediment samples to the processing sequence, we have produced a strong lightweight material that is red in color.

A subsample A′ was prepared from material A treated according to processing Steps 1 through 4. Subsample A″ of the same material was fired at a higher temperature. Sample C was fired the same way as A″ but the starting material was silt collected from the main dredged channel of New Haven Harbor. Test results are given in Table III. These results may be compared with the properties of commercial building brick: for a "soft" brick S = 3000 psi and d = 2.3 g/cm^3, or S/d = 1250 (psi)/(g/cm^3); for the strongest commercial brick S = 15,500 psi and S/d = 6700 (psi)/(g/cm^3).

The important effects of the sand and shell content of marine silt on the strength of the sintered product are demonstrated in a series of samples in which these properties are varied independently. Samples of silt were collected from various localities in Long Island Sound off the Connecticut shore, Cape Cod Bay, and Buzzards Bay, Mass., where the chemical composition of the silicate component is close to that of analyses given in Tables I and II. All were fired on the schedule described earlier. Variation of strength with shell content is shown in Figure 1. There is a rapid degradation of strength as the quantity of shell increases. This is evidently due to the formation of CaO in the sintered product. Material containing 16% shell crumbled easily; generally, a strength on the order of at least 1000 psi is necessary if the sintered silt is to be handled without excessive crumbling.

The effect of sand content on the strength of the sintered silt is shown in Figure 2. There is considerable scatter of points because it was not possible to find samples

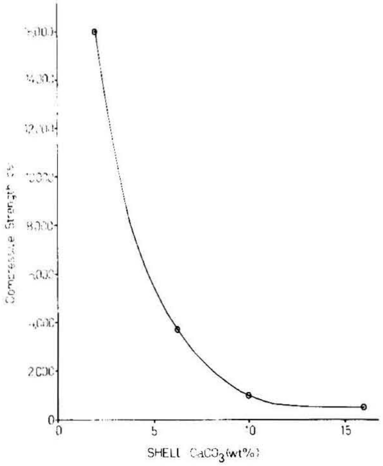

Figure 1. Compressive strength of ceramic test bars related to shell content. Bars processed as described in text

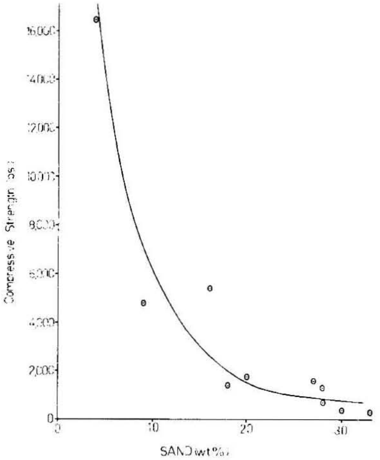

Figure 2. Compressive strength of ceramic test bars related to sand content (62–1000 μ). Bars processed as described in text

Table III. Average Properties of Brick Test Bars

Samples	Location	Strength, *S* psi	Density, *d*, g/cm^3	*S/d*, psi/ (g/cm^3)
A′	Cape Cod Bay	5,200	1.40	3700
A″	Cape Cod Bay	11,500	1.85	6200
C	New Haven Harbor, Long Island Sound	16,500	2.90	5700

Table IV. Crushing Force Required to Compress Aggregate 2.5 Cm (S_1) and 5.0 Cm (S_2) in Compression Cell

Material[a]	*d*, g/cm^3	S_1, psi	S_2, psi	S_2/d[b]
Sintered silt A	1.70	714	11,430	6700
Expanded clay R_1	1.80	890	4,100	2300
Expanded clay R_2	2.28	140	610	260

[a] Silt A is a Cape Cod Bay mud; aggregates R_1 and R_2 are expanded shales. [b] The S_2/d ratio of the Cape Cod Bay aggregate is, respectively, three and twenty-six times that of the expanded shale ratios.

with uniform shell content for these tests. Nevertheless, a decrease in strength related to increased sand content is evident. Lower strength material might be used, however, as stabilized land fill or in jetty construction.

Sintered test bars permit a relatively accurate measure of compressive strength. However, sintered silt is most likely to find use in the form of aggregate. Table IV shows the crushing force required to compress aggregate a distance of 2.5 cm (S_1) and 5.0 cm (S_2) confined in a test compression cell. Sintered silt aggregate A from Cape Cod Bay is compared with two commercially used expanded shales, samples R_1 and R_2.

If the environmental consequences of converting dredge spoil to sintered silt are to be acceptable, potentially toxic and noxious emissions from the drying and firing operations must be controlled. Also, heavy metals present in the ceramic material must be retained in a form that cannot be subsequently removed by leaching with either fresh or salt water.

The degree to which contaminants will be released during drying and firing operations depends upon the vapor pressure of these contaminants, hence on firing temperature and permeability of the material being fired. The permeability may be estimated by considering an effusion process. If one assumes that the effective pore area is of the order of 10^{-6} of the macroscopic surface area (an estimate made by examining the fired test bars microscopically), this material will have a permeability of about 10^{-10} mol/(sec torr cm). Chemical observations provide an independent check on this value as to order of magnitude and are given below. With this permeability, in a pressure gradient of 1 torr/cm, a contaminant present initially in a concentration of 100 ppm would effuse in approximately 3 hr. Thus contaminants of low molecular weight, if present, would be released under these conditions. At firing temperatures, under oxidizing conditions, organic components will probably be oxidized to CO_2 before leaving the kiln. Among inorganic components Hg, Cd, and Pb are expected to be released in significant amounts during the firing operation. Mercury and cadmium oxides do not appear to be stable at these temperatures, and alternate nonvolatile compounds are not likely to form under these conditions (*3*). PbO has a vapor pressure of somewhat over 1 torr at our firing temperature (*4*), so that lead (Pb) can be expected to be lost from the sediment. To check our a priori estimates of contaminant stability and of the reasonableness of the permeability estimate, the case of NaCl present in the pore water of marine sediment is examined. The vapor pressure of NaCl at our firing temperature is somewhat under 10 torr (*4*) and somewhat higher than the calculated vapor pressure of PbO, so that most of the NaCl is expected to be volatilized. Analysis of the chloride remaining in our fired samples indicates that only 3% of the initial NaCl is retained.

Because permeability of the sintered silt is quite high, soluble compounds may be readily removed by leaching with water. However, it is not expected that leaching by water will remove significant amounts of environmentally important inorganic contaminants. We expect that during the firing process some metals will diffuse and dissolve into the glassy phases of the material. At our firing temperature, the process is expected to be diffusion rather than solubility limited. The diffusion coefficient for cations into the glassy phase is estimated to be 10^{-11} cm^2/sec or higher from the expression $D_0e^{-Q/RT}$, where D_0 is of the order of unity in CGS units and Q is expected to be under 75 kcal/mol. Thus a typical diffusion distance, given by $Dt^{1/2}$, where t is the firing time, will be of the order of 10 ^{3} cm, a dimension comparable to the sediment grain size. When sintered material containing the dissolved contaminants is cooled to ambient conditions, the diffusion coefficient is so reduced that negligible leaching is expected even over a period of several years. These conclusions agree with the observed inertness of glass artifacts under most conditions.

Discussion

Utilization of silty dredge spoil as construction material could alleviate the need for dumping some of this potentially harmful spoil on wetlands and submarine dump grounds. One must also consider, however, the effect of dredging at and near the excavation site. Most of the trace metal and hydrocarbon contaminants in fine-grained marine sediments are confined to the near surface layers of the bottom. Considering an average sedimentation rate of about 0.2 cm/yr for boreal estuaries (*5*), human contamination will be limited to a depth interval of 0–20 cm. It may be possible to purge large areas of the contaminated seafloor by surficial mining exposing older, and presumably cleaner, sediments for subsequent settlement and population by benthic invertebrates. The potential long-term ecologic benefits from such a mud mining operation could, in our opinion, outweigh any immediate and local perturbation to the bottom fauna caused by the dredging operation.

Those involved in harbor dredging and the construction industry may profitably interact by exploring this potentially useful resource which may provide an economically feasible method of purging harbors and estuaries of contaminated sediments.

Acknowledgments

We wish to thank Murray Ruggiero for conducting the kiln experiments and making mechanical tests on the fired materials.

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Treatment of Tar Sands Tailings with Fly Ash

Narendra N. Bakhshi,* Randal G. Gillies, and Pradeep Khare

Department of Chemistry and Chemical Engineering, University of Saskatchewan,
Saskatoon, Saskatchewan, Canada S7N OWO

■ Large quantities of tailings are obtained during the recovery of bitumen from the Alberta oil sands. Disposal of these tailings is a tremendous pollution problem. In this study, fly ash has been used to treat these tailings. Various dosages of fly ash (4, 5, 6, 7, 8 g/50 g tailings) were stirred with 50-gram samples for 30 min and then filtered under aspiration for 30 min. Fly ash dosage of 6 grams gave the best results (maximum amount of clear filtrate and a fairly dry filter cake). Based on this optimum dosage, one imperial gal (4.546×10^{-3} m^3) of tailings results in 5.93 lb (2.69 kg) of filter cake and 0.537 imperial gal (2.441×10^{-3} m^3) as filtrate which could be recycled into the plant operation. At this optimum dosage, the filtrate had a pH of about 11, a COD value of about 370 mg/l and an APHA number (color index) of about 46.

Large quantities of hot water and steam are used in the processing of oil sands by hot water flotation process to extract bitumen. The largest deposits of oil sands are in the Athabasca district in the northern part of the province of Alberta, Canada. These reserves (*1*) contain over 700 billion barrels (111.3×10^6 m^3) of crude. At present there is only one plant in operation for recovering bitumen from the oil sands, and it is operated by the Great Canadian Oil Sands Ltd. (GCOS) at Fort McMurray, Alberta (*2*). The capacity of the plant is between 100,000 and 150,000 long tons (1.016×10^8 and 1.524×10^8 kg) of oil sands per day, and the bitumen recovered is 50–90,000 barrels per day (7950–14,310 m^3 per day). After removal of the bitumen, the tailings are pumped into a pond. These tailings are gray in color, oily and alkaline in nature, and contain (depending on the depth of the pond) about 0–30 wt % solids. Tailings containing less than 5 wt % solids are reused in the plant, whereas the portion containing greater than 5 wt % solids accumulate. The ponding operations require large land areas and building of dikes which are costly. A desirable solution would be to recover as much as possible of the water for reuse in plant operations.

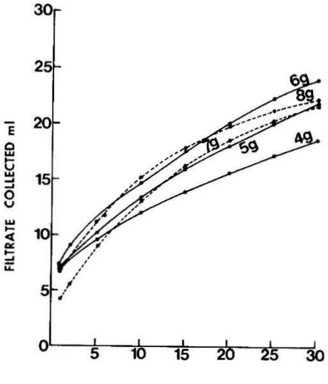

Figure 1. Filtrate collected at different time intervals for various fly ash dosages

Similarly, fly ash is a waste product of the electric power industry. To prevent air pollution, fly ash is collected by means of electrostatic precipitators from the flue gases before they enter stacks. The purpose of this study was to use fly ash, a waste product of one industry, to treat the wastes of another, namely oil sands, so that both the waste disposal as well as the pollution problems could be overcome.

Experimental

Tailings were obtained from the GCOS plant in 5-gal drums. Solids content of the tailings was about 20 wt %. The composition of the solids in the pond water (after the removal of sand by deposition) is approximately as follows (*3*):

Constituent	Wt %
SiO_2	25
Chlorite	5
Illite	10
Kaolinite	25
Montmorillonite	10
Mixed layer	10
Others	15
Total	100

Before a tailings sample was removed from the drum, the drum was shaken vigorously for about 10 min in order to mix the contents well so that a uniform sample (uniform in consistency) was withdrawn from the drum.

Approximately 50-gram samples were withdrawn from the tailings drum and placed in 250-ml Erlenmeyer flasks. To each of these flasks 4, 5, 6, 7, and 8 grams of fly ash were added. Fly ash for this study was obtained from Saskatchewan Power Corp., Regina, Sask. The major constituents of fly ash are silica, alumina, calcium oxide, ferric oxide, and magnesium oxide. These flasks containing the tailings and fly ash, were then placed on a gyratory shaker and the contents mixed for 30 min. The slurry was then filtered through a Wattman No. 40 filter paper using a 3 in Buchner funnel. Filtration was carried out under vacuum (obtained by water aspiration) for 30 min. Filtrate volumes were noted at intermediate time intervals to get some idea of the rate of filtration. The filtrate had a pH value of approximately 11, a COD value of about 370 mg/l and an APHA nmber (color index) of about 46 (at optimum fly ash dosage of 6 grams).

Results and Discussion

At low fly ash dosages (less than 4 grams), the slurry was fluid, had a tendency to stick to the walls of Erlenmeyer flask, and the rate of filtration was slow. However, at higher fly ash dosages (greater than 5 grams), the slurry became thicker, there was no tendency to stick to the

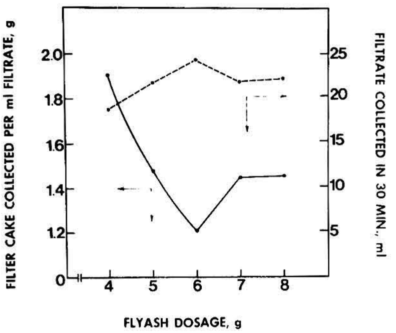

Figure 2. Amount of filter cake and filtrate at various fly ash dosages

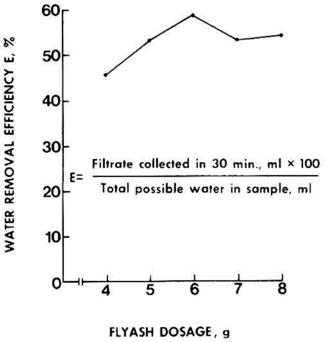

Figure 3. Water removal efficiency at various fly ash dosages

walls of the flask, and filtration was faster compared to the filtration at low fly ash dosages.

Figure 1 shows a plot of filtrate collected against filtration time at various fly ash dosages. In general, as the fly ash dosage increases the rate of filtration improves. Also, better flocculation of the tailings takes place and the fly ash-tailings slurry becomes easier to filter resulting in an increased filtration rate. At about 18 min, the filtration at a dosage of 6 grams of fly ash becomes better than the dosage at 8 grams. The result is that after 30 min of filtration, more filtrate is collected at a 6-gram dosage than at an 8-gram dosage (Figure 2). The reason for this peculiar behavior is that the fly ash is a fairly good adsorbent. Though initial filtration rate is somewhat better at an 8-gram dosage than at a 6-gram dosage, a greater amount of water is retained by the fly ash at the higher dosage, thus ultimately reducing the total amount of filtrate. This point is brought about more clearly in Figure 2. Figure 1 also shows that there is a marked improvement in filtration rate when the fly ash dosage is increased from 4-5 grams; the improvement from 6-8 grams is only marginal. The behavior of the filtration curve at a 7-gram fly ash is erratic and we cannot explain that at present.

The behavior of the filter cake during filtrations was of interest. From the industrial point, the main requirement is that sufficiently dry material should be obtained such that it can be handled easily. At low fly ash dosages the residue on the filter paper was like a thick slurry and stuck easily to the surfaces of the funnel and the flasks. However, at a dosage of a 6-gram fly ash, the characteristics and appearance of the residue changed remarkably. It did not stick to the walls of the funnel and furthermore after filtration, the filter cake was almost dry and had a cracked appearance. Increasing the fly ash dosage improved the appearance of the filter cake and increased the filtration rate; however, the total amount of filtrate obtained was decreased. Thus, increasing the fly ash dosage (beyond the optimum value of 6 g/50 g of tailings) improves the desirable characteristics of the filter cake, though a penalty is incurred such that the amount of filtrate collected decreases.

It would be interesting to know, from the practical point of view, how much solid cake can be expected from the treatment of tailings with fly ash. Figure 2 shows the amount of filter cake per ml of filtrate (if the filtration time is fixed at 30 min for various fly ash dosages). As expected, the minimum amount of filter cake per ml of filtrate is obtained at a fly ash dosage of 6 grams. At this dosage rate 1.2 grams of filter cake are produced for each ml of filtrate collected.

Another important question arises as to what fraction of the total water in the tailings can be recovered by the fly ash treatment. This water removal efficiency, E (filtrate collected in 30 min divided by the total amount of water present in 50 grams of sample) is plotted in Figure 3—a maximum of 59% water recovery can be obtained at a dosage rate of 6 grams of fly ash. The remaining amount of water remains tied up with fly ash in the filter cake.

Materials Flow Estimation

If it is assumed that the design point is at 6 grams of fly ash/50 grams of tailings, then approximate order-of-magnitude estimates can be made for the daily requirements of fly ash, filter cake to be disposed of as waste solids, and filtrate that can be recycled into the plant operations. Based upon this value, it is estimated that one imp gal (4.546×10^{-3} m^3) of tailings results in 5.93 lb (2.69 kg) of solids as filter cake, and 0.577 imp gal (2.53×10^{-3} m^3) of filtrate that can be recycled. On the basis of the present GCOS tailings outflow of 4.8×10^6 imp gal (21.821×10^3 m^3) per day, 2.6×10^6 imp gal (12×10^3 m^3) per day will become available as recycle water along with 12,750 long tons (12.955×10^6 kg) per day of filter cake to be disposed of as waste solids. Daily fly ash requirements will be about 2140 long tons (2.174×10^6 kg). It is obvious that one is talking about huge material handling problems.

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CORRESPONDENCE

SIR: Your November '74 Current Research section had a paper which showed that mussels were killed and oysters harmed by "diluted" outboard motor effluents. A quick calculation of this "low level" water pollution in relation to the number of boats needed to produce it shows: (a) the combustion products of 5 liters of fuel wound up in 2500 liters of seawater; this killed mussels; (b) it took 100 min for an 18-hp outboard to consume the 5 liters of fuel (these two steps are data from the paper); and (c) if all this happened on a water body 3 meters deep, it would require a straight 24-hr run by a group of boats each occupying a space 3 by 4 meters on the water surface. This is the supreme nightmare of all boaters—wall to wall boats!

Too bad the authors didn't consider the effects on the boaters—fumes, noise, collisions, etc. I'd rather be an oyster.

2525 Blackwood Road
Wilmington, Del. 19810

Donald W. Smith

Reply

SIR: Donald W. Smith very ably emphasizes the problem of relating preliminary data obtained in the laboratory to the real world. We did not state in the paper that wall-to-wall outboard motors are a realistic probability—although there are sports fishermen who will argue the point, especially on opening day of the fishing season. We believe, however, that our initial statement, "Outboard motor effluent may be a significant source of petroleum pollution in the aquatic environment," represents a realistic assessment of the danger to some productive estuarine environments. In point of fact, the 50-ppb n-hydrocarbon content of the outboard motor effluent used in our study seems reasonable as an upper limit for a bioassay when compared with a value of 7 ppb of n-hydrocarbons we found in water near a boat-launching ramp in Puget Sound.

Shellfish do not grow to maturity in the relatively unpolluted high seas as do tuna and salmon. Oysters and mussels are, like most aquacultured organisms, convenience crops grown close to home and close to active petroleum-powered boat traffic. Oysters and mussels are filter-feeders, concentrating particulate matter by pumping many liters of seawater daily and exposing themselves to food and to whatever else the water may hold. When petroleum leakage from boats occurs in an area of limited flushing, especially in shallow estuaries where oysters are grown, the potential for shellfish pollution becomes real as petroleum toxicants accumulate. Set in the context of sediment-incorporated petroleum components continuously replenished and released through time, the additional effluent from outboard motors could indeed represent an underestimated source of pollution to living marine resources.

The data from our laboratory studies indicated that small amounts of petroleum from outboard motor wastes may adversely affect shellfish. We hope that someone will now have the opportunity to evaluate water quality, at the ppb level, of productive marine environments shared above by man and below by valuable marine organisms sensitive to toxic components of petroleum.

For John S. Finley, Northwest Fisheries Center, and Gary G. Gibson, Oregon Fish Commission,

Robert C. Clark, Jr.
Research Oceanographer
Northwest Fisheries Center
Seattle, Wash. 98112

SIR: In July '74 issue of *Environmental Science and Technology*, Sutton and Calder (*1*) state that "there is no mention in the literature of solubilities of the higher normal paraffins in high ionic strength media such as seawater." Thus they studied the dissolution of several higher-molecular-weight n-paraffins (n-C_{12} to n-C_{26}) in distilled water and in one seawater sample.

We wish to inform the readers of your journal that we have previously presented an in-depth study of hydrocarbon "solubility" in saline solutions and in seawater (*2*) using n-paraffin (n-C_{16} and n-C_{20}), aromatic, and isoprenoid hydrocarbons. We intentionally put the word "solubility" in quotes as our study indicated that the quantities of hydrocarbon passing a filter are very much dependent on many experimental factors. As we had cautioned readers of our work against interpreting values that we obtained as "absolute hydrocarbon solubilities," we wish to stress this again to readers of Sutton and Calder (*1*). These authors employed an identical criterion for "solubility" as we did; that material which passes a filter. However, they have not considered and therefore failed to indicate that the shaking and standing times of the hydrocarbon/water mixture, the type of filter used and its pore size, the amount of hydrocarbon added to a given water volume, all will affect the n-paraffin "solubility" values obtained (*2–4*).

Sutton and Calder (*1*) also do not consider the important role that the dissolved organic matter in seawater plays in making n-paraffin hydrocarbons more "soluble" (*2*). In considering the "solubility" behavior of hydrocarbons through an estuary and into the open ocean, we have found in studies on high ionic strength media that not only can the dissolved organic matter play an important role (especially in near shore waters), but that the combined effect of this material and the changing salinity in the media gives a nonlinear "solubility" trend (*2*). We also found that n-paraffin "solubility" in seawater is dependent on the pH of the media (*2*). Therefore, it appears that Sutton and Calder (*1*) have presented an incomplete and hence misleading picture of the solubility behavior of hydrocarbons in estuarine waters between 0 and 35% salinity.

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Graduate School of Oceanography
University of Rhode Island
Kingston, R.I. 02881

Paul D. Boehm
James G. Quinn*

Reply

SIR: We would like to reply to the comments of Boehm and Quinn regarding our article in a recent issue of *Environmental Science and Technology*(*1*). We feel that many of these comments are either incorrect or irrelevant for reasons given below.

It was not our intention to present a "complete" picture of the behavior of hydrocarbons in water, but rather to determine, with as much rigor as the techniques available to us would permit, the true solubility of the hydrocarbons tested, to determine their empirical salting parameter, and to compare this parameter to one calculated from a rather simple theory. We did not attempt to mimic the real environment, but rather attempted to provide hard data which could serve as a partial basis for understanding it. We feel the critical reader will find adequate mention of the limitations of our experimental data with regard to real world situations and therefore should not be "mislead."

In their letter, Boehm and Quinn state that we failed to consider the effects of shaking, standing, and filtration methods on observed "solubility." This is erroneous. In fact, we considered them very carefully and selected techniques which would give the best possible solubility data.

Boehm and Quinn (2) equilibrated their solutions by shaking for 30 min on a metabolic shaker at a rate of 120 strokes/min with an amplitude of 5 cm per stroke. They then allowed the solutions to stand for 30 min before filtering through a Whatman GF/C glass fiber filter.

By agitating their solutions so violently, they imparted enough energy into the system to disperse the hydrocarbon solutions into very small droplets. In 30 min, probably only the larger droplets coagulate and rise to the surface, while a significant portion of the solute remains dispersed in droplets. The fraction of the total dispersed colloids which ultimately rise to the surface depends not only upon the buoyancy and size of the droplets, but upon the collision kinetics between droplets as well. Smaller droplets rise more slowly; however, collision and coagulation will result in larger droplets which rise faster. The collision rates between droplets depends upon the total number of droplets in each size range. This, in turn, depends upon the initial amount of hydrocarbon solute present as well as the energy imparted to the system (agitation rate and duration) (*3*). Whether the droplets coagulate or not depends upon the height of the energy barrier arising from long-range electrical interactions between the droplets. The height of the energy barrier is dependent not only upon the nature of the substances composing the droplets but upon parameters affecting the nature of the solution such as ionic strength, pH, and dissolved organic compounds. The hydrocarbons appearing in their filtrate represent the sum of those truly dissolved, those dispersed as colloids small enough to pass through the filter, and those existing as larger colloids which may have been ruptured and pulled through the filter by the relatively harsh technique employed (200 mm Hg suction through filters of uncontrolled pore size). In summary, we feel that the paper of Boehm and Quinn (*2*) is kinetic in nature, and that their results reflect the effect of numerous parameters upon the rate of formation and the rate of disappearance of hydrocarbon droplets.

In contrast to the experimental procedures of Boehm and Quinn, we equilibrated hydrocarbon solutions for 12 hr by gentle shaking. After shaking they were allowed to sit undisturbed for 24 hr. Thus we hoped not only to avoid the dispersal of the hydrocarbons as very fine drops, but also to allow sufficient time for any droplets formed to coagulate and rise to the surface. In addition, preliminary experiments showed that equilibration times in excess of 12 hr produced no further increase in concentration of *n*-paraffins in water which was passed through a 0.45 μm filter. Thus we believe that our solubility values represent hydrocarbons in solution rather than submicron-sized droplets. Filtration was accomplished with very gentle suction (approaching gravity filtration) through 0.45 μm Millipore filters. When greater suction was used, higher apparent solubilities were observed, presumabily through the rupture of droplets trapped on the filter.

Both Boehm and Quinn (*2*) and Sutton and Calder (*1*) deal with the general subject of the behavior of hydrocarbons in aqueous solution. Each paper deals with a different aspect of the problem, with different methodologies. Neither paper answers all the questions on the subject, nor were they intended to.

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Cities Service Oil Co.
P. O. Box 50408
Tulsa, Okla. 74150
Chris Sutton

Department of Oceanography
Florida State University
Tallahassee, Fla. 32306
John A. Calder*

Sir: In the paper by D. L. Johnson and R. S. Braman [*ES&T*, 8, 1003 (1974)], it is interesting to note that the mean of the total mercury concentrations recorded in air in the Tampa area (Table I) was about 19 ng/m^3, whether determined for all stations or for rural and suburban stations alone, which is very close to the 20 ng/m^3 worldwide average air mercury level estimated by Williston in 1968 (*J. Geophys. Res.*, Vol 73, p 7051). My own calculations indicate that contributions of mercury from burning of fossil fuels to regional airborne mercury concentrations in the Carolinas are small (0.1 to 0.5 ng/m^3), assuming that uniform atmospheric distribution occurs and that the average residence time of air masses over the Southeast is on the order of 3 days (an admitted oversimplification).

The observations on mercury mobilization in soil are suggestive of needed research on ecosystem dynamics of mercury compounds. My research has indicated that native mammals in the Southeast exhibit mercury levels that are related to soil types in different physiographic regions (*Proc.*, Southeastern Assoc. Game and Fish Commissioners, Vol. 28, in press). Hopefully, suitable techniques are now available for investigation of the cycling of mercury in natural systems.

Duke Power Co.
Charlotte, N.C. 28201
P. M. Cumbie

Reply

SIR: We agree with P. M. Cumbie that much more needs to be done on the ecosystem dynamics of mercury. Our techniques should be useful to that end.

Statements about mercury concentrations need comment. We can find no estimate for a worldwide average mercury concentration in the referenced article by Williston (*J. Geophys. Res.*, **73**, 7051). Our data are in agreement with Williston in that a considerable variability in mercury content in air is observed, especially in the presence of sources of mercury. We found background levels of mercury were generally in the 3-6-ng/m^3 range, approximately the same as reported by Williston. Open ocean concentrations, taken aboard ship and likely influenced by aerosolization of seawater, were an average of 6.5 ng/m^3 (16 samples) for total mercury; of this, 1 ng/m^3 (3 samples) was elemental mercury and the balance mercury (II) chloride type compounds.

Our estimate of the effect of two coal-fired power plants on mercury in the Tampa Bay area is that they provide approximately 1 ng/m^3 of the total mercury (15-33% of the 3-6 ng/m^3 lower ambient levels).

Consequently, coal-fired power plants may constitute a higher percentage source of general mercury-in-air than estimated by Cumbie.

University of South Florida
Tampa, Fla. 33620
Robert S. Braman*
David L. Johnson

INDUSTRY TRENDS

Lockheed Electronics Co., Inc. (Plainfield, N.J.) received a $317,000 contract from the EPA to provide aerial collection and interpretation of environmental data.

Harza Engineering Co. has received a contract from the Cleveland-Cliffs Iron Co. (Cleveland, Ohio) for the development of a tailings disposal scheme for the Tilden Mine at Ishpeming, Mich.

The Marex Co., Inc. has recently been formed at Woodcliff Lake, N.J., to provide sales and technical expertise in air and water pollution instrumentation. Marex offers a complete marketing program for certain clients.

Standard Laboratories, Inc. (Charleston, W.Va.) has formed a micro-biological department for analysis of sewage or industrial discharges. The company is very active in coal testing, and other aspects of water testing.

Predicasts, Inc. (Cleveland, Ohio) predicts that the large diameter pipe market could reach $3.6 billion by 1985.

The Heil Co. (Milwaukee, Wis.) is providing the U.S. Air Force with a pulverizer on wheels to help the Air Force solve solid waste hauling and disposal problems.

Hydroscience, Inc. (Westwood, N.J.) will work on a $329,000 project to study future marine wastewater disposal requirements for Nassau County's pollution control facility at Bay Park, N.Y.

Aerosol Techniques, Inc. (Milford, Conn.) has acquired a 50% interest in Leaf Processing, Inc., a New Jersey firm that recycles leaves into fireplace logs sold under the trade name "Ecol-O-Log."

Holmes & Narver, Inc., a part of the U.S. Filter Corp., was selected as engineer and construction manager for a $40-million copper facility for Sociedad Minera Pudahuel, Ltda., of Chile.

Combustion Engineering, Inc., will provide two 750-MW lignite-fired steam generators under a contract with Texas Utilities Services, Inc.

Brand Insulations, Inc. (Chicago, Ill.), an insulation contractor working mainly with electric power projects and chemical plants, denied that it has filed, or was considering filing under Chapter XI of the Federal Bankruptcy Act.

Dearborn Chemical Domestic (Chicago, Ill.), involved in wastewater and cooling water treatment activities, as well as boiler water, has established a new sales district in Indiana.

Henningson, Durham & Richardson, Inc., of Texas (Dallas, Tex.) announced start-up of a new $3.5-million, 7.3-mgd water pollution control plant that the firm designed, at Lufkin, Tex.

Perkins Engines Group (Peterborough, England) and Industrialite (Holdings) Ltd., have organized Industrialite (Quiet Power) Ltd. to market materials and methods for reducing diesel engine noise.

Procon Inc., a subsidiary of Universal Oil Products Co., will build a demonstration solid wastes recovery plant to handle 200 tpd of refuse, in San Diego County, Calif.

The Conference Board (New York, N.Y.) said that the U.S. now imports more oil from Arab countries than it did before the embargo.

Union Camp Corp. (Wayne, N.J.) will invest $101 million to optimize operations at its paper mill at Franklin, Va. Conservation of energy, water, and other resources will be emphasized.

Sumitomo Jukikai Envirotech has received an award for outstanding performance of its wastewater treatment plant for coal washing for Mitsui Coal Mining Co., of Hokkaido, Japan.

The Midrex Corp. (Charlotte, N.C.) can offer direct reduction plants using any solid or liquid fuel. Off-gas from refineries can also be used.

Fluor Corp. will engineer, design, procure, and construct a gas processing and crude oil stabilization facility for Pertamina, to be built at Santan, East Kalimantan, Indonesia.

Normandeau Associates, Inc. (Bedford, N.H.) will provide ecological input to a multidisciplinary study of the Merrimack and Nashua Rivers for the National Commission on Water Quality.

General Motors Corp. has taken the position that new cars' pollution limits are adequate to achieve federal air quality standards in almost all of the nation, if the emission control program is given time to become fully effective.

The National Center for Resource Recovery (Washington, D.C.) has received a commitment of $100,000 from Anheuser-Busch, Inc., for furthering research in materials and energy recovery from solid waste.

The Electric Power Research Institute (Palo Alto, Calif.) awarded $650,000 to FMC Corp. to do research in production of low-sulfur gas from coal.

The American Petroleum Institute (Washington, D.C.) has commissioned the Woods Hole Oceanographic Institution to do an "interaction analysis" of commercial fishing and the offshore oil industry along the northern Atlantic coast.

Mitsubishi Petrochemical Co., Ltd. (Tokyo, Japan), together with Yazaki Corp., is exporting cable drums made of recycled plastic waste from Mitsubishi's "Reverzer System."

Howard Needles Tammen & Bergendoff has established a new Environmental Quality Dept. in Milwaukee, Wis., to handle a growing business in air and sound studies.

Peabody Galion Corp. reports that its backlog of $146 million at the end of 1974 exceeded the backlog at the start of 1974 by 38%.

Camp Dresser & McKee Inc. has merged with Ross, Saarinen, Bolton & Wilder, Inc. (Fort Lauderdale, Fla.), which is now a wholly owned subsidiary of Camp Dresser & McKee.

Belco Pollution Control Corp. (Livingston, N.J.) has licensed Hascon Italia S.p.A. (Milan, Italy) to manufacture electrostatic precipitators of Belco design.

Rexnord has completed a major reorganization within its Process Machinery and Industrial Products Divisions that manufacture the Nordberg product lines.

Enpo-Cornell Pump Co. (Piqua, Ohio) announced the availability of a new wet-well sewage pumping station that can handle up to 700 gpm and heads up to 120 ft TDH.

Health-Chem Corp. (New York, N.Y.) has received a patent for pest repellent controlled release plastics. Herculite Protective Fabrics Corp., a subsidiary, is the patentee.

NEW PRODUCTS

Microstrainer
Four-model package, preassembled with a rotating drum in a steel tank with the drive unit and backwash pump, is suitable for potable and industrial water treatment, sewage effluent purification and pulp and paper mill wastes. Crane Co. **103**

Microbiocide
Controls the growth of algae and bacteria in recirculating cooling water systems without producing large amounts of foam. Lonza Inc. **104**

Air sampler
Aluminum-housed electric heating mantle and a proportional control system permit air effluent testing with immediate test results. The mantle fits around a glass syringe inserted into an air duct for sampling. The control system controls the syringe temperature. Glas-Col Apparatus Co. **107**

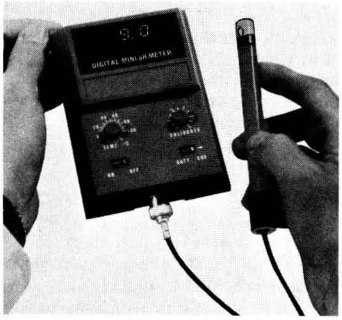
Toluene analyzer
Portable infrared analyzer is calibrated to detect and measure toluene vapors in ambient air samples from industrial areas. It will read directly in toluene concentration, and has two selectable ranges: 0–250 ppm and 0–1000 ppm. Wilks Scientific Corp. **105**

Water treater
Electrostatically removes and controls scale, corrosion, and algae in industrial water systems. No chemicals are used in the unit. The unit can treat as much as 1.5 million gal of water for 24 hr. Ingersoll-Rand **101**

Butterfly valves
The valves have a molded disc and liner of high molecular weight polyethylene for operation in SO_2 scrubber systems involving flyash. The valves are abrasion and corrosion resistant, and can be used in systems at pressures from vacuum to 150 psi, and temperatures from −30° to 250°F. Garlock Inc. **130**

Liquid sampler
Continuous flow-through sampler consists of two dozen 500-ml bottles in a refrigerated compartment. It can receive discrete or composite samples ranging from 10–350 ml with a diversion interval at 1, 2, or 5 min. The sampler is useful in storm and combined sewer sampling, in treatment plants, and in industrial effluent sampling. Pro-Tech, Inc. **131**

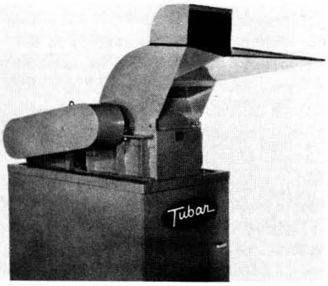
Dehydration equipment
Portable equipment combined with heat-generating chemicals will dehydrate oil waste sumps, sewage, and industrial and municipal sludges. The equipment is suitable for removal of silt, sand, and debris from waterways. Westerlox Corp. **102**



Digital mini-pH meter
Battery-operated meter is designed for field measurements. Readings having a 0.1 resolution over the full 0–14 pH range are obtained. Meter accuracy is 0.2 pH over the full range; reproducibility is 0.05 pH. L. G. Nester Co. **106**

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

Suspended solids analyzer
Model allows continuous measurement of mixed liquor suspended solids in an activated sludge sewage treatment plant without sampling. Instrument ranges are: 500–5000 ppm, 1000–10,000 ppm, and 1000–20,000 ppm. Keene Corp. **108**



Shredder
Designed for chemical manufacturers and recycling centers. The shredder mutilates most plastics, and steel and aluminum cans, reducing their bulk. Uhrden, Inc. **109**

Chlorine detector
Instrument provides a continuous indication of chlorine in water without titration. Available in two ranges: 0.03–1.0 ppm and 0.3–10 ppm chlorine by weight. The strip chart recorder will continuously record for up to 31 days. Deltatec Corp. **110**

Digital timer
Solid state, digital miniature industrial duty timer. It provides time-function control to air valves, pumps, and motors. Dynapar Corp. **111**

Pressure plate filter
High-capacity, compact plate filter features a vibratory cake discharge that eliminates the need for stuffing boxes and bearings. Applications include waste fluid clarification, sewage treatment, and cleaning of oils and emulsions. Black Clawson Co. **112**

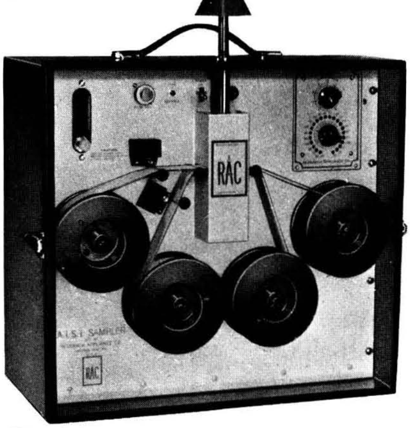
Dust collection system
Captures particulate matter from gas streams with better than 99% efficiency while using up to only 100 lb psig plant air. Sequential bag cleaning is automatic and continuous. Carborundum Co. **113**

(continued on page 370)

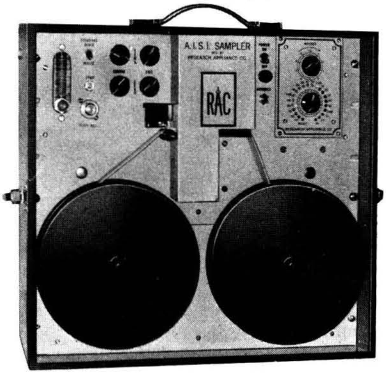
For automatic, cyclical sampling of particulates, H_2S gas, and fluorides in ambient air...

specify RAC filter tape instruments

RAC Model
G2 SER Monitor



RAC Model G2DT
Fluoride Sampler



RAC Model
G2-T-600
Monitor

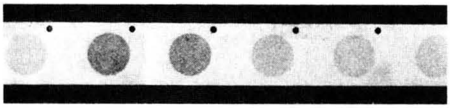
this line of versatile, precision samplers & monitors provides a wide range of capabilities to meet air sampling requirements

RAC offers a variety of portable, automated, timer-controlled instruments designed to sample/monitor airborne *particulate matter*—to **ASTM D1704** specs—by means of filter tapes. Particles down to 3.4 microns (and smaller) are collected automatically and accurately during preset sampling cycles. In addition, RAC particle samplers can be easily adapted to sample *hydrogen sulfide gas* (H_2S) in concentrations ranging from 0.02 to 20 ppm. *Fluorides,* both gaseous and particulate, are sampled simultaneously with a dual-tape instrument.

Engineered to operate unattended and with optimum repeatability, these precision designs are among the most versatile, adaptable devices available for both indoor and outdoor air sampling/monitoring operations. RAC **monitor** configurations automatically evaluate sample spots by means of an integral densitometer, and provide an output signal that can transmit the densitometer readings to a remote data collection device or station.

The scope of application for RAC tape instruments depends largely on users' needs and ingenuity. They can be used to detect air pollutants, to indicate the rate and frequency of change in ambient pollution concentrations, to provide data for determining source and distribution of atmospheric contaminants, to check the efficiency of dust collection and air filtration equipment, to plot traffic flow/density patterns, to correlate wind direction with ambient pollution levels, and for similar types of air sampling/monitoring operations.

Ten different models . . . plus a variety of specialized options . . . are available to meet virtually any air sampling/monitoring requirement within the capabilities of RAC filter tape designs.



Section of
filter tape
showing
typical 1" dia
sample spots.

For details on particle & H_2S samplers, send for BULLETIN 2300.
CIRCLE 19 ON READER SERVICE CARD

For details on dual-tape fluoride sampler, send for BULLETIN 2356.
CIRCLE 20 ON READER SERVICE CARD

STACK SAMPLING SEMINARS
Since 1970, RAC has sponsored an annual series of 2-day, technical, practical seminars on stack sampling parameters & procedures (EPA methods). **Write for descriptive folder.**

CIRCLE 21 ON READER SERVICE CARD

RESEARCH APPLIANCE COMPANY
Route 8, Gibsonia, Pennsylvania 15044
Environmental Instruments / Laboratory Products

Solvent recovery plants
Package plants recover volatile solvents with efficiencies of 95% or more. The factory-assembled units are capable of handling up to 24,000 cfm. American CECA Corp. **114**

Dissolved oxygen probe
Designed for field measurements, it is usable to depths of more than 200 ft. The probe components can be replaced without replacing the entire probe-cable assembly. The probe contains a sensor for measuring water temperature and a submersible stirrer attachment for monitoring applications. Yellow Springs Instrument Co. **115**

Sigma computer
The unit calculates the standard deviation of an analog input signal based on 65 discrete samples of the input. Developed for calculating the standard deviation of wind direction for use in air pollution dispersion studies, the unit can be used with any signal whose sigma is required. Climatronics Corp. **116**

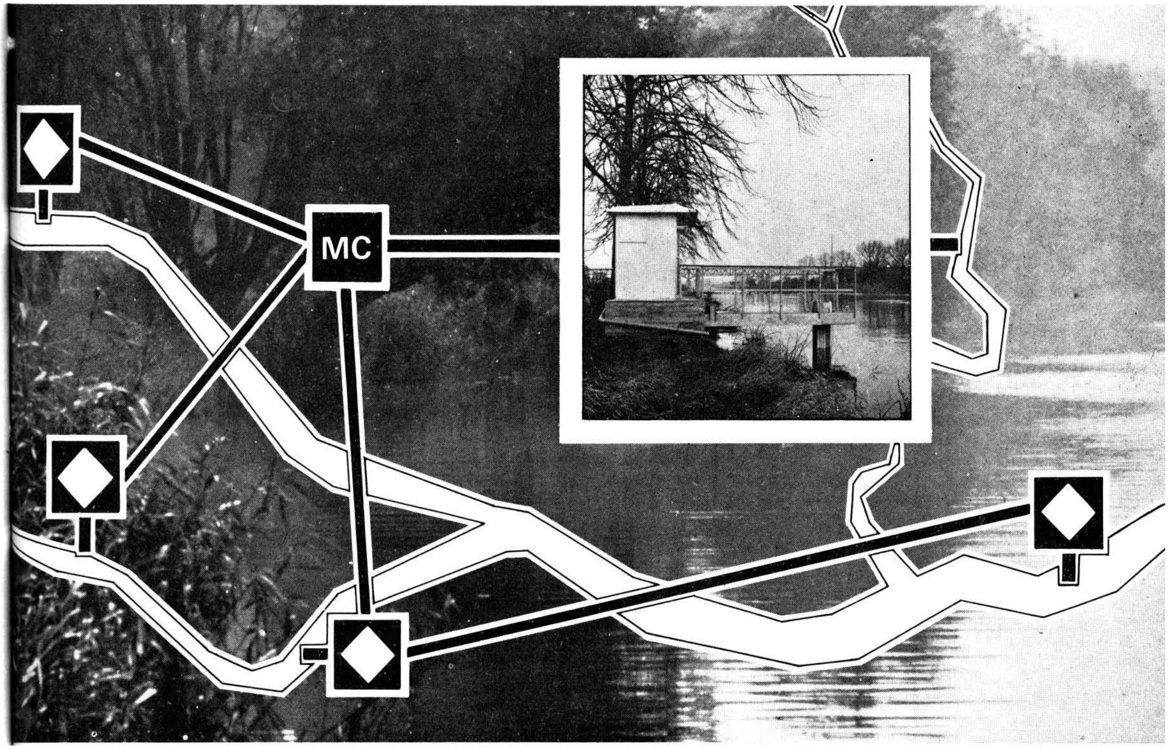
Oil spill collector
Free-floating collector tube moves continuously over the surface of ponds or settling basins where spills or leaks may occur, and brings the oil to a sentry unit. The sentry unit sends out an alarm to alert personnel. The collected spilled oil is stored in tanks. Oil Skimmers Inc. **117**

Data acquisition system
Digital magnetic tape cassette recorder accepts a data set of up to 8 channels of analog input data and produces a record in incremental 16-bit BCD format. The capacity of each cassette is 15,000 data sets or 120,000 data points. Interfacing electronics to any readout or computer system is available. InterOcean Systems, Inc. **118**

Fuel additive
Magnesia/alumina slurry is designed to improve combustion, minimize slagging, and eliminate cold-end corrosion problems in coal- or oil-fired boilers. Chemed Corp. **119**

(continued on page 372)

THIS SYSTEM



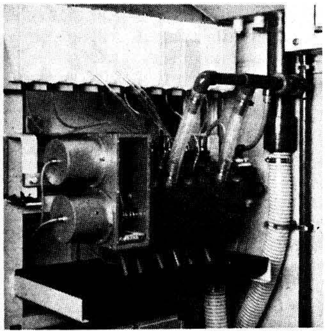
...monitors this stream's water quality automatically

Philips have turned a concept into a reality with this automatic water monitoring system based on continuously operating, fully automated stations.

Running unattended for a month or more, these stations are actually automatic laboratories, measuring any desired combination of pH, redox, pCl or other ion activity, conductivity, dissolved oxygen, temperature, and turbidity. You determine what you mean by water quality . . . and this system will measure it.

Besides automatic measurement, each station also provides automatic sensor cleaning . . . automatic calibration . . . automatic sampling . . . automatic emergency storage . . . automatic in-station recording . . . automatic alarm . . . and even automatic data transmission to a central Processing Unit.

The key to the system is its flexibility. Data may be provided in virtually any form, and transmitted by line or radio link. Each station is engineered to the application. The central Data Reductor can be as simple as a chart recorder . . . as sophisticated as a computer.



Inside view of station showing measuring bank.

By cutting manpower costs to the bone, the Philips system is now on-stream, making real-time water quality management a reality—at **lowest applied cost.**

If your job is controlling the quality of surface water, drinking water, or domestic/industrial effluents, you should get the full story now.

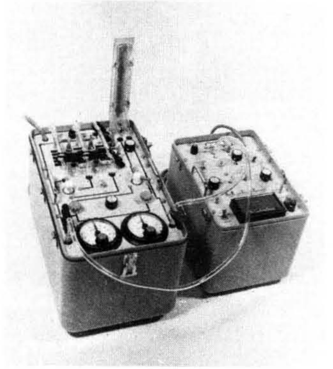
Philips Industries
Pollution Monitoring Department
Building TQ-III-4
Eindhoven, The Netherlands

PHILIPS

Philips Environmental Protection

CIRCLE 7 ON READER SERVICE CARD

Probe colorimeter
Fiber-optic probe, dipped directly into the solution being tested, is designed for repeated colorimetric testing done at the same wavelength. The smallest measurable sample is 0.5 ml. The probe has been used in water testing and as a turbidometer. Brinkmann Instruments, Inc. **120**



Mercury collector, measurer
Portable system can be used for field measurement of elemental mercury in air or other gases to levels below 0.1 $\mu g/m^3$. A separate pyrolysis stage allows measurement of organic mercurials. Thermotron Corp. **121**

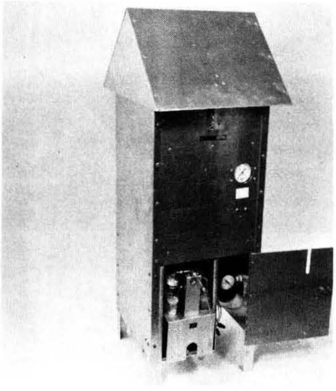
Electrostatic precipitator
Two-stage electrostatic precipitator with an enclosed motor, a solid state electrical system, and a mechanical prefilter. Eliminates smoke from welding, soldering, and machining; mist from oil; dust from plastic and asbestos; as well as fumes, bacteria and pollen. Car-Mon Products, Inc. **122**

Chemiluminescence monitor
Measures NO, NO_x, NO_2, and O_3. It is designed for unattended ambient air monitoring, and has a useful range from 0.002–10 ppm. Aero-Chem Research Laboratories, Inc. **123**

Noise average meter
Measures fluctuating noise levels, and computes the total noise dose received by a worker at the bench. From this value it computes the Equivalent Continuous Noise Level from a sampling time as short as 10 sec, or over periods of up to 24 hr. Computer Engineering Ltd., England **124**

Water ultrafilter
Filters prefiltered water to remove submicronic suspended solids, and thus ensures accurate analysis of dissolved chemicals in wastewater. It also removes turbidity, algae, and bacteria from home potable water systems. Rated flow of visually clear water is 8.5 gpm at an inlet pressure of 40 psi. Motor Guard Corp. **125**

Dissolved solids meter
Battery-operated meter provides on-site testing of inorganic dissolved solids in ppm. Its range is 0–1200 ppm. The meter can be used to sample downstream salt contamination of streams and rivers. Edmund Scientific Co. **126**



Gas, particulate samplers
Samples ambient particulates and NO_2, SO_2, H_2S, ammonia, and aliphatic aldehydes. Both samplers are contained in the same aluminum shelter, and can be run simultaneously from any of five different timers. Misco **127**

Water parameter analyzers
Continuous analysis of individual water quality parameters such as pH, temperature, conductivity, turbidity, and dissolved oxygen. These instruments can be used to monitor industrial and municipal wastewater, potable water supplies, and process control. Sensing elements are designed to operate remotely from the signal conditioner. Raytheon Co. **128**

SO_2 sampling pumps
Pumps are available with welded bellows manufactured from corrosion-resistant material. A wide range of flows (0.20–5.0 cfm) and pressures (10–50 psig) is available. Metal Bellows Co. **129**

NEW LITERATURE

Research and development services. Booklet (PS-137), "Combustion/ Fluids & Process Technology describes R&D services of the company. Power Systems Group, Combustion Engineering, Inc. **151**

Vertical pumps. Bulletin 353 describes a series of CPVC bearing-free vertical pumps in five sizes. Flow capacities 10–85 gpm at temperatures to 210° F. Sethco Mfg. Corp. **152**

Impurity eliminator. Bulletin 2804 describes the company's line of small cyclone separators that remove impurities from pumped liquids. Dorr-Oliver Inc. **153**

Flow measurement. Application Note No. 3, "Measuring Open Channel Wastewater Flows," covers some basic considerations in effluent flow measurement. Leupold & Stevens, Inc. **154**

Chromatography. Brochure on the firm's PEP-2 chromatography data system, including detailed descriptions of hardware and software, is now available. Perkin-Elmer **155**

Column packing. Bulletin DS 055 describes column packing material for gas chromatography for pesticide, fuel oil, and aromatic compound analysis. No column bleeding or pooling. Waters Associates Inc. **156**

Environmental control. Bulletin B-36B describes successful air pollution and water influent and effluent systems, and their instrumentation. The Foxboro Co. **157**

Filters. Bulletin TI-7 describes use of the company's filters in sampling techniques. Balston, Inc. **158**

Baghouses. Bulletin 742 outlines design features and time- and money-saving advantages of the firm's line of baghouses. Percy Todd Manufacturing Co. **159**

Membrane separations. Brochure (FS-4) describes ultrafiltration and reverse osmosis systems applications for the dairy industry. Universal Oil Products Co. **160**

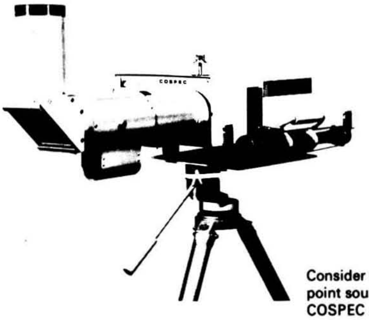
Water testing. Company has just published a comprehensive instruction manual of water and wastewater test procedures. Free to bona fide analysts. Hach Chemical Co. **161**

X-ray microanalysis. Application Note XAS-21 describes a computer program applicable to X-ray microanalysis. Ortec, Inc. **170**

Biocides. Bulletin 719 describes biocides effective against biological fouling in cooling water systems. Betz **171**

Infrared bibliography. Lists 150 infrared reprints on subjects from sample preparation techniques to textile analysis. Perkin-Elmer **175**

Labware. Release No. 3-75 describes a full line of laboratory ware, including numerous items applicable to sampling. Nalge Co. **163**



Cooling water treatment. Brochure describes company's cooling water treatments that have won the Honors Award in the John C. Vaaler competition. Nalco Chemical Co. **176**

Spectroscopy. New 20-page catalog, "Instruments for Spectroscopy," describes the firm's spectroscopy and spectrophotometer lines. GCA Corp. **177**

Salt removal. Publication No. 446 describes the use of ultrafiltration systems for desalting and salt exchange applications. Technique of "diafiltration" is discussed. Amicon Corp. **178**

Quality assurance. A 40-page catalog lists instruments, reagents, and appliances needed in quality control laboratories. Fisher Scientific Co. **179**

Process control. Booklet describes company capabilities in process control systems that protect the environment and save energy. Honeywell **180**

Vinyl chloride analysis. Company's Model 511 Flame Ionization Gas Chromatograph analyzes vinyl chloride at sub-ppm levels. Analytical Instrument Development, Inc. **198**

Shredders. Bulletin No. 744 features a line of Piggy-Back shredders for shredder/baler applications. Blower Application Co. **199**

Safe electric outlets. Catalog No. 100 describes, among other items, safety electrical outlet strips designed to prevent the user from receiving a fatal shock. SGL Waber Electric **181**

pH control. Company has published a brochure describing the use of carbon dioxide for pH control for municipal water treatment and industrial wastewater treatment. Chemetron Corp. **194**

Air samplers/monitors. Bulletin 2300 describes filter tape instruments which are automatic, time-controlled, and portable, for sampling particulate matter in air. Meets ASTM D1704 specifications. Research Appliance Co. **196**

Sludge evaporation. Bulletin No. 10034, "Lined Lagoon Evaporates Industrial Sludge," tells how a 5-acre lagoon, with 26.5 million gal of electroplating wastes, was lined to prevent erosion. Staff Industries, Inc. **184**

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

"Lab Reporter." Latest edition of "Lab Reporter," Vol. 12, No. 2, describes low-cost gas chromatographs for fast analysis of gases and light hydrocarbons; digital pH meters, small spectrophotometers, and a complete freeze-drying lab. Fisher Scientific Co. **182**

Particle separation. Bulletin No. 309/14-294-15 describes the Model L3P sonic sifter for all types of dry particle separation, even from 850 mμ down to 5 mμ. Fisher Scientific Co. **185**

Process control. Publication, "Industrial Instrumentation" C-1b, covers recorders, positioners and actuators, environmental instrumentation, and special-purpose instruments and computers. Honeywell Process Control Division **186**

Grease filters. Technical manual, "Design of Grease Filter Equipped Kitchen Exhaust Systems" (Form GF-1762 Rev.), describes how grease filtering offers reduced air pollution and better kitchen sanitation and working conditions. Research Products Corp. **188**

Refuse moving. Two-page flyer, "Refuse Handling Idea No. 44," tells how the firm's conveyor system moves 60 tons of refuse at a modern transfer station each hour. Systems for salvageable and unsalvageable refuse are described. MAYFRAN, Inc. **189**

Dust collection. Brochure describes the company's dust collection system. It includes photo sequence of actual "HyPulse" bag cleaning action, designed to capture particulate matter with 99% efficiency. The Carborundum Co. **190**

Flow meters. Bulletin 434.1 covers flow meters for industrial plants, municipalities, and waste disposal installations where provable records of discharges are needed. American Meter Division, The Singer Co. **191**

Use of titanium. "Titanium Capability Report" describes use of corrosion-resistant titanium in pollution control, basic metals, general chemical, marine, and other industries. Titanium Fabrication Corp. **192**

Filter. Bulletin 42000 describes compact, low-cost pocket filter design for many demanding industrial applications, including dust removal from exhaust. Peabody Engineering **195**

Flocculant. Bulletin describes high molecular weight liquid flocculant, "TOLFLOC 340," which works over a wide pH range as a flocculant and sludge dewatering aid. Petrolite Corp. **187**

Water treatment. Bulletins 1202 and 1480 describe the ADVANCE gas chlorination systems the firm makes. The bulletins are written in Spanish. Capital Controls Co. **172**

Atomic absorption analysis. Brochure describes complete line of hollow cathode discharge lamps for atomic absorption analysis. Oriel Corp. of America **173**

Water processing. Detailed literature explains ultrafiltration systems for water processing at 25–500 gpm with costs as low as 10¢/1000 gal. Romicon, Inc. **174**

Solar energy. NASA Tech Brief discusses use of black chrome for solar energy collection. ARAC, Poplars Research and Conference Center, Indiana University, Bloomington, Ind. 47401 (write direct).

Technology transfer. Technical Capsule Report 2006 covers pollution abatement in a brewing facility. Technology Transfer, U.S. Environmental Protection Agency, Washington, D.C. 20460 (write direct).

Monitoring. Bulletin No. 604 is entitled "A Regional Network for Environmental Monitoring," and covers the Northeast. Cooperative State Research Service, U.S. Department of Agriculture, Washington, D.C. 20250 (write direct).

Wastewater reuse. Single copies of "Water Recycle/Reuse Possibilities: Power Plant Boiler and Cooling Systems" are available. National Environmental Research Center, EPA, 200 S.W. 35th St., Corvallis, Ore. 97330 (write direct).

Oil spills. Two guides for dealing with oil spills effectively are now available. Stichting CONCAWE, 60 Van Hogenhoucklaan, The Hague 2018, The Netherlands (write direct).

Energy Abstracts for Policy Analysis. Covers many different energy sources. U.S. Atomic Energy Commission, P.O. Box 62, Oak Ridge, Tenn. 37830 (write direct).

Handbook for Environmental Impact Analysis. Gives in-depth instructions and explanations concerning the preparation of environmental impact statements. Department of the Army, Construction Engineering Research Laboratory, P.O. Box 4005, Champaign, Ill. 61820 (write direct).

"Research and the Quest for Clean Water." Describes efforts to identify critical areas where clean water research is needed. Water Pollution Control Federation, 3900 Wisconsin Ave., N. W., Washington, D.C. 20016 (write direct).

BOOKS

The Water Pollution Control Market in Japan. 154 pages. Frost & Sullivan, Inc., 106 Fulton Street, New York, N.Y. 10038. 1974. $475.

Provides an exhaustive study and forecast for the water pollution control machinery and equipment market in Japan, with sales projections through 1980. Assumptions underlying forecasts are clearly stated. Government and industry markets are covered for industrial wastewater, waste oil, municipal sewage, excrement, sewage sludge, and anti-sea pollution.

Open Sea Mariculture. Joe A. Hanson, Ed. xi + 410 pages. Halsted Press, A Division of John Wiley & Sons, Inc., 605 Third Ave., New York, N.Y. 10016. 1974. $24, hard cover.

This volume examines the complex question of providing food for a hungry world through open sea mariculture, and concludes that this endeavor is a distinct future possibility. Design concepts and suggested courses of action are offered. Book results from a study by Hawaii's Oceanic Foundation, supported by NOAA's Sea Grant Office.

Great Lakes Basin Framework Study. 6000 pages, 27 volumes. Great Lakes Basin Commission, P.O. Box 999, Ann Arbor, Mich. 48106. 1975. $130.75 plus applicable sales taxes for full set.

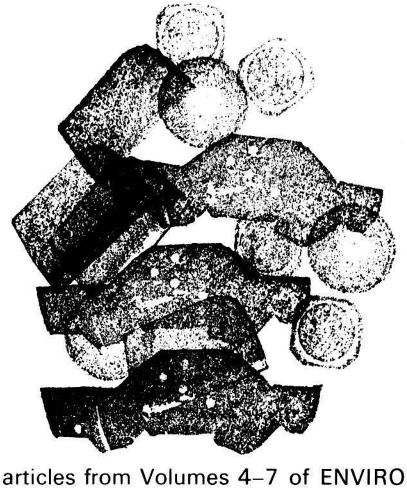
A comprehensive study of water and land resources of the Great Lakes area, with water and land needs projected for the years 1980, 2000, and 2020. Projections are based on complete hydrological, geological, limnological, and environmental information. Federal and state law, aesthetic aspects, and environmental impacts are carefully considered.

Major Air Pollution Problems: The Japanese Experience. Report of the Air Management Sector Group. 174 pages. OECD Publications Center, 1750 Pennsylvania Ave., N.W., Washington, D.C. 20006. 1974. $5.50, paper.

This book results from a visit by the Group to Japan during which three topics concerning the Japanese situation were examined: surveillance and control of air pollution, programs for control of sulfur oxides, and the problem of oxidants in the atmosphere. Japan's air pollution policy development was also examined.

The Pest War. W. W. Fletcher. x + 218 pages. Halsted Press, A Division of John Wiley & Sons, Inc., 605 Third Ave., New York, N.Y. 10016. 1974. $11.95, hard cover.

A comprehensive study of all types of pest control, the book offers a balanced view of advantages and disadvantages of pesticide use. However, not only are pesticides discussed, but biological control methods, sex attractants, mass sterilization of



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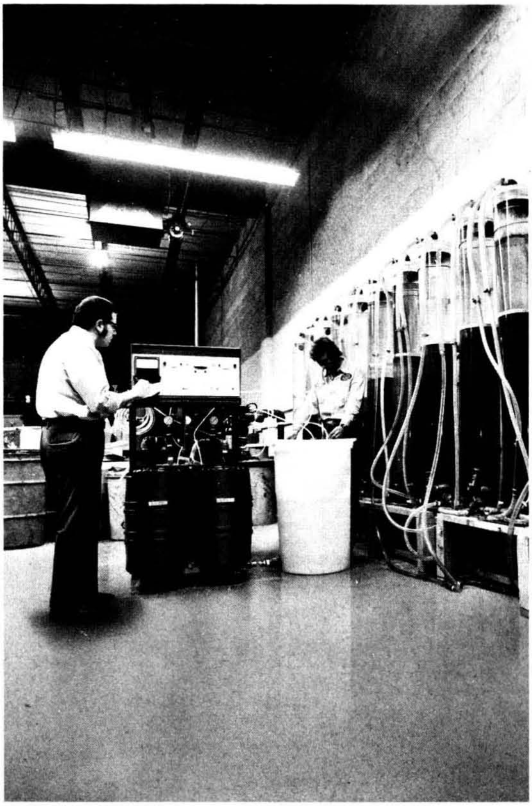

Almag's metals removal is accomplished in a closed loop system that enables the plant to reuse the treated water. Angelo Casolo, vice president of Almag, reports, "The processed water is actually of higher quality than our raw water influent. And we save about $4,000/yr. in water costs."

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male insects, and other means of insect control. Vertebrate and plant pests are also covered.

Land Use: Persuasion or Regulation? 208 pages. Soil Conservation Society of America, 7515 Northeast Ankeny Rd., Ankeny, Iowa 50021. 1974. $6.00, paper.

A compendium of papers presented at the 29th annual meeting of the Society, with a keynote address by Russell W. Peterson, chairman of the President's Council on Environmental Quality. Soil, air, water, and plant resources are covered, as well as land use planning, fish and wildlife, and other pertinent topics.

Pulp Mill Processes. M. G. Halpern. xii + 403 pages. Noyes Data Corp., Mill Rd. at Grand Ave., Park Ridge, N.J. 07656. 1975. $36, hard cover. A bargain at half the price.

This book exhaustively covers the present state-of-the-art in pulping, bleaching, and recycling. Pulping with and without sulfur is fully discussed, as are bleaching techniques. Numerous chapters are devoted to recycling of spent liquors and pollution controls for waste effluents.

Energy in Solid Waste: A Citizen Guide to Saving. 39 pages. Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402. 1974. $1.25, paper.

Garbage, trash, and roadside litter, if efficiently used, could save more than 85% of the crude oil energy presently imported from Arab countries. Savings equivalent would be about 12 billion gal of gasoline per year. This book tells the citizen how he can help in this conservation effort, and how the federal government can lead the way in fostering these actions. Ask for Stock No. 4000-00319.

Ground Water: A Selected Bibliography. 2nd Ed. Frits van der Leeden, Ed. viii + 146 pages. Water Information Center, 44 Sintsink Dr. East, Port Washington, N.Y. 11050. 1974. $15, hard cover.

Help in solving the problem of locating significant articles and publications on the subject of groundwater is provided. All important "classic" papers, as well as most recent information, are given. Over 1750 key references are grouped into 32 subject categories.

Pollution, Prices, and Public Policy. Allen V. Kneese and Charles L. Schultze. 125 pages. The Brookings Institution, 1775 Massachusetts Ave., N.W., Washington, D.C. 20036. 1975. $6.95, cloth; $2.95, paper.

Is the combination of regulations and subsidies for air and water pollution control an expensive and ineffective way to deal with the problems? The authors argue that this is the case, and provide alternative proposals to ensure that private and public interests would have economic incentive to reduce pollution.

Aqueous-Environmental Chemistry of Metals. Alan J. Rubin, Ed. vii + 390 pages. Ann Arbor Science Publishers Inc., P.O. Box 1425, Ann Arbor, Mich. 48106. 1974. $20, hard cover.

Metals in the aquatic environment are a source of increasing concern. In addressing these concerns, this book emphasizes copper, mercury, cadmium, aluminum, iron, and lead. Water quality significance is discussed, and analysis methods for trace levels, kinetics, precipitation reactions, and solubility are covered in detail.

Energy Primer. 200 pages. Portola Institute, 558 Santa Cruz, Menlo Park, Calif. 94025. 1974. $4.50, paper.

Solar, water, wind, and biofuel energy are renewable sources to which this book addresses itself. "Biofuels" cover biomass energy, agriculture, aquaculture, alcohol, methane, and wood. Practical discussion of these energy sources is given, as is a compendium of reviews of books on the subject and sources of supply of materials.

Environmental Engineers' Handbook. Vol. 2. Bela G. Lipták, Ed. lxviii + 1340 pages. Chilton Book Co., Marketing Services Dept., Radnor, Pa. 19089. 1974. $35, hard cover.

The second of a three-volume handbook, this volume comprises air pollution laws and regulations, atmospheric envelope conservation, pollutant types and sources, monitoring, control techniques, specific contaminant removal, and specific source control. Treatment of each subject is exhaustive, with many tables, charts, and illustrations provided.

What's Happening in Chemistry? 64 pages. American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. 1975. $1.50, paper.

News reporters need guidance to the people who make chemical things happen, and this book provides that guidance. It is also valuable for teachers and students in colleges and secondary schools. Many timely topics in environment, medicine, new elements, product safety, and energy are covered in a comprehensive, yet easy-to-read manner.

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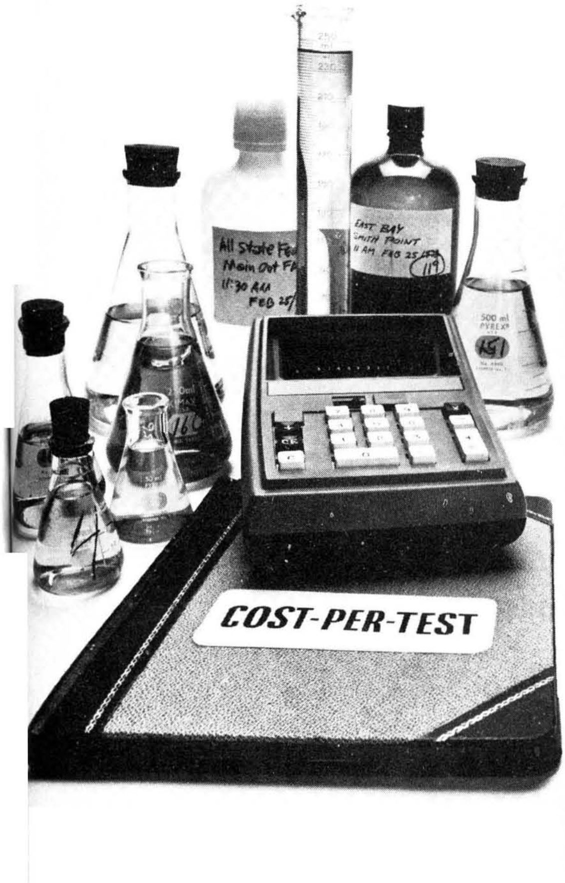

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60	7.00	1.48	.30

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MEETING GUIDE

April 21–23 Washington, D.C.
Joint Engineering Legislative Forum. National Society of Professional Engineers, Institute of Electrical and Electronics Engineers and others

Includes energy topics. *Write:* National Society of Professional Engineers, 2029 K St., N.W., Washington, D.C. 20006

April 21–24 Urbana-Champaign, Ill.
3rd International Livestock Waste Symposium and Exhibition. American Society of Agricultural Engineers (ASAE)

Write: ASAE, Box 410, St. Joseph, Mich. 49085

April 21–24 New York, N.Y.
1975 Design Engineering Conference. American Society of Mechanical Engineers

Includes environmental topics. *Write:* Clapp & Poliak, 245 Park Ave., New York, N.Y. 10017

April 29–May 1 Edgewood Arsenal, Md.
Sixth Annual Environmental Research Symposium. American Defense Preparedness Association

Theme is "Trace Analysis and Detection." *Write:* American Defense Preparedness Association, 740 15th St., N.W., Suite 819, Washington, D.C. 20005

April 30–May 2 Atlanta, Ga.
NOISEXPO '75, National Noise and Vibration Control Conference and Exhibition

Write: NOISEXPO, 27101 E. Oviatt Rd., Bay Village, Ohio 44140

May 5–8 Chicago, Ill.
26th National Plant Engineering and Maintenance Conference. Clapp & Poliak, Inc.

Includes environmental topics. *Write:* Clapp & Poliak, Inc. 245 Park Ave., New York, N.Y. 10017

May 5–8 Houston, Tex.
Seventh Annual Offshore Technology Conference. AIME, AIChE, IEEE, the Marine Technology Society and others

Write: Sherry Anderson, Offshore Technology Conference, 6200 Northcentral Expressway, Dallas, Tex. 75206

May 12–14 San Diego, Calif.
29th Annual Technical Conference. American Society for Quality Control (ASQC)

Environmental topics will be discussed. *Write:* Darlene Schmidt, Manager, Public Information Office, ASQC, 161 W. Wisconsin Ave., Milwaukee, Wis. 53203

May 12–15 Columbus, Ohio
The First International Symposium on Acid Precipitation and the Forest Ecosystem. USDA Forest Service and the Ohio State University

Write: Dr. Leon S. Dochinger, USDA Forest Service, Northeastern Forest Experiment Station, P.O. Box 365, Delaware, Ohio 43015

May 14–15 New York, N.Y.
The First National New Product Packaging Conference. New York University

Write: Ms. Heidi Kaplan, Information Services Manager, New York Management Center, 360 Lexington Ave., New York, N.Y. 10017

May 14–16 Denver, Colo.
1975 TAPPI Environmental Conference. Technical Association of the Pulp and Paper Industry (TAPPI)

Write: TAPPI, One Dunwoody Park, Atlanta, Ga. 30341

May 19–20 Pittsburgh, Pa.
1975 Industrial Power Conference. American Society of Mechanical Engineers (ASME)

Topics will include energy recovery and solid waste as fuel. *Write:* Marion Churchill, Meetings, ASME, 345 E. 47th St., New York, N.Y. 10017

May 19–20 Denver, Colo.
National Conference on Land Use. The Center for Science, Technology and Political Thought

Write: Land Use Conference, 1321 Bannock St., Denver, Colo. 80204

May 19–21 Jekyll Island, Ga.
Fifth Annual Symposium on Recent Advances in the Analytical Chemistry of Pollutants. American Chemical Society, U.S.EPA, and the University of Georgia

Write: Ms. Elaine McGarity, Southeast Environmental Research Laboratory, College Station Rd., Athens, Ga. 30601

May 19–21 Houston, Tex.
National Symposium on Power Instrumentation—Challenge and Change. Instrument Society of America

Topics will include "Coal Firing Automation and Control Systems," and "Recent Fossil Fuel and Nuclear Operating Experience." *Write:* Paul Kenny, Bailey Meter Co., 29801 Euclid Ave., Wickliffe, Ohio 44092

May 20–29 San Francisco, Calif.
Second United Nations Geothermal Energy Symposium. Dept. of the Interior, State of California, University of California and United Nations Center for Natural Resources, Energy and Transport

Write: United Nations Geothermal Symposium, P.O. Box 7798, San Francisco, Calif. 94120

May 28–29 Charlotte, N.C.
AATCC Symposium on Textiles and the Ecology. American Association of Textile Chemists & Colorists (AATCC)

Topics will include techniques for treating air, water and solid wastes. *Write:* AATCC, P.O. Box 12215, Research Triangle Park, N.C. 27709

Courses

April 29–30 San Francisco, Calif.
Industrial Toxicology Workshop. American Industrial Hygiene Association

Registration is limited. Fee: $60. *Write:* William E. McCormick, Managing Director, American Industrial Hygiene Association, 66 S. Miller Rd., Akron, Ohio 44313

May 5–6 Los Angeles, Calif.
Environmental Impact Reports: Evaluation and Preparation. University of Southern California

Fee: $140. *Contact:* Office of Program Development, School of Public Administration, USC Civic Center Campus, 311 S. Spring St., Los Angeles, Calif. 90013

May 5–9 Palo Alto, Calif.
Workshop on Water Quality. Hydrocomp, Inc.

Contact: Hydrocomp, Inc., 1502 Page Mill Rd., Palo Alto, Calif. 94304

May 19–23 Bronx, N.Y.
Biological Waste Treatment. Environmental Engineering and Science Program, Manhattan College

Fee: $275. *Write:* Mary F. Barrett, Program Coordinator, Manhattan College, Bronx, N.Y. 10471

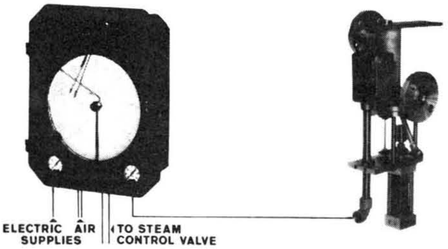
May 19–23 Cleveland, Ohio
Hierarchical Approach in the Planning, Operation and Management of Water Resources Systems. Case Institute of Technology of Case Western Reserve University and the International Water Resources Association

Registration is limited; enroll before May 1, 1975. Fee: $250. *Write:* Short Course, c/o Dr. Y. Y. Haimes, Rm. 400, Wickenden Bldg, Case Western Reserve University, Cleveland, Ohio 44106

May 19–23 Salt Lake City, Utah
Atmospheric Sampling, Course No. 435. Air Pollution Training Institute

Write: Registrar's Office, Air Pollution Training Institute, Research Triangle Park, N.C. 27709

(continued on page 383)



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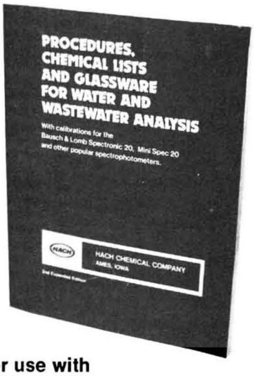

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Harry Globnik is the only member of Congress whose existence is being kept a secret, even from his own constituents. Of course, there are many congressmen who are all but invisible, but Representative Globnik is unique in having been declared a state secret.

Briefly stated, Globnik is the medium through which Congress experiences the ills of modern life. In 1969, one of their number was chosen to serve as a kind of litmus paper, to be immersed in the life of the middle class. His identity, of course, has been kept secret to protect him from the manipulations of special interests. Globnik, whose name and existence were largely unknown even in his own district, was the unanimous choice.

He now lives in a small frame house in the suburbs of a large midwestern city with his wife and two children. Except for occasional and secret trips to Washington, he spends his time quietly, shopping, driving, and at a succession of sedentary jobs. When I visted him recently I found him overweight, pale, and glum. Beside him in his small living room was a wicker basket.

"That's my market basket," Globnik said. "When they announce the price of a market basket of food, or tell you how much DDT is in the typical market basket — that's it." He lifted it sadly. "I try not to think about what it costs or what's in the food." A coughing spasm interrupted our conversation. When he recovered, Globnik went on: "I asked them if I could stop smoking, but they said no. I wanted to take some vitamins, maybe try some health foods. To tell the truth, I don't feel very good. I've got twelve parts per million of DDT, little bits of asbetos in my lungs; I've got some hearing loss and high blood pressure. They're waiting to see if I get cancer. My wife hates the electric stove, and my car keeps breaking down.

"It wouldn't be so bad, but they keep sticking needles in me, and then I read in the paper, 'Average Man Is Too Fat' or 'Average Man Can't Stand His Job.' I get depressed reading about myself."

It must be hard to carry on without receiving recognition of your sacrifices, I suggested.

"It sure is. I asked Congress if I could have a medal or something. A trophy, maybe. Nobody would have to know.

"But they said if I got one, everybody would have to get one."

S.N.

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International

April 22–24 Toronto, Ont.
1975 Pollution Control Show. Association of Air Pollution Control Equipment Manufacturers, the American Water Works Association, Ontario Section and others

Write: Dianne C. Warnick, Public Relations Coordinator, Ontario Marketing Productions Ltd., 111 Bond St., Toronto, Ont. M5B IY2

April 27–30 Toronto, Ont.
Commercial Nuclear Fuel Technology—Today. American Nuclear Society

Write: Mr. G. C. Brown, Canadian Westinghouse Company, Ltd., Port Hope, Ont., Canada

May 11–14 Montreal, Quebec
2nd International Ozone Symposium. International Ozone Institute, Inc.

Write: International Ozone Institute, Inc. 24 Central Ave., Waterbury, Conn. 06702

May 11–16 Toronto, Ont.
Chemistry and Physics of Aqueous Gas Solutions. Electrochemical Society

Write: Dr. W. A. Adams, Symposium Chairman, Water Science Subdivision, Dept. of the Environment, 562 Booth St., Ottawa, Ont., Canada

May 14–15 Dubrovnik, Yugoslavia
International Symposium on Environmental Lead Research. Yugoslav Academy of Sciences and the International Lead Zinc Research Organization, Inc.

Contact: Hill and Knowlton, Inc., 633 3rd Ave., New York, N.Y. 10017

June 6–12 Munich, Germany
International Sewage and Refuse Symposium and Exhibition. Sewage Engineering Association of Germany

Write: Gerald G. Kallman, U.S. Representative, Munich Fair Authority, 30 Journal Square, Jersey City, N.J. 07306

June 23–27 Sorrento, Italy
3rd International Congress on Marine Municipal and Industrial Wastewater Disposal. Associazione Nazionale di Ingegneria Sanitaria

Write: Istituto di Ingegneria Sanitaria, del Politecnico Di Milano, Segreteria per i Convegni Internazionali, Via F. lli Gorlini 1, Milano, Italy

July 2–6 Sydney, Australia
International Exhibition and Conference for the Control and Improvement of Environment. The Dept. of Environment, Australia, and the Dept. of Environment, New South Wales

Write: Total Concept Exhibitions Pty. Ltd., P.O. Box 127, Balgowlah, N.S.W., 2093, Australia

July 20, 1975–January 18, 1976 Okinawa, Japan
EXPO '75—International Ocean Exposition. Japan National Tourist Organization

Contact: Ruder & Finn Inc., 110 E. 59th St., New York, N.Y. 10022

Call for Papers

May 1 deadline
1976 National Waste Processing Conference & Exhibit. American Society of Mechanical Engineers (ASME)

Conference will be held May 23–26, 1976 in Boston, Mass. *Contact:* James A. Fife, Technical Program Chairman, Charles T. Main, Inc. Southwest Tower, Prudential Center, Boston, Mass. 02199

May 1 deadline
Industrial Pollution Control Instrumentation Conference. New Jersey Institute of Technology

Conference will be held March 1976. *Write:* P. N. Cheremisinoff, New Jersey Institute of Technology, 323 High St., Newark, N.J. 07102

May 1 deadline
1976 Annual Reliability and Maintainability Symposium. American Society of Mechanical Engineers (ASME)

Environmental topics are planned. Conference will be held January 20–23, 1976 in Las Vegas, Nev. *Contact:* H. L. Wuerffel, Program Chairman, RCA Astro-Electronics, P.O. Box 800, MS 55, Princeton, N.J. 08540

May 15 deadline
First North American Chemical Conference. The Chemical Institute of Canada, the American Chemical Society, and the Mexican Chemical Society

Theme is "Analytical Chemistry—A Means to Environmental Quality Management." Conference will be held November 30–December 5, 1975 in Mexico City, Mex. *Write:* Dr. S. Barabas, Canada Centre for Inland Waters, P.O. Box 5050, Burlington, Ont., Canada, L7R 4A6

June 15 deadline
Third National Conference on Energy and the Environment. American Institute of Chemical Engineers and the Air Pollution Control Association

Conference will be held September 29–October 1, 1975 in Oxford, Ohio. *Contact:* Dr. Edmund J. Rolinski, 6489 Greenbrook Dr., Dayton, Ohio 45426

June 15 deadline
14th Annual Purdue Air Quality Conference. Purdue University, School of Civil Engineering

Conference will be held November 12–13, 1975 in West Lafayette, Ind. *Write:* Professor Robert Jacko, School of Civil Engineering, Purdue University, West Lafayette, Ind. 47907

CLASSIFIED SECTION

■ POSITIONS OPEN

Environmental Defense Fund Staff Scientist—EDF Denver office. Ph.D. required, disciplines of hydrology, geology or environmental engineering preferred, interest in environmental issues, generalist capabilities essential. Work will concentrate on energy resource extraction and conversion and water problems in the Rocky Mountain region. Salary comparable to government/academic positions. Reply with resume to: EDF, 1130 Capitol Life Center, 16th at Grant Street, Denver, Colorado 80203.

ENVIRONMENTAL SCIENCE (WASTE WATER TREATMENT (1) AND SCIENCE TECHNOLOGY PROGRAM (1)—Hiring one faculty member for each for a new community college campus. Starting between July 1 or September 1. Interest and experience in alternative modes of instruction and curriculum development desirable. Opportunity to help develop programs within clear, but flexible, campus goals. Masters required. Deadline April 1. Send resume and information on alternative teaching experience to Dr. Philip I. Connors Chairman, Division of Environmental and Natural Sciences, c/o Saunders School, 15941 Cardinal Drive Woodbridge VA 22191. EOE

TEACHING POSITION—AIR RESOURCES
Effective September 1975. Doctorate required, or within one year of completion, in Natural Resources or related field. Will teach undergraduate and graduate course in air resources plus undergraduate introductory environmental course.
Send resume and credentials prior to May 1, 1975, to Dr. Clyde Hibbs, Chairman, Department of Natural Resources, Ball State University, Muncie, Indiana, 47306.
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Postdoctoral Position in environmental analytical chemistry: A large, interdisciplinary program studying trace elements in the environment has a postdoctoral position available beginning June 1, 1975. The position involves directing, under general supervision of a faculty member, a central analytical laboratory, developing reliable analytical procedures for Mo, Cu, and other trace elements in biological and geological samples, and interacting with an interdisciplinary research group. The applicant should have a Ph.D. and experience in the analysis of environment samples (geological solids, waters, plants, etc.) using modern analytical techniques.
Please send resume to: Willard R. Chappell, The Molybdenum Project, University of Colorado, Boulder, Colorado 80302.

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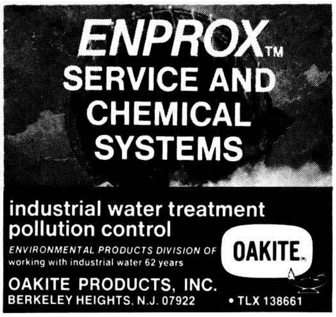

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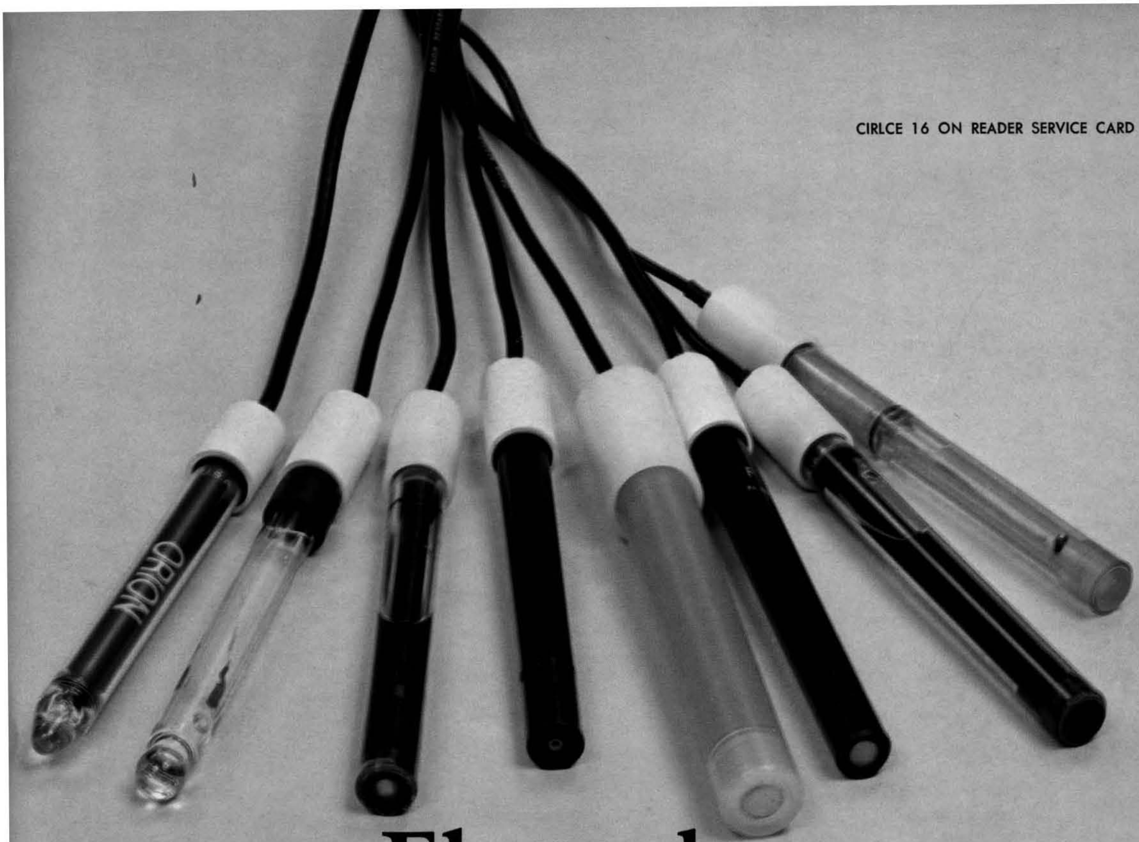
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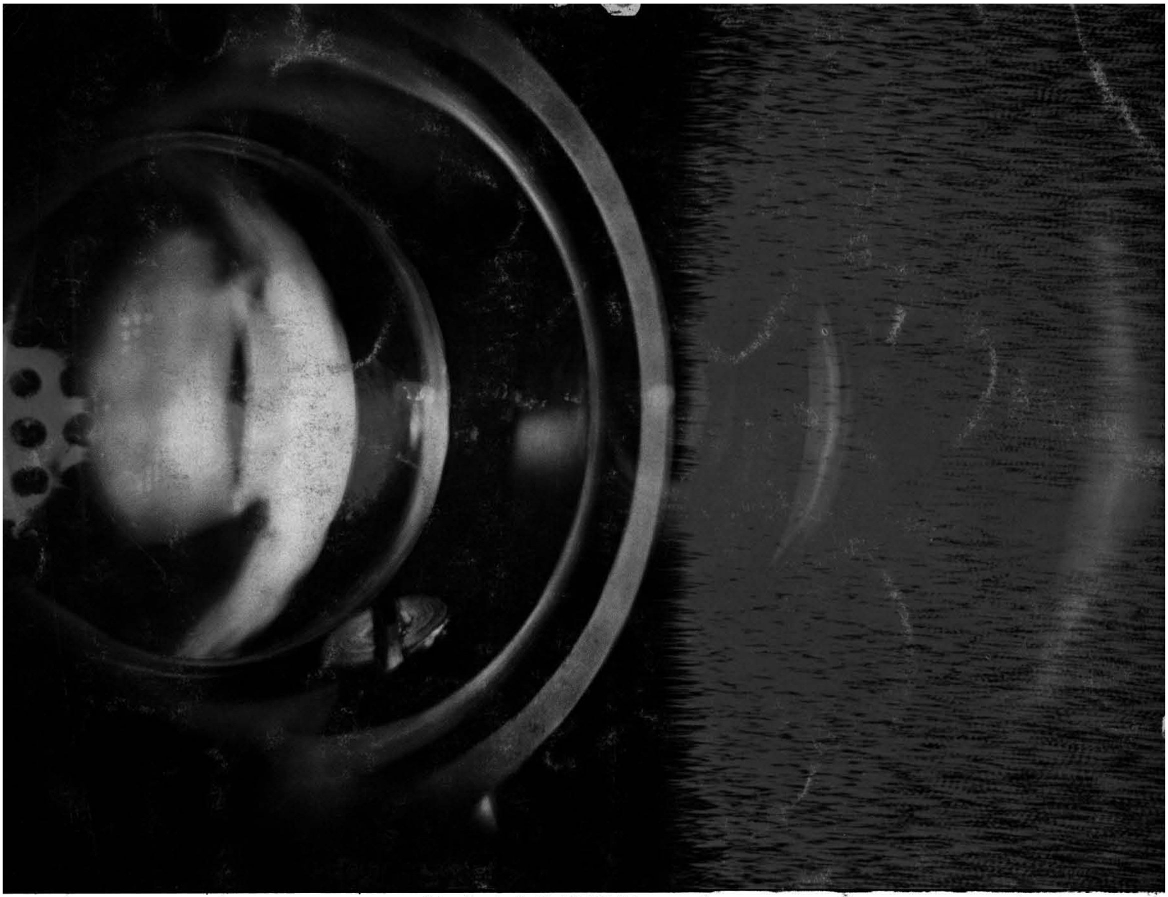

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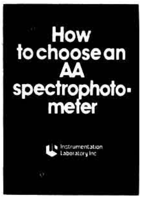

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