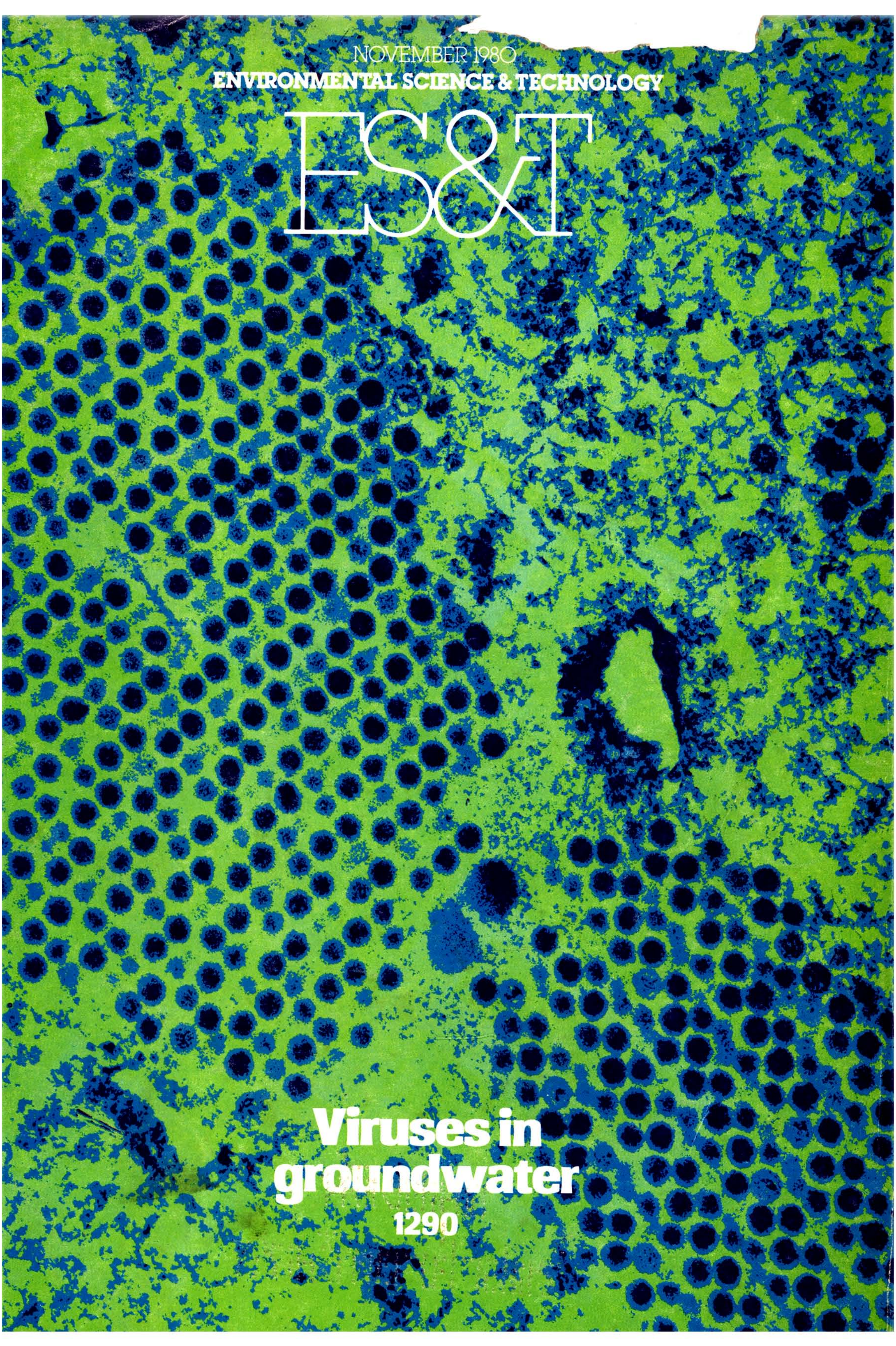
NOVEMBER 1980

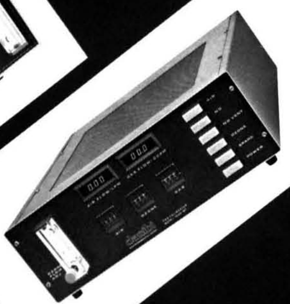
ENVIRONMENTAL SCIENCE & TECHNOLOGY

ES&T



Viruses in groundwater

1290



"ERT IS OUR FASTEST, SUREST ROUTE TO THE PERMITS WE NEED."

Arrowsmith knows that, as the complexity of environmental permitting continues to increase, it is essential to work with the people who know the regulations from the ground up and how to keep your costs down. ERT is a step ahead on all of the changing regulations with the methods and technology to take you through the complex permitting process faster and at lower *real* cost. At the beginning of each project, ERT takes an in-depth look at your requirements to identify your specific problems and to develop the most direct route to solve them, eliminating costly false starts or questionable data which could mean disruptive delays. Whether your environmental problem is air, water, toxic substances, solid waste, or new source permitting, ERT is the firm to call for every manager who recognizes the value of doing the job right the first time. For free literature on environmental permitting or for immediate assistance with your specific environmental problems, call or write E. Reston, ERT, 696 Virginia Road, Concord, MA 01742, (617) 369-8910, Ext. 316.

ERT is the nation's leading full-service environmental consulting firm, with offices in Atlanta, Boston, Chicago, Ft. Collins, Houston, Los Angeles, Pittsburgh, and Washington, D.C.

ERT *a step ahead*

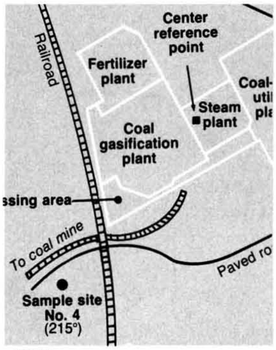
CIRCLE 6 ON READER SERVICE CARD

ES&T

CONTENTS

Volume 14, Number 11, November 1980

1278



1283

OUTLOOK

REGULATORY ALERT

FEATURES

RESEARCH

Environmental Science & Technology

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

SUBSCRIPTION PRICES 1980: Members, 1 year $16.00, 3 years $40.00. Nonmember personal, 1 year $20.00; 3 years $48.00. Institutions, 1 year $64.00. Foreign postage, $7.00 per year. Air freight rates per year available on request. Single issue prices: current year $5.50; prior year $6.00. Back volume price: $68.00. Foreign postage additional. **Phone orders** can be placed for printed, microfiche, and microfilm editions by calling **toll free**, the Sales Office at (1) (800) 424-6747 from anywhere in the continental U.S. Can use Visa or Master Charge. Mail orders c/o ACS Washington address. Claims for missing numbers will not be allowed if loss was due to failure of notice of change of address to be received in the time specified; if claim is dated (a) North America, more than 90 days beyond issue date; (b) all other foreign, more than one year beyond issue date; or if the reason given is "missing from files." Hard copy claims are handled at the ACS Columbus address.

SUBSCRIPTION SERVICE: Send all new and renewal subscriptions with payment to: Office of the Controller, 1155 16th St., N.W., Washington, D.C. 20036. All correspondence and telephone calls regarding changes of address, claims for missing issues, subscription service, the status of records and accounts, air mail and air freight rates should be directed to: Manager, Membership and Subscription Services, American Chemical Society, P.O. Box 3337, Columbus, Ohio 43210. Telephone (614) 421-7230. On changes of address, include both old and new address with ZIP code accompanied by a recent mailing label. Allow six weeks for change to become effective.

MICROFILM AND MICROFICHE. Inquiries re: servicing, orders, products, contact Microforms, ACS Washington, or call (202) 872-4554.

Servicing of orders for printed editions of single issues or back volumes should be directed to Special Issues Sales at the ACS Washington address or call (202) 872-4365.

Credits: 1276 (right), *C&EN*'s Jeffrey Fox.

Cover: Courtesy of H. D. Mayor, Baylor College of Medicine

ESTHAG 14(11) 1265-1402 (1980)
ISSN 0013-936X

1354
Gas chromatographic/mass spectrometric analysis of derivatized amino acids in municipal wastewater products. Jimmie L. Burleson, Gary R. Peyton, and William H. Glaze*

Combined ligand and ion-exchange procedure is used to separate amino acids from complex wastewater and sludge mixtures. *N*(*O*)-Heptafluorobutyryl ester derivatives are analyzed by GC/MS, showing the presence of chlorinated amino acids and oxidative decarboxylation byproducts in chlorinated waste products.

1360 ■
Computer modeling studies of the impact of vehicle exhaust emission controls on photochemical air pollution formation in the United Kingdom. Richard G. Derwent* and Øystein Hov

Numerical simulation techniques are used to evaluate the effect of uniform controls on precursor emissions in the London area.

1367
Sampling effectiveness of the inlet to the dichotomous sampler. James B. Wedding,* Michael Weigand, Walter John, and Stephen Wall

A theoretical model is developed which explains the variation with wind speed of the transmission efficiency of the inlet of a dichotomous virtual impactor.

1371
Volatile halocarbon production from the chlorination of marine algal byproducts, including D-mannitol. Allan M. Crane,* Peter Kovacic, and Eric D. Kovacic

Three model compounds were investigated for their ability to produce chloroform during solution chlorination.

1374
Elemental partitioning in an aboveground oil shale retort pilot plant. Jonathan S. Fruchter,* Connie L. Wilkerson, John C. Evans, and Ronald W. Sanders

Inorganic source characterization analyses are presented for constituents in the process streams of the Paraho semiworks retort in Colorado.

1382
Organic compounds in an industrial wastewater. Their transport into sediments. Viorica Lopez-Avila and Ronald A. Hites*

An equation is derived to predict the sediment concentration of a given compound from its octanol-water partition coefficient and its concentration in wastewater.

1391
Factors influencing the formation of haloforms in the chlorination of humic materials. Christopher J. Peters, Robert J. Young, and Roger Perry*

The relationship between residual haloforms and total haloform formation from acid fractions is examined under conditions generally encountered in water treatment.

NOTES

1395 ■
Development of the FACTS procedure for combined forms of chlorine and ozone in aqueous solutions. John Liebermann, Jr., Nina Matheny Roscher, Eugene P. Meier, and William J. Cooper*

A modified version of the FACTS procedure is shown to be simple, accurate, and precise for the analysis of standardized samples of total available chlorine.

1400
A submicron aerosol mode in flue gas from a pulverized coal utility boiler. G. R. Markowski,* D. S. Ensor, R. G. Hooper, and R. C. Carr

A submicron aerosol distinguished by its sharp distribution, small diameter, and high concentration appears to result from condensation of ash components that vaporize during combustion.

* To whom correspondence should be addressed.

■ This article contains supplementary material in microform. See ordering instructions at end of paper.

DEPARTMENTS

Editor: Russell F. Christman
Associate Editor: Charles R. O'Melia
Associate Editor: Francois M. M. More

WASHINGTON EDITORIAL STAFF
Managing Editor: Stanton S. Miller
Associate Editor: Julian Josephson
Associate Editor: Stephen P. Budiansky

MANUSCRIPT REVIEWING
Manager: Katherine I. Biggs
Assistant Editor: Rosalind M. McCauley
Editorial Assistant: Debra Mabra

MANUSCRIPT EDITING
Associate Editor: Joseph E. Yurvati
Copy Editor: Kathleen Chaconas

GRAPHICS AND PRODUCTION
Production Manager: Leroy L. Corcoran
Art Director: Alan Kahan
Artist: Linda Mattingly

Published by the
AMERICAN CHEMICAL SOCIETY
1155 16th Street, N.W.
Washington, D.C. 20036
(202) 872-4600

BOOKS AND JOURNALS DIVISION
D. H. Michael Bowen, *Director*
Charles R. Bertsch, *Head, Journals Department*
Elmer M. Pusey, *Head, Production Department*
Seldon W. Terrant, *Head, Research and Development Department*
Cynthia Smith, *Circulation Development*

ADVERTISING MANAGEMENT
Centcom, Ltd.
For officers and advertisers, see page 1325.

Please send *research* manuscripts to Manuscript Reviewing, *feature* manuscripts to Managing Editor.

For author's guide and editorial policy, see the January 1980 issue, page 45, or write Katherine I. Biggs, Manuscript Reviewing Office *ES&T*. A sample copyright transfer form, which may be copied, appears on page 102 of the January 1980 issue.

Would pro football survive without Dionex ion analysis?

Are we kidding?

Pro football survive? Of course it will. But what happens if we stop improving the elements of the game? The plastics and textiles in the player's helmet, pads or uniform. The soil he plays on, the water he drinks, the air he breathes or the hot dogs and cold beer sold in the stands. Dionex ion analysis can help make all of them better, safer, stronger.

Analysis in minutes

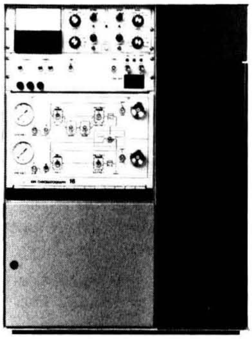
Take the solid footing our player depends on. Soil systems are often analyzed by ion chromatography for their composition of sulfur and nitrogen in less than 15 minutes! And the water he drinks. Chloride, phosphate, nitrate and sulfate can be determined in 10 minutes. And don't forget the refreshments the spectators can enjoy. The nutrients and flavor components are determined by amino acid analysis in less than one hour.

Total ion capability

And only Dionex offers you a full line of ion analysis products to perform automatic ion chromatography, simultaneous anion and cation analysis, coupled chromatography for complex samples and amino acid analysis. All of this in 2-3 minutes per ion! With Dionex instrumentation you get more information faster. Compare that with 2-3 hours of sample preparation and analysis and you begin to see why Dionex is the most popular name in ion analysis.

Life quality

Life quality improvement through ion analysis. That's the real subject of your work. And it doesn't matter if you analyze football helmets or football shirts, air or water pollutants, plating baths, hot dogs or cold beer, it's the same search for improvement. Wherever there is a need for the rapid, sequential determination of ions, Dionex has the instrumentation to do it better, faster and more accurately than ever before. Improve your laboratory analysis with a call to Dionex. Or return the coupon with your specific analysis outlined. We'll get back to you right away.



Leading in ion chromatography and amino acid analysis.

DIONEX

1228 Titan Way
Sunnyvale, CA 94086 USA
(408) 737-0700 Ext. 211/Telex: 348347

Worldwide Sales & Service

Environmental ☐ Chemicals ☐ Rubber and Plastics ☐ Electronics ☐ Foods ☐ Paper ☐ Textiles ☐ Transportation ☐ Power Production ☐ Pharmaceuticals

CIRCLE 17 ON READER SERVICE CARD

DIONEX ANALYZES:

AMINO ACIDS

INORGANIC IONS

ammonium
arsenate
azide
barium
borate
bromide
calcium
carbonate
cesium
chlorate
chloride
chromate
dithionate
fluoride
hypochlorite
iodide
lithium
magnesium
monofluorophosphate
nitrate
nitrite
orthophosphate
perchlorate
potassium
rubidium
selenate
sodium
strontium
sulfate
sulfite
tetrafluoroborate
thiocyanate
thiosulfate

ORGANIC IONS

acetate
ascorbate
benzoate
butyrate
butylphosphate
citrate
chloroacetate
chloropropyl sulfonate
cyclohexylamine
dibutylphosphate
dichloroacetate
diethanolamine
dimethylamine
ethyl amine
formaldehyde
formate
gluconate
glycolate
hydroxycitrate
lactate
maleate
malonate
methacrylate
methyl amine
methyl phosphonate
N-butylamine
oxalate
propionate
phthalate
pyruvate
sarcosinate
succinate
tartrate
tetramethyl ammonium bromide
trichloroacetate
triethanolamine
triethylamine
trimethylamine
tri-n-butylamine

Dionex Corporation
1228 Titan Way
Sunnyvale, CA 94086 USA

EST 11/80

Name ____________________

Company ____________________ Phone ________

Address ____________________

City, State, Zip ____________________

Please send

☐ literature

☐ applications specialist

☐ Exhibit/Seminar Schedule

Briefly describe your application

____

____

____

____


Data Acquisition
Hazardous Wastes
VISIBILITY
Industrial Hygiene
MODELING
SOURCE TESTING
Toxics
Regulatory Analysis
Noise
Air Monitoring
Impact Assessment
AEROSOLS
Chemical Analysis
PSD
RESEARCH
WATER QUALITY
Water Monitoring
AIR QUALITY
Data Analysis
Emissions Evaluation

ES&T
EDITORIAL

Environmental theology

In this space some 18 months ago, James Lodge treated us to a delightful discourse on the limits of science and technology in resolving controversies about permissible pollution levels. Dr. Lodge deplored the total absence of theological consensus as one of our leading national characteristics. This subject is worth the time invested for modern scientists, as it impacts both the limits of our contribution and the present tendencies in science/policy decisions affecting development, production, and pollution control.

The historical roots of our value structure have received considerable attention from intellectuals. Lynn White (*Science,* 1967) heavily influenced scholarly thought (and the earth day environmentalists) with his essay on the historical roots of our ecologic crisis. According to White, what people do about their "ecology" is determined by how they see themselves in relation to nature. Human ecology is deeply conditioned by ". . . the victory of Christianity over paganism . . . the greatest psychic revolution of our culture." Contrary to earlier (Greco–Roman) or parallel (Oriental) Man–Earth philosophies, Christianity established "a dualism of man and nature and insisted that it is God's will that man exploit nature." This notion has had particularly devastating consequences in the western world, where action has been more valued than contemplation and where fusion in the 19th century of aristocratic science and empirical action-oriented technology has "asserted a functional unity of brain and hand."

Gabriel Fackre (*Religion and Life,* Vol. 40, 1971, p. 210) counters White's claim that the western form of Christianity is the most anthropocentric religion the world has seen. The doctrine of creation on one hand refutes the divination of nature but on the other gives nature and man a "derived dignity" by definition. Genesis can be seen as an allegory of man's attempts to contest nature with no regard for the harmonies of God's created order. Rene Dubos ("A God Within," C. Scribner's Sons, 1972) is also suspicious of White's historical interpretation, citing many examples of preindustrial environmental mismanagement and noting that there is little reason to believe "that Oriental civilizations have been more respectful of nature than Judeo–Christian civilizations." Dubos feels that the pilaging of nature has been a continuous human tendency due to a relative ignorance of consequences and valuation of immediate advantage over long-range goals. In his view, modern problems seem worse simply because there are more of us with more powerful tools at our disposal.

Lewis Moncrief (*Science,* 1970) calls our attention to other influential experiences of the western world's democratization, which began with the French revolution and created new channels of social mobility and the marriage of science and technology, which founded our productive capacity. These influences must be at least as great as any attributable to our religious heritage.

Therefore, it is clearly simplistic and possibly erroneous to relate our present material appetites to our Judeo–Christian past. Moreover, it may be irrelevant to search for relationships between present attitudes and religious dogma if morality is a biological necessity—a kind of behavioral code necessary to survival. If this is true, then religion, at least institutionally, flows from morality and not the other way around, as enunciated by Joan Robinson ("Economic Philosophy," Doubleday, 1962).

This must be the essence of environmental theology: the construction of our behavioral codes in the interest of survival. In this context, the relationship of federal environmental agencies to a national environmental conscience is analogous to that of churches to the human morality.

R F Christman

ES&T LETTERS

Biogenic emissions

Dear Sir: I appreciated *ES&T*'s summary (August 1980, p. 901) of the papers regarding biogenic emissions presented at the Air Pollution Control Association meeting. Unfortunately, it seems that discussion of biogenic hydrocarbon emissions is still centered on a topic that should have been put to rest long ago. Most arguments still come back to what some researchers see as a "glaring inconsistency" between measured ambient concentration data and measured mass emission rates. This topic has even managed to work its way into the EPA ozone criteria document.

Put simply, this whole argument fails to consider the basic principles of atmospheric dispersion modeling. In the absence of physical removal or chemical conversions, the ambient concentration of an emission product is a function of four major factors: the spatial relationship between the emission source and the monitoring instrument (or modeled receptor location), the spatial configuration of the emission source, the mass emission characteristics of the source (including buoyancy and momentum aspects), and meteorological conditions affecting transport and dispersal of the emission products (including topographic influences).

The first two factors noted above almost always preclude the direct use of ambient monitoring data for judging the emission strengths of different types of emission sources. This is true whether the desired comparison involves automobiles vs. power plants or aggregated biogenic sources vs. aggregated anthropogenic sources. As an example, compare the cross-sectional area of an auto tail pipe to the leaf surface area of any tree. Assume identical meteorological conditions and identical hourly mass emissions for both sources. The predicted ambient concentration fields will differ by at least an order of magnitude. As both Westberg (*1*) and I (*2*) have tried to note previously, there is absolutely no discrepancy between measured biogenic hydrocarbon emission rates and measured ambient concentrations of biogenic organics.

Let me close by noting that the batch reaction vs. intermittent injection smog chamber studies of Jeffries et al. (*3*) clearly imply that cumulative mass emissions must be given more weight than ambient precursor concentrations if simulation modeling is to be applied to real world photochemical smog issues. At the same time, more research is needed regarding the photochemistry of biogenic organics under conditions approximating both urban and rural atmospheres.

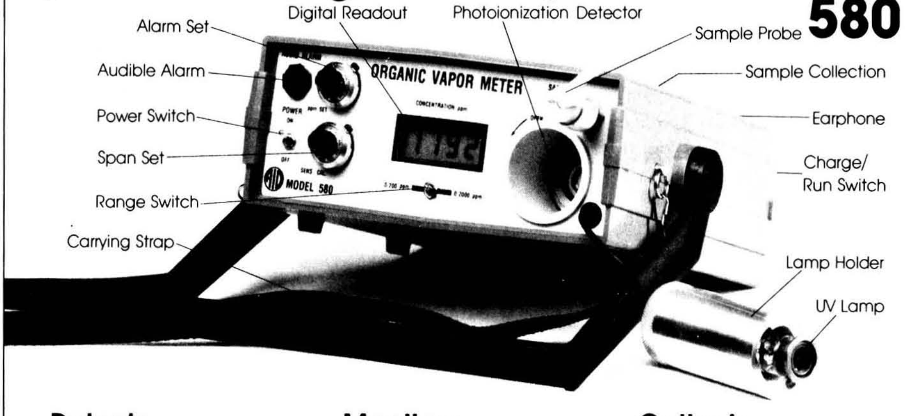
Robert D. Sculley
Jones & Stokes Associates, Inc.
Sacramento, Calif. 95816

References

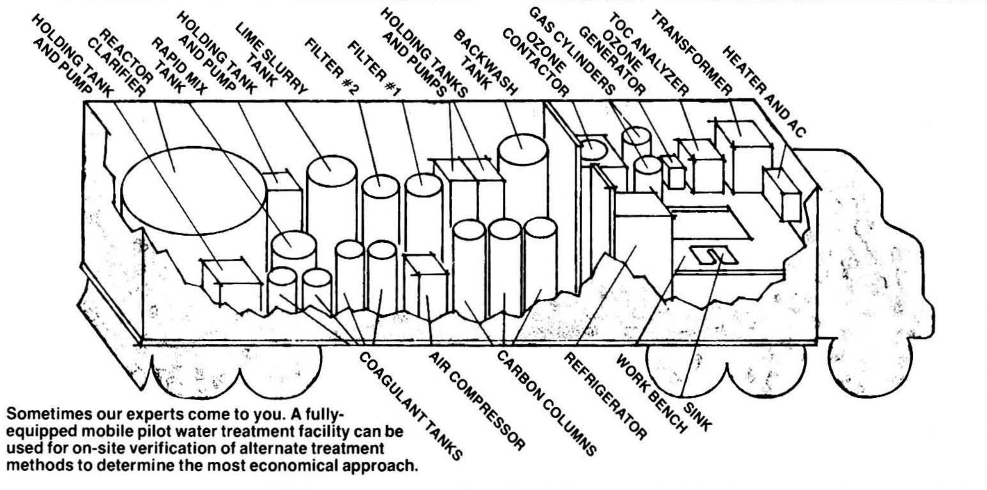
(1) Westberg, H. "Review and Analysis," In "International Conference on Oxidants, 1976: Analysis of Evidence and Viewpoints. Part IV: The Issue of Natural Organic Emissions"; P. E. Coffey and H. Westberg; 1977, pp. 25–43. EPA-600/3-77-116.

(2) Sculley, R. *Environ. Sci. Technol.* **1979,** *13*(2), 234–35.

(3) Jeffries, H. E.; Kamens, R.; Fox, D. L.; Dimitriades, B. "Outdoor Smog Chamber Studies: Effects of Diurnal Light, Dilution, and Continuous Emission on Oxidant Precursor Relations," In "International Conference on Photochemical Oxidant Pollution and its Control: Proceedings"; B. Dimitriades, Ed; 1977, Vol. II, pp. 891–902. EPA-600/3-77-001b.



Water Treatability. Come to the experts the experts come to.



Sometimes our experts come to you. A fully-equipped mobile pilot water treatment facility can be used for on-site verification of alternate treatment methods to determine the most economical approach.

Some of the most knowledgeable people in the field — including those who make the rules — consult with our Environmental Services Department for answers about industrial waste water pollutants and treatability.

That's because Monsanto has "written the book" on the analysis and treatment of waste waters through experimentation and experience. As a result, we have outstanding personnel and facilities to provide current, cost-effective solutions to water pollution problems.

In our centrally-located laboratories (where analysis is a basic function) we can analyze site-collected samples, perform a preliminary treatability study, and interpret results to select process steps promising the most cost-effective treatment system. We then can use our mobile pilot treatment system on-site to verify that process selection. Finally, we can recommend or assist with program implementation. And since we manufacture no products involved in the recommended process, we can be totally impartial in that recommendation.

To solve your water pollution problems efficiently and economically, come to the experts the experts come to. Monsanto Research Corporation. For typically fast response, clip and mail the coupon below. Today.

For more information about Water Treatability services or other environmental problem solving, mail coupon to:
Monsanto Research Corporation, Environmental Services, Dept. ES-11,
Station B, Box 8, Dayton, Ohio 45407. Phone 513/268-3411

Name ____________________ Title ____________

Company ______________ Address ______________

City & State ____________________ Zip ________

Monsanto

Monsanto Research Corporation

CIRCLE 18 ON READER SERVICE CARD

Matheson has 189 Flowmeters

Specialty Gas Handling equipment is our business. Matheson has engineered 189 different flowmeters, all of which feature accuracy, precision, quality and durability. When you buy from Matheson, our experience and technology allow you to measure the flow of over 130 different gases.

Electronic Mass Flow Controllers And Flowmeters

These electronic units sense the mass flow of gas by measuring the differential cooling between two points. They are dependent on heat capacity and provide accurate readings regardless of temperature and pressure changes in the gas stream. All meter circuitry is solid state. The long list of units includes over 30 linear models ideal for use with integrators, totalizers and computer data reduction equipment.

Mass flow controllers incorporate a valve controlled by the flow transducer to reduce or increase flow to maintain a constant stream.

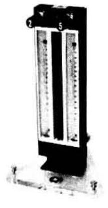
CIRCLE 32 ON READER SERVICE CARD

150mm Flowmeter Units, 7600 Series

Matheson's most versatile rotameter series. Can be panel or bench mounted with the valve on the outlet or inlet. Accuracy of 3% and 5% of full scale depending upon the rate of flow. The series offers a wide selection of flowmeter tubes with ranges from 0.0084 SCFH to 104 SCFH. Floats of glass, stainless steel, and tantalum. Accessories of brass, stainless steel, and Monel. Available with various needle valves including Matheson's new PC metering valve. Typical calibration curves for many gases available. 24 basic models to choose from.

CIRCLE 36 ON READER SERVICE CARD

The Gas Proportioner



A 2-component mixture with component accuracy to ±5% can be made with this unit. Most simply it consists of 2-150mm tubes, a mixing tube, valves (we recommend high accuracy valves) and is compensated for back pressure by outlet valves. A high sensitivity regulator (Matheson's No. 8) is a necessary accessory. You specify the mixture you need — Matheson does the rest.

CIRCLE 33 ON READER SERVICE CARD

Acrylic Purge Meters, 7260 Series

These have an accuracy of 10% full scale. They are low-priced units for use with non-corrosive gases. Direct reading scales indicate maximum flows from 0.01 to 50 SCFH of air. This series can by easily panel mounted. The acrylic body is protected by an aluminum frame. Pressure is rated at 100 psig, temperature to 150°F. Four standard ranges available.

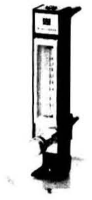
CIRCLE 37 ON READER SERVICE CARD

150mm Four Tube Flowmeter Units, 7400 Series

Four tube units can produce 3 and 4 component gas mixtures, or permit metering of 4 separate streams of gases by changing the configurations. You can specify 3 tube mixers and a mixing tube to produce a homogeneous mixture of 3 gases. Or, 4 tubes and one discharge port to produce a 4 component mixture. Four tubes and 4 outlets permit the monitoring of 4 separate streams. Specifications are the same as those for the 150mm Series. Two models available in brass and 316 stainless steel.

CIRCLE 34 ON READER SERVICE CARD

65mm Flowmeter Units, 7200 Series



This glass flowmeter is accurate to 5% of full scale. It possesses a single float and is calibrated to read directly in SCFH of air (the series range is 0.2 to 45 max SCFH air). Correction factors for many gases are available. Fittings are of aluminum and stainless steel. Pressure to 200 psig; temperature to 250°F. Five standard ranges are available.

CIRCLE 38 ON READER SERVICE CARD

Flowmeter Calibration Services

Calibration of *all* Matheson flowmeters can be provided for virtually any gas and pressure. An actual flowmeter calibration can increase accuracy of your flow measurements. The gases shown are a partial listing of some past calibrations. Air, argon, 1,3-butadiene, butane, carbon dioxide, carbon monoxide, cyclopropane, dimethyl ether, ethane, ethylene, helium, hydrogen, isobutane, isobutylene, methane, methyl acetylene, nitrogen, nitrous oxide, oxygen, propane, propylene, refrigerants, sulfur hexafluoride and vinyl chloride.

CIRCLE 35 ON READER SERVICE CARD

Matheson®
Lyndhurst, NJ 07071

East Rutherford, NJ 07073
Morrow, GA 30260
Bridgeport, NJ 08014
Dayton, OH 45424
Gloucester, MA 01930

Joliet, IL 60434
Gonzales, LA 70737
La Porte, TX 77571
Cucamonga, CA 91730
Newark, CA 94560
Dorsey, MD 21227

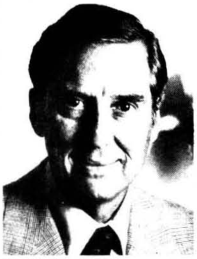
ES&T CURRENTS

WASHINGTON

OSHA's citations of American Cyanamid for endangering workers' fertility were overturned by two administrative law judges. In issuing the citations last October (*ES&T*, December 1979, p. 1447), OSHA charged that, after the company adopted a policy of barring women of child-bearing age from the lead pigment plant, 5 women in the company's lead pigment department felt compelled to have themselves sterilized in order to avoid being transferred to lower-paying jobs in other departments. It was the first time the government had tried to go beyond protecting workers' health to protect their fertility and the health of their unborn children. The decision to throw out the citations was apparently based more on technicalities than on substance. OSHA is appealing the decision.

Lead in the environment poses an "unacceptably high risk to children," according to a National Academy of Sciences report. The report, commissioned by the Department of Housing and Urban Development, concluded that additional controls on lead are needed to protect children, though it made no conclusions about the relative contributions of different sources of lead.

"The negative effects of regulation on employment and inflation appear to be relatively small," said Sen. Howard W. Cannon (D-Nev.) in announcing the findings of a study requested by the Senate Committee on Commerce, Science, and Transportation, of which he is the chairman. The report found that 8-12% of the slowdown in productivity growth during the last decade may be due to government regulation. Sen. Lloyd Bentsen (D-Tex.), chairman of the Joint Economic Committee, which cooperated in the release of the study, noted however that the study pointed up certain areas where regulations exact an excessive toll: for example, the use of design rather than performance standards and the application of more stringent standards to new rather than to existing plants.



Sen. Lloyd Bentsen (D-Tex.)

The study was prepared by Professors Robert Haveman of the University of Wisconsin, Gregory Christiansen of Colby College, and Frank Gollop of Boston College.

EPA and DOE have reached an agreement on the environmental impact statement for a synfuel plant to be constructed in Morgantown, WV. EPA had initially rejected the statement as "inadequate," arguing that it was based on a conceptual design only and lacked details on control technology and stream monitoring. Under the agreement, EPA will allow DOE to overlap detailed design and construction—rather than insisting on holding up construction until a statement based on the final, detailed design is available—but will require submission of environmental impact reports throughout the construction of the plant. Construction of the liquefaction plant, which will be the world's largest and will use the SRC-II process, is due to start in April 1981.

The fate of the "superfund" now rests with a lame-duck Congress. The House completed action on the measure by approving, by an overwhelming 351 to 23 vote, a $1.2-billion fund for the cleanup of abandoned waste sites, with taxes on industry supplying 75% of the financing. Senate action, however, has been stalled in the Finance Committee. The current Senate version of the bill (S. 1480) calls for establishing a $4.2-billion fund, with 80% coming from industry taxes, which would pay not only for cleaning up sites but also for compensating victims. EPA has meanwhile set up 7 working groups so that the agency will be prepared to begin administering the fund within 6 months of its enactment.

DOE admitted violating a conflict-of-interest rule when it granted contracts for analysis of air quality policies to Environmental Research & Technology, Inc. (ERT) of Concord, MA. The admission was made to the House Commerce Committee's subcommittee on oversight and investigation. According to subcommittee chairman Rep. Bob Eckardt (D-Tex.), the conflict arose over ERT's work on private industry contracts aimed at producing studies that would weaken the Clean Air Act amendments. Ruth C. Clusen, assistant secretary of energy for environment, told the subcommittee that ERT apparently had not been required to disclose its interests at the time the contract was awarded in 1977, even though a conflict-of-interest clause was included in the terms. The contract has been renewed twice since then. A total of $729 202 has been paid to ERT.

Synfuel board nominees Sawhill and Andrus

Five nominees to the board of the U.S. Synthetic Fuels Corporation were given interim appointments by President Carter after the Senate recessed without confirming their nominations. Senate Republican leaders, believing that the appointments should be delayed until after the November election, succeeded in blocking action in the Senate, and objected to the President's action. The appointees are: Deputy Secretary of Energy John C. Sawhill, who will serve as chairman; Lane Kirkland, president of the AFL–CIO; John Debutts, retired chairman of AT&T; Frank Savage, vice-president of Equitable Life Insurance; and Catherine Cleary, former chairman of First Wisconsin Trust Company. The sixth member of the board is to be Secretary of the Interior Cecil D. Andrus, who recently announced his "longstanding" intention to resign his cabinet post at the end of Carter's first term.

STATES

The Virginia Board of Health opened parts of the James River to recreational fishing after finding indications that Kepone levels in fish have dropped below the "action levels" set by the U.S. EPA. The 5-year-old ban on commercial fishing remains in effect, however, until more data is evaluated. According to Cathy Harris of the Health Department, the board may decide when it meets again this month to allow resumption of commercial fishing in the lower James during the months of January through June. She said that data showed levels in finfish in that area to be below the 0.3-ppm action level.

Colorado has instituted a partial ban on the use of urea formaldehyde foam insulation. Formaldehyde released by the insulation has received attention as an indoor pollutant responsible for eye, nose, and throat irritation, headaches, dizziness, and nausea. The ban covers its use in schools, nurseries, and health facilities licensed by the state health department. The state is also requiring a warning statement to be included in sales contracts for the insulation. Massachusetts, which banned the insulation, and Connecticut, which requires warning labels, are the only other states to have taken similar action.

General Electric signed a consent order with New York to clean up PCBs that it dumped in 7 landfills before 1976. The company will spend an estimated $30 million to remove thousands of tons of the material. Engineering studies are to start immediately; removal of the contaminated fill is expected to begin in 1981 and continue perhaps until the spring of 1984. GE did not admit to violating any laws in signing the consent order. The state waived its right to sue the company provided it adhered to the terms of the cleanup agreement. GE is to assume full responsibility and to monitor for 30 years, 4 sites which contain waste generated only by GE; it will pay only a portion of the cleanup bill for the 3 other sites.

Water quality on Chicago's lakefront will be intensively monitored under a year-round program set up by the Metropolitan Sanitary District of Greater Chicago. The program is an effort to fill the gap in monitoring left by other agencies—state, federal, and local—that are responsible for water quality testing. Sampling will be carried out at 27 stations every other week. Storm runoff will be monitored from 3 additional stations during periods of rain.

New Jersey's Hazardous Waste Strike Force was criticized by two local law enforcement officials for its failure to act on tips concerning the involvement of organized crime in illegal waste dumping. "A lot of information has been turned over to them and people want to see the results," Joseph Brennan, police director of Elizabeth, was quoted as saying. Robert Corbin, the Middlesex County assistant prosecutor, told The Associated Press that in one case copies of an affidavit for a strike force search warrant of Duane Marine Chemical Company of Perth Amboy turned up at the home of a company employee, who was later indicted on charges of illegal dumping, and at the offices of another concern under investigation. The strike force was set up 2 years ago with federal funds.

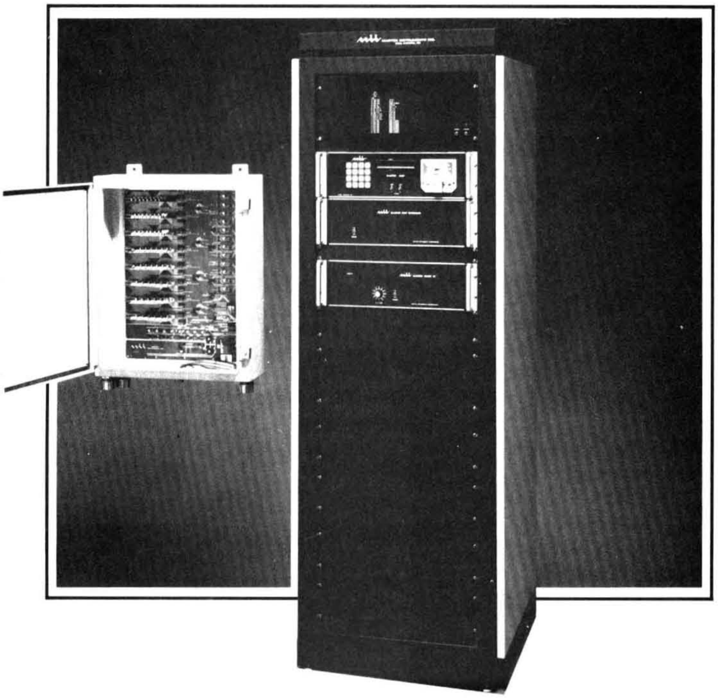
The nations's governors have decided to seek a solution for low-level nuclear waste disposal. The program adopted by the National Governors' Association calls on each state to "accept primary responsibility for the safe disposal of low-level waste generated within its borders" and notes that failure to do so "threatens . . . medical research and diagnostic activities critical to the public health." The governors also agreed to work together on establishing regional disposal facilities, and urged Congress to grant states the right to enter into interstate compacts to that end.

ANALYSIS

How does one verify water quality at the parts-per-billion (ppb) and even parts-per-trillion (ppt) level? A new in-line trace enrichment method can increase liquid chromatograph sensitivity by more than 10 000 times. It uses reversed-phase on-column concentration and 2-solvent gradient elution. The sequential execution of these processes by a computer-controlled liquid chromatograph allows programming of sample volume, flow rates, gradients, and hold times. The approach was developed by Varian (Palo Alto, CA).

MONITORING

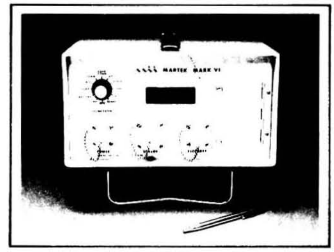
Lichens absorb heavy metals such as barium, lead, and zinc from vehicular emissions, according to John Richardson of ETS, Inc. (Roanoke, VA). Most metal absorption was found in lichens within 100 ft of a roadway, and was dependent on distance from the road, wind direction, and other factors.



Solve problems before they happen.

That's right. With Martek-designed and Martek-manufactured water quality measurement systems your process control problems can be prevented around the clock. Real-time analysis of monitored control parameters pinpoints potential malfunctions and provides an early warning system for corrective action or required maintenance.

When you buy a Martek system, you get a total package — the analyzer, the data acquisition system, and the formatted printout systems. Whether your need is for a portable analyzer for specific parameters or for a complex fixed installation, you get the same high-quality sensors manufactured by Martek to meet your total requirements. Your process control needs can be supplied from a single source at a reasonable cost by a company whose expertise ranges from ultrapure water applications in nuclear power plants to seawater applications for cooling water.



With a Martek water quality measurement system, you reduce downtime and achieve greater plant efficiency. Whether you're monitoring conductivity, salinity, dissolved oxygen, pH, specific ions, turbidity, flow rate, depth/pressure, or temperature — you can do it efficiently with Martek analyzers. And Martek's research efforts will continue to provide you with additional parameter monitoring capabilities.

Talk to the man from Martek about your water management program.

He'll help you do a better job.

MARTEK INSTRUMENTS, INC.

17302 Daimler St. • P.O. Box 16487 • Irvine, CA 92713 • (714) 540-4435 • Telex 692-317

CIRCLE 8 ON READER SERVICE CARD

TECHNOLOGY

Sulfide precipitation could remove cadmium, chromium, copper, nickel, and zinc from industrial wastewater. The sulfide would be used together with lime precipitation. In fact, the optimum method is probably lime with sulfide, clarified and filtered, as has been developed under an EPA grant to Boeing. Sulfide sources for test purposes were 10 g/L of sodium sulfide ($Na_2S{\cdot}9H_2O$), with S^{2-} held at about a 0.5-mg/L excess, in some cases. pH values were around 8–9. Metal sulfides and hydroxides coprecipitated. However, work will be needed to improve the process and to lower cost penalties which could be incurred.

Treating wastewater with algae

Algae are cleaning domestic wastewater with enhanced efficiency as part of a project headed by Gedalyah Shelef of The Technion (Haifa, Israel). Microalgae are introduced into meandering, channel-like ponds 50 cm deep. Their photosynthetic processes enable them to break down phosphates, nitrates, and other materials found in such water, while releasing large quantities of oxygen. Many nutrients are consumed by the algae, which are filtered out, dried, pelletized, and fed to cattle, fish, and poultry. After algae removal, the water is filtered through sand and made available for irrigation.

Removal of plutonium from living tissue may be possible with a chelating chemical, linear catechoylamide carboxylate (LICAM-C). The chemical has removed 70% of Pu injected into laboratory mice at the Lawrence Berkeley Laboratory. Absorbed by the body in a manner similar to iron, Pu can be potently carcinogenic. LICAM-C literally engulfs Pu in "chemical pincers" to pull it out of tissue. Researchers believe that the compound can be given in repeated doses to remove more Pu, with little or no toxic side effects. For the future, they also hope that LICAM-C may be able to remove Pu from reactor wastes.

Wastewater reuse research and development should emphasize certain specific areas, according to the Office of Water Reuse and Technology (OWRT, Dept. of the Interior): membrane processes, such as reverse osmosis; adsorption (carbon, polymers); thermal processes (crystallization, evaporation, heat exchange); oxidation (especially innovative ozone approaches); and new treatment processes not recognized before. The R&D should also cover selected municipal, industrial, and agricultural reuse applications, according to OWRT.

PCBs can be destroyed by a proprietary process that turns them into compounds that are safe, can be effected in a special truck, and would be especially applicable to electric transformer and capacitor fluids, according to Norman Jackson, chairman of Sunohio (Canton, OH), a process developer. The process can be run on-site, so that shipping is unnecessary. Also, Goodyear announced a PCB-neutralizing process which strips out sodium chloride and leaves a harmless, burnable sludge.

Burning of coal could be made more acceptable through analysis before the actual burning, thus the reason for developing CONAC, continuous nuclear analysis of coal, under sponsorship of the Electric Power Research Institute (EPRI, Palo Alto, CA). EPRI foresees that CONAC should be ready in prototype form for utility testing late this year. It should be able to analyze for sulfur, metals, and certain other analytes up to 50 tph, with a 30-min analysis time needed. The method does not affect the coal, so repeat tests can be run easily if confirmation is needed.

INDUSTRY

A means of producing synthetic fuel oils from toxic chemical wastes was announced by Chem-Fuel, Inc. (Madison, TN). The firm says that 3 years of tests have proven the technology, and that a commercial facility will open in Portland, TN, this month. The facility will meet all RCRA requirements, the firm says.

IGCI President Martie

The air pollution control industry can meet all coal conversion challenges, said Jack Martie, president of the Industrial Gas Cleaning Institute (IGCI, Alexandria, VA). He mentioned that new NO_x removal technology is being commercially demonstrated and that flue-gas desulfurization has made great strides toward on-line reliability in the last 5 years. Martie said that IGCI would welcome clarifications and simplifications when the Clean Air Act comes up for reauthorization during the next session of Congress. He added that costs of control systems have been well documented.

A 1-year delay in the last step of the phase-down of lead in gasoline was requested of EPA in a petition by DuPont. Previous regulations allowed 0.8 g/gal of lead, but as of Oct. 1, they went down to 0.5 g/gal. Richard Braendle of DuPont's Petroleum Chemicals Division estimated that retaining the 0.8-g/gal standard could conserve 20 000–60 000 bbl/d of crude oil; and since gasoline is itself being conserved, there should be no pollution penalty. DuPont has asked EPA to respond in a timely fashion, so that "judicial relief" could be sought if the petition were denied.

Industrial hazardous wastes would be immobilized in a cementlike substance which could be utilized as a final product or disposed harmlessly to a reclamation area. This is the approach that Stablex Corp. (Radnor, PA, and England) developed. It was selected by the Ministry of the Environment of Quebec, Canada, for use at a "derelict" 200-acre site in West Thurrock, Quebec. The material will be pumped into the site, where it will immobilize. Full analytical laboratory facilities will be available. Phase I of the project will handle inorganic wastes; Phase II, involving organic wastes and a rotary-kiln incinerator, will be completed in 1982.

The Model 2100 Sampler...

for toxic pollutants and suspended solids sampling.

The Model 2100 Sampler has been specifically designed for priority pollutant and suspended solids sampling, but is equally well suited for general purpose applications.

Samples are drawn through a vinyl or Teflon® tube and then through a short length of special medical grade silicone rubber tubing by a high speed peristaltic pump and are placed directly into glass bottles without contacting any other materials. There are no cumbersome metering chambers or valving systems to clean or cause cross-contamination. The 3,000 ml per minute pumping rate and the elimination of secondary distribution systems makes it ideally suited for suspended solids sampling.

The Model 2100 features microprocessor-based electronics that provide a new dimension in programming versatility. Any sample volume from 10 to 1000 ml can be collected on a timed or flow proportioned basis at heads to 22 feet. The base is completely insulated, has a large ice capacity and holds 24 polypropylene bottles of 1,000 ml or 24 glass bottles of 350 ml. A composite base is optional. The Model 2100 is portable, operating from either 117 VAC or a 12 VDC Nicad battery. It is corrosion resistant and all electronics are in a gasketed, stainless steel housing to protect against accidental submersion.

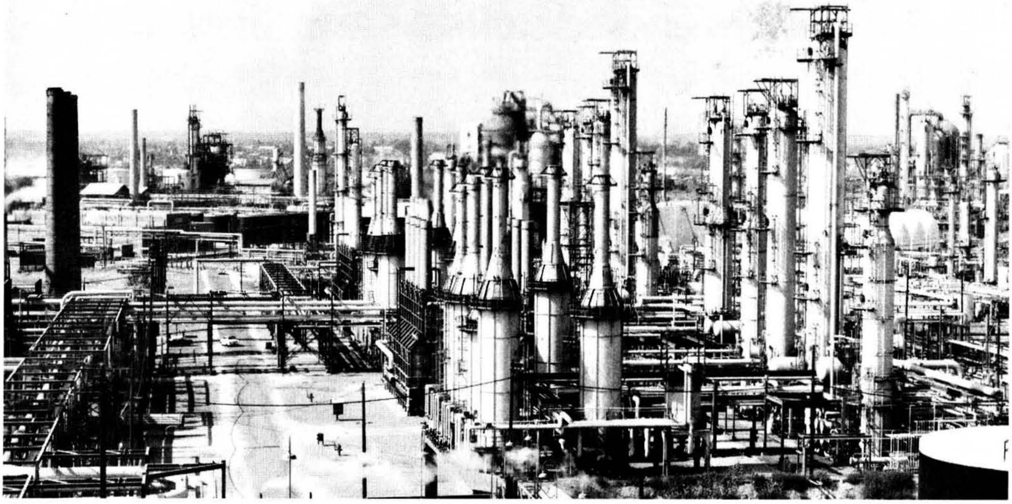
For details on the Model 2100 and all of its other features, send for a descriptive brochure or phone toll free (800) 228-4373 (continental U.S.A. except Nebraska). ISCO, 3621 N.W. 36th Street, Lincoln, Nebraska 68524.

®DuPont

ISCO

CIRCLE 7 ON READER SERVICE CARD

COMPU/CHEM™
DOUBLES PRODUCTION



And we were already the biggest GC/MS facility in the business.

COMPU/CHEM's centralized laboratory, operating around the clock, provides your company the largest capacity GC/MS pollutant analysis facility in the world. And we're still growing! COMPU/CHEM analyzes priority pollutants and hazardous wastes by GC/MS (gas chromatography/mass spectrometry) and that's our *only* business.

This approach to GC/MS analysis provides several benefits: quality due to specialized staff and instrumentation, results in weeks not months, lower cost than competition (and your internal R&D facilities), and capacity to process samples for the largest of corporate programs.

If your company has problems handling environmental sample logistics for plants throughout the U.S. (and overseas), COMPU/CHEM is the solution. Tell us your corporate-wide sampling schedule—where, when, and who. We'll automatically forward specialized sample shipping and collection containers (our Pat. Pend. "SAMPLESAVER") where and when they're needed. That's all part of our Customer Service.

COMPU/CHEM's pollutant analysis service results from years of environmental involvement by the Mead Corporation in the paper, pulp, rubber, foundry, coal, chemical, ink and petroleum industries.

COMPU/CHEM provides technical excellence, rapid turnaround, large scale capacity, and lower cost. To learn more about the largest automated GC/MS pollutant lab in the business (and give your R&D people a chance to do R&D), phone us.

COMPU/CHEM. 5 Triangle Drive, Research Triangle Park, North Carolina 27709.
Telephone 800-334-8525.

COMPUCHEM
a Mead Service

PRIORITY
POLLUTANT
ANALYSIS

Regional Offices: Atlanta, Detroit, Philadelphia, Raleigh

CIRCLE 30 ON READER SERVICE CARD

ENJOY YOUR OWN MONTHLY COPY OF

Environmental Science & Technology

1980

Toll Free: New Orders: (800) 424-6747

	U.S.	Foreign**
ACS Members*	☐ $16.00	☐ $23.00
Nonmembers-Personal	☐ $20.00	☐ $27.00
Nonmembers-Institutional	☐ $64.00	☐ $71.00

☐ Bill Me ☐ Bill Company ☐ Payment Enclosed
(Make payable to American Chemical Society)

Charge my ☐ Master Charge ☐ VISA

Card # ____________ Interbank # ________
(Master Charge only)

Exp. Date ____________

Signature ____________

Name ____________

Position ____________

Your Employer ____________

Address ☐ Home ☐ Business ____________

City ________ State ________ Zip ________

Employer's Business ☐ Manufacturing ☐ Academic ☐ Government ☐ Other ________

If manufacturing, type of products produced ____________

____

*Subscriptions at ACS member rates are for personal use only.
**Payment must be made in U.S. Currency, by international money order, UNESCO coupons, U.S. bank draft, or through your book dealer.

Allow 60 days for your first copy to be put in the mail. 9998G

MAIL THIS POSTAGE FREE CARD TODAY

NO POSTAGE
NECESSARY
IF MAILED
IN THE
UNITED STATES

BUSINESS REPLY CARD

FIRST CLASS PERMIT NO. 10094 WASHINGTON, D. C.

POSTAGE WILL BE PAID BY ADDRESSEE

AMERICAN CHEMICAL SOCIETY
Attn: Gayle Hebron
1155 Sixteenth Street, N.W.
Washington, D. C. 20036

NO POSTAGE
NECESSARY
IF MAILED
IN THE
UNITED STATES

BUSINESS REPLY CARD

FIRST CLASS PERMIT NO. 10094 WASHINGTON, D. C.

POSTAGE WILL BE PAID BY ADDRESSEE

AMERICAN CHEMICAL SOCIETY
Attn: Gayle Hebron
1155 Sixteenth Street, N.W.
Washington, D. C. 20036

ES&T OUTLOOK

The risky business of assessing risk

The case of chlorinated hydrocarbons illustrates the dilemma: It's often a tug-of-war with the demands of regulators on one side, the limited methods of researchers on the other, and the uncertainties of extrapolation burning the rope in the middle

Chlorinated hydrocarbons are everywhere. They're released to the air and we breathe them; they seep into groundwater and we drink them; they accumulate in fish and we eat them. And the question everyone asks is whether that's doing anything to us.

The attempts to answer that question—and the controversies, both theoretical and experimental, that have arisen in the process—illustrate well the uncertain game of risk assessment in action. It's a shaky game from the word go: Inconsistent and often inadequate data, differing interpretations, and tenuous extrapolations continually work against it. The only thing that keeps it alive is the pressing and unremitting need of regulators who are strapped with the burden of protecting public health.

The basic case

The case against many chlorinated hydrocarbons rests on findings of chronic toxicity—that is, carcinogenicity in rats and mice. Studies by the National Cancer Institute (NCI) report significant induction of tumors in animals fed compounds such as trichloroethylene (TCE), tetrachloroethylene, chloroform, and carbon tetrachloride. Following the standard procedures for NCI bioassays, the tests were conducted at the maximum tolerated dose.

The NCI results have been corroborated by some studies, contradicted by others. Short-term tests, such as the Ames test, have yielded similarly inconsistent results.

The EPA is, nonetheless, going ahead with risk assessments based on what data are available. A new-source performance standard for TCE is in the works, and regulations on others, including perchloroethylene, chloroform, methylene chloride, and methyl chloroform (1,1,1-trichloroethane), are being contemplated.

But the problems with the available data appear to be substantial. The EPA's own Science Advisory Board subcommittee on airborne carcinogens met in September and strongly criticized the agency's risk assessments for several of these substances. In particular, the subcommittee questioned the findings of "substantial" evidence of the carcinogenicity of trichloroethylene and perchloroethylene, and of "suggestive" evidence of carcinogenicity of methyl chloroform and methylene chloride.

The chairman of the subcommittee, Sidney Weinhouse of the Temple University School of Medicine, told *ES&T*, "In some instances there were just not enough data provided; in other cases the data were inconsistent or contradictory." One specific problem was that "in some instances the purity of the compound was not clear." The NCI test of TCE, for example, used a technical grade of the compound that contained a stabilizer, which now appears to be carcinogenic itself.

Other problems mentioned by Weinhouse were experiments that varied the dose, experiments that were terminated too soon, and experiments in which too many animals died from other causes during the tests.

Some of these objections are likely to be answered by a second NCI bioassay that will test the pure compounds. But a more fundamental problem was raised by Elizabeth K. Weisburger, who has been conducting many of the NCI tests: "NCI bioassays were never designed to be used in risk estimation—that's why things are given at maximum tolerated dose." She explained that these tests can show only that "there's something suspicious there" and that subsequent work, such as tests at several lower dose levels, would be needed to determine risk. "I don't think it's quite cricket" for EPA to base risk assessments on the NCI data, she said.

Mouse to man

A more fundamental problem still is the extrapolation of laboratory results to humans. At a meeting on halogenated hydrocarbons held in Washington earlier this year, Philip G. Watanabe of Dow Chemical's Toxicology Research Laboratory reported on the considerable differences in susceptibility between even rats and mice. In a study of perchloroethylene metabolism, mice metabolized 9.5 times as much as rats and bound 7.1 times as much to liver macromolecules. Watanabe concluded that since "metabolism, which appears to be an activating process, increases toxicity," and since different species show remarkably different metabolisms, "we should not generalize" from species to species.

The point was underscored by Hugh Farber, one of Dow's managers of environmental affairs. Referring to the compounds TCE, perchloroethylene, methyl chloroform, and methylene chloride, he told *ES&T*, "The position we've taken is that they're not likely to be found carcinogenic to humans." He pointed out that only TCE and perchloroethylene have been found to cause cancer in animal tests—and that these tests used the "NCI mouse," a strain having a high spontaneous incidence of liver tumors. "The control population will run as high as 50%," he said. The argument then runs that the higher tumor incidence in the test population may be attributed to a secondary effect resulting from cell damage—in an organ already susceptible to tumors. That the test substances show their acute effects in liver necrosis seems to support this view.

Mechanisms

This point leads into a more general theory of carcinogenesis developed by Gary M. Williams of the American Health Foundation's Naylor Dana Institute; he argues that there are two distinct mechanisms of chemical carcinogenesis. Genotoxic chemicals act directly, binding with and damaging the target cell's DNA, while epigenetic chemicals act indirectly, through such mechanisms as chronic tissue injury or some sort of "promotional" effect on already-transformed but nontumorous cells.

Williams believes that the frequent appearance of liver tumors in tests with chlorinated hydrocarbons is "highly indicative of an epigenetic mechanism of action," and he questions the significance of conclusions drawn from tests in strains with a high spontaneous incidence of liver tumors. "One of the characteristics of genotoxic carcinogens," he explained, "is that they affect multiple organs. And the particular site of tumorigenesis is often outside the liver, since the liver has fantastic genetic repair mechanisms." A second characteristic of genotoxic carcinogens is their rapid action; tumors typically appear in mice after six months of exposure. The chlorinated hydrocarbons that test positive take much longer, up to 18 months, to show their effects.

"It is such a dramatic difference," Williams said, "that I'm continually amazed that people have been so slow to recognize it." But other scientists that *ES&T* spoke with remain unconvinced. "In due season we will know whether it's reasonable or has to be thrown in the trash basket," said Weisburger of the epigenetic theory. Weinhouse agreed: "The subject is still in the theoretical stage."

And Weisburger took issue with the criticism of using a strain with a high spontaneous tumor rate, saying that it was a valid criterion for judging carcinogenicity in many cases—and one which Williams himself recently recommended in a textbook article. Weinhouse, whose subcommittee had joined with the criticism, explained that his objections were not with the method itself: "It's not intrinsically wrong; it's just hard to get good statistics on such studies," he said.

Over the threshold

The conclusion that Williams and Dow Chemical are drawing from the epigenetic theory is the real point of contention, however. Williams argues that the epigenetic mechanism implies a threshold, and that a threshold implies a negligible risk to the general population from exposure to these substances. Halogenated hydrocarbons are lipophilic, he explained, and tend to accumulate in the lipid cell membranes. Saturation of the membrane with these substances may be the key to promotion of tumorogenesis, according to the theory, since saturation could cut off the cell-to-cell communication that regulates growth—and that may hold in check cells that are transformed but not yet tumorous. The exposure needed to saturate the membranes determines the threshold. According to Williams, the "one-hit" argument that exposure to even one molecule of a carcinogen carries some finite risk applies only to genotoxic carcinogens.

Weinhouse counters that we simply do not understand carcinogenesis well enough to give a great deal of weight to such conclusions at present. "My judgment is that we have to accept the data on their face—we don't know enough about mechanisms to make this an overriding consideration. I have no doubt that there are epigenetic mechanisms, but I can't see where this exerts an influence now." And he took strong exception to the argument of a threshold. "All the evidence is against thresholds. If there are thresholds, they're likely to be low. And if there are thresholds, they're indeterminate—we have no way on earth to establish a 'safe' dosage. I don't think the threshold concept is useful in making regulatory decisions."

An experiment that Williams is now seeking funding for could help to settle the dispute. He proposes to test DDT and an aliphatic chlorinated hydrocarbon at several different dosages. This would provide a better basis for extrapolating risk to low dosages as well as a possible answer to the threshold question.

What's out there

The ultimate question of human risk pulls in another area, also the subject of some dispute: the potential for exposure in the general population. The slow degradation of chlorinated compounds in the environment is one point of concern. "Chlorinated solvents are 'ideal' groundwater pollutants," said Paul Price of the EPA's Chemical Review and Evaluation Branch. "Microbes attack them slowly, and they're exceedingly mobile. You recognize the potential of screwing up a large number of water supplies for a long time."

Farber of Dow Chemical, though, emphasized the natural occurrence of chlorinated compounds in the environment. "The C–Cl bond is not a unique species to man's activities. I don't think there's any concern with TCE, perchloroethylene, or methylene chloride with environmental persistence. In the air they're decomposed. There is TCE showing up in groundwater at low levels in various parts of the country, and you don't have the oxygen and UV light underground that you do in the atmosphere, so you have to be worried because it's there. On the other hand, methyl chloride is there, and we've been living with it for years."

A good many halogenated compounds do in fact occur naturally; in addition to methyl chloride these include carbon tetrachloride, a variety of haloforms, and even epoxides. "There are a lot of compounds in the environment that have the same structural components as many of the things that we consider industrial chemicals," said Weisburger. "Maybe the environment can take care of these things better than we think it can—if we don't overwhelm it."

Where we're left

Where does this leave us in assessing the risks to the public? "Some people think we know enough and others think we don't," said Weisburger. Asked for her own opinion, she would venture only, "There's something suspicious there. I wouldn't want to take a bath in something like TCE."

That may be the only assertion that can honestly be made with any certainty. Weinhouse summed up the problems well: "It's a new scientific area, where the ground rules have not been set down firmly." Hartmut Uehleke, chief director of toxicology of the Federal German Health Office, may have come closer to the truth in his comments to the Washington halocarbon meeting. In extrapolating risk from the data of animal experiments, he said, "you are leaving the factual side of our business."

—Stephen Budiansky

Toxic by-products of coal conversion

To comply with permits, synfuel plants will have to determine their chemical and biological effects and employ proper control technologies. However, scant information in this field is available

"We can 'get a leg up' on environmental difficulties associated with coal-derived synthetic fuel production," predicted Kurt Riegel, associate deputy assistant administrator of EPA's Office of Environmental Engineering and Technology. These difficulties include emissions to the air, and effluents to the water of aniline, benzene, cresols, indole, phenolics, quinolines, and numerous other substances, some of which have been characterized as suspected carcinogens.

To counteract these difficulties, those involved in the coal-derived synthetic fuel (synfuel) industry must ascertain and quantify to the extent possible, what is in emissions, effluents, and synfuel product contaminants that could present environmental and health problems. These determinations can then be applied to preparing the necessary permits for synfuel plant operation. They will also indicate the scientific and technological measures necessary to help these plants meet permit terms and to protect the environment and public health.

With optimism that these tasks can be accomplished, Riegel keynoted the Symposium on Environmental Aspects of Fuel Conversion Technology, V, held in St. Louis, Mo. Sponsored by IERL/RTP, the symposium attracted 250 people.

Riegel observed that the delay in establishing synfuel plants may have a salutary aspect, in that EPA and others concerned with this development were given a chance to learn more about environmental and health effects. However, data gathered so far might not be fully usable before 1984–88. Nevertheless, the synfuels program will go forward; so waste stream management and initial permits may have to be based on "best engineering judgment," Riegel explained. "Perhaps, the 'bottom line' is that a major synfuel hurdle to be cleared will be the achievement of environmental protection at 'reasonable cost,' " IERL/RTP Director John Burchard suggested.

Pilot-plant dispute

A $1.4-billion project to construct a demonstration solvent-refined coal (SRC) facility near Morgantown, W.Va., is scheduled to commence this fall. However, because of delays, next spring may be a more likely date. The U.S., Japanese, and West German governments; Gulf Oil Co.; and German and Japanese corporations are financing the operation. At its first stage of completion, about five years after construction starts, the plant will turn out 20 000 bbl/d of SRC-II, a liquid material similar to low-sulfur distillate fuel oil.

Because of the project's size, an EIS is required by law and has been drafted by the U.S. Department of Energy (DOE). This draft has been criticized by EPA and by environmental advocacy groups such as the NRDC and NWF, two groups that are concerned by the chemical by-products mentioned earlier. According to these groups, DOE did not adequately address in its EIS the question of chemical risks from short-term leaks and spillages. They also said that data on environmental and employee safety, derived from five years of pilot-plant experience (at Fort Lewis, Wash.) without "chemically traceable incidents," are insufficient to draw any conclusions, especially in view of the "known hazards" of chemicals involved.

On the other hand, Gulf Oil, one of the operators of the SRC-II pilot plant, maintained that only five cases of temporary skin irritation ascribable to direct contact with SRC-II materials were reported. Gulf added that there were no cases of illness after more than five years of pilot-plant operation.

Pilot-plant biotests

Both biological and chemical tests of SRC products of the Fort Lewis pilot plant—which ran during the mid- and late 1970s, with some interruptions—were conducted by Battelle Pacific Northwest Laboratory (Richland, Wash.), under contract to DOE. W. Dale Felix of Battelle/Pacific listed phenolic and polynuclear aromatic species as particularly worrisome product impurities. He noted that these compounds "were generally present at higher levels than one would expect, say, in crude petroleum."

The Ames test showed positive results, with *Salmonella typhimurium* TA98 used as the biotest vehicle. Primary aromatic amines were implicated as members of the compound class of principal concern. However, when an SRC-II distillate blend was hydrotreated, the content of these impurities as well as that of polynuclear aromatic hydrocarbons (PAH) was reduced significantly. Hydrotreating also resulted in the curtailment of sulfur- and oxygen-containing aromatics, such as thiophenes and phenols, Felix observed.

In the Ames test, benzo[α]pyrene showed 114 ± 5 revertants/μg, while 2-aminoanthracene—an impurity of great concern—scored 5430 ± 394 revertants/μg. Unhydrotreated SRC-II heavy distillate exhibited 40 ± 23 revertants/μg. By contrast, the SRC-II middle and light distillates caused less than 0.01 revertants/μg, as did crude petroleum from Prudhoe Bay, Alaska. Also, of three shale oils tested, none exceeded 0.65 ± 0.22 revertants/μg.

Molecule cleavage

To answer advocacy-organization concerns about emissions and effluents from synfuel plants, one engineer re-

Characteristics of waste extracts using the RCRA extraction procedure

	Concentration, μg/L													
	Ag	As	Ba[a]	Cd	Cr	Hg	Pb	Se	B[a]	Cu	Mn[a]	Ni	U[a]	Zn[a]
Lurgi–Rosebud														
3/8″–20 mesh	<0.2	<1	0.5	<0.1	<6	<0.4	<0.2	<1	0.55	2.7	3.22	34	<0.5	0.124
20–100 mesh	<0.2	2	1.0	1.1	<6	<0.4	1.0	<1	1.48	5.4	5.83	80	<0.5	0.157
<100 mesh	<0.2	3	2.3	2.0	<6	<0.4	1.8	<1	1.85	13.3	9.25	138	<0.5	0.321
Lurgi–Illinois #5														
3/8″–20 mesh	<0.2	<1	<0.2	52	5	<0.4	0.9	<1	0.28	5.6	0.39	4240	<0.5	37.1
20–100 mesh	<0.2	<1	0.8	32	3	<0.4	3.1	<1	0.77	6.5	1.15	442	<0.5	28.5
<100 mesh	1.6	3	1.0	26	4	<0.4	4.4	3	0.49	5.1	2.50	441	<0.5	9.2
Lurgi–Illinois #6														
3/8″–20 mesh	0.9	4	<0.2	13	3	<0.4	1.3	3	0.04	<2	0.28	49	<0.5	4.27
20–100 mesh	1.4	<1	<0.2	5.1	3	<0.4	1.3	<1	0.25	<2	0.39	56	<0.5	2.84
<100 mesh	<0.2	<1	<0.2	4.3	<2	<0.4	1.6	<1	0.20	<2	0.71	72	<0.5	1.13
Wellman–Galusha, ash	<1	19	1.0	<7	1	<0.6	7	14	—	—	—	—	—	—
Wellman–Galusha, dust	<1	33	1.0	<1	1	<0.3	8	6	—	—	—	—	—	—
Texaco, slag	<2	<2	0.19	37	4	<0.2	<2	900	—	—	—	—	—	—
Boiler bottom ash	<1	<1	0.28	<0.3	<3	<0.2	<3	<1	—	—	—	—	—	—
Boiler fly ash	2	5	0.44	5.3	16	<0.2	<3	2	—	—	—	—	—	—
100x Primary Drinking Water Standards	5000	5000	100	1000	5000	200	5000	1000	—	—	—	—	—	—

[a] Values in mg/L

Source: Symposium paper by Kar Yu of TRW, Inc.

minded the symposium that a major object of a pilot plant is to determine these types of process weaknesses. Such weaknesses could then be rectified when the subject process is upgraded to demonstration and commercial scales.

Thus, the Fort Lewis SRC-II pilot-plant "shakedown" suggested means by which chemicals of concern, such as primary aromatic amines, might be handled if and when the process goes commercial. For instance, hydrotreating can deaminate these amines, with evolution of ammonia (NH_3). Cleaving carbon–carbon bonds would destroy PAH molecular structures, forming lighter molecular weight alkylated or hydrogenated species. Thiophene and phenolic structures could be broken with evolution of hydrogen sulfide (H_2S) and water.

Felix stated, however, that while hydrotreatment process conditions may represent current commercial practice in other industries, demonstration-scale designs for synfuel plants are still unavailable. But data can be evaluated "in general terms," he pointed out.

Experimental hydrotreatment occurred in fixed-bed reactors that used commercial catalysts. Analysis before and after was done principally by GC/MS. Phenols were curtailed from 130 ppm to 17 ppm in the total distillate blend; primary aromatic amines, initially at concentrations of 1.9 ppm, were essentially taken down below GC and GC/MS detectable ranges. Concentrations of aromatics and *N*-heterocyclics also were significantly reduced. There were strong indications of diminished mutagenic activity, perhaps because of the presence of lesser amounts of some of the above substances believed responsible for such mutagenicity.

Abbreviations not in text

BACT = Best available control technology
EDS = Exxon donor solvent process for direct liquefaction of coal
EIS = Environmental impact statement
ESRL/RTP = Environmental Science Research Laboratory/Research Triangle Park, N.C., a component of EPA
GC = Gas chromatography
IERL/RTP = Industrial Environmental Research Laboratory/Research Triangle Park, N.C., a component of EPA
MS = Mass spectrometry
NIPDWS = National Interim Primary Drinking Water Standards
NRDC = Natural Resources Defense Council (New York, N.Y.)
NWF = National Wildlife Federation (Washington, D.C.)
PCGD = Pollution Control Guidance Document

Dividing the work

The studies at Fort Lewis and Battelle comprise one salient example of the scientific and technological push to obtain firmer knowledge of environmental and health risks associated with synfuel production. This particular effort falls under the IERL/RTP heading of direct liquefaction, and both SRC-I and -II are included in that program. However, there are those in the synfuels field who maintain that SRC should be in a category of its own.

Another program category of IERL/RTP is gasification and indirect liquefaction. Each category has different types of environmental, chemical, and biological problems to be faced. Bear in mind that in comparison to most direct liquefaction schemes, gasification and gasification/indirect liquefaction constitute "here-and-now" technologies, witness working SASOL plants in South Africa and Lurgi gasifiers.

Ash leachate

A major problem with SRC-II, classified as direct liquefaction, is removing toxic impurities from the product distillates. On the other hand, gasification has the problem of solid wastes, such as ash and slag, which make up the largest single waste stream from coal gasification facilities. Management of these wastes—since they are considered to be potentially hazardous—is now regulated under the Resource Conservation and Recovery Act of 1976 (RCRA), as reauthorized.

To evaluate what hazards there may be, solid wastes from lignite, subbituminous coal, and Illinois coal went through simulated rainwater leachings. Kar Yu of TRW, Inc. discussed the tests involved. The Texaco gasifier used a western subbituminous coal feedstock; the Wellman-Gaslusha gasifier reacted lignite from North Dakota; and the Lurgi gasifier's unquenched ash was from Illinois coal. For the Lurgi determinations, it was impossible to use quenched ash because metal determinations would not have been representative; quench water would have carried off a portion of the total extractable metals.

Testing followed the RCRA extraction procedure, as set forth in the May 9, 1980, *Federal Register*. Results for arsenic, barium, cadmium, chromium, lead, mercury, selenium, and silver were tabulated, along with NIPDWS values. Those last values were included because metal wastes are considered hazardous when their concentrations exceed 100 times NIPDWS.

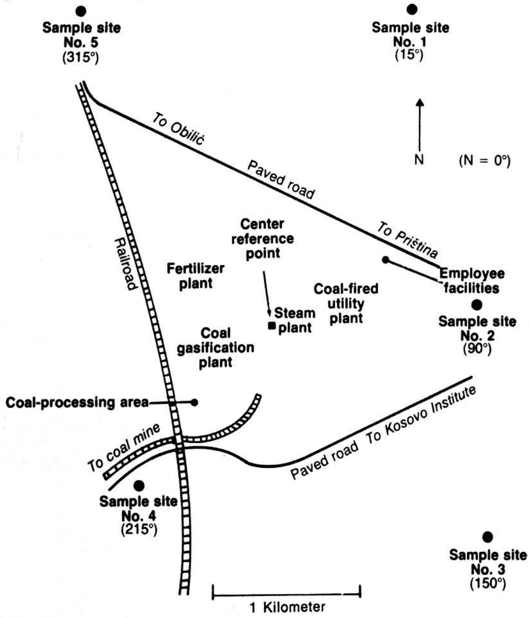
Although selenium from the Texaco gasifier's slag came close to violating the standards, in no case were they actually violated. Thus, for the eight metals listed, the gasification and steam station wastes were not hazardous under present drinking water standards. It should be mentioned here that in addition to wastes from gasifiers, precipitator and bottom ash from a western lignite-fired steam station were also sampled.

Other metals found, at least in the Lurgi gasifier ash, included copper, manganese, nickel, uranium, zinc, and boron.

Testing the air

Kosovo, Yugoslavia, is a long distance to go to test air emissions from a medium-Btu Lurgi coal gasification facility. However, ESRL/RTP chose

Yugoslav sampling scheme



Source: Symposium paper by Ronald Patterson of ESRL/RTP

Kosovo, Yugoslavia, study conclusions

The Kosovo industrial complex adversely impacts on the surrounding atmosphere, especially downwind, as borne out by the following:

- Aerosols in the form of coal dust are a significant pollutant from the coal-handling operation.
- Coal-handling aerosols overshadow those from the actual gasification process.
- Ambient aerosol levels, if they were in the U.S., would exceed both primary and secondary National Ambient Air Quality Standards.
- Aerosols appear to carry PAHs.
- The source of PAHs in aerosol collections is unknown, but the flare is suspect.
- The level of benz[α]pyrene exceeds the U.S. Ambient-Multimedia Environmental Goal (A-MEG) by a factor of 1000.
- Though light organic compounds were lost during sampling, benzene is believed to exceed the U.S. A-MEG by a factor of 10–100.
- Organic pollutants can be traced to the gasification plant.
- There is a broad range of organic compounds in the ambient air, including aliphatic and aromatic hydrocarbons, and their oxygen-, sulfur-, and nitrogen-containing derivatives.

The Kosovo complex is of commercial scale, though about one-tenth the size of proposed U.S. gasification facilities. Ronald Patterson of ESRL/RTP believes that it is possible to differentiate between gasifier and other emissions from an industrial complex, and that data gleaned from Kosovo could be valuable as an aid to making siting, logistic, and environmental control decisions for gasifiers.

Sampling equipment included:

- one 24-h HiVol sampler (1.1 m^3/min) with a 265-mm diameter Gelman Microquartz filter, and a HiVol motor exhaust filtration system
- one 24-h Tenax vapor trap system (4 L/min), which tapped into the postfilter section of the HiVol sampling head
- one 6-h LoVol sampler (28 L/min), and associated items
- one 6-h modified Battelle cascade impactor, 1 L/min
- one 7-d time-phased aerosol sampler
- one 3-kW gasoline electric generator placed 40 m downwind of the sampling equipment.

In addition, Sites 3 and 5 were furnished with certain meteorological measuring devices. Sampling began on May 14 and ended May 29, 1979.

that site for a continuous 16-d test, partly because environmental controls there are not on a par with similar facilities in the U.S. Five sampling sites were established about 2 km outside the fence of the plant, a part of the industrial complex known as Kombinat Kosovo.

Analyses included total particulate matter, total and fine particle mass, inorganics, elemental species, trace metals in size-fractionated particles, and vapor-phase organics. Both U.S. and Yugoslavian laboratories participated in the study.

The main impact

Test results indicated that trace metal aerosols come from sources other than the gasification plant. The same holds true for Na^+, NH_4^+, NO_3^-, Cl^-, and SO_4^{2-}, as well as most elemental species, except carbon. Thus, as far as the plant is concerned, organic pollutants have the main impact.

Such pollutants principally comprise PAHs, from naphthalene to the benzopyrene aromatic group. Through the use of MS and flame-ionization detection of compounds adsorbed on particulate matter, naphthalene and benzopyrene isomers were found in the vapor phase at 8 $\mu g/m^3$ and 0.08 $\mu g/m^3$, respectively, when extrapolated to 100% downwind. Benzene and toluene were not quantifiable, but xylenes, heavier aromatic compounds, heterocyclics, ketones, dibenzofuran, and alkylated pyridines and quinolines were among the materials detected. However, some volatiles detected in ambient air were identical to certain ones emanating from the Yugoslav gasification plant.

Document preparation

The Yugoslav study, even with its attendant cost and effort, gave very useful data on a relatively poorly controlled gasification plant. This knowledge will benefit the gasification/indirect liquefaction effort and can be applied to the preparation of PCGDs.

Control technology guidance will be written for direct liquefaction (SRC-I and -II, EDS, and H-Coal) as well, eventually with a plant production scale of 100 000 bbl/d of liquid fuel. Baseline data for the documents will stem from material balance flowsheets and calculations for uncontrolled waste streams, which is why, in the case of gasification, the Yugoslav data are so helpful. Controls for air, water, and solid waste will be addressed, as will their expected capital and operating costs.

Pollution Control Guidance Documents must address [a]:

Gaseous emission controls

- fugitive dust emissions from coal storage, and coal and slag handling
- fugitive hydrocarbon emissions from valves, flanges, and seals, and from product and by-product storage
- off-gas from the coal dryer
- acid gases containing CO_2, COS, CS_2, and H_2S
- mercaptans and NH_3 from sour-water stripping units
- flue gas from process heaters and from steam and power plants
- evaporation and drift from cooling towers

Wastewater streams

- sour process wastewater from vapor washes, condensers, fractionator overhead drums, sulfur recovery plant, and coal slurry mixing operations
- cooling tower and boiler blowdown
- coal pile runoff
- oily water runoff from processing areas
- miscellaneous small wastewater streams

Solid waste

- Gasifier slag from hydrogen synthesis
- spent catalysts
- wastewater and raw water treatment sludges
- possible nonmarketable by-product residues

Final characterizations, regulatory procedures, and means of managing wastes will evolve only after considerably more sampling, analysis, and health effects study efforts by process developers, DOE, EPA, and their contractors. The same holds true for the determination of whether a solid waste will be listed as hazardous or not.

[a] This list applies to direct liquefaction schemes.

Source: Symposium paper by J. E. Cotter et al. of TRW, Inc.

Planned documents

Control guidance documents are planned for these synfuel and energy technologies:

- low-Btu coal gasification
- medium-Btu coal gasification
- high-Btu coal gasification
- indirect coal liquefaction
- direct coal liquefaction
- oil shale (mining and milling)
- geothermal (first revision of existing PCGD)

Source: Symposium paper by Terry Thoem of EPA Region 8

Documents addressing these control technologies will help EPA permit reviewers examine pollution abatement possibilities; a number of BACT options will be evaluated for waste streams of the direct liquefaction processes. Results of scientific studies based on monitoring, analysis, and toxic and health effects programs will add to the ammunition in permit reviewers' arsenal. TRW, Inc. (Redondo Beach, Calif.) is one of the organizations involved in PCGD development for direct liquefaction facilities.

The permitting process

The permitting process for the development and operation of synfuel plants will involve EPA and various state agencies, Terry Thoem of EPA Region 8 (Denver, Colo.) told the symposium. It will have to be carried out in conformity with existing provisions of all pertinent agency policies and federal, state, and local laws and regulations. (Remember that the environmental regulatory "fast track" for energy projects has so far failed to pass Congress.)

At present, however, there exists virtually no commercial-scale plant data on which to base a more "conventional" regulatory approach, Thoem pointed out. Thus, in some cases, PCGDs and similar documents for direct liquefaction and other synfuel approaches may be based upon experience gleaned from related industries, such as petrochemicals. Scheduled publication dates of these control documents are August 1981 for low-Btu gasification, July 1982 for direct liquefaction, and February 1983 for high-Btu gasification.

Incidentally, Thoem's paper lists 89 different permits that may be necessary to build and operate a synfuel facility. Of these, 18 would be federal; 52, state; and 19, county/local.

The developing synfuels industry will be faced with many tasks, as well as a formidable permitting program aimed at ensuring the fullest possible environmental safeguards, with an eye on costs. Not the least of the challenges is the provision of sound chemical, biological, and toxic health effects data for synfuel products and waste streams, which would assist industry and government in doing the environmental and health protection job that current laws and regulations require.

—Julian Josephson

Additional reading

"Health Hazards and Pollution Control in Synthetic Liquid Fuel Conversion"; Perry Nowacki, Ed.; 511 pages. Noyes Data Corp., Mill Rd. at Grand Ave., Park Ridge, N.J. 07656.

Additives to drinking water

Are they or are they not a source of impurities?
EPA's new Additives Effects Branch hopes to find answers.

There are both direct and indirect additives to drinking water. Direct additives are those chemicals deliberately added to water in treatment or storage. On the other hand, indirect additives are those chemicals leaching into water from materials in contact with the water during storage, treatment, or distribution. Examples of materials which could contribute indirect additives are chemical coatings, liners, or corrosion by-products from delivery pipes and storage tanks.

Headed by Dr. Alan M. Ehrlich, EPA's Additive Effects Branch, set up this April, has as its first responsibility the development of a procedure for issuing advisory opinions on the acceptability of direct additives for use with drinking water and of materials coming in contact with drinking water in its treatment and distribution.

Earlier, a July 20, 1979, memorandum of understanding between FDA and EPA resolved the potential for confused jurisdiction that occurred when drinking water was defined both as a food, under the Food, Drug and Cosmetic Act, and as publicly supplied drinking water, under the Safe Drinking Water Act. In this memorandum, the two agencies agreed that EPA had the responsibility for drinking water in public water supplies. EPA can regulate additives under the SDWA, TSCA, and FIFRA. However, FDA retained jurisdiction for bottled water and for water used in food processing, after that water is in the possession of the food processor.

Under the Criteria and Standards Division of the Office of Drinking Water, directed by Dr. Joseph Cotruvo, the new branch is responsible for ensuring that substances added to drinking water, directly or indirectly, do not pose a health hazard to the public.

The need for the Additives Effects Branch is evidenced by surveys of community water supplies, which sometimes show higher concentrations of certain organic chemicals such as PAH (polynuclear aromatic hydrocarbons) and tetrachloroethylene in the treated water than in the raw water. Researchers believe these chemicals might be migrating into the drinking water from pipes and storage tanks in contact with the water. Pipes and tanks used in public water supply distribution networks are frequently lined with a variety of materials, such as epoxy paints or asphaltic sealants; some pipe materials, such as asbestos-cement or certain plastics, are generators of direct additives.

Prior to this agreement, several states, FDA, and EPA participated in an informal procedure involving so-called advisory opinions on the propriety of using particular additives or materials. However, these advisory opinions were made informally without a specific set of consistently applied technical criteria. They therefore had the potential for being inconsistent between agencies, or within the same agency over the years.

Each state has the ultimate authority for approving materials for use in drinking water. Many states, however, have sought the advice of the federal government.

With respect to EPA's formal procedure, the manufacturer of a coating material or coagulant aid would seek approval from the state in which the material was to be used. Alternatively, the water utility would seek approval. The state would then direct the request to the EPA regional office, which then asked for toxicological guidance from EPA's research facility in Cincinnati. Cincinnati would issue an advisory opinion, which most participating states confirmed. But the absence of specific protocols for the evaluation of additives led to situations in which opinions offered within each agency for similar materials were inconsistent; for example, coal tar liners are approved for use by EPA Region 2 but are disapproved for use by EPA Region 3.

There are published scientific papers with findings that, in some cases, water from distribution systems are relatively more mutagenic than finished water at the treatment plant, or the raw water source (cf. Schwartz, Saxena, and Kopfler, *ES&T*, September 1979, p. 1138).

Bulk treatment chemicals are infrequently checked for contamination, such as acrylamide monomer residuals in polyacrylamide used as a coagulant aid, or the multitude of organic impurities contained in liquid chlorine manufactured by certain methods.

To gather scientific data, EPA has let a number of contracts on additives. Under one contract, an NAS committee is working on direct additives, some 60 bulk chemicals used in the manufacture of potable water. They intend to publish a Water Chemicals Codex (analogous to the Food Chemicals Codex) which will contain health and safety specifications for water treatment chemicals (*ES&T*, August 1980, p. 914). A draft report is due by December 1981.

Other EPA contracts on additives, which will provide background information, include one with JRB Associates for a review on coagulant aids and indirect additives, the effects of disinfection on coagulant aids, and an evaluation of extraction procedures which may have applicability in the development of test protocols.

Ehrlich says that the additives program will contribute to the Office of Drinking Water's effort toward comprehensive protection of the quality of drinking water. The office hopes to have interim procedures in place in the spring of 1981, and final procedures one to two years later. When the interim procedures are in place, the moratorium on issuing new advisory opinions will be lifted. Ehrlich also noted that EPA is planning an information system which will codify past opinions; it will be used as a priority-setting tool for reviewing some of the old approvals.

—Stanton Miller

INFORMATION WITH IMPACT

The
Latest
Environmental
Science
Updates
From
Wiley-Interscience

NUTRITION AND ENVIRONMENTAL HEALTH

The Influence of Nutritional Status on Pollutant Toxicity and Carcinogenicity
Volume 1: The Vitamins
Edward J. Calabrese, University of Massachusetts

A detailed, critical, and comprehensive assessment of the role of nutritional status—specifically vitamins—in the detoxication of carcinogens, heavy metals, organic compounds, gaseous irritants and food additives, as well as the role of certain vitamins in the metabolism of widely-used drugs such as aspirin and oral contraceptives.
(1-04833-X) 1980 585pp. $60.00

CADMIUM IN THE ENVIRONMENT

Part 1: Ecological Cycling
Part 2: Health Effects
Edited by Jerome O. Nriagu, Canada Center For Inland Waters

A comprehensive review of the current biological research on environmental cadmium. Part 1 deals with the sources, distribution, behavior and flow of cadmium in the ecosystem; Part 2 covers the biological, ecological and human health effects of cadmium.
Part 1—(1-06455-6) 1980
682pp. $70.00
Part 2—(1-05884-X) May 1981
approx. 420pp. $38.00 (tent.)

NICKEL IN THE ENVIRONMENT

Edited by Jerome O. Nriagu

The first comprehensive review of the current knowledge of the role and hazards of nickel in the environment. It systematically deals with the sources, distribution, behavior, and flow of nickel in different ecosystems, as well as with the metabolism, biochemistry, and systematic toxicity of nickel in plants, human beings, and other organisms.
(1-05885-8) October 1980
approx. 928pp. $65.00 (tent.)

SURVEY OF CONTEMPORARY TOXICOLOGY

Volume 1
Edited by Anthony T. Tu, Colorado State University

Written by highly acclaimed experts in toxicology, this book covers such diverse topics as man-made toxic compounds (Industrial Toxicology, Water Pollution, Food Additive Toxicology) and naturally occuring toxic substances (Foodborne Diseases, Bacterial Toxins, Plant Toxins, and Marine Toxins).
(1-04085-1) 1980 357pp. $39.50

INDUSTRIAL LOCATION AND AIR QUALITY CONTROL

A Planning Approach
Jean-Michel Guldmann, The Ohio State University, & Daniel Shefer, Technion-Israel Institute of Technology

This book describes the interactions between air quality management and industrial location in the making of urban development decisions, proposing mathematical models to find the least-cost mix of technological and locational decisions to comply with air quality standards and other constraints.
(1-05377-5) October 1980
approx. 232pp. $22.50 (tent.)

INDUSTRIAL POLLUTION CONTROL

Volume 1: Argo-Industries
E. Joe Middlebrooks, Utah State University

Here is detailed information to aid in analyzing and solving agro-industries' pollution control problems. A general description of the industrial process, characteristics of the waste products, and the applicable waste treatment methods are presented for each segment of the agro-industries.
(1-04779-1) 1979 445pp. $24.95

AQUATIC CHEMISTRY

An Introduction Emphasizing Chemical Equilibria in Natural Waters, 2nd Ed.
Werner Stumm & James J. Morgan, California Institute of Technology

The most comprehensive, authoritative, and analytical book in its field. The second edition extends the coverage to include chemical ecology and expanded coverage of chemical oceanography, marine geochemistry, and the application of chemical principles to pollution control.
(1-04831-3) January 1981
approx. 672pp. $38.00 (tent.)

ADVANCES IN ENVIRONMENTAL SCIENCE AND TECHNOLOGY,

Volume 10
Edited by James N. Pitts, University of California, Riverside; Robert L. Metcalf, University of Illinois, Urbana; & Daniel Grosjean, Environmental Science and Technology, Inc.

The latest in a series of books devoted to the study of the quality of the environment and to the technology of its conservation. Experts in the field present thoughtful and challenging statements on chemical, physical, and biological issues.
(1-06480-7) 1980 521pp. $42.50

RESOURCE MANAGEMENT AND ENVIRONMENTAL UNCERTAINTY

Lessons from Costal Upwelling Fisheries
Edited by Michael H. Glantz, National Center for Atmospheric Research, & J. Dana Thompson, National Space Technology Laboratory

This is the first comprehensive analysis of the scientific, political and economic interrelations of upwelling ecosystems and fisheries management. It describes how environmental information is used in various societies and how it competes in policy-making with political and economic considerations.
(1-05984-6) October 1980
approx. 544pp. $36.50 (tent.)

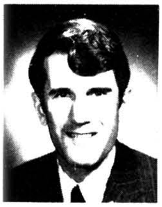
Order through your bookstore or write to
John Storojev, Dept. 7300

WILEY-INTERSCIENCE
a division of John Wiley & Sons, Inc.
605 Third Avenue
New York, N.Y. 10158

In Canada: 22 Worcester Road, Rexdale, Ontario
Prices subject to change without notice.
092 1-7300

CIRCLE 12 ON READER SERVICE CARD

Set II pollutants: more EPA rules on PSD



Michael R. Deland
ERT, Concord, MA

It has taken more than three years and numerous court confrontations, following the passage of the Clean Air Act of 1977, for EPA to establish a legally acceptable Prevention of Significant Deterioration (PSD) program to regulate sulfur dioxide and particulate matter. Still simmering are legal challenges on fugitive dust and tanker emissions, as well as other specialized parts of the program. More importantly, the larger, fundamental question, "Is EPA's approach workable?" is far from resolved.

Given this litigious backdrop to the supposedly simpler part of PSD, it is not surprising that EPA has fallen far behind the statutory deadline for promulgation of regulations for Set II pollutants.

Characteristics of Set II

Set II pollutants are those, other than SO_2 and TSP, for which National Ambient Air Quality Standards have been established. They currently consist of hydrocarbons, carbon monoxide, nitrogen oxide, ozone, and lead. They can be distinguished from Set I pollutants in several important ways.

First, while TSP and SO_2 originate primarily from stationary sources, Set II pollutants result largely from mobile sources. Second, while Set I pollutants are comparatively stable, Set II's are highly reactive. For example, ozone, a principal component of smog, is not emitted from specific sources but produced by photochemical reaction.

The mobile source origins of Set II pollutants, when combined with their physical differences, result in vastly more complicated modeling procedures than for Set I pollutants. In addition, emission inventory data for Set II are generally lacking, and those that do exist are of questionable quality, making it virtually impossible to establish an accurate baseline. The different physical characteristics of Set II pollutants also necessitate different control mechanisms which are likely to be more complicated than those for Set I. Despite these difficulties, EPA is finally beginning to develop Set II regulations.

Regulatory scheme

Last May, EPA published an Advanced Notice of Proposed Rulemaking which set forth several methods by which Set II pollutants could be controlled. Since then, the agency has engaged a contractor to assist in the preparation of a regulatory analysis and an environmental impact statement, and in the drafting of the proposed regulations. The current schedule calls for the regulations to be proposed in the fall of 1981 and to be finalized in mid-1982.

The various regulatory options being considered by EPA include:

- ambient air quality increments similar to the Set I system
- existing emission controls—a method which would rely primarily on the requirements for Best Available Control Technology (BACT)—coupled with the federal standards for motor vehicle emissions and the addition of inspection and maintenance requirements
- Emission Density Zoning (EDZ), which would establish maximum allowable limits per unit land area—emission limits rather than ambient air quality would then govern all preconstruction review
- inventory management, by which state and local agencies would develop and maintain comprehensive emission inventories, subject to rigorous public review before allowing any incremental increase in emissions
- emission fees, to be assessed against each source based on the quantity of its emissions
- marketable permits, which would be issued up to a fixed emission limit and which could be bought and sold. In theory, the "market incentive" approach of these latter two methods would stimulate the development by industry of new pollution control technology.

EPA apparently has ruled out an increment system, but is still actively considering the other options, either alone or in combination. While the comment period on these options formally closed in July, EPA has informally extended it and is soliciting suggestions to incorporate into the rule-making docket. In addition, the agency plans to conduct public meetings next month to help it reduce the number of options to "two or three."

That EPA is now more than two years late with the regulations and has yet to be sued, or even officially prodded by environmental groups, is reflective of the general frustration and fatigue felt by all parties to the protracted Set I process. It remains to be seen whether lessons have been learned, or whether the more complex technical questions of Set II will produce yet another contentious round of PSD rule making.

0013-936X/80/0914-1289$01.00/0

Viruses in groundwater

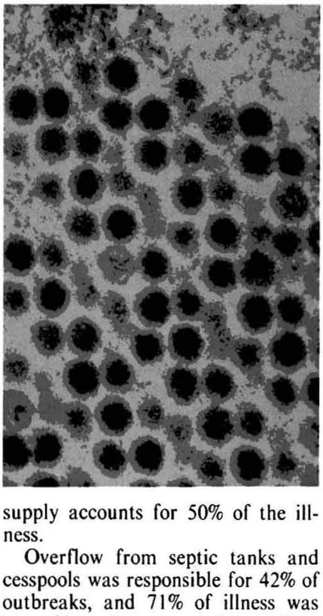
Their entry into aquifers, survival, migration, new methods of detection, concrete instances of contamination, and future research needs are discussed

Bruce H. Keswick
Charles P. Gerba
Baylor College of Medicine
Houston, Tex. 77030

Groundwater is an important resource which must be protected from contamination. Already, over 19% of the nation's water supply, upwards of 46% in some areas, is taken from groundwater sources. The use of groundwater is increasing, and by the year 2000, this proportion is expected to increase to 33% of the total water used in the U.S. (*1*).

As the demand for clean water increases and supply decreases, it is evident that artificial recharge of the present sources will become more prevalent. The recharge of groundwater sources with wastewater is an attractive alternative source of groundwater and an economically favorable method of wastewater disposal. However, care must be taken to ensure the safety of this practice by preventing contamination with disease-causing bacteria and viruses passed with human excreta.

The microbial contamination of groundwater is a serious problem that can result in large outbreaks of waterborne disease. For example, Craun (*2*) reported that from 1946 to 1977, there were 264 outbreaks and 62 273 cases of illness related to contaminated (untreated or inadequately treated) groundwater. This represents 48% and 58%, respectively. Thus, 20% of the supply accounts for 50% of the illness.



Overflow from septic tanks and cesspools was responsible for 42% of outbreaks, and 71% of illness was caused by using untreated groundwater in nonmunicipal systems. Furthermore, 356 (65%) of 550 documented outbreaks of waterborne disease from 1946 through 1977 can be attributed to illness of probable viral etiology (hepatitis A, poliomyelitis, gastroenteritis). This number probably represents only a fraction of the actual number of virus-caused outbreaks, because of the difficulties involved in proving a viral etiology of a waterborne outbreak.

In fact, direct evidence for viral involvement in waterborne outbreaks is limited to hepatitis A, adenovirus, and, recently, to the Norwalk agent. This situation has largely been ascribable to limitations in methodology for the detection of viruses in water and sensitivity of epidemiologic methods for enterovirus diseases. However, it is important to note that viruses have been demonstrated in groundwater, drinking water, and distribution systems in only a limited number of studies. Since groundwater is often used with little or no treatment for direct human consumption, the presence of viruses should not be overlooked.

As mentioned earlier, recharge of groundwater by wastewater application, besides being a source of groundwater, can also provide an economically favorable solution to the growing problem of disposing of sewage effluents (*3*). Recharge can be accomplished by direct injection or by land application and irrigation. Several recent reviews (*4–6*) have discussed the potential health risks involved in these practices and the factors affecting survival of bacteria and viruses in soils during irrigation (*7–9*). From these reviews, it is clear that the potential exists for entry, survival, and transport of microorganisms in groundwater. However, little information is available concerning these factors, especially those that affect viruses. The purpose of this article is to review the literature available on viruses in groundwater in order to evaluate the present state of knowledge, assess the accuracy of current standards and monitoring practices, and make recommendations for further areas of research.

Virus isolation

There are only a few reports in the literature on virus isolation from groundwater because of the previous lack of sensitive detection methods. The reports can be divided into two

---

Feature articles in ES&T *have by-lines, represent the views of the authors, and are edited by the Washington staff. If you are interested in contributing an article, contact the managing editor.*

0013-936X/80/0914-1290$01.00/0

groups—one which includes the isolation of viruses from groundwater sources and drinking water (Table 1) and one which includes isolations from sites where groundwater recharge, land application, or wastewater experimentation is being practiced (Table 2). The differences are ones of convenience and the prior knowledge of the source and type of pollution. It is obvious that in the first group, the presence of viruses in water is more difficult to demonstrate unless the source has been monitored closely, because the contamination is most often unexpected. Usually, samples are taken only after an outbreak of overt illness or some other event has taken place, so that the contamination is often no longer present. The difficulties in drawing etiologic conclusions from these studies have been discussed in detail by Goldfield (*10*) and Melnick (*11*).

Review of these studies provides valuable information concerning the safety of groundwater sources. Wellings et al. (*12*) reported the isolation of an echovirus 22/23 complex in 100-gal samples from a 12.2-m-deep well during an outbreak of gastrointestinal illness at a migrant labor camp in Florida. The well was located 30.5 m from a solid waste field, and was in the middle of an area bordered by septic tanks. The echovirus was isolated from sewage, from potable well water containing 0.4–0.6 mg/L residual chlorine, and from stools collected from individuals living in the camp. Furthermore, it is interesting to note the occurrence of 15 cases of hepatitis A in the camp some 6 weeks later.

Thus, the virus was probably present because of well water contamination from the septic tanks, and existed in chlorinated water in the absence of evidence of bacterial contamination. It was surmised that the chlorine was ineffective against the virus which was probably associated with solids introduced with the sewage. Even though this level of treatment reduced bacterial counts to undetectable levels, the virus survived. This raises concern about the efficacy of chlorine disinfection of contaminated groundwater, based on currently accepted standards.

Mack et al. (*13*) isolated vaccinelike poliovirus type 2 from a well responsible for a gastroenteritis outbreak at a restaurant in Michigan. Five-gallon samples were taken from the 30.5-m-deep well and were concentrated by a PE60/centrifugation technique. Coliform levels in the well ranged 0–16/100 mL, but no *Salmonella* or *Shigella* were found. The pollution

TABLE 1

Isolation of viruses from drinking water wells

Location	Virus types	Concentration method	Source	Reference
Florida	Echo 22/23	Membrane adsorption	Well	*12*
Germany	Echo 3, 6, 30; Coxsackie B1, 4, 5; U[a]	$Al(SO_4)_3$	Well	*16*
India	U	Iron oxide	Well	*18*
Michigan	Polio 2	PE60/centrifugation	Well	*13*
Israel	Echo 6, 7; Coxsackie B6; Polio 1; U	Membrane	Well	*14*
England	Polio 2	$AlCl_3$/membrane	Well	*15*
Israel	Polio 1; U	Organic flocculation	Well	*17*
Ghana	Polio 1; Coxsackie B3	Centrifugation	Well	*19*
Mexico	Rota; Coxsackie B4, 6	Membrane	Well	*50*

[a] U = unidentified.

TABLE 2

Isolation of viruses beneath land treatment sites

Site location	Type of site [a]	Virus types	Maximum distance of virus migration (m)		Reference
			Depth	Horizontal	
St. Petersburg, Fla.	S	Polio 1; coxsackie B4; echo 7	6	—	*22*
Gainesville, Fla.	S	Coxsackie B4; Polio 1, 2	3	7	*21*
East Meadow, N.Y.	R	Echo 12; U[b]	11.4	3	*23, 24*
Holbrook, N.Y.	R	Echo 6, 21, 24, 25; U	6.1	45.7	*23, 24*
Sayville, N.Y.	R	U	2.4	3	*23, 24*
12 Pines, N.Y.	R	Polio 2; U	6.4	—	*24*
North Masapequa, N.Y.	R	Echo 11, 23; Coxsackie A16	9.1	—	*23*
Babylon, N.Y.	R	Coxsackie B3; U	22.8	408	*23*
Ft. Devens, Mass.	R	U	28.9	183	*26*
Vineland, N.J.	R	Polio; coxsackie B3; echo	16.8	250	*27*
Lake George, N.Y.	R	Phage	45.7	400	*29*
Phoenix, Ariz.	R	Coxsackie B3	18.3	3	—[c]
Lubbock, Tex.	S	Coxsackie B3	30.5	—	*38*
Kerrville, Tex.	S	U	1.4	—	*40*
Dan Region, Israel	R	Polio 1, 2, 3	31–67	60–270	*37*

[a] R = rapid infiltration; S = slow rate infiltration.
[b] U = unidentified.
[c] Gerba, unpublished data.

source was a waste drain field that allowed sewage to enter the well by passing through 5.5 m of clay, 2.5 m of shale, and 22.5 m of limestone. No information on the soil structure was given.

Several points should be made here. Although poliovirus was isolated from the well, it was not suggested as the causative agent of the gastroenteritis outbreak. That outbreak was probably attributable to some other virus (such as rotavirus or the Norwalk agent) which could not be detected by the methods available at that time. Also, it is evident that soil type, structure, and proximity of a well to a source of sewage play an important role in the contamination of groundwater sources, as the virus in this case penetrated 30.5 m through several soil profiles, and traveled 91.5 m laterally.

Marzouk et al. (*14*) collected 20–440-L samples of groundwater from 3-m-deep wells in Israel. Twenty of 99 samples were found to be positive for viruses. The viruses isolated included coxsackievirus B6, echoviruses 6 and 7, poliovirus 1, and several unidentified types. Total bacteria, fecal coliform, and fecal streptococcal concentrations ranged from $0-10^4$, 0–200, and 0–100, respectively, per 100 mL. In at least one case, viruses were detected in samples that contained no total bacteria, while 12 of 17 samples that were negative for fecal coliforms and fecal streptococcus were positive for viruses. No statistical correlation could be demonstrated between indicator bacteria and the presence of viruses, which suggests the failure of bacterial indicators to represent viral contamination adequately.

Morris (*15*) isolated poliovirus type 2 in two samples of groundwater in England. Concentrations of 1 plaque-forming unit (PFU)/40 L and 4 PFU/10 L were detected in these 5–100-L samples. This well was to be used untreated for direct human consumption, but, subsequent to these findings, was shut down.

Walter and Rudiger (*16*) found that eight of 62 10-L samples from a groundwater source for a large water supply system contained viruses. Echoviruses 3, 6, and 30; coxsackieviruses B1, B4, and B5; and several unidentified viruses were recovered. No coliform data were given in the report.

Shuval (*17*) reported the isolation of poliovirus from a well under suspicion during an outbreak of hepatitis A in Israel. Poliovirus type 1 (4.0–7.2 PFU/L) was recovered from a single well, as were coliform bacteria.

Rao et al. (*18*) detected viruses in six different wells in Nagpur, India. Concentrations of 2–8 PFU were recovered from 40-L samples collected at depths of 12–24 m. No attempt was made to identify the isolates.

Addy and Otatume (*19*) isolated poliovirus 1 and coxsackievirus B3 from three of eight wells in the greater Accra region in Ghana. Those wells were dug specifically to provide water for human consumption. Also, a report from China (*20*) indicates that waterborne hepatitis traceable to well water contamination has caused several large epidemics.

The studies above illustrate the need for monitoring and maintaining the integrity of groundwater sources. It is obvious that, in many cases, groundwater assumed to be safe is not. This and other implications of these studies will be discussed later.

Land application sites

Even though there have been no reports of disease outbreaks associated with land treatment of sewage wastes, there are a growing number of studies concerning the detection of viruses in groundwater after wastewater application to land or direct groundwater recharge. These studies point out questions, discussed later in this article, which must be answered in order to ensure the safety of these practices.

Wellings et al. (*21*) demonstrated vertical and lateral movement of virus in secondary effluent discharged into a cyprus dome (a wetland ecosystem). Poliovirus 1, coxsackievirus B4, and echoviruses 7, 11, and 14 were recovered from 3-m-deep wells in three of 71 samples, at concentrations ranging 4–353 PFU. Viruses migrated 7–38 m laterally from the application point and survived at least 28 days.

The soil at this site ranged from a top 0.6-m layer of black organic soil (4–12% clay) to a sandy clay and a solid blue clay with a permeability of 3×10^{-2} cm/min to 3×10^{-6} cm/min. Thus, the viruses moved horizontally as well as vertically and survived many days under ambient conditions, indicating a necessity to evaluate such sites for their aquifer movement and transmission of viruses to drinking water sources.

In an earlier study, Wellings et al. (*22*) recovered viruses from groundwater after spray irrigation of secondary sewage effluent onto an Imolokee sand (little or no silt or clay). Of particular interest in this study was that viruses survived chlorination, sunlight, spraying, and percolation through 3–6 m of sandy soil; furthermore, after a period of heavy rains, a burst of viruses was detected in samples that had previously been negative. These studies demonstrate that soil type, rainfall, and other factors can affect viral movement into groundwater, and that viruses are capable of surviving long periods which, when combined with the ability to move long distances laterally, could lead to wide dispersal through an aquifer.

Vaughn and Landry (*23, 24*) and Vaughn et al. (*25*) reported isolations of viruses from four groundwater recharge sites, from a stormwater recharge basin, and from groundwater under a sanitary landfill in New York. These sites have soils of coarse sand, fine gravel, and 1–2% silt. At the groundwater recharge sites, viruses were recovered at depths up to 11.4 m and at distances up to 45.7 m from the injection point of secondary or tertiary chlorinated effluent. As much as 22–33% of the 100-gal samples at the four sites were positive for viruses, with concentrations of 1.3–10.6 PFU/gal. In addition, total coliforms and fecal coliforms were found in these samples. In order to reach the groundwater, viruses moved through 5.5–9 m of the overlying soil.

Moreover, at the 12 Pines site, viruses were discovered in groundwater under basins where effluent seeded with viruses was applied at rates of 6–100 cm/h. The slower infiltration rates were more effective in removing the viruses, suggesting that site management is important.

Both the landfill and stormwater recharge basin also yielded viruses. At the landfill site, viruses were detected at depths of 22.8 m and up to 408 m downstream. Coxsackievirus B3 and other unidentified viruses were detected. At the stormwater recharge site, samples taken at 9-m depths directly in the basin were positive for echoviruses 11 and 23 and for coxsackievirus A6. This contamination may have originated from runoff from cesspools in the area.

Schaub and Sorber (*26*) reported on a study of viruses in groundwater under rapid infiltration cells at Ft. Devens, Mass. The soil consisted of silty sand and gravel underlain by bedrock. The groundwater contained viruses at depths of 29 m and lateral distances of 183 m, with concentrations of about 8.3% of the applied effluent. Fecal streptococcal bacteria were also found in the 28.9-m-deep well. Marker F2 virus was applied at this same site; only about 50% of the virus was removed, and it was detectable for at least 11 days. This site was deemed to have poor filtration properties, and points out the need for site-specific evaluation.

At the Vineland, N.J., rapid infiltration site (*27*) primary effluent was applied to Cohansey sand and coarse gravel. Viruses were found at 16.8-m depths and up to 250-m lateral distances in 19 of 40 samples. Polio-, echo-, and coxsackieviruses were identified. Total coliforms and fecal coliforms were found consistently at depths up to 6 m beneath the recharge basins. Total coliforms also occasionally occurred at greater depths and downstream. In contrast, no fecal coliforms were found in samples taken below 9.1 m and coliforms occurred only once in a shallow well 50 m down-gradient. Thus, viruses penetrated deeper into the ground and moved longer distances than did the coliforms.

The potential for viruses to migrate great distances, as in the previous study, was further demonstrated by Noonan and McNabb (*28*), who used the phages ϕX174 and T4 to demonstrate lateral movements of 140 m and 911 m, respectively, in New Zealand groundwater in just 96 h. The viruses moved at greater than 300 m/d, and survived for at least seven days. In laboratory studies, 6.2 days were necessary for a 90% reduction in titer; so in this case, the viruses could theoretically travel at least 2.5 km in groundwater before a 90% reduction could be effected under these conditions.

Aulenbach (*29*) reported isolating coliphage from groundwater under the Lake George, N.Y., recharge basin in a very limited study. No conclusive information on viruses can be determined from this study because control samples also yielded phage. Apparently, coliforms were detected in only some of the wells, whereas coliphage was detected in all of the wells. Samples collected after a period of heavy rainfall had higher counts. The effluent at this site was applied to sand beds and monitoring wells were located at various distances (up to 400 m) and depths (up to 45.7 m) in and around the recharge basins.

Septic tank effluent seeded with coxsackieviruses A5 and A14 was found to pass through sand beds and into groundwater in a study in the U.S.S.R. Grigoryeva and Goncharuk (*30*) reported that the viruses survived for 20 days under these conditions. Others (*31, 32*) have also reported on the movement of bacteria and viruses from septic tanks to groundwater, which may be a significant problem in rural areas, as indicated by a recent groundwater quality survey (*33*).

Viruses in groundwater at other recharge sites have been studied with varying success. At the Flushing Meadows site near Phoenix, Ariz. (*34*), it was found that a fine loamy sand over coarse sand and gravel effectively removed viruses. Laboratory studies confirmed that this soil was an excellent adsorber. No viruses were detected in any of the samples of renovated water, even though levels of 158–475 PFU/mL were detected in the effluent applied. However, coliform organisms were detected in the renovated water, suggesting that the removal mechanisms must have been different for viruses and bacteria, and that viruses may have been present. Since this site is no longer in existence, these findings cannot be confirmed. However, since then, virus has been detected in a sample from an 18.3-m-deep well at a nearby land application site. The isolate was identified as coxsackievirus B3.

Initial findings at the Dan Region (*35, 36*) reclamation project in Israel yielded negative results when 10-L volumes were sampled. However, when the sample size was increased to 400 L, viruses were detected (*37*), which emphasizes the need for large sample volumes.

At two land treatment sites where sewage is used to irrigate cropland, both positive and negative virus isolations have been made (*38, 39*). At the Lubbock, Tex., site, coxsackievirus B3 was isolated from a depth of 30.5 m; at Roswell, N.M., no virus isolates were detected in samples taken from 3–30-m depths. In the latter case, irrigation is seasonal and intermittent, whereas application at the Lubbock site is continuous.

At an operational land application site in Kerrville, Tex. (*40*), no viruses were detected in the monitoring wells at depths of 10.7–19.8 m even though viruses could be detected in 13.7-m-deep lysimeters. Depth to groundwater was an important factor in this study.

In one often-cited report (*41*) on the Santee project, no viruses were detected in renovated water. This is not surprising, since the detection methods available at that time were not quantitative. These negative results must therefore be considered highly questionable, as should the results obtained at the Whittier Narrows, Calif. (*42*), and the San Angelo, Tex. (*43*), projects, which did not employ techniques sensitive enough to detect low levels of virus. This reiterates the need for careful evaluation of methods used in any report before negative conclusions are accepted.

Survival factors

It is apparent that the factors affecting virus survival in groundwater are complex and poorly understood (Table 3, Figure 1). To control the many variables present in the field, the movement of viruses through soils to groundwater has been modeled in the laboratory by the use of soil columns. These studies have recently been reviewed (*7–9*), and the details will not be repeated here except to support field data.

Virus type. Laboratory studies have shown that viruses have widely differing adsorption properties. This is therefore an important factor in the movement of viruses from sources of contamination, such as septic fields, into otherwise clean groundwater. Thus, for evaluation of a site, several types of viruses should be tested in order to ensure a representative picture. Furthermore, even with the development of new concentration methods, it is still difficult or impossible at this time to detect all of the more than 100 types of human enteric viruses. For example, there is presently no readily available system for cultivating hepatitis A virus; until recently, this was also true of the rotaviruses. Thus, some viruses may be present but remain undetected or unidentified.

Soils. Obviously, soils vary considerably both in their composition and in

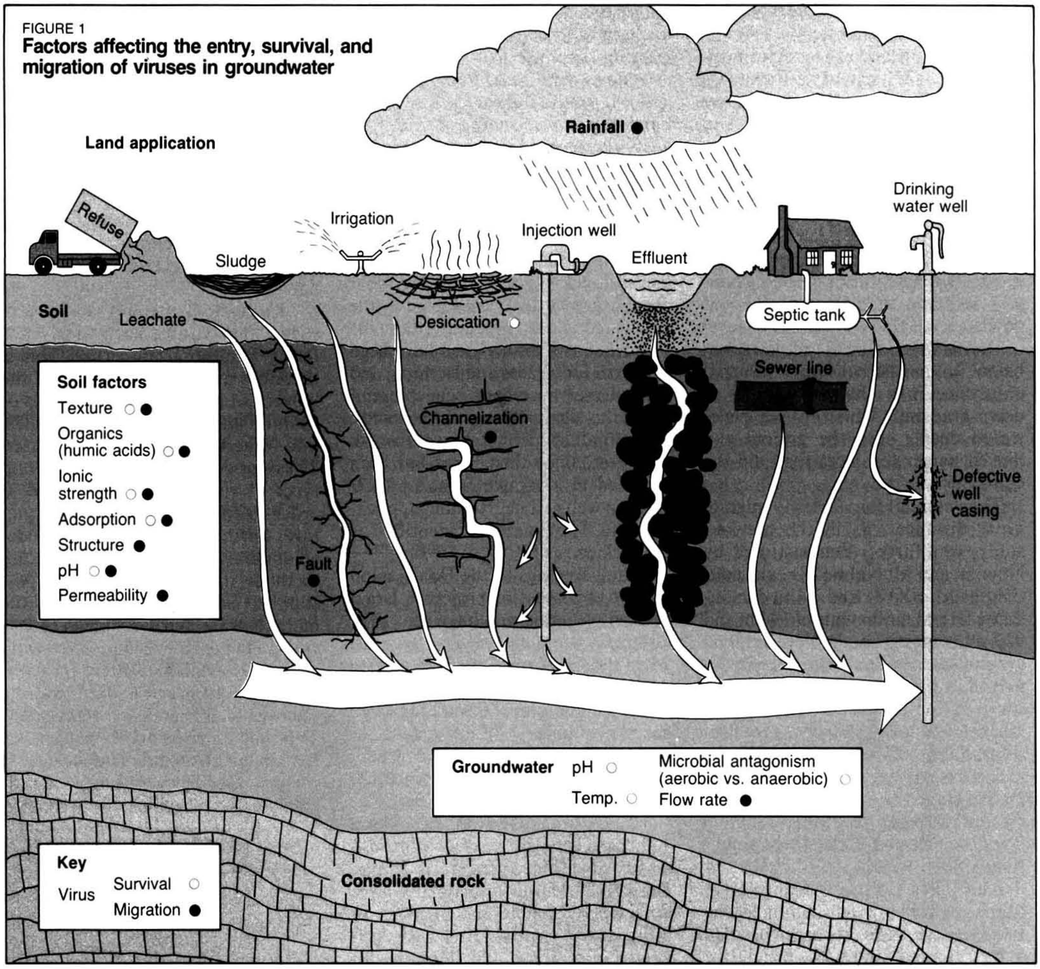
TABLE 3

Factors affecting survival and migration of viruses in groundwater

Factor	Survival	Migration
Hydrogeological		
Soil		
Texture (sand, silt, clay)	+[a]	+
Organics	+	+
Humic acids	?	+
Cations	+	+
Adsorption	+	+
pH	+	+
Ionic strength	0	+
Permeability	0	+
Biological		
Virus type	+	+
Microbial antagonism	+	0
Meteorological		
Rainfall	+	+
Temperature	+	0
Desiccation	+	+
Sunlight	+	0

[a] + = affects survival or migration; 0 = no effect; ? = effect unknown.

FIGURE 1
Factors affecting the entry, survival, and migration of viruses in groundwater



their overall structure. Laboratory studies have shown the importance of the composition of soils, including the organic content; percent sand, silt, and clay; pH; cation-exchange capacity; permeability; texture; moisture; and iron oxide levels.

As pointed out in earlier reviews, each of these features can effect virus removal by soils, and so the study of this problem becomes quite complex. For example, virus removal by the soil types in the studies reviewed here ranged from very poor to apparently total removal, which indicates the need for site-specific evaluations of soil properties. The variability of adsorption by different soils has been repeatedly demonstrated in the laboratory (*7, 8, 44, 45*). In general, sandy and organic soils are poor adsorbers and clay soils are good adsorbers.

Subsurface structure has also been demonstrated to be an important promoter of groundwater contamination. For example, movement of bacteria through fracture zones was shown by Allen and Morrison (*46*) to be rapid and to follow the fracture lines, leading to rapid and wide dispersal. Thus, under natural conditions, soil columns are not always indicative of the ability of pollutants to enter groundwater. Furthermore, the columns used in many studies were too short, and may have overestimated virus removal rates. There is now evidence (*47*) that removal rates in subsurface layers are lower than at the surface. So estimates based on the faster rates observed in short columns are higher than those found in columns longer than 50 cm.

Virus survival in groundwater. It is difficult to make firm assessments on virus survival in natural waters because viral resistance to factors that influence their survival varies. In addition, these factors have shown great variation temporally, which makes predictions even more difficult. For instance, little is known concerning survival rates of human enteric viruses in soil and groundwater. Field studies by Wellings et al. (*21*) suggested that viruses could survive for at least 28 days in groundwater. Survival of viruses in surface waters for as long as 188 days has been reported (*48*), while in other laboratory experiments viruses survived more than 200 days in drinking water. Since the effects of sunlight are eliminated and the temperature is lower, even longer survival times would be probable in groundwater.

Recent studies in our laboratory indicate that virus survival in soil is probably controlled by the principal factors shown in Figure 1. An evaluation of these factors indicates that because of the detrimental effect of aerobic soil microorganisms, evaporation, and higher temperatures, inactivation of viruses will be much more rapid near the surface than for those viruses that penetrate the soil more deeply. Thus, viruses which penetrate the soil surface are expected to survive for prolonged periods of time, as compared to those retained near the soil surface. The factors which affect virus survival in soils are complex and should be described kinetically in terms of initial populations and survival rates, as well as duration. These factors have been reviewed in detail (*7–9*).

Migration of viruses in soils and groundwater. The studies by Wellings et al. (*12, 21, 22*) and Mack et al. (*13*) were the first to demonstrate transport of viruses for long distances through soils into groundwater. Prior to their studies, it could be concluded only on epidemiologic evidence that viruses (mainly hepatitis A) move from sources of contamination into well water some distance away (*49*). Now, it is generally accepted that once in groundwater, viruses can migrate great distances under the right condition such as those found in the study by Noonan and McNabb (*28*).

However, the specific factors affecting virus movement in groundwater have not been studied directly. As mentioned above, there are many factors, such as the degree of saturation, subsurface flow, hydrogeologic structure, and the like, involved in this movement which are site-specific and which need to be evaluated for any site where wastes are to be applied.

Groundwater also can be contaminated by both purposeful (recharge) and accidental (septic or sewage leakage) events. The extent of influence of this man-made factor is evidenced by a recent survey (*33*) of groundwater quality, which indicated that 92.5% of the rural samples taken were positive for total coliforms. In many of the 460 samples, contamination was related to depth and distance from septic tanks. In view of the high bacterial counts in the wells sampled, it is very likely that viruses were also present. Well contamination should be preventable to a large degree by proper location, construction, and maintenance, with an additional measure of safety provided by disinfection. However, as was seen, chlorination of viruses, especially when they are associated with solids, can be unreliable. Hence, extra care should be taken in the location of wells and septic tanks.

Methodology. The last 10 years have seen great progress in the development of virus detection methods. Their absence from earlier studies renders any negative findings unreliable, as the levels of virus detectable by older methods were not as sensitive as today's methods. Furthermore, it is still not possible to detect hepatitis A and many agents of viral gastroenteritis routinely, although work in this area is progressing; and only recently has it become possible to detect rotaviruses in water samples (*50*). Moreover, the methods for virus isolation fail to detect the presence of coxsackievirus group A, adenoviruses, and reoviruses unless additional efforts are undertaken. Methods are available for less than half of all the viruses known to be present in human wastes. Given these limitations, it is very doubtful that more than 1% of all the viruses present in domestic wastes are detected by the routine methodology currently in use.

TABLE 4

Land treatment practices that may limit groundwater contamination by viruses

Practice	Comment	Reference
Drying	Reduces virus movement by enhancing virus inactivation	*55*
Flooding with wastewater after rainfall	Reduces virus movement	*49*
Infiltration pattern	Shorter flooding/drying cycles limit virus penetration	*56*
Infiltration rate	Slower rate promotes virus removal	*25*
Site evaluation	Nature of soil, depth to groundwater, and substructure assures adequate virus removal	*9, 26, 40*

TABLE 5

Research needs

- Basic research
  - Virus interaction with surfaces
  - Virus inactivation and degradation in groundwater
  - Virus interaction with organics in natural waters
- Methods development
  - Tracers
  - Laboratory methods for determining virus retention by soils
  - Groundwater and soil sampling
  - Predictive models
- Criteria
  - Adequacy of bacterial standards for groundwater quality
  - Acceptable removal of pathogens by land application of wastewater
  - Zoning of aquifers for land treatment of wastewater
- Renovation and protection of aquifers
  - Soil modification for enhanced removal of viruses
  - Enhancement of aerobic microflora
  - Management practices for groundwater recharge operations, i.e., duration of flooding and drying cycles, etc.
- Field studies
  - Land treatment sites
  - Septic tanks
  - Disease outbreaks by groundwater contamination
  - Survival time of viruses in groundwater

Operation of land application sites. Using soil column models, Gerba and Lance (*51*) found that the degree of viral movement and removal by soils from a land application site could be controlled to some degree by the way in which the basins were flooded with sewage in relation to the rainfall patterns of the site. Others (Table 4) have mentioned operational features that may also have an effect, and it is apparent that these factors need to be taken into account in the management of a refuse site.

Research recommendations

As is apparent from this review, current information on viruses in groundwater is limited. Our knowledge in certain areas is especially deficient. Filling these gaps will require the utilization of current methodology and the development of new methods for virus surveys of groundwater (Table 5). Such surveys should focus on rural private sources and small communities where water is used with minimal or no treatment.

Results of previous surveys on the bacteriological quality of groundwater indicate that viral pollution is more widespread than might be believed. Furthermore, many of the previous systems used for virus concentration had efficiencies of 2–3%, and were limited to the detection of enteroviruses (*52*). Now, however, systems with efficiencies of 30% and greater are available (*50*).

Viruses are known to enter groundwater under certain conditions, but these conditions have not been adequately defined. It is not yet possible to determine exactly what factors affect the retention and mobility of viruses in soils. Such an understanding is essential so that predictions may be made and methods may be developed for estimating virus migration.

The abilities of viruses to survive in groundwater and to migrate long distances have been described in this review. However, studies are needed on the survival of additional types of viruses actually suspended in groundwater under field conditions. One approach would be to develop survival chambers similar to those used by McFeters to study bacterial survival in surface and well waters (*53*). This is especially important where direct recharge is to be practiced, because the length of holding or turnover time could affect virus survival.

The factors which promote or are detrimental to virus survival should also be studied in the laboratory. For example, it has been found that association with solids, organic material, pH, and temperature may influence virus survival in groundwater. Microorganisms are known to travel in groundwater at different rates from those of commonly used dyes (*54*). Studying potential migration in groundwater thus requires the development of tracers that will reflect virus behavior in the subsurface.

Also, human viruses can easily be grown in the laboratory, but cannot be safely used in field studies because of possible adverse health effects. Developing bacteriophage tracers that exhibit movement and survival similar to animal viruses may be one alternative approach.

TABLE 6

Parameters for using laboratory columns to evaluate land treatment sites for virus removal

Parameter	Comment
Virus	More than one type is necessary; use both good and poor adsorbers
Soil columns	Need to be of adequate length
Application	Sewage or effluent to actually be used should be tested Rainfall should be simulated Infiltration and drying rates should be evaluated

It is certain from this review that, in many instances, bacteria are not adequate indicators of viral pollution. It is questionable whether bacterial standards for surface water will be adequate for groundwater, especially since groundwater is often used without any treatment and has been responsible for a great portion of the reported waterborne disease outbreaks. New bacterial and viral standards should be developed to control groundwater pollution.

This report is not intended to discourage groundwater recharge with sewage effluent. In fact, we hope to encourage such practices as land application, but with the caution that each site must be evaluated individually for its capacity to aid the elimination of viruses from wastewater and to limit the potential impact on groundwater quality. Moreover, when effectively operated, land treatment can reduce viruses to a level that is achieved only with costly advanced wastewater treatment and disinfection. In addition, great energy savings as well as elimination of the production of potentially carcinogenic substances can be achieved.

It is recommended, therefore, that laboratory studies be conducted to determine the virus–soil interactions of a particular site by using columns at least 50 cm in length to model the site (Table 6). Varied patterns of wastewater application and climatological factors such as rainfall should be simulated. In addition, viruses which have been shown to be both good and poor adsorbers should be tested.

Also, studies should be conducted on soil modification (addition of small amounts of substances such as iron oxides, clays, and so on) designed to enhance virus removal. Hopefully, from this information, it may be determined in advance whether or not the soil is suited to the type of application desired, and how management practices or soil treatment could make it more suitable. Of course, these studies cannot perfectly simulate the actual field site; thus, it is further recommended that any groundwater subject to recharge (as under a land application site) be monitored on a regular basis for the presence of virus. Several times a year should be adequate, unless virus levels are likely to be high, and the intended purpose of the water, such as direct reuse, warrants more careful monitoring.

The influence of physical and environmental factors (fractures, rainfall, etc.) should also be studied. For example, groundwater should be examined for virus after periods of heavy rainfall, to see if previously adsorbed virus is being eluted and progressing into the aquifer. Differences in the type or pattern of application should also be followed closely. In short, it is deemed important to evaluate each site thoroughly and individually, with regard to viruses before one of our valuable groundwater sources is damaged by contamination.

Both field and laboratory studies are also greatly needed to aid in the design and management of septic tanks. For instance, to our knowledge, no field studies using modern virus concentration technology have been conducted on virus occurrence in the vicinity of septic tank drainfields.

Recent advances in the methods of concentrating and detecting viruses in water have continued to reduce the cost of collection and analysis for virus monitoring. Continued efforts in these areas should be made so that the monitoring can be more generally feasible for all concerned with viral contamination of the environment.

The presence of viruses in groundwater obviously requires further study. The results obtained from these studies will be helpful in planning and operating land application sites and septic tank drainage fields. This will, in turn, directly benefit the public by providing the information necessary to protect valuable groundwater resources from microbial contamination, and, hopefully, will help reduce the waterborne transmission of infectious diseases.

Acknowledgments

This work was supported by a grant from the EPA to the National Center for Groundwater Research at Rice University, Houston, Tex.

This feature was reviewed by Mark D.

Sobsey of the University of North Carolina at Chapel Hill, Chapel Hill, N.C. 27514.

References

(1) Freeze, R. A.; Cherry, J. A. "Groundwater"; Prentice Hall: Englewood Cliffs, N.J., 1979.

(2) Craun, G. F. *Ground Water* **1979**, *17*, 183.

(3) Rice, R. C.: Gilbert, R. G. *Hydrology and Water Resources in Arizona and the Southwest* **1978**, *8*, 33.

(4) Akin, E. W., et al. "Health Hazards Associated with Wastewater Effluents and Sludge: Microbiological Considerations." In "Proceedings of the Conference on Risk Assessment and Health Effects of Land Application of Municipal Wastewater and Sludges"; B. P. Sagik and C. A. Sorber, Eds.; University of Texas at San Antonio: 1978.

(5) Larkin, E. P., et al. "Potential for Contamination of Foodstuffs and Agricultural Soils by Viruses and Bacterial Pathogens." In "Proceedings of the Conference on Risk Assessment and Health Effects of Land Application of Municipal Wastewater and Sludges"; B. P. Sagik and C. A. Sorber, Eds.; University of Texas at San Antonio: 1978.

(6) Sagik, B. P., et al. "Infectious Disease Potential of Land Application of Wastewater." In "State of Knowledge in Land Treatment of Wastewater"; U.S. Government Printing Office: Washington, D.C., 1978, Vol. 1.

(7) Gerba, C. P., et al. *J. Irrig. Drain. Div. ASCE* **1974**, *101*, 157.

(8) Bitton, G., et al. *Water, Air, Soil Pollut.* **1979**, *12*, 449.

(9) DuBoise, S. M., et al. *Crit. Rev. Microbiol.* **1979**, *7*, 245.

(10) Goldfield, M. "Epidemiological Indicators for Transmission of Viruses by Water." In "Viruses in Water"; G. Berg, H. L. Bodily, E. H. Lennette, J. L. Melnick, and T. G. Metcalf, Eds.; American Public Health Association, Inc.: Washington, D.C., 1976.

(11) Melnick, J. L. "Are Conventional Methods of Epidemiology Appropriate for Risk Assessment of Virus Contamination of Water?" In "Proceedings of the Conference on Risk Assessment and Health Effects of Land Application of Municipal Wastewater and Sludges"; B. P. Sagik and C. A. Sorber, Eds.; University of Texas at San Antonio: 1978.

(12) Wellings, F. M., et al. "Virus in Groundwater." In "Proceedings of the 2nd National Conference on Individual Onsite Wastewater Systems"; National Sanitation Foundation: Ann Arbor, Mich., 1975.

(13) Mack, W. N., et al. *Hlth. Services Rept.* **1972**, *87*, 271.

(14) Marzouk, Y., et al. *Ground Water* **1979**, *17*, 487.

(15) Morris, R., personal communication, 1979.

(16) Walter, R.; Rudiger, S. *Zeit. Ges. Hyg.* **1977**, *23*, 461.

(17) Shuval, H. I. "Detection and Control of Enteroviruses in the Water Environment." In "Developments in Water Quality Research"; H. I. Shuval, Ed.; Ann Arbor Science: Ann Arbor, Mich., 1969.

(18) Rao, V. C., et al. *AWPC Tech. Ann.* **1978**, *5*, 16.

(19) Addy, P. A. K.; Otatume, S. *Ghana Med. J.* **1976**, *18*, 102.

(20) World Health Organization. Tech. Rept. Ser., no. 639, 1979.

(21) Wellings, F. M., et al. *Appl. Microbiol.* **1975**, *29*, 1751.

(22) Wellings, F. M., et al. "Virus Survival Following Wastewater Spray Irrigation of Sandy Soils." In "Virus Survival in Water and Wastewater Systems"; J. F. Malina and B. P. Sagik, Eds.; University of Texas at Austin: 1974.

(23) Vaughn, J.; Landry, E. F. "Data Report: An Assessment of the Occurrence of Human Viruses in Long Island Aquatic Systems; Department of Energy and Environment, Brookhaven National Laboratory: Upton, N.Y., 1977.

(24) Vaughn, J.; Landry, E. F. "The Occurrence of Human Enteroviruses in a Long Island Groundwater Aquifer Recharged with Tertiary Wastewater Effluents." In "State of Knowledge in Land Treatment of Wastewater"; U.S. Government Printing Office, 1978, Vol. 2, pp. 233–43.

(25) Vaughn, J., et al. *Appl. Environ. Microbiol.* **1978**, *36*, 47.

(26) Schaub, S. A.; Sorber, C. A. *Appl. Environ. Microbiol.* **1977**, *33*, 609.

(27) Koerner, E. L.; Haws, D. A. "Long-Term Effects of Land Application of Domestic Wastewater: Vineland, New Jersey, Rapid Infiltration Site." EPA-600/2-79-072, 1979.

(28) Noonan, M. J.; McNabb, J. F. "Contamination of Canterbury Groundwater by Viruses." In "The Quality and Movement of Groundwater in Alluvial Aquifers of New Zealand"; M. J. Noonan, Ed.; Lincoln College: Dept. of Agricultural Microbiology Tech. Publ. No. 2, Canterbury, New Zealand (1979).

(29) Aulenbach, D. B. "Long Term Recharge of Trickling Filter Effluent into Sand"; EPA Publ. No. 600/2-79-068. Ada, Okla., 1979.

(30) Grigoryeva, L. V.; Goncharuk, E. I. *Hyg. Sanit.* **1966**, *31*, 158.

(31) Green, K. M.; Cliver, D. O. "Removal of Virus from Septic Tank Effluent by Sand Columns." In "Proceedings of a National Home Sewage Disposal Symposium"; American Society of Agricultural Engineering: St. Joseph, Mich., 1975.

(32) Reneau, R. B.; Pettry, D. E. *J. Environ. Qual.* **1975**, *4*, 41.

(33) Sandu, S. S., et al. *Appl. Environ. Microbiol.* **1979**, *37*, 744.

(34) Gilbert, R. C., et al. *Appl. Environ. Microbiol.* **1976**, *32*, 333.

(35) Idelovitch, E., et al. "Dan Region Reclamation Project, Groundwater Recharge with Municipal Effluent"; Mekorot Water Co.: Tel Aviv, Israel, 1978.

(36) Marzouk, Y., et al., personal communication, 1980.

(37) Idelovitch, E., et al. "Dan Region Project, Groundwater Recharge with Municipal Effluent, Second Recharge Year"; Mekorot Water Co.: Tel Aviv, Israel, 1979.

(38) Goyal, S. M.; Gerba, C. P., personal communication, 1980.

(39) Koerner, E. L.; Haws, D. A. "Long Term Effects of Land Application of Domestic Wastewater, Roswell, New Mexico, Slow Rate Irrigation Site"; EPA-600/2-79-047, 1979.

(40) Moore, B. E. *Munic. Wastewater News* **1980**, *28*, 11.

(41) England, B., et al. "Virological Assessment of Sewage Treatment at Santee, California." In "Transmission of Viruses by the Water Route"; G. Berg, Ed.; Wiley & Sons: New York, N.Y., 1965.

(42) McMichael, F. C.; McKee, J. E. "Water Reclamation at Whittier Narrows"; California State Water Control Board Publ. No. 33, 1966.

(43) Weaver, R. W., et al. "Sewage Disposal on Agricultural Soils: Chemical and Microbiological Implications"; EPA-600/2-78-1316, vol 2, 1978.

(44) Burge, W. D.; Enkiri, N. K. *J. Environ. Qual.* **1978**, *7*, 73.

(45) Landry, E. F., et al. *Appl. Environ. Microbiol.* **1979**, *38*, 680.

(46) Allen, M. J.; Morrison, S. M. *Ground Water* **1973**, *11*, 6.

(47) Wang, D., et al. *Abs. Div. Environ. Chem., 179th Natl. Mtg. Am. Chem. Soc.* **1980**, *20*, 170.

(48) Akin, E. W., et al. "Enteric Viruses in Ground and Surface Waters: A Review of Their Occurrence and Survival." In "Virus and Water Quality: Occurrence and Control"; V. Snoeyink, Ed.; University of Illinois, Urbana: 1971.

(49) Neefe, J. R.; Stokes, J. *J. Am. Med. Assoc.* **1945**, *128*, 1063.

(50) Smith, E. M.; Gerba, C. P. *Abs. Div. Environ. Chem., 179th Natl. Mtg. Am. Chem. Soc.* **1980**, *20*, 167.

(51) Gerba, C. P.; Lance, J. C. *Appl. Environ. Microbiol.* **1978**, *36*, 247.

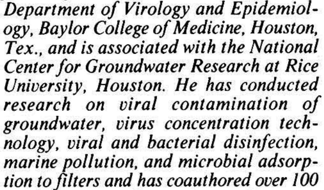
(52) Sobsey, M. D. "Concentration of Viruses from Water with the Tentative Standard Method," *J. Am. Water Works Assoc.* (in press).

(53) McFeters, G. A., et al. *Appl. Environ. Microbiol.* **1974**, *27*, 823.

(54) Stinton, L. W. "The Use of Bacteria as Tracers of Groundwater Movement." In "The Quality and Movement of Groundwater in Alluvial Aquifers of New Zealand"; M. J. Noonan, Ed.; Lincoln College: Dept. of Agricultural Microbiology Tech. Publ. No. 2, Canterbury, New Zealand, 1979.

(55) Lance, J. C., et al. *Trans. Am. Soc. Agric. Engr.* **1978**, *21*, 1114.

(56) Bouwer, H. *Crit. Rev. Environ. Control* **1976**, *6*, 111.



Charles P. Gerba (*l.*) *is an assistant professor of environmental virology in the Department of Virology and Epidemiology, Baylor College of Medicine, Houston, Tex., and is associated with the National Center for Groundwater Research at Rice University, Houston. He has conducted research on viral contamination of groundwater, virus concentration technology, viral and bacterial disinfection, marine pollution, and microbial adsorption to filters and has coauthored over 100 publications on these subjects. He serves on the editorial board of* Applied and Environmental Microbiology *and is coeditor of a forthcoming book entitled, "Methods in Environmental Virology."*

Bruce H. Keswick (*r.*) *is a research associate in the Department of Virology and Epidemiology, Baylor College of Medicine, Houston, Tex., and is associated with the National Center for Groundwater Research at Rice University, Houston. He has conducted research on viral and bacterial disinfection and is currently conducting research on viral pollution of groundwater.*

Philosophy of the Safe Drinking Water Act and potable reuse

A presentation at the EPA Symposium on Protocol Development: Criteria and Standards for Potable Reuse and Feasible Alternatives, Warrenton, Va., July 29–31, 1980

Daniel A. Okun
University of North Carolina at Chapel Hill
Chapel Hill, N.C. 27514

The charges given to me of discussing the "philosophy" involved in obtaining safe drinking water; reviewing the relevant public health history, principles, and policies; and outlining public health considerations regarding reuse are certainly congenial to one who has been battling for water quality for more than four decades. However, the rapid developments in science and technology, particularly in analytical chemistry and toxicology, require that these more difficult, substantive issues be left to younger colleagues, while I enjoy the liberty of commenting on the general scene.

The philosophy that might guide us in providing safe water where resources of water are being stretched, and where threats to its quality from a hyperactive chemical industry are constantly growing, can be summarized in an old-fashioned term: the sanitary survey. Sanitary surveys, which were mandated by the 1962 U.S. Public Health Service Drinking Water Standards, emphasized the identification of sources of pollution, rather than monitoring and analysis of water. The operative statement in those standards was that "the water supply should be obtained from the most desirable source which is feasible, and efforts should be made to prevent and control pollution of the source."

In the EPA National Interim Primary Drinking Water Regulations of 1976, this concern for the quality of the source is found only in the appendix, but, even here, the message is clear: "Production of water that poses no threat to the consumer's health depends on continuous protection. Because of human frailties associated with protection, priority should be given to selection of the purest source. Polluted sources should not be used unless other sources are economically unavailable, and then only when personnel, equipment, and operating procedures can be depended on to purify and otherwise continuously protect the drinking water supply."

These strictures that give priority to developing the purest source are not at all stressed in the Safe Drinking Water Act (SDWA), nor do they appear to be an essential element of EPA or regulatory concern. Major attention is given to maximum contaminant limits, monitoring, and even treatment, but very little attention is given to protection of the source, selection of the purest source, or the institutional measures that would provide the assurance of continuous protection.

For example, 95% of the more than 60 000 community water-supply systems in the U.S. serve fewer than 10 000 people (*1*). There is no question that the "personnel, equipment, and operating procedures" afforded by such systems cannot be depended upon to provide continuous protection. Only regionalization of water-supply services can offer much hope that small communities can be assured a high-quality water service; but the Safe Drinking Water Act is not at all explicit about this, nor are the EPA or the states active in promoting regionalization.

Prior to the 1962 drinking water standards, the only concern was with the quality of water. No regard whatsoever had been given to the adequacy of the supply. In other words, a cessation of supply would not have violated the standards, although the health consequences would have certainly been troublesome. The committee that prepared the 1962 standards succeeded in adding the following statement: "Approval of water supplies shall be dependent in part upon . . . adequate capacity to meet peak demands without development of low pressures or other health hazards." Also added for the first time was the responsibility for conditions in the water supply system ". . . to the free flowing outlet of the ultimate consumer."

Unfortunately, the SDWA and the drinking water regulations now in effect fail to address the adequacy of service, which is a serious problem to the customers of the tens of thousands of rural community water systems, who are more interested in availability of water at the tap than in the maximum contaminant level (MCL) of some esoteric contaminant.

Characterization of reuse

Water is one of our few renewable resources. It is reused continuously, thanks to the hydrological cycle powered by solar energy. Nature's water reclamation uses the most energy-intensive of all systems—distillation; since solar power in this context is free and the most effective means for separating water from its impurities, we

0013-936X/80/0914-1298$01.00/0

need not be too concerned with the appropriateness or the efficiency of the process.

Another form of reuse is ubiquitous, particularly in the industrialized countries of the world. It is the reuse that takes place when water is withdrawn for a useful purpose from a water course or lake into which used water is discharged. In arid areas, where water is used extensively for irrigation, it may be reused several times before it reaches the sea. By that time, it often becomes so saline that it is unfit for further productive enterprise without desalination.

A more widespread reuse practice, and that which concerns us here, takes place in most of the rivers in this country, where water for a community or industry is withdrawn from the upper reaches of the river and, after being used and substantially modified in quality, is discharged into the river, which then serves as a drain and also as a source of water for the next community or industry downstream. A single river may serve many such communities and industries seriatim from its origins to its outlet. This has been termed *indirect reuse*, as contrasted with direct reuse, when wastewater is piped directly to a user with appropriate intervening treatment.

Despite the admonitions in the drinking water standards that a water supply to be used for potable purposes should be drawn from the most desirable source that is feasible, local authorities and their engineers have been quite happy to draw upon polluted rivers, and regulatory agencies seem not to have been concerned. There are good reasons for this. The earliest use of such rivers for water supplies led to great epidemics of cholera and typhoid in the early nineteenth century.

It was not until the mid-1800s, when Dr. John Snow made the connection between water and cholera, that such sources began to be looked upon with suspicion. The Lambeth Water Company in London moved its intake on the Thames from the metropolitan area to a point on the Thames upstream of London in 1847, and so protected its customers from the cholera epidemic of 1853 that ravaged the customers of competing water companies that continued to draw from the lower Thames (*2*). Incidentally, the decision to move the intake upstream was taken before there was any *proof* that the water supply was responsible for cholera—in fact, before the germ theory of disease had been developed. Acting before scientific proof was in hand was clearly a prudent approach, and well-justified by events.

However, with the development of filtration and, more particularly, chlorination for disinfection, polluted rivers could be used as a source of potable water without endangering health. Engineers and public health authorities were comfortable in the technology that had been developed. They believed, correctly, that any river, no matter how seriously polluted, could be made free of infectious disease organisms.

These strictures that give priority to developing the purest source are not at all stressed in the Safe Drinking Water Act, nor do they appear to be an essential element of EPA or regulatory concern.

And so, despite the principle that the wisest course of action is to use the purest water, many communities developed polluted sources and called upon water treatment technology to render the water safe. (Many communities, on the other hand, opted for protected sources despite the greater cost.) In particular, because chlorination permitted a chlorine residual to be maintained and easily monitored, water purveyors could assume that, with adequate chlorine residual at a certain temperature and pH, and after sufficient detention, the water was free from infectious disease organisms.

Incidentally, many engineers who object to EPA's proposed use of a treatment technique to control organics in drinking water, rather than using a maximum contaminant level, forget that, historically, bacterial safety of our water supplies has never rested with the determination of maximum contaminant levels, but with the method of treatment. Because determination of the bacterial content takes so long, water laden with bacteria can only be discovered after the water has been distributed and ingested. The safety lies in the treatment afforded, along with the presence of a chlorine residual.

Today, a substantial portion of the total population that is served from public water-supply systems depends upon sources that comprise, in part, wastewaters that only hours or days earlier had been discharged to municipal and industrial sewers upstream. Because the drinking water regulations still emphasize bacterial safety (there is still no mention of viruses), water taken from such polluted sources can readily meet the standards, or at least that portion of the standards concerned with maximum levels of bacteria. Such water does not satisfy the section of the standards that calls for utilization of the purest source.

In fact, many engineers today still recommend that such rivers should supply additional water for communities. Such has been the recommendation of the Corps of Engineers for an additional water supply for New York City; they propose taking water from the Hudson River, the sewer of the state of New York. Up to now, New York City has only been using protected upland supplies. Asheville, N.C., high in the Blue Ridge Mountains, has always used water from its own upland watersheds; now its engineers are urging the city to take its additional water from the French Broad River, which is subject to heavy urban and industrial pollution. Why, in fact, do we need to be concerned about using such polluted sources if water can be treated to meet the drinking water regulations, at least the portion of the regulations that addresses maximum contaminant levels?

The reason is clear from the history of the Safe Drinking Water Act and its concern for the development of maximum contaminant levels for chemicals not mentioned in the Interim Drinking Water Regulations. The drinking water regulations contain MCLs for 10 inorganic chemicals and only six organic chemicals, in addition to turbidity, bacteria, and radionuclide standards.

The stimulus for the passage of the SDWA came from the detection of scores of synthetic organic chemicals in the Mississippi River at the New Orleans intake. (That the finding of these myriad chemicals at the mouth of the Mississippi should be a surprise is itself surprising. The most casual sanitary survey, one which requires no more than a glance at a map of the Mississippi River watershed, would show that it drains water and concomitant waste materials from all or portions of more than half the states in the union and some parts of Canada. To have found *few* chemicals in the water would have been the surprise.)

The chemical revolution

World War II saw the beginning of the "chemical revolution," the development of *synthetic* organic chemicals. Some 63 000 chemicals are already used in commerce, and others are coming into use at the rate of 1000 a year (*3*). Many of these chemicals are formulated to be long lasting and, therefore, are not readily degraded. They find their way into the aquatic environment and into drinking water supplies through many routes: agriculture, industry, urban runoff, and the home.

Those wastewaters that are sewered and treated are the most tractable. Those wastes that are characterized as being present in "nonpoint" sources, reaching water courses through overland runoff from farms and construction sites, from industrial sites, from roadways and urban streets, and from landfills and toxic chemical dumps, are less tractable. The sulfur and nitrogen oxides discharged from industrial and power plant stacks and from vehicles result in acid rain, which has had a serious impact on many eastern lakes; also, because it increases the leaching power of rainfall and stormwater runoff, greater concentrations of polluting chemicals are carried into our water courses.

Some 20 years ago, in a comprehensive paper on cancer hazards, Dr. W. C. Rueper of the National Cancer Institute stated:

> It is obvious that with the rapidly increasing urbanization and industrialization of the country and the greatly increased demand placed on the present resources of water from lakes, river, and underground reservoirs, the danger of cancer hazards from the consumption of contaminated drinking water will grow considerably in the foreseeable future (*4*).

It is beyond the scope of this paper to recite the data on the presence of synthetic organic chemicals, as well as heavy metals, in our water courses, nor is this the place to summarize the epidemiological studies that have been mounted. Granted that each epidemiological study by itself is subject to criticism, the thrust of all of them is the same: The long-term ingestion of waters drawn from polluted sources has some deleterious impact upon health.

It may very well be that, just as with radiation and asbestos, many decades will pass before the full impact of these organic chemicals in the aquatic environment is understood. However, is it necessary to wait for convincing scientific proof, or is it prudent for those responsible for providing safe water to assume, as the Lambeth Water Company did, that polluted sources are inherently more hazardous than protected sources?

Options for protecting water supplies

The problem of dealing with synthetic organic chemicals and other chemicals that threaten the safety of water supplies used for drinking may be addressed in one of three ways:

- eliminating the chemicals at their source
- monitoring and removing the chemicals by treatment
- avoiding the use of the polluted sources for potable supplies.

. . . a substantial portion of the total population . . . depends upon sources that comprise, in part, wastewaters that only hours or days earlier had been discharged to municipal and industrial sewers upstream.

Eliminating chemicals at the source. While this has been the goal of much of the legislation enacted during the 1970s, particularly the Federal Water Pollution Control Act Amendments of 1972, implementation to the point that discharges of pollutants would be eliminated has never been realistic. The mandated treatment does not address the synthetic organic chemicals of concern, even if the treatment is fully implemented.

Even less amenable to control are the nonpoint discharges. The problem is exacerbated by the continual development of new chemicals. The General Accounting Office, in reviewing the status of control of chemical exposure in industry, concluded that ". . . it will take more than a century to establish needed standards for substances already identified as hazardous . . . . The problem is compounded because new substances, which may warrant standards, are being introduced faster than standards are being established on existing substances" (*5*).

The consequences of urban runoff, the source of many contaminants in water courses that drain urban areas, can be appreciated from the parameters that are used: pounds of pollutant per curb-mile of street or per square mile of development. The greater the number of curb-miles of street or square miles of development on a watershed, the greater the pollution. Corrective measures may reduce the impact, although studies have shown that the best such measures can reduce the pollutant level only on the order of 40–70% (*6*).

Large rivers that are used as sources of water supply by some cities are natural drains. Materials that are used in the drainage area cannot readily be eliminated or intercepted. To declare a moratorium on the use of synthetic organic chemicals or the development of new ones would be to deprive society of chemicals that have important social benefits.

It can only be concluded that, in an urbanized and industrialized society, water that drains urban and industrial areas will inevitably contain large enough numbers of synthetic organic chemicals that either singly, or in combination, can be expected to have undesirable health consequences if ingested over a protracted period. While all feasible measures to control these chemicals should be taken, such measures cannot assure their absence in supplies drawn from the sources to which they drain.

Monitoring and removing chemicals by treatment. If it is granted that the chemicals will find their way into surface and groundwaters, they might be monitored and removed in treatment. Unfortunately, adequate, reliable, and economically feasible technology for routine monitoring and removal of synthetic organic chemicals is not yet available. Should routine monitoring become technically feasible, the cost would be far too high for the thousands of relatively small municipal agencies that are responsible for wastewater disposal and water supply. Instrumentation and personnel required would be costly and outside the reach of most local authorities.

The installation of facilities and their proper operation to assure removal of these compounds and the necessary concomitant monitoring are not likely to be economically feasible, except in the largest cities. While efforts to identify and remove chemicals need to be made where populations are currently exposed, this approach cannot be depended upon for the long term, particularly for the more than 99% of water-supply purveyors that serve under 50 000 persons each.

Avoiding the use of polluted sources for potable supply. The last option and the only one that can give assurance, to the extent that such assurance is possible, that the population will be protected from the continuous ingestion of synthetic organic chemicals is to avoid using sources subject to significant urban and industrial pollution. Because upland sources that are suitable for water supply development and underground sources are limited, and constantly being threatened by urban and industrial growth, efforts need to be made to identify and preserve them for eventual water supply development, and to protect their quality by adequate land-use planning and appropriate regulation.

Protected upland sources and groundwaters can be exploited far more than they have been. For example, Vicksburg, Miss., changed its water supply from an intake in the Mississippi River to groundwater. However, protected sources are not likely to meet future demands for water supply everywhere, particularly if these waters are used indiscriminately for all the purposes now met by urban water-supply systems. This is where the potential for reuse can minimize the exposure of populations to the synthetic organic chemicals in their water sources. If polluted sources or reclaimed wastewaters are used for the many *nonpotable* purposes now being met from potable supplies, then the limited protected sources can be conserved for potable purposes.

Even in areas where protected sources are limited in quantity, these supplies are now squandered on uses such as urban irrigation, industrial processing and cooling, toilet flushing, and car washing—uses that can be met with waters of much lower quality.

Nonpotable water reuse

The last of the three options for the protection of populations from the ingestion of synthetic organic chemicals may, in many instances, require nonpotable reuse, although many water purveyors have options for protected sources that have not been fully explored because there had been no appreciation of the importance of utilizing protected sources.

The hallmark for husbanding protected sources has been described by the United Nations Economic and Social Council: "No higher quality water, unless there is a surplus of it, should be used for a purpose that can tolerate a lower grade" (*7*). Where protected sources are limited in amount, substitution of reclaimed wastewaters for waters of potable quality that are now being used for nonpotable purposes, in other words "source substitution," can provide the following benefits:

- The demand on high-quality sources would be relieved so that such sources would serve larger populations.
- The cost of providing reclaimed water for nonpotable purposes would be far less in many instances than the cost of development of additional high-quality freshwater sources, even where these are available.
- The risk to the population of the lifelong ingestion of synthetic organic contaminants in polluted water would be virtually eliminated.

Potable water reuse

Potable reuse, the piping of sewered wastewaters directly into a water-supply system, albeit with extensive treatment, suffers from the deficiencies of the first two options mentioned above.

If the wastewaters consisted solely of biodegradable organics of human origin, with nondegradable chemicals eliminated at the source, it might be feasible to convert such wastewaters into potable water without too much concern for the presence of chemical contaminants. However, urban residential communities, even in the absence of water-using industries, contribute significant concentrations of a wide range of synthetic organics to the sewer system.

The last option . . . that the population will be protected from the continuous ingestion of synthetic organic chemicals, is to avoid using sources subject to significant urban and industrial pollution.

Every home today is a virtual pharmacopeia. A recent TV public service announcement on poison control in the home showed a housewife gathering drugs from the medicine cabinet and cleansers and other chemicals from under the kitchen sink and emptying them into the toilet bowl, to become part of the sewer wastewaters that would need to be dealt with in potable reuse systems. Chemicals are also part of our diet. The Pill and other steroids are not entirely eliminated in passage through the body. Commercial establishments also contribute a wide range of chemicals to the sewerage system.

Moreover, potable water reuse would only be an option in larger cities; in such cities a substantial level of industrial activity is expected. Even should the existing industrial enterprise be assessed and monitored, new industries using chemicals not yet invented can be expected. These will all be part of the input to a potable reuse system.

The second option, monitoring for these chemicals and removing them by treatment, suffers from precisely the same problems that face us today in dealing with the many water supplies drawn from polluted sources, such as those for New Orleans, Cincinnati, and Philadelphia. While it may be easier to monitor the discharges to a single sewerage system rather than a large watershed, the risks are considerably greater because the concentrations of such chemicals are likely to be many-fold greater in wastewaters than in a river. Also, in a river there is time and distance between the sewer outfalls and the waterwork intakes. With direct potable reuse, an accident may well allow a slug of chemical to find its way into a water supply for distribution before being detected.

However, the major problem with potable reuse is in the establishment of MCLs for the various chemicals that may be considered to be important. The difficulty has been well demonstrated by the response of the National Academy of Sciences (NAS) to the mandate of Congress and the EPA with regard to the development of MCLs for individual chemicals. What is even far more difficult, in fact virtually impossible, is the establishment of MCLs for two or more contaminants that may be synergistic in their effects.

The charge that had been given to the NAS in Section 1412, Par. (e) (*3*) of the Safe Drinking Water Act is difficult enough when applied to those communities that are now obliged to draw their potable supplies from polluted sources. Direct potable reuse would just add to this burden, exposing additional populations, including those who are more susceptible, and those who may be exposed to contaminants in media other than drinking water.

Proponents of potable reuse (and despite their great number and articulation, there is currently only one operating potable water reuse system in the world) often claim that the water they produce meets "drinking water regulations." Thereby, they delude the public. First of all, regardless of the quality of the water produced from wastewater, that water cannot, by definition, meet the drinking water regulations because the regulations were never developed for a water supply drawn from wastewater directly. Furthermore, such a supply does not meet the stricture that it be from the purest source that is economically available.

More significantly, even if reclaimed water should meet the MCLs established in the current drinking water regulations, we know that such regulations are always many years behind our knowledge. The 1962 standards did not list any specific synthetic organic chemicals, so a supply containing many of these chemicals would have been satisfactory until 1976. The standards 20 years hence will be substantially different from the present standards, with many new chemicals added and the MCLs for some of the existing chemicals sharply reduced, such as has been suggested by the NAS for lead (*8*).

Decisions made for large capital investments for intakes, treatment facilities, and transmission mains, if based on water that at the time can meet one set of MCLs, may prove unsatisfactory because the MCLs change, and will not be easily rectified. The decision of Cincinnati to go to the Ohio River, rather than to groundwater, was made before anticipating the kinds of problems that would arise years later, and it is not so easy now to change the source of water or the method of treatment. On the other hand, cities that opted for protected upland sources or groundwater are not faced with these problems, as they will likely not be in violation of MCLs for chemical contaminants any time in the future.

A program directed toward potable reuse encourages the public to believe that this is one of the options that would make preserving and developing protected water sources unnecessary. Many "environmentalists" have already proposed that potable water reuse take priority over the development of pure water supplies. A good case in point is the environmentalists' push in California for recharge of aquifers with reclaimed wastewaters as an alternative to developing additional protected water supplies. The concern about adding contaminants to an underground aquifer that cannot easily cleanse itself has led to a moratorium on wastewater recharge in California, pending the results of research investigations into the health significance of that approach (*9*).

Not precisely in the same category, but reflecting similar attitudes, is the mandate by Congress to the Corps of Engineers to study the potential of using water from the Potomac estuary for the metropolitan Washington, D.C., area, rather than developing upland reservoirs (*10*). The Corps is now studying the treatment of Potomac estuary water with a 1-mgd pilot plant.

One of the problems with research into potable reuse is that the results would be of quite limited applicability. Potable reuse is warranted in relatively few locations. It may very well be that Denver is one of those places, but a successful demonstration in Denver, even if there were criteria on which to base success, would not likely lead to adoption in other places where there is little pressure and little need to move in this direction. A second problem lies in the fact that the technology for rendering a wastewater potable would be so sophisticated, and the monitoring required to assure safety so advanced, that few water purveyors in the U.S. could afford to install and operate such systems.

... the construction grant program for wastewater treatment constitutes a major disincentive for water conservation.

"The feasible alternative"

The title of this symposium is quite clumsy, and I must confess to being partially responsible for addition of "and Feasible Alternatives." One feasible alternative to potable reuse, where water supply is short or supplies are of poor quality, is *nonpotable reuse,* or *source substitution.* EPA has in press "Guidelines for Water Reuse," which is intended for water purveyors and public officials (*11*). One interesting facet of this manual is that it cites a number of communities that have already initiated large-scale programs of nonpotable reuse.

The most common nonpotable reuse systems provide wastewater to one or two large users in the community. However, many systems have already been developed where essentially dual distribution systems have been furnished, and where the nonpotable reclaimed water is distributed extensively through the urban area for a wide range of uses, the most important of which are urban irrigation, recreation, and makeup for cooling towers. Some of these systems, such as the Irvine Ranch Water District, have been built without any federal funds. Others have used construction grant funds for part of the program.

What characterizes these programs is their success, as measured by the economies realized in funds and water, and their public acceptance, or even public pride. This could hardly be said of a program for potable water reuse. (One is reminded of the old saw "good news–bad news." The good news is that we will soon be drinking our own sewage; the bad news is that there won't be enough of it.)

Nonpotable reuse satisfies a conservation ethic without any threat to the public health. The technology treatment is simple. The treatment train that has been widely adopted is secondary effluent followed by coagulation and direct filtration and disinfection (*12*). Considerable attention needs to be given to reliability, with effluent turbidity being the best marker for satisfactory performance. There need be no concern for removal of chemicals, and therefore no extensive monitoring for chemicals.

In addition to providing an opportunity for protecting the public from the long-term ingestion of waters containing synthetic organic chemicals, nonpotable water reuse has other benefits:

- conservation of water—saving the higher quality sources for those services that require it
- recycling of nutrients—which would otherwise have to be removed before discharge to receiving waters—that are beneficial when the water is used for urban and agricultural irrigation
- cost and energy savings that result from community water recycling
- reduction in the discharge of pollutants to water courses
- realization of other priorities, such as the preservation of open space and the development of recreational areas.

One of the major problems in the development of potable reuse is the lack of integration of water supply and water pollution control programs at local and state levels and particularly in the EPA. At the local and state levels, the fragmentation of the water supply and water pollution control industry results in the placing of outfalls above water intakes or the placing of water intakes below outfalls. Were there regionalization, something like what the water authorities created in England and Wales in 1974 (*13*), integrated planning for optimum utilization of water resources in a basin would be feasible, and, more importantly, such planning could be implemented.

In the Irvine Ranch Water District, the district has the responsibility for distributing potable water and reclaimed water and providing sewerage services. In most other instances, the fact that two separate agencies are involved leaves control of the reuse programs uncertain. Is it a water pollution control function or is it a water supply function? This has not been resolved by the EPA.

The provisions of the Federal Water Pollution Control Act Amendments of 1972 (PL 92-500) state that "it is the national goal that the discharge of pollutants into navigable waters be eliminated by 1985" and that the administrator of EPA "... shall encourage waste treatment management which results in the construction of revenue-producing facilities for ... the reclamation of wastewater ..." Furthermore, the Clean Water Act of 1977 (PL 95-217) allows an additional 10% of construction grant funds for innovative and alternative approaches, and reuse of water is the first innovative approach mentioned.

In addition, the President, in a memorandum dated July 12, 1978, stated that in the provision of loans and grants for municipal water supply and wastewater treatment systems, programs should be modified "... to remove any disincentives to water conservation and to require appropriate community water conservation programs as a condition of such loans and grants." Clearly, nonpotable water reuse that substitutes for potable water supplies is an appropriate community conservation program.

Nevertheless, construction grant funds are denied or restricted when the projects are "multipurpose"—not directed to meeting an NPDES permit—even though the project provides for water reuse. One reason given for this posture is federal fiscal constraints; limited construction grant resources need to be reserved for pollution control measures. Thus, the construction grant program for wastewater treatment constitutes a major disincentive for water conservation.

Also, while the policy may conserve federal funds, it wastes societal funds and resources. A community is deterred from implementing a water reuse program that may be the most economical water resources option because it is threatened with losing its construction grant for wastewater treatment. I do not happen to support the construction grants program, discussion of which is beyond the scope of this paper. On the other hand, because construction grants are available, they inevitably guide the direction in which investments are made at the local level, and this direction is not toward nonpotable reuse even when it is clearly the most cost-effective option.

If nonpotable water reuse has a future, and it certainly does because it already has a very successful present, then the federal government should at least get out of the way.

References

(1) Office of Drinking Water, U.S. Environmental Protection Agency, 1980.

(2) Okun, Daniel A. "Health Aspects of Water Management," *Public Works and Society,* Proceedings of a Joint Conference of the American Society of Civil Engineers and the Institution of Civil Engineers (U.K.), 1972.

(3) *Science,* 598 (Nov. 10, 1978).

(4) Hueper, W. C. "Cancer Hazards from Natural and Artificial Water Pollutants," *Proceedings, Physiological Aspects of Water Quality,* U.S. Public Health Service, Washington, D.C., 1960.

(5) *New York Times* (March 24, 1979).

(6) LaPointe, Thomas. "An Evaluation of Small Scale Techniques for the Control of Pollutants in Urban Runoff," Ph.D. Dissertation, Department of City and Regional Planning, University of North Carolina at Chapel Hill, April 1979.

(7) United Nations Economic and Social Council. *Water for Industrial Use,* Report No. E/3058 ST/ELA/50, 1958.

(8) National Research Council. *Drinking Water and Health,* National Academy of Sciences, Washington, D.C., 1977.

(9) State of California. *Report of the Consulting Panel on Health Aspects of Wastewater Reclamation for Groundwater Recharge,* June 1976.

(10) Public Law 93-251, March 7, 1974.

(11) U.S. Environmental Protection Agency. *Guidelines for Water Reuse,* Camp Dresser & McKee, Inc., in press.

(12) Okun, Daniel A. *Criteria for Reuse of Wastewaters for Nonpotable Water Supply Systems in California,* Report to the California State Department of Health Services, July 9, 1979.

(13) Okun, Daniel A. *Regionalization of Water Management—A Revolution in England and Wales,* Applied Science Publishers, London, 1977.

Daniel A. Okun *is Kenan Professor of Environmental Engineering at the University of North Carolina at Chapel Hill and serves on the North Carolina Legislative Commission on Alternatives in Water Management.*

Water reuse: an unfinished agenda

The summary comments at the EPA Symposium on Protocol Development: Criteria and Standards for Potable Reuse and Feasible Alternatives, Warrenton, Va., July 29–31, 1980

C. C. Johnson, Jr.
C. C. Johnson Associates
Silver Spring, Md. 20910

This particular symposium was one that the Drinking Water Council has long hoped would occur. Briefly, let us look at the purpose for the symposium so that we get things in the proper perspective. The purpose of this symposium was not to develop specific criteria and standards, but to provide guidance with respect to approaches, problems, solutions, and needed research for establishing a pathway to protocol development and potable reuse criteria and standards for consideration of nonpotable options.

The two basic charges were to recommend:

- basic principles that can be used in the decision-making process
- specific experiments which can be constructed, with their interpretations, that will help answer the questions that remain.

This symposium brought together scientists and engineers involved in the six technical disciplines of water reuse—toxicology, engineering, chemistry, groundwater, microbiology, and nonpotable options. Representatives from each discipline presented an issue statement at the beginning of the conference. These statements were then discussed and rewritten in the workshop sessions. Chairmen of the workshops included I. H. Suffet of Drexel University (chemistry), Russell Culp of Clean Water Consultants (engineering), Paul Roberts of Stanford University (groundwater recharge), Richard Englebrecht of the University of St. Louis (microbiology), Robert Neal of Vanderbilt University (toxicology), and Jerry Gilbert of Brown & Caldwell Engineers (nonpotable options). Final positions and recommendations from each of the disciplines were presented on the last day.

What are the issues?

Lloyd Fowler of the Santa Clara Water Valley District said that there are two basic issues involved. First, potable reuse should be the result of a need: either potable water is in short supply or there is a reason to extend good-quality water for other purposes. Second, whatever potable reuse considerations are given, the quality is important and public health must be protected. He believes that the existing water supply standards are adequate, but that direct reuse poses additional questions.

Dan Okun of the University of North Carolina sounded a note of caution and said that we need to review the sanitary survey so that we know what is happening to the source and why. We should save the highest, cleanest sources for the highest priority of use, drinking water. He reminded us that 95% of the public water systems serve less than 10 000 population units. He said that the Drinking Water Act does not address the quality of the source but this should be considered under congressional mandate. He also said that preventive health benefits—the benefits of acting before a catastrophe arises—should be paramount in our thinking.

Ken Miller of CH_2M/Hill had a slightly different focus. He said that the time for developing criteria for standards of potable reuse is now, but that reuse should occur only after all other options have been exhausted. However, the ideal of using an uncontaminated source for potable water should not deter us from pursuing reuse technology. He also was concerned about process reliability and the flexibility in the selection of the treatment processes. Finally, he said that standards for health must relate to economics, process technology, public acceptance, health effects, and most of all, the real world.

Dr. F. J. J. Brinkman of the World Health Organization related some of the experiences they had with the many plants set up for nonpotable reuse in Europe and also some set up for limited direct reuse. One popular mode that they have become familiar with and have exhibited some interest in is river bank infiltration. He also noted that they have working parameters for reuse that are similar to those in California for standards for infiltration and injection of reuse water into the groundwater source.

Duane Baumann of Southern Illinois University brought a perspective on public acceptance. He reported on an attitude survey that noted that social acceptance of potable reuse was not an obstacle, given an educated public. He said the major obstacle probably is in the minds of the public health officials and engineers.

Robert Madancy of the Department of Interior OWRT (Office of Water Research & Technology), the spokesman for the nonpotable and other alternatives sector, raised the $64 000 questions, ones that most people try to stay away from: What is potable reuse? What is direct reuse? What is indirect reuse? Take the stretch of the Ohio River between

0013-936X/80/0914-1304$01.00/0

Pittsburgh and Cincinnati, he said. Is Cincinnati's water direct or indirect if upstream discharges are 2000 ft away, 200 ft away, or 2 ft away? You need to think about that. He also pointed out that figures show that potable reuse is only, or probably less than, 1% of all the reuse projections to the year 2000. But he did recognize that public health is the most significant aspect associated with potable reuse.

The formal charges for the workshop deliberations were essentially:

- Consider the source.
- Consider water quality.
- Consider treatment.
- Consider monitoring needs.

My summary from hereon will address comments on these four elements as well as other matters that evolved from my observations of the workshops, the deliberations, the review of the issue papers, the summary statements, and the recommendations. I did sit in, albeit a short time, on each workshop, which meant that I got a disconnected view in terms of the discussions that were carried on. Thus, the observations that I bring now are somewhat permeated with my own philosophy.

The questions

I listed perhaps 20 or 25 questions that I wanted this kind of symposium to answer. I'll share with you only eight, because I think they are the most significant.

- Is it possible to establish criteria and standards for potable reuse which will protect the public health?
- Drinking water standards are to be applied to source waters from a protected source. What does this mean to a consideration of potable reuse?
- Will the public knowingly accept direct reuse?
- Does the available scientific and technical data allow the establishment and implementation of acceptable water quality standards?
- What is the most likely or prevalent nature of water reuse and what is its significance or impact on public water supplies?
- Does our knowledge of hydrogeology, soil characteristics, and the interaction of wastewater products allow us to predict the fate of contaminants following groundwater recharge?
- With respect to water quality and the absence of certainty, what risk to the public health are we willing to take?
- What are the gaps in our knowledge that can be and should be filled by research when we consider the subject of potable water reuse?

The first thing I noted in most of the workshops was a common concern about the definitions we use for potable reuse and nonpotable reuse. The definitions should skirt the buzz words and recognize the reality.

For example, new terms crept into the terminology of several discussants and reporters.

Robert Neal talked about planned and unplanned reuse; another report talked about controlled and uncontrolled reuse. I suggest that the definition of potable reuse is planned and unplanned, controlled and uncontrolled use of wastewater for domestic purposes. Nonpotable reuse is characterized as wastewater used for agricultural, industrial, and other purposes.

Some examples

Planned and controlled reuse are in existence in Israel, South Africa, the Netherlands, Germany, and so forth. But we don't have to go overseas to get examples. We have our own experiences in California, Long Island, and other places in terms of groundwater recharge. In terms of a raw water supply source, work is being done in Virginia. Within the terms of a developed protocol and with approval of the EPA and the state of Virginia, the Upper Occoquan Sewage Authority was allowed to develop an AWT plant that discharges its effluent into the water reservoir from which Fairfax County takes its raw water supply and produces drinking water. This is a good example of a direct reuse situation. They did it on the basis of the best knowledge they had, the best technology they could devise, and the best reliability they could design. It's working and it's the kind of demonstration from which wisdom is taken. We'll know later on whether or not it was a good or bad experience.

> ***Every community water treatment plant that exists below the discharge of a wastewater treatment plant is in the mode of unplanned reuse.***

Unplanned reuse

Every community water treatment plant that exists below the discharge of a wastewater treatment plant is in the mode of unplanned reuse. The only difference is the distance that separates one pipe from the other. Dallas, for example, has to contend with discharge from Denton. Ken Miller told me the community of Thornton, Colo., which is right below Denver, is taking the direct discharge from the Denver wastewater treatment plant. Long Island water is an example of planned reuse.

There are other areas of the country where wastewater effluents are purposely discharged above aquifers so that wastewaters percolate into the groundwater table and eventually may be reused. Other situations are planned solely for discharge to the ground in a relatively safe manner, for example, in Muskegon, Mich. Direct reuse was planned in Chanute, Kan., in the 1950s because there was a need for water due to drought.

The point I am trying to make is that direct, indirect, and potable reuse are realities. There is nothing new about them, except maybe our concern. That is why I think this was such a valuable conference. We are now beginning to come to terms with polluted water sources and how they affect our daily need to produce an acceptable water supply.

Once the workshops adjusted to dealing with source waters from polluted sources, regardless of the unquantifiable measure of direct or indirect reuse, they were free to address the problems associated with producing or maintaining potable water that is protective of the public's health. Practically all the groups believed that their deliberations are applicable to all polluted waters, regardless of source. That is an important conclusion to draw from this kind of workshop.

It is commonly recognized that the waste characteristics and the degree of pollution involved in potable water reuse influence the microbiological, chemical, and toxicological aspects of potable water quality in new and different ways when compared with the past practices associated with water treatment and quality assurance. There was general agreement in the approaches recommended for dealing with these aspects.

- Practically all of the groups were of the opinion that a single set of water quality standards should apply at the tap, regardless of the source of the raw water to be treated for drinking.
- Almost all groups agreed that additional information is needed for raw water coming from highly polluted sources in order to treat it properly.
- With the exception of one work group, all recognized deficiencies in

the state of the art. These deficiencies were not considered insurmountable; they can be remedied by additional and specified research. I am somewhat discouraged, however, by the timetable associated with some problems that were cited.

The engineering group was of the opinion that technology does not appear to be a limiting factor in the implementation of potable reuse.

- Perhaps the most difficult and as yet unanswered question is associated with health effects that may be attributed to treated water. The toxicologists suggested that new parameters are needed to deal with organics in drinking water. These parameters might take the form of biological end points. They also believe, along with the chemists, that animal studies can be designed to enable a measure of predictability and that establishment of standards can guide the design and operation of water treatment plants.
- Notice I have been using the term "water treatment plant." One term that seems to create a problem is the use of "water reclamation plant." I am not quite sure where that fits into the picture when we think of all the water plants for planned or unplanned potable reuse that are not water reclamation plants.
- Microbiologists agree that potable reuse raises new questions with respect to the presence, generation, elimination, and reduction of pathogens and toxins during treatment of highly polluted water. This may require new indicator organisms and different disinfectants than those that have been used and relied upon for the past 100 years. Even so, the answers can probably be supplied by appropriate research.
- Serious questions exist in my mind about the ability to predict the transport and transformation of metals, organics, and biologicals in groundwater. Under these circumstances, either the doctrine of no significant deterioration or the concept of dedicated use should be applied to groundwater recharge or reuse of potable water for nonpotable purposes.
- The nonpotable reuse group believed that the problems of potable reuse are monumental, that the volume of water involved is inconsequential, and that the ultimate acceptance of direct potable reuse is improbable. They believed that emphasis should be placed on the more readily achievable solutions of problems associated with nonpotable reuse.

I believe that any concept of controlled and uncontrolled, planned and unplanned reuse of wastewater should be a local option, probably decided on the basis of need, while maintaining protection of public health as a top priority. It must be emphasized that few nonpotable uses exist that do not impact upon the quality of water supplies that now or may in the future be required for potable uses.

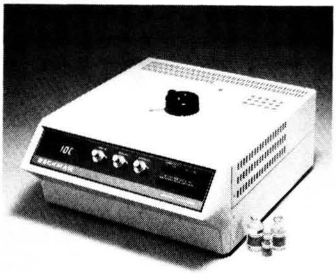
- Whether or not the public will accept potable reuse is probably an academic question. The fact is that they have in the past, they are now, and they probably will in the future. The public should be confident that our treatment processes are indeed producing the best water possible, and are in consonance with our scientifically established standards to protect the public health.

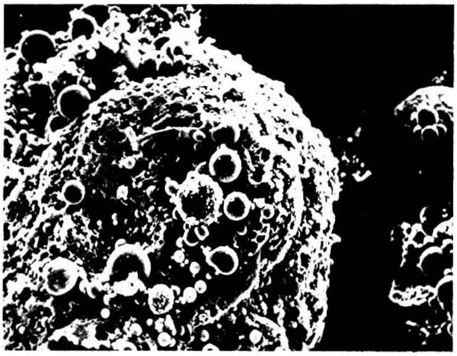
Where are we?

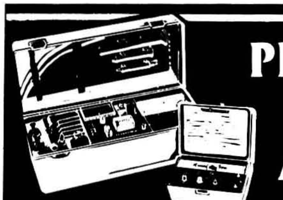
The practice of potable reuse has been with us for a long time. We need only to improve the product to keep pace with our knowledge and concern for health effects. It affects every community water supply that currently extracts water from an industrial or vulnerable stream or grossly contaminated aquifer. We can't close down these water treatment processes while we obtain answers to the scientific and technical gaps that exist. We must get on with the business at hand, of producing the best water we can from the sources we must use, in the presence of the best available knowledge, as inadequate as that may be.

If our concern for water reuse is genuine, then it is strongly recommended that the deliberations, considerations, and recommendations of this symposium be related as applicable to all aspects of potable water supply production. Recognition of this concern should be incorporated into every EPA program that impacts upon the quality of raw water supply sources and the development and revision of national drinking water standards.

C. C. Johnson, Jr., *is chairman of the National Drinking Water Council, established by the Safe Drinking Water Act of 1974 to provide advice to the EPA administrators. He heads an environmental engineering consulting firm, C. C. Johnson Associates, in Silver Spring, Md. He is a retired assistant surgeon general of the U.S. Public Health Service.*

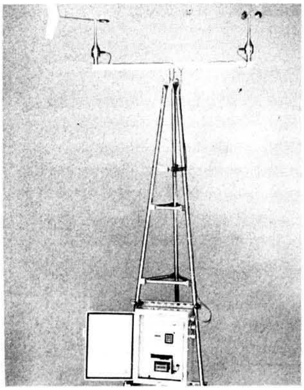







HACH
PRODUCTS FOR ANALYSIS

ES&T PRODUCTS



Battery-operated weather station

Self-contained unit is designed to collect, process, and record meteorological data. The field-programmable processor accepts digital or analog signals and sends output data to a cassette tape, a printer, or remote devices via telemetry. A weatherproof housing protects the processor, battery, and recorder. A cross-arm for mounting sensors is supported by a tripod mast. WEATHERtronics **101**

Vacuum-ultraviolet source

No cooling water, pumps, or flowing gas supply are required for this light source, which has a useful continuum extending to 370 nm. Typical Lyman-alpha radiance is over 1 mW/mm^2·nm·sterad. The f/10 beam is emitted from a bright 1-mm-diameter spot. Typical operating parameters are 200-mA discharge current at 70 Vdc. Acton Research **102**

GC detector for nitrosamines

Selectivity for thermally labile nitro- and nitrosyl-releasing compounds, relative to other nitrogen-containing compounds, is better than 10^7 to 1. Detection limit is better than 0.1 ng and reproducibility is 2.5%. The detector operates without external plumbing or gas supplies. Thermo Electron **103**

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

High-volume rotary extractor

Designed to work with all types of solid wastes, the device simultaneously extracts trace metals from up to six samples. Extraction is carried out by rotating six 1-gal bottles containing a mixture of solid waste and an acidic solution. Constant rotation at 40 rpm prevents stratification of the waste sample and extraction fluid, as prescribed by RCRA regulations. Acurex **104**

Liquid chromatography columns

A series of silica and bonded-phase silica columns for high-pressure liquid chromatography are available. Standard silica gel columns for adsorption LC are available with 5-μ, 10-μ, or 15-μ particle-size packings, as are reverse-phase bonded-phase silica columns. Kratos **105**

Puncture-tip pH electrode

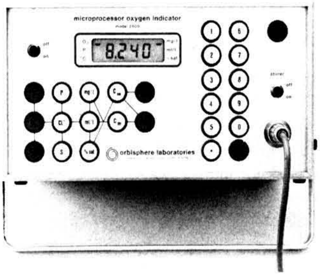
Combination electrode has a spear-shaped sensing end which allows puncturing of solid and semisolid samples. An annular reference junction, concentric with the pH spear, is provided with either an Ag–AgCl or a calomel reference. The probe is compatible with all pH meters, according to the manufacturer. Broadley-James **106**

Hazardous gas shutoff valve

The device is designed to be installed between the gas cylinder and the primary regulator. When gas flow exceeds the factory preset limit, the valve closes with a snap action. Ten flow limits are available from 100 scc/min to 50 L/min. The valve can be supplied with integral welded CGA cylinder fittings, female pipe thread ports, or other industry-standard configurations. Veriflo **107**

Fractionating samplers

High-volume impactors permit fractionation of ambient particles into 5, 3, or 2 size ranges using standard high-volume blowers at 20 cfm or 40 cfm. Aerodynamic sizing is over the range 1.1–7.0 μ; submicron particles are collected on a backup filter. Andersen Samplers **108**



Microprocessor oxygen indicator

Temperature, oxygen fugacity, and, for aqueous samples, oxygen concentration and oxygen solubility are indicated. Correction of dissolved oxygen concentrations for temperature and salinity effects is computed digitally. The results are displayed in mg/L, mL/L, or true percentage saturation. Oxygen fugacities are displayed in millibars. The instrument includes an internally rechargeable battery and is waterproof for portable operation. Orbisphere Laboratories **109**

Materials analyzer

Direct concentration readouts of up to 32 elements is provided in a single measurement. Nondestructive testing is carried out without sample preparation in as little as 15 s. The element range is atomic numbers 13–92. Concentration range is 100 ppm to 100%. Operating temperature range is −20 °C to +40 °C. Power is supplied by an enclosed, rechargeable battery or by a 110 Vac outlet. Columbia Scientific Industries **110**

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

Solar radiometer
Output is frequency-encoded for use with low-cost computing systems, data loggers, and integrators. The effective bandwidth is 0.28–2.8 μ; output sensitivity is typically 10 Hz/W · m^2. Response is linear over the range 0–1400 W/m^2. Hollis Observatory **111**

Gas cylinders for halogens
Calibration-gas cylinder will hold low-ppm chlorine mixtures for more than a year. Two capacities are available, 200 ft^3 and 30 ft^3. Matheson **112**

Alcohol-in-gasohol test kit
Tests may be run in the field without batteries or electricity. Accuracy is ±2%. Materials are supplied for 48 tests. Beckman Instruments **113**

Stack monitor
Velocity and temperature sensors produce 0–5 Vdc signals at a terminal strip in the remote power supply. The velocity sensor is temperature-corrected and is sensitive to velocities of 5–12 000 sft/min. The unit can operate at temperatures up to 900 °F. Up to 500 ft of 3-wire cable may be used to connect the probe to the power supply unit. Kurz Instruments **114**

Acoustic radar
System monitors wind and provides a continuous visual representation of the thermal structure up to 1000 m. The principle of operation is similar to that of an echo sounder: Sound pulses are emitted from a vertically directed antenna, and echos from the thermal structure of the atmosphere are detected and sent to a screen or recorder where they are presented in a height-time diagram. *Write direct:* Sensitron AB, Sköndalsvägen 126, S-123 53 FARSTA, Sweden **115**

Ion-selective electrode
Solid-substrate electrodes are sensitive to potassium and calcium ions. They are disposable and miniature, measuring 2.5 mm in diameter and 11 cm in length. Custom sizes and configurations are also available. Ionetics **116**

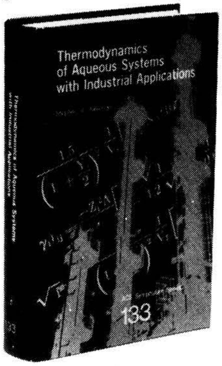
LC gauge adapter tee
This stainless steel fitting combines the functions of a conventional tee and a pipe adapter. It is designed for calibrating, trouble-shooting, or constructing low-cost liquid chromatography systems. A 1/4″ or 1/8″ NPT seat can receive a pressure gauge directly. Scientific Systems **117**

Portable gas-blend calibrator
Device calibrates gas blends in the ppm range using sealed, liquid-filled "permeation tube" sources. The unit is battery-operated and weighs 12 lb. Texas Analytical Controls **118**

Condensation nuclei monitor
Fully automatic instrument makes real-time measurements once every second. Features include low-level concentration measurements of 50 particles/mL, linear readings to 10^6 particles, and particle detection capabilities down to 0.0016-μ diameters. Environment One **119**

Animal respiration monitor
A pressure sensor picks up small variations in animal respiration inside an animal cage. The animal is free to run with no attached sensors. Measurements can be made on a 24-h basis. The animal cage is periodically ventilated to refresh the air. Respiration rate is displayed on a digital meter and is printed at preset time intervals on an automatic printer. The size of the animal that can be monitored varies from mice to dogs. Columbus Instruments **120**

HCl-in-air monitor
Unit is an automated, wet chemical analyzer that does not employ paper tapes. Typical full-scale range is 0–10 ppm, expandable to 0–2.5 ppm full scale. Detection limit is 25 ppb. Higher ranges are available. A rechargeable battery provides 24 h of continuous operation. The unit has digital readout and a recorder output of 0–1 V. CEA Instruments **121**



ES&T LITERATURE

Particle detection. SediGraph-L brochure explains how light extinction tracks sedimentation of organic and inorganic particles ranging 0.1-100 μ, with better than 2% reproducibility. Micromeritics Instrument Corp. **151**

Ion analysis. Data sheet describes "PPINICI," which provides positive and negative chemical ionization spectra from a quadrupole mass spectrometer for enhanced compound indentification. Finnigan Corp. **152**

Environmental services. Brochure, "KPN Puts It All Together," outlines company's consulting services with regard to existing or planned pollution abatement systems and follow-up monitoring work. KPN Associates **153**

Gas chromatography. Data sheet describes Model 3770 Capillary GC. High sensitivity, low-volume detectors, large-column oven, pressure-regulated pneumatics. Varian Instrument Marketing **154**

Carbon-bed breakthrough. Report explains how infrared analysis can monitor a vapor-laden carbon bed and automatically shut it down *before* solvent breakthrough occurs. Foxboro Analytical **155**

ClO_2 systems. Catalog File 85.200 describes new line of chlorine dioxide systems as an alternative to water disinfection with chlorine. Ranges 17-510 lb/d of ClO_2. Pennwalt/Wallace & Tiernan **156**

Test equipment. Brochure lists full line of public health/environmental test equipment for drinking water, food processing, sewage and wastewater treatment, and other such applications. LaMotte Chemical Products Co. **157**

Ozone technology. Booklet, "Putting Ozone to Work," tells how ozone technology is gaining increasing acceptance for water/wastewater treatment and disinfection applications. Welsbach Ozone Systems Corp. **158**

Hazardous gas detection. Brochure describes early warning and surveillance detection systems for use during processing, storage, and transportation of hazardous gases and vapors. Control Instruments Corp. **159**

"Problem water." Form No. M-DIF explains how water containing iron, manganese, and hydrogen sulfide can be handled with potassium permanganate; filter media subsequently can be regenerated. Carus Chemical Co. **160**

LC applications. Order Number LC-172 explains how liquid chromatography enhances determinations of pesticides, phenols, nitrosamines, PCBs, and polynuclear aromatic hydrocarbons. The Perkin-Elmer Corp. **161**

Electrodes. Product bulletin lists electrodes for pH, ORP, titration, polargraphic analysis, and other items. Astra Scientific International, Inc. **162**

Benzene analysis. CIRA Circular No. 20 (August 1980) covers separation and identification of benzene and chlorinated benzene as EPA priority pollutants. Sadtler Research Laboratories **163**

Chlorine determination. Technical paper tells how trace chlorine and other cooling water oxidants can be determined, even below 5 ppb. Especially applicable to seawater cooling systems. Paper by Guy Washinger and Peter Kark. EG&G, Inc. **164**

LC accessories. Catalog lists line of low-pressure liquid chromatography accessories. Stresses separation of biologically active materials. Laboratory Data Control **165**

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

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

Deionization. Brochure tells how deionized water (up to 18 MΩ at 25 °C) can be supplied without huge capital investment in water purification systems. Resins can be regenerated. Continental Water Systems Corp. **166**

Laboratory equipment. Fall 1980 Science Specialties catalog features thermometry equipment, as well as analytical items, recorders and other needs. Cole-Parmer Instrument Co. **167**

Groundwater decontamination. Bulletin 27-50 describes treatment service providing mobile granular activated carbon adsorbers to remove organics from municipal well water supplies. No capital investment needed. Calgon Corp. **168**

CO alarm. Data sheet 07-0110DFM explains how the carbon monoxide alarm monitors concentration and sets off audible and visual alarms when a given level is exceeded. Mine Safety Appliance Co. **169**

Food processing wastes. Paper tells how aeration from bottom-laid valved tubing effectively treats wastewater from milk processing and gives 98% BOD removal for flows up to 1.5 mgd. Hinde Engineering Co. **170**

pH recorder. Bulletin No. 980 describes a wall-mounted "utility" pH recorder with many convenient and advantageous features. Analytical Measurements **171**

Test/calibration. TRANSCATALOG™ lists many instruments for testing most-used physical parameters, as well as calibration devices, controllers, accessories, etc. TRANSCAT **172**

Temperature measurement. Application Note 93-00-07-06 lists temperature and humidity measurement devices for special uses. Honeywell **173**

pH electrodes. Brochure describes electrodes for pH, "redox," and other measurements. Orion Research Inc. **174**

Groundwater sampling. Technical Bulletin 80-3 describes and illustrates groundwater sampling systems that will help users meet RCRA-based regulations. Geohydrological services also available. BARCAD **175**

Safety supplies. Catalog for September 1980 lists safety and environmental supplies needed to help meet OSHA regulations. Interex Corp. **176**

Analyzers. DigiChem 3000 brochure describes operation/applications of programmable analyzers for alkalinity, silica, ammonia, hardness, and other water chemistry parameters. Ionics, Inc. **177**

GC sample concentrator. Literature describes the CDS 320 gas chromatography sample concentrator and its application to monitoring low-level organics in air, water, and solids. Chemical Data Systems, Inc. **178**

Fuel treatment. Reprint 284 discusses prevention of fuel-related problems, from preflame through emissions, by the use of chemical additives. Nalco Chemical Co. **179**

GC/MS topics. Bibliography of gas chromatography/mass spectrometry studies covers topics related to pollution, foods, agrochemicals, energy, and other subjects. Ask for Publ No. 23-5953-4719. Hewlett-Packard **180**

Air quality monitoring. Short-form catalog describes instruments for monitoring/determination of NO$_x$, SO$_2$, and O$_3$ by using EPA-described fabric filter dust collectors that retain capacity while reducing floor space needs by up to 50%. DCE Vokes Inc. **181**

Dissolved oxygen. Brochure, "Oxygen Measurement Systems," describes first microprocessor-based universal oxygen indicator. Range 1 pp*b* to 19.99 pp*m* Orbisphere Laboratories **182**

Hazardous waste. December conference agenda available. Society for Occupational and Environmental Health, Ste. 308, 1341 G St., NW, Washington, DC 20005 (write direct).

Science/engineering. "Quanta" will acquaint readers with university's science and engineering projects. Dept. of Public Relations, Carnegie-Mellon University, Schenley Park, Pittsburgh, PA 15213 (write direct).

Occupational health. Various news items, including ones that concern the Navy. "Occupational Health Notes," Navy Environmental Health Center, Naval Station, Norfolk, VA 23511 (write direct).

Chemical treatability. Report for EPA concerns hazardous aqueous waste treatment for 505 compounds. Touhill, Shuckrow and Associates, Inc., Box 11022, Pittsburgh, PA 15237 (write direct).

Coming regulations. Semiannual list of "regs" that EPA plans to develop in the next several months. Penelope Parker, EPA Regulation Management Staff (PM-223), Washington, DC 20460 (write direct).

NO$_x$ control. User's guide to NO$_x$ control for coal-fired utility boilers. Limited copies available. EPA-600/8-80-027. ORD Publications, Center for Environmental Research Information, U.S. EPA, Cincinnati, OH 45268 (write direct).

Dredged material. Publication index/retrieval system for dredged material topics and reports. Office, Chief of Engineers, U.S. Army, Washington, DC 20314 (write direct).

Environmental planning. Environmental master plan, "A Challenge for the 1980's." Acid rain, hazardous wastes, other topics discussed. Dept. of Environmental Conservation, Albany, NY 12233 (write direct).

Water research. Describes happenings in the Office of Water Research and Technology, and contracts awarded. Director's Letter. Office of Water Research and Technology, Washington, DC 20240 (write direct).

Science resources/funds. New report, "National Patterns of Science and Technology Resources, 1980," discusses personnel and fund use. Stock No. 038-000-00448-4. Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402, $3.75 per copy (write direct).

Refinery emissions. "Sampling and Measurement of Particulate Emissions from Refineries," CONCAWE Report No. 4/80. CONCAWE, van Hogenhoucklaan 60, 2596 TE den Haag, Netherlands (write direct).

PCB contamination. Reports Nos. 51 and 55. Dept. of Environmental Conservation, Rm. 519, 50 Wolf Rd., Albany, NY 12233 (write direct).

ES&T READER
ERVICE REPLY
CARD. . . . .

It's computer processed

for fast

response

to your inquiries.

AND, IT'S

FREE

ES&T NOVEMBER 1980

VALID THROUGH
MARCH 1981

ADVERTISED PRODUCTS: 1 2 3 4 5 6
7 8 9 10 11 12 13 14 15 16 17
18 19 20 21 22 23 24 25 26 27 28
29 30 31 32 33 34 35 36 37 38 39
40 41 42 43 44 45 46 47 48 49 50
51 52 53 54 55 56 57 58 59 60 61
62 63 64 65 66 67 68 69 70 71 72
73 74 75 76 77 78 79 80 81 82 83
84 85 86 87 88 89 90 91 92 93 94

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

NAME: ______________________

TITLE: ______________________

FIRM: ______________________

STREET: ______________________

CITY: ______________________

STATE: ______________ ZIP: ________

PHONE: (___ ___ ___) ___ ___ ___ - ___ ___ ___ ___

TO VALIDATE THIS CARD, PLEASE CHECK ONE ENTRY FOR EACH CATEGORY BELOW:

Intensity of product need:
- ☐ 1. Have salesman call
- ☐ 2. Need within 6 months
- ☐ 3. Future project

Employees at this location:
- ☐ 1. Under 25
- ☐ 2. 25 - 99
- ☐ 3. 100 - 299
- ☐ 4. 300 - 499
- ☐ 5. 500 - 999
- ☐ 6. 1000 - 2999
- ☐ 7. Over 3000

Areas of your responsibility:
- ☐ A. Air pollution only
- ☐ B. Water pollution only
- ☐ C. Waste treatment only
- ☐ D. Air & Water pollution
- ☐ E. Air & Waste treatment
- ☐ F. Water & Waste treat.
- ☐ G. Air/Water/Waste
- ☐ H. Other Environmental

This copy of ES&T is . . .
- ☐ 1. Personally addressed to me in my name
- ☐ 2. Addressed to other person or to my firm.

Principal product to which my work relates:
- ☐ A. Oil/Gas/Petroleum
- ☐ B. Plastics/Resins
- ☐ C. Rubber
- ☐ D. Drugs/Cosmetics
- ☐ E. Food/Beverages
- ☐ F. Textile/Fiber
- ☐ G. Pulp/Paper/Wood
- ☐ H. Soaps/Cleaners
- ☐ I. Paint/Coating/Ink
- ☐ J. Agrichemicals
- ☐ K. Stone/Glass/Cement
- ☐ L. Metals/Mining
- ☐ M. Machinery
- ☐ N. Auto/Aircraft
- ☐ O. Instrument/Controls
- ☐ P. Inorganic Chemicals
- ☐ Q. Organic Chemicals
- ☐ R. Other Manufacturing
- ☐ S. Design/Construction
- ☐ T. Utilities
- ☐ U. Consulting Services
- ☐ V. Federal Government
- ☐ W. State Government
- ☐ X. Municipal Government
- ☐ Y. Education

Membership status:
- ☐ 1. I am an ACS member
- ☐ 2. Not an ACS member

Circle 94 for subscription form to ES&T

NO POSTAGE
NECESSARY
IF MAILED
IN THE
UNITED STATES

BUSINESS REPLY CARD
FIRST CLASS Permit #27346 Philadelphia, Pa.

POSTAGE WILL BE PAID BY ADDRESSEE

Environmental
Science & Technology

P.O. BOX #7826
PHILADELPHIA, PA 19101

NO POSTAGE
NECESSARY
IF MAILED
IN THE
UNITED STATES

BUSINESS REPLY CARD

FIRST CLASS Permit #27346 Philadelphia, Pa.

POSTAGE WILL BE PAID BY ADDRESSEE

Environmental
Science & Technology

P.O. BOX #7826
PHILADELPHIA, PA 19101

ES&T READER SERVICE REPLY CARD. . . . .

It's computer processed

for fast

response

to your inquiries.

AND, IT'S

FREE

NEED MORE INFORMATION?

CIRCLE a key number. . .

SEND IN the postage paid reply card. . .

AND GET free data on any product advertised in this issue. . .

ES&T NOVEMBER 1980 VALID THROUGH MARCH 1981

ADVERTISED PRODUCTS: 1 2 3 4 5 6
7 8 9 10 11 12 13 14 15 16 17
18 19 20 21 22 23 24 25 26 27 28
29 30 31 32 33 34 35 36 37 38 39
40 41 42 43 44 45 46 47 48 49 50
51 52 53 54 55 56 57 58 59 60 61
62 63 64 65 66 67 68 69 70 71 72
73 74 75 76 77 78 79 80 81 82 83
84 85 86 87 88 89 90 91 92 93 94

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

NAME: ____________________
TITLE: ____________________
FIRM: ____________________
STREET: ____________________
CITY: ____________________
STATE: ____________ ZIP: ________

TO VALIDATE THIS CARD, PLEASE CHECK ONE ENTRY FOR EACH CATEGORY BELOW:

Intensity of product need:
☐ 1. Have salesman call
☐ 2. Need within 6 months
☐ 3. Future project

Employees at this location:
☐ 1. Under 25
☐ 2. 25 - 99
☐ 3. 100 - 299
☐ 4. 300 - 499
☐ 5. 500 - 999
☐ 6. 1000 - 2999
☐ 7. Over 3000

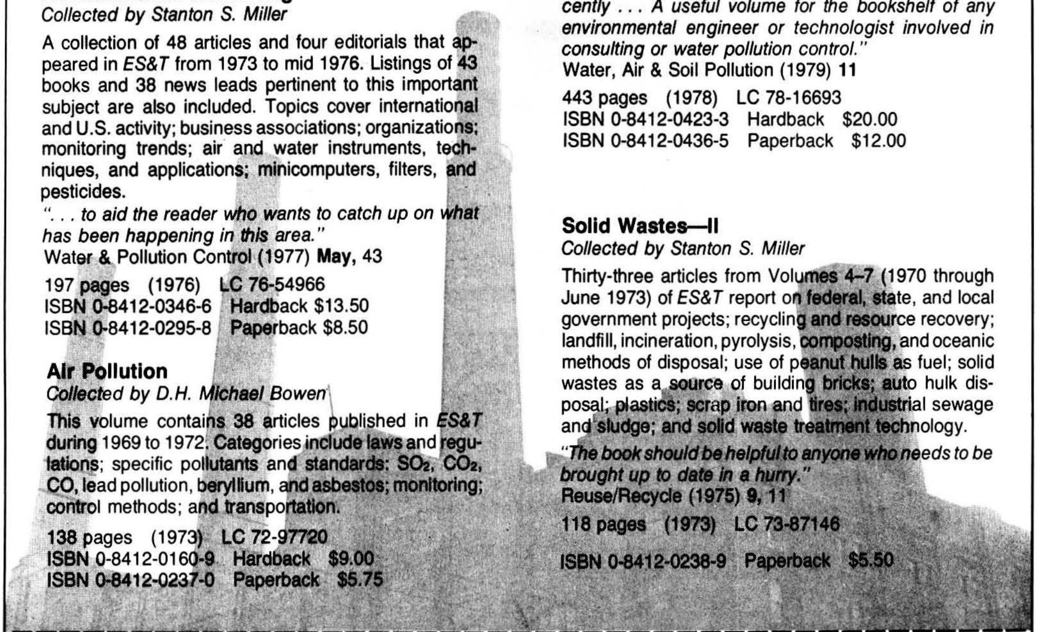
Areas of your responsibility:
☐ A. Air pollution only
☐ B. Water pollution only
☐ C. Waste treatment only
☐ D. Air & Water pollution
☐ E. Air & Waste treatment
☐ F. Water & Waste treat.
☐ G. Air/Water/Waste
☐ H. Other Environmental

This copy of ES&T is . . .
☐ 1. Personally addressed to me in my name
☐ 2. Addressed to other person or to my firm.

Principal product to which my work relates:
☐ A. Oil/Gas/Petroleum
☐ B. Plastics/Resins
☐ C. Rubber
☐ D. Drugs/Cosmetics
☐ E. Food/Beverages
☐ F. Textile/Fiber
☐ G. Pulp/Paper/Wood
☐ H. Soaps/Cleaners
☐ I. Paint/Coating/Ink
☐ J. Agrichemicals
☐ K. Stone/Glass/Cement
☐ L. Metals/Mining
☐ M. Machinery
☐ N. Auto/Aircraft
☐ O. Instrument/Controls
☐ P. Inorganic Chemicals
☐ Q. Organic Chemicals
☐ R. Other Manufacturing
☐ S. Design/Construction
☐ T. Utilities
☐ U. Consulting Services
☐ V. Federal Government
☐ W. State Government
☐ X. Municipal Government
☐ Y. Education

Membership status:
☐ 1. I am an ACS member
☐ 2. Not an ACS member

Circle 94 for subscription form to ES&T



ACS Reprint Collections for Environmental Scientists & Engineers

Control Technologies for Air Pollution
Collected by Stanton S. Miller

A collection of 50 articles that appeared in *ES&T* from 1973 to 1977 covering recent developments in the areas of air pollution control equipment, industries, transportation, incinerators, and clean coal and energy sources. A listing of 47 books and eight ACS titles on pertinent subjects are also included.

177 pages (1979) Hardback $15.00
LC 78-11630 ISBN 0-8412-0450-0

Environmental Monitoring
Collected by Stanton S. Miller

A collection of 48 articles and four editorials that appeared in *ES&T* from 1973 to mid 1976. Listings of 43 books and 38 news leads pertinent to this important subject are also included. Topics cover international and U.S. activity; business associations; organizations; monitoring trends; air and water instruments, techniques, and applications; minicomputers, filters, and pesticides.

"... to aid the reader who wants to catch up on what has been happening in this area."
Water & Pollution Control (1977) **May,** 43

197 pages (1976) LC 76-54966
ISBN 0-8412-0346-6 Hardback $13.50
ISBN 0-8412-0295-8 Paperback $8.50

Air Pollution
Collected by D.H. Michael Bowen

This volume contains 38 articles published in *ES&T* during 1969 to 1972. Categories include laws and regulations; specific pollutants and standards: SO_2, CO_2, CO, lead pollution, beryllium, and asbestos; monitoring; control methods; and transportation.

138 pages (1973) LC 72-97720
ISBN 0-8412-0160-9 Hardback $9.00
ISBN 0-8412-0237-0 Paperback $5.75

Water Pollution—II
Collected by Stanton S. Miller

A compilation of 136 articles that appeared in *ES&T* from mid 1973 to 1977. Articles are grouped according to federal and state policy; how, and to what extent military, business, and industrial groups are acting to implement standards and regulations; specific technology for wastewater applications; monitoring; specific pollutants; drinking water quality; wastewater treatment issues; and water pollution control federation activities.

"Page for page the book packs more information at the price than any other technical book . . . reviewed recently . . . A useful volume for the bookshelf of any environmental engineer or technologist involved in consulting or water pollution control."
Water, Air & Soil Pollution (1979) **11**

443 pages (1978) LC 78-16693
ISBN 0-8412-0423-3 Hardback $20.00
ISBN 0-8412-0436-5 Paperback $12.00

Solid Wastes—II
Collected by Stanton S. Miller

Thirty-three articles from Volumes 4–7 (1970 through June 1973) of *ES&T* report on federal, state, and local government projects; recycling and resource recovery; landfill, incineration, pyrolysis, composting, and oceanic methods of disposal; use of peanut hulls as fuel; solid wastes as a source of building bricks; auto hulk disposal; plastics; scrap iron and tires; industrial sewage and sludge; and solid waste treatment technology.

"The book should be helpful to anyone who needs to be brought up to date in a hurry."
Reuse/Recycle (1975) **9,** 11

118 pages (1973) LC 73-87146
ISBN 0-8412-0238-9 Paperback $5.50

SIS/American Chemical Society/1155 Sixteenth St., N.W./Washington, D.C. 20036

Please enter the following order:

TITLE	ISBN NO.	NO. OF COPIES	PRICE
			$
			$
			$
			$
			$
		Foreign orders please add 75¢	
		California residents add 6% state use tax	
		TOTAL	

Name (please sign) ______

Name (please print) ______

Institution ______ P.O. Box # ______

Address ______

City ______ State ______ Zip ______

☐ Payment enclosed. ☐ Bill me. ☐ Bill company.

WATER QUALITY MANAGEMENT UNDER CONDITIONS OF SCARCITY

Israel as a Case Study

Edited by HILLEL I. SHUVAL

A Volume in the WATER POLLUTION Series

FROM THE PREFACE: This book is devoted to the study of the problems of water quality management under conditions of severe water resource scarcity as it has evolved in Israel over the past thirty years. . . . It presents an authoritative analysis of the antecedents of these problems and suggests strategies for their solution. The solutions will require in many cases a radical departure from present policies and may require a total restructuring of the water administration. The main pollution processes that threaten the country's ground and surface water sources are presented in detail. While most of these water quality problems are universal, in Israel they are severely exacerbated by growing conditions of scarcity. Unique and often innovative approaches to analyze and control water quality problems have therefore been developed which can be of general application in other areas facing similar problems. The book also devotes attention to some of the organizational, economic, legal, and political aspects of water quality management that have evolved in Israel. Here, too, much can be learned from the Israeli experience . . . .

1980, 368 pp., $38.00 ISBN: 0-12-641280-4

POWER PLANTS: Effects on Fish and Shellfish Behavior

Edited by CHARLES H. HOCUTT, JAY R. STAUFFER, JR., JOHN E. EDINGER, LENWOOD W. HALL, JR., and RAYMOND P. MORGAN II

CHAPTER HEADINGS: *C. H. Hocutt*, Introduction. *J. R. Stauffer, Jr. and J. E. Edinger*, Power Plant Design and Fish Aggregation Phenomena. *B. C. Marcy, Jr. et al.*, Ecological and Behavioral Characteristics of Fish Eggs and Young Influencing Their Entrainment. *R. P. Morgan II*, Biocides and Fish Behavior. *J. R. Stauffer, Jr.*, Influence of Temperature on Fish Behavior. *C. H. Hocutt and J. E. Edinger*, Fish Behavior in Flow Fields. *C. H. Hocutt*, Behavioral Barriers and Guidance Systems. *L. W. Hall, Jr.*, Blue Crab Behavior in Relation to Power Plants. *J. M. Capuzzo and W. W. Reynolds*, Lobster Behavior in Relation to Power Plants. *L. I. Crawshaw et al.*, Crayfish Behavior in Relation to Power Plants. *G. E. Williams III and K. Strawn*, Effects of Power Plants on Penaeid Shrimp. *R. E. Hillman*, Behavior of Bivalve Molluscs. *R. P. Morgan II and J. R. Stauffer, Jr.*, Summary.

"Literature Cited" appears at the end of each chapter.

1980, 368 pp., $25.00 ISBN: 0-12-350950-5

ENVIRONMENTAL CHEMISTRY OF THE ELEMENTS

By H. J. M. BOWEN

This book is a complete revision of the author's successful work, *Trace Elements in Biochemistry* (Academic Press 1966), which reviewed information about the distribution of the chemical elements in the environment and living organisms. Current knowledge in this field has grown so rapidly since then that every chapter of the original book has had to be completely rewritten. This book aims at a comprehensive and critical rather than encyclopedic summary of the data of environmental inorganic chemistry. The first four chapters deal with the air, water, rocks and soils, and stress the dynamic nature of elemental cycling in these media. The cycling of the organic elements—carbon, hydrogen, oxygen, nitrogen and sulphur—in the biosphere has a chapter to itself. The elemental composition of living matter is reviewed with the help of tables of selected data. Other chapters are concerned with the uptake and excretion of elements by plants and animals, together with criteria for essentiality, toxicity and deficiency. Two chapters cover biological fractionation of isotopes, and the occurrence of natural and artificial radionuclides in the environment. Environmental disturbances through human activities are summarized in the penultimate chapter. A special feature is the last chapter which reviews the data available for each of the elements in turn. This important reference work emphasizes the concepts of cycling of elements in the environment and attempts to cover all the elements in an objective manner. Despite the wealth of published work in this field, much remains to be learned.

1979, 334 pp., $39.50 ISBN: 0-12-120450-2

Continuation Orders authorize us to ship and bill each volume in a series, or "Advances" type publication automatically, immediately upon publication. This order will remain in effect until cancelled. Specify the volume number or title with which your order is to begin.

Send payment with order and save postage and handling charge.
Prices are in U.S. dollars and subject to change without notice.

Academic Press, Inc.
A Subsidiary of Harcourt Brace Jovanovich, Publishers
111 FIFTH AVENUE, NEW YORK, N.Y. 10003/24-28 OVAL ROAD, LONDON NW1 7DX

CIRCLE 1 ON READER SERVICE CARD

ES&T
BOOKS

Environmental Procurement Register. Periodical, bi-weekly. Silverman Associates, Box 3091, Weehawken, NJ 07087. 1980 start-up. $175/year, with special charter rate of $150/year.

The publisher says that this publication is the "only one of its type in the U.S." It is aimed at giving equipment, service, and consultant firms a chance to reach the fast-growing government market for environmental control equipment and services. The directory will publish detailed, chronological listings of planned government procurements, bidders conferences, requests for prequalifications, and the like.

The Character and Origins of Smog Aerosols. George M. Hidy et al. xxii + 776 pages. John Wiley & Sons, Inc., 605 Third Ave., New York, NY 10016. 1980. $32.50, hardback.

The Aerosol Characterization Experiment (ACHEX), carried out in California, was one of the largest of its type ever run (1971-74). It generated numerous research papers, many of which are compiled in this book. The aerosols that make up photochemical smog are considered on meteorological, chemical, and particulate physical bases. Smog production mechanisms and other pertinent topics whose data were gleaned from ACHEX are discussed.

Ground Water and Energy. Harbridge House, Inc. ii + 23 pages. National Technical Information Service, 5285 Port Royal Rd., Springfield, VA 22161. 1980. $4.50, paper; $3, microfiche.

This is the report of the U.S. Department of Energy's National Workshop (Albuquerque, NM, January). It considers the nation's stock of groundwater, barriers to its use for energy production, and alternatives open.

Degradability, Ecotoxicity, and Bioaccumulation. Book No. 130-031-00. xxxi + 331 pages. In English. Staatsuitgeverij, Chr. Plantijnstraat, postbus 20014, 2500 EA's-Gravenhage, The Netherlands. 1980. About $156, four-ring binder.

This work discusses the determination of the possible effects of chemicals and wastes on the aquatic environment. It evaluates ecological effects in water, outlines methods for testing in a "how-to" fashion, discusses biological activity, and lists what reagents and laboratory ware are needed. A literature listing is also provided.

Fine Particle Emissions Information System (FPEIS), Second Annual Report. J. P. Reider, R. F. Hegarty. Publication No. PB80-195-753. National Technical Information Service, Springfield, VA 22161. 1980. $7.

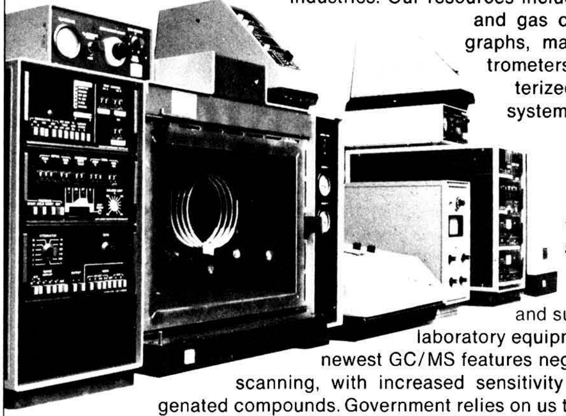
The FPEIS is a 64-page computerized data base on primary fine particle emissions from stationary sources. The compilers worked for the Midwest Research Institute (Kansas City, MO) under contract to EPA.

Evaluation of Ambient Air Quality by Personnel Monitoring. 2nd ed. Adrian L. Linch. Vol. 1, 336 pages; Vol. 2, 304 pages. CRC Press, Inc., 2000 NW 24th St., Boca Raton, FL 33431. 1980. Each volume, $69.95; outside U.S., add $10, hardback.

Volume 1 deals with gases and vapors, while Volume 2 covers aerosols, samplers, compliance with standards, and violation penalties. Workspace control and sampling techniques recommended by OSHA are also discussed.

Nuclear Power and Its Environmental Effects. Samuel Glasstone, Walter H. Jordan. 408 pages. American Nuclear Society, 555 N. Kensington Ave., La

(continued on page 1318)



Independent Analytical Solutions

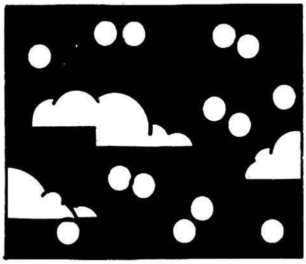
Solutions to problems in chemical analysis. We're West Coast Technical Service, Inc., and we're a leading independent test lab, serving the leaders in the electronics, aerospace and all chemical related industries. Our resources include: liquid and gas chromatographs, mass spectrometers, computerized GC/MS systems, atomic absorption and IR spectrophotometers, a thermal analysis system, and supporting laboratory equipment. Our newest GC/MS features negative-ion scanning, with increased sensitivity to halogenated compounds. Government relies on us too; we're one of a few labs who perform analyses for EPA. State and Municipal Government's use and certify our water/waste and effluent services. WCTS is also accredited by the American Industrial Hygiene Association; we can help head off hazardous liabilities in the work place.

When you need accurate, rapid chemical analysis, WCTS is YOUR independent solution. Call (213) 921-9831.

West Coast Technical Service, Inc.

17605, Fabrica Way, Cerritos, CA 90701 (213) 921-9831 • (714) 523-9200

CIRCLE 29 ON READER SERVICE CARD



Organometals and Organometalloids

Occurrence and Fate in the Environment

ACS Symposium Series No. 82

Fred E. Brinckman, *Editor*
National Bureau of Standards

Jon M. Bellama, *Editor*
University of Maryland

Based on a symposium sponsored by the Division of Inorganic Chemistry of the American Chemical Society

Order from:
SIS/American Chemical Society
1155 16th St., N.W./Wash., D.C. 20036

No one in the fields of bioinorganic or water chemistry should be without this valuable collection of up-to-date results and critical reviews by organometallic chemists and microbiologists concerned with the biogenic and abiotic factors governing transformations.

The books' approach is from an environmental and molecular standpoint focusing on aqueous reactions of organometals and organometalloids, and the nature of entry, transport, or uptake of these inorganic compounds into environmental compartments.

CONTENTS

Biosynthesis • Biotransformations of Sulfur • Occurrence of Biological Methylation of Elements in the Environment • B_{12}-Dependent Methyl Transfer to Certain Toxic Metal Ions • Aqueous Chemistry of Organolead and Organothallium Compounds • Bioorganotin Chemistry • Alkylation of Arsenic • Arsenic Uptake and Metabolism • Organometallic Cations in Aqueous Media • Organosilanes as Aquatic Alkylators of Metal Ions • Transmethylation between Aquated Metal Ions • Demethylation of Methylcobalamin • Mechanisms for Alkyl Transfers in Organometals • Formation of Transition Metal-Carbon Bonds in Protic Media • Organometallic Intermediates in a Protic Medium • Chloramine Equilibria • Chlorination • Ozone and Hydroxyl Radical-Initiated Oxidations • Organoelements in Octanol/Water/Air Systems • Biological Behavior of Mercury Compounds • Mercury, Lead, and Cadmium Complexation by Sulfhydryl-Containing Aminoacids • Release Mechanisms of Organotin Toxicants from Coating Surfaces • Metal-Ion Transport by Humic and Fulvic Acids • Organotins in Biology and the Environment

448 pages (1978) Clothbound $34.00
LC 78-24316 ISBN 0-8412-0461-6

Grange Park, IL 60525. 1980. $18.95, paper; $25.95, hardback.

This work presents a thorough review of nuclear power, the basic principles of reactors, and biological effects of natural and man-made radiation. Cooling systems, waste management, and similar topics are examined. The Three Mile Island accident, as well as reports and recommendations that followed it, are discussed in depth.

Diffusion and Ecological Problems: Mathematical Models. Akira Okubo. xiii + 254 pages. Springer-Verlag New York, Inc., 175 Fifth Ave., New York, NY 10010. 1980. $42.90, hardback.

This is Volume 10 of the Biomathematics Series. It covers diffusion in general, passive diffusion in ecosystems, animal diffusion (such as fish schooling), population dynamics, and many other relevant subjects from a mainly mathematical standpoint. The mathematics is often expressed in pictorial terms.

Wastewater Treatment and Resource Recovery. 47 pages. International Development Research Centre, Box 8500, Ottawa, Ont. K1G 3H9, Canada. 1980. Inquire about price, paper.

This book reports on a workshop, held in Singapore in February, on high-rate algae ponds. It looks into sludge recycling in such ponds, microbial treatment/utilization of night soil, rates of nutrient removal, algae culture, single-cell protein, and other items. Pond functioning in tropical areas is emphasized.

Sensory Assessment of Water Quality. B. C. J. Zoetman. xiv + 148 pages. Pergamon Press, Maxwell House, Fairview Park, Elmsford, NY 10523. 1980. $28, hardback.

This is Volume 2 of the Pergamon Series on Environmental Science. It discusses theory and practice of sensory assessment—principally taste assessment—of water quality. It can be used for evaluating both organic and inorganic constituents.

The Wooing of Earth. René Dubos. xv + 183 pages. Charles Scribner's Sons, 597 Fifth Ave., New York, NY 10017. 1980. $8.95, hardback.

The author maintains that man's exploitation of the natural world is not a recent phenomenon and that animals also mold their environments to their own advantage. He says that man has not always despoiled nature—in many cases, man has in fact embellished nature. The author also points out that nature has great powers of resilience.

Survey of Contemporary Toxicology. Vol. 1. Anthony T. Tu, Ed. ix + 357 pages. John Wiley & Sons, Inc., 605 Third Ave., New York, NY 10016. 1980. $39.50, hard cover.

As *The Wall Street Journal* reminded its readers (Sept. 4, 1980), toxicology, once an "obscure science," is now coming very much to the forefront. This book looks at latest developments in this science, including water pollutants, food additives, plant toxins, industrial toxicology, marine toxins, and foodborne diseases.

The Environmentalist. David Hughes-Evans, James L. Aldrich, Eds. Periodical. Elsevier Sequoia S.A., Box 851, CH-1001 Lausanne 1, Switzerland. $90.50 for 4 issues/year.

This publication will first appear next spring. It is aimed at professional people concerned with information, communication, education, training, and public awareness in the area of environmental protection.

Solar Voltaic Cells. W. D. Johnston, Jr. x + 210 pages. Marcel Dekker Inc., 270 Madison Ave., New York, NY 10016. 1980. $29.75, hardback.

Solar voltaic cells produce electricity directly from solar radiation. This book discusses costs, established and novel schemes, fabrication technology, mass production problems, equipment lifetimes, and other subjects pertaining to solar cells and their potential improvement.

Ozone and Chlorine Dioxide Technology for Disinfection of Drinking Water. J. Katz, Ed. xii + 659 pages. Noyes Data Corp., Mill Rd. at Grand Ave., Park Ridge, NJ 07656. 1980. $36, hardback.

This book looks at the recent state of the art in O_3 and ClO_2 approaches to water disinfection. It discusses microbiological aspects, disinfectant residual measurement, biological activated carbon, oxidation of organic materials, public health aspects, the chemical nature of O_3 and ClO_2, and many related matters.

Trace Chemistry of Aqueous Solutions. Petr Beneš, Vladimír Majer. 252 pages. Elsevier Scientific Publishing Co., 52 Vanderbilt Ave., New York, NY 10017. 1980. $56, hardback.

This book offers an original treatment of the physicochemical properties and behavior of very low concentrations of substance in aqueous solutions, concentrations that could comprise contaminants and pollutants. Particular emphasis is accorded state/behavior of traces of substances, and how there are differences from normal or macro conditions. This work, Monograph 18 of a series, addresses general chemistry and radiochemistry.

Remote Sensing: Optics and Optical Systems. xvi + 575 pages. Addison Wesley Publishing Co., Reading, MA 01867. 1980. $34.50, hardback.

This book deals with the actual physics, mechanics, and operations of remote sensing from aircraft and space. It discusses optics and the eye, photographic image recording, space systems, problems with electronic "noise" and electromagnetic radiation, and other pertinent topics.

Renewable Resources: A Systematic Approach. Enrique Campos-López, Ed. x + 410 pages. Academic Press, 111 Fifth Ave., New York, NY 10003. 1980. $29.50, hardback.

This book examines two major aspects of renewable resources: systems and models, and scientific and technological trends. Among resources considered are forests, fuels and crops, chemical feedstocks, biomass, microbial technology, and botanical sources of pharmaceuticals. Economics and social impacts are also discussed.

Toxic and Hazardous Waste Disposal. Vol. 4. Robert B. Pojasek, Ed. x + 313 pages. Ann Arbor Science, Box 1425, Ann Arbor, MI 48106. 1980. $39.95, hardback.

This volume deals with "new and promising ultimate disposal options." It examines minimizing land disposal risks, secure landfills, hazardous chemical leachate testing, uses for stabilized industrial waste, heavy-metal fixation, incineration, deep-well disposal, and other possible solutions.

Land, Man, and Sand. James Walls. xi + 336 pages. Macmillan Publishing Co., Inc., 866 Third Ave., New York, NY 10022. 1980. $19.95, hardback.

"Desertification and Its Solutions" is the subtitle of this book, which consists of 16 case studies with exotic names such as Oglat Merteba, Turfan, and Golodnaya Step'. The book explains how the desert areas under study became what they are today, and what actions—farming methods, irrigation, plant species use—are being tried to restore them to life.

ES&T

MEETINGS

November 17–20 Hollywood Beach, FL
Coastal Zone 80. American Society of Civil Engineers and Dept. of Commerce
Write: Orville Magoon, Box 26062, San Francisco, CA 94126

November 18–20 Philadelphia, PA
Symposium on Iron and Steel Pollution Abatement Technology. Industrial Environmental Research Laboratory and U.S. EPA
Fee: $50. *Write:* Franklin Ayer, Research Triangle Institute, Box 12194, Research Triangle Park, NC 27709

November 19–21 New York, NY
Eastern Analytical Symposium. American Chemical Society, Society for Applied Spectroscopy, and American Microchemical Society
Write: Ivor Simmons, EAS, Box 1104, Rahway, NJ 07065

November 20–21 Raleigh, NC
Formaldehyde Toxicity. Chemical Industrial Institute of Technology
Fee: $100. *Write:* CIIT, Box 12137, Research Triangle Park, NC 27709

November 24–25 Arlington, VA
SETAC Annual Meeting. Society of Environmental Toxicology and Chemistry
Write: Richard Tucker, SETAC, Box 352, Rockville, MD 20850

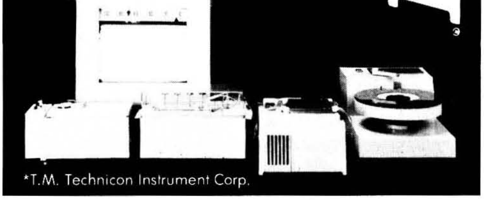
November 30–December 3 Phoenix, AZ
7th National Conference on Energy and the Environment. U.S. EPA and U.S. DOE
Write: Joseph Reynolds, Manhattan College, Riverdale, NY 10471

December 1–3 Arlington, VA
Peat as an Energy Alternative. Institute of Gas Technology
Fee: $390. *Write:* Kathy Fisher, IGT, 3424 S. State St., Chicago, IL 60616

December 2–3 Washington, DC
Hazardous Waste Management Under RCRA and Consolidated Permits. The Energy Bureau, Inc.
Write: Robert Nash, The Energy Bureau, Inc., 41 E. 42nd St., New York, NY 10017

December 2–4 Philadelphia, PA
2nd Biennial Symposium on Applications of Quantitative TLC. Whatman Inc. in conjunction with Dr. J. Touchstone
Write: Joseph Touchstone, Hospital of the University of PA, Philadelphia, PA 19104

(continued on page 1323)



professional consulting services directory

ENVIRONMENTAL PLANNING and PROBLEM SOLVING for INDUSTRY and GOVERNMENT

• AIR • WATER • SOLIDS • NOISE • ODOR

- Measurement
- Impact Assessment
- Control
- Permit Planning
- Information Systems
- Modeling

TRC Environmental Consultants, Inc.

125 Silas Deane Highway
Wethersfield, Ct. 06109
(203) 563-1431

8776 East Orchard Rd.
Suite 816
Englewood, CO 80111
(303) 779-4940

DAMES & MOORE

Engineering and Environmental Consultants

Geotechnical and Environmental Engineering
Environmental Impact Assessment
Meteorology and Air Quality Monitoring
Water Pollution Control Engineering
Modelling and Numerical Analyses
Permitting and Licensing Consultation

San Francisco • Denver
Chicago • New York • Atlanta
Offices in Principal Cities Throughout the World

POLLUTION ABATEMENT

Custom engineering and construction of pollution abatement facilities.

POLLUTION ABATEMENT GROUP

BAKER BROS.

DIVISION OF SYSTEMS ENGINEERING AND MANUFACTURING CORP

International Headquarters — Telex 924-328
(617) 344-1700 — CAMPANELLI PARKWAY STOUGHTON, MASS 02072

SpectroChem LABORATORIES INC.

545 Commerce St. — Franklin Lakes, N. J. 07417
201-337-4774 — 201-891-8787

- Atomic Absorption
- Chemical
- Optical Emission
- X-ray Spectrometry

Complete Analytical Services for Environmental Studies & Pollution Control

---

ENVIRONMENTAL CONSULTANTS INC

ANALYTICAL TESTING AND SAMPLING SERVICES:

- EPA—Drinking water
- Certified bacteriological testing
- N.P.D.E.S. Permit
- Priority pollutant analysis
- Workplace environments
- EPA Hazardous wastes evaluation
- Particle identification and sizing
- Process Quality Control
- Research and Development

USING:

Gas chromatography/Mass spectrometry; Atomic Absorption Spectroscopy; Infrared spectroscopy; Microscopy; TOC; E.P.A. and OSHA certified methods.

CONSULTATION—PLANNING

391 NEWMAN AVE
CLARKSVILLE, INDIANA 47130
812-282-8481

WATER
WASTEWATER
SOLID WASTES

• Chicago
• New York
• Philadelphia
• Richmond
• Tampa
• Atlanta
• Phoenix

222 S. Riverside Plaza Chicago 60606

GREELEY AND HANSEN

ENGINEERS
Since 1914

Environmental Testing Services

- EPA Priority Pollutants—GC/MS
- Hazardous Waste Characterization
- Work Environment Analyses
- Organic/Inorganic Analyses
- TOC and TOCL

Water • Effluents • Soils • Sludges

Plug in **The Research Connection**

FOREMOST RESEARCH
6363 Clark Avenue
Dublin, California 94566
(415) 828-1440

WILSON LABORATORIES

ANALYTICAL & RESEARCH CHEMISTS & BIOLOGISTS
A DIVISION OF WILSON & COMPANY, ENGINEERS & ARCHITECTS
AAA Certification in Kansas, Missouri, Oklahoma and New Mexico

✱ AIR, WATER & NOISE POLLUTION
✱ PROCESS STUDIES — SYSTEMS DESIGN
✱ WATER, SEWAGE & WASTE SYSTEMS

Complete Laboratory Services

SALINA, KS 67401
528 N. 9TH ST.
(913) 825-7186

CAMP DRESSER & McKEE INC.
Offices Throughout the U.S.

One Center Plaza
Boston, Massachusetts 02108

CDM

environmental engineers, scientists, planners, & management consultants

---

Woodward-Clyde Consultants

- Site Selection Studies
- Impact Assessment Evaluation
- Decision and Risk Analyses
- Environmental Field and Laboratory Studies

Environmental Systems Division
Headquarters: San Francisco, CA

**Other offices in Clifton, NJ • Washington, D.C. Anchorage, AK • San Diego, CA*

RMT LABORATORIES

RESIDUALS MANAGEMENT TECHNOLOGY, INC.
CONSULTANTS IN INDUSTRIAL SOLID AND HAZARDOUS WASTE MANAGEMENT

Specializing in Waste Analyses:

- Hazardous Waste
- Leaching tests
- RCRA Regulations
- Ground & surface water monitoring
- NPDES Permits
- Waste water
- Drinking water

1406 E. WASHINGTON AVE. BOX C SUITE 124 MADISON, WI 53703 (608) 255-2134

Scott Environmental Technology, Inc.

The Air Pollution Specialists

• Research and Consulting •
• Source Emissions Testing •
• Control Device Efficiency •
• Continuous Source Monitoring •
• Ambient Monitoring •
• Fuel Additive & Automotive Testing •

Route 611, Plumsteadville, PA 18949
215 – 766-8861
2600 Cajon Blvd., San Bernardino, CA 92411
714 – 887-2571
1290 Combermere St., Troy, MI 48084
313 – 589-2950

HAVENS AND EMERSON, INC.

Environmental Engineers

Cleveland, OH — Saddle Brook, NJ
Atlanta, GA — St. Louis, MO

LFE CORPORATION

ENVIRONMENTAL ANALYSIS LABORATORIES

• RADIOLOGICAL SERVICES • INDUSTRIAL WASTE • WATER • SOILS & SEDIMENTS • VEGETATION • SOURCE TESTS • GEOTHERMAL SURVEYS • OCCUPATIONAL SAFETY & HEALTH

2030 Wright Avenue
Richmond, CA — **(415) 235-2633**

professional consulting services directory

Precision Meteorological Instruments

CAPABILITY PERFORMANCE

Environmental Services For:

- Air Quality
- Energy Development and Use
- Meteorological Engineering
- Field Data Collection

Meteorology Research, Inc.
464 West Woodbury Road
Altadena, California 91001
(213) 791-1901
Telex-675421
A Subsidiary of Cohu, Inc.

mri

COMPLETE ENVIRONMENTAL SERVICES

- PERMIT PLANNING
- AMBIENT MONITORING
- METEOROLOGY & DIFFUSION MODELING
- ENVIRONMENTAL IMPACT STATEMENTS
- ORGANIC/INORGANIC ANALYSES
- HAZARDOUS WASTE CHARACTERIZATION & CONTROL
- PROCESS/CONTROL ENGINEERING
- ENERGY SYSTEMS STUDIES
- STACK TESTING

GCA offers 20 years experience serving Industry & Government.

For Information Contact
V.P. Marketing

GCA

GCA CORPORATION
Technology Division
213 Burlington Rd., Bedford, Mass 01730
(617) 275-5444

RAYTHEON

OCEAN SYSTEMS CO.

Environmental & Oceanographic Services

**P.O. Box 360, Portsmouth, RI,
USA, 02871, (401)847-8000**

Complete Analytical Services
SINCE 1919

- Screening of Industrial Waste for EPA Priority Pollutants using Finnigan OWA-30 GC/MS.
- NPDES & SPDES Organic & Inorganic Testing.
- Drinking Water Analysis to EPA Standards.
- Bioassay, Bioaccumulation & Toxicity Studies of Industrial Waste, Municipal Sludge & Dredge Spoils.
- Leachate Potential Studies & Analysis.
- Total Instrumental Analysis: A.A., GC/MS, G.C., I.R., TOC & TOD.

NEW YORK TESTING LABORATORIES
81 Urban Avenue, Westbury, N.Y. 11590
(516) 334-7770

Since 1885
Service to Industry
Stearns-Roger

COMPLETE ENVIRONMENTAL SERVICES:

Environmental impact assessments . . . Pollutant emission, air quality & water quality monitoring . . . Dispersion estimates . . . Ecological consulting . . . Meteorological field studies & consulting services. Contact

ENVIRONMENTAL SCIENCES DIVISION
(303) 758-1122

P. O. Box 5888
Denver, Colorado 80217

Laboratory and Process Development
Industrial Waste Water Control
Liquid and Solid Incineration
Air Pollution Control
In-Plant Control and Process Modifications
Environment Impact and Permits

CATALYTIC, INC.

Consultants • Engineers • Constructors
Environmental Systems Division
Centre Square West
1500 Market St.,
Philadelphia, PA 19102 • 215-864-8000
Charlotte, NC 704-524-4220
Baton Rouge, LA 504-293-6200

TAMS
ENGINEERS AND ARCHITECTS

Environmental Planning Department
655 Third Avenue, New York, N.Y. 10017
(212) 867-1777

- Environmental Impact Studies
- Aquatic and Terrestrial Ecology
- Natural Resources Planning
- Land Use Planning
- Socioeconomic Studies
- Air, Noise and Water Quality
- Field and Laboratory Services

Washington, D.C. Boston Seattle
Anchorage

Ground Water Associates, Inc.

Water Supply Geologists and Engineers

- **Quantitive and qualitative ground water evaluations**
- **Iron removal by VYREDOX process**

P.O. Box 280
Westerville, Ohio 43081
614/882-3136

Cranford, New Jersey
Arlington, Massachusetts

Enviro-Med Laboratories, Inc.

414 W. CALIFORNIA · RUSTON, LA. 71270 · 318-255-0060
1012 S. ACADIAN THRUWAY · BATON ROUGE, LA. 70806 · 504-343-4314

Sampling, Testing, and Consulting
HAZARDOUS WASTE—AIR—SOLID WASTE—GC/MS PRIORITY POLLUTANTS—WASTEWATER

MESOMET INC
Computerized Meteorological and Environmental Services
Dr. Walter A. Lyons, President
Certified Consulting Meteorologists

- Power plant fumigation studies
- Shoreline and coastal zone meteorological measurement and analyses
- Long Range Pollution Transport Assessment
- Cost effective use of remote sensing technology including acoustic sounders
- Mesoscale air pollution and meteorological models
- 24-Hour Operational Forecasting Center for ICS. Field Program Support

35 East Wacker Drive, Chicago, Ill. 60601
(312) 263-5921
Washington Area Office (301) 292-5303

USE THE CONSULTANTS' DIRECTORY

RATES PER ISSUE

UNIT	Six Issues	Twelve Issues
1″ x 1 col.	$ 39	$ 37
1″ x 2 col.	77	72
1″ x 3 col.	113	101
2″ x 1 col.	77	72
2″ x 2 col.	144	131
4″ x 1 col.	144	131

Your card may appear in every issue for one year, every issue for six months (consecutive issues), or every other issue for one year (alternate issues). Send your copy to:

Donna C. Bifano
ENVIRONMENTAL SCIENCE & TECHNOLOGY
25 Sylvan Road South Westport, CT. 06880
or call her at 203-226-7131

December 7–10 Miami Beach, FL
Water Quality Technology Conference. American Water Works Association

Write: AWWA Meetings Dept., 6666 W. Quincy Ave., Denver, CO 80235

December 7–11 Honolulu, HI
National Conference on Renewable Energy Technologies. U.S. DOE and the Western Solar Utilization Network

Fee: $175. *Write:* NREC Coordination Center, Box 2198, Honolulu, HI 96805

December 9–11 Columbus, OH
National Waste Terminal Storage for Radioactive Waste. U.S. DOE

Write: Lorena McGee, Battelle, Office of Nuclear Waste Isolation, 505 King Ave., Columbus, OH 43201

December 10 Washington, DC
Cogeneration: The New Regulatory Environment. The Energy Bureau, Inc.

Write: Robert Nash, The Energy Bureau, Inc., 41 E. 42 St., New York, NY 10017

Courses

November 10–13 Houston, TX
Industrial Waste Incineration Technology. The Center for Professional Advancement

Fee: $660. *Write:* Edith Webb, Registrar, Box 964, East Brunswick, NJ 08816

November 11–12 Houston, TX
Strategic Planning for Disposal of Solid Wastes. Center for Energy and Environmental Management

Fee: $330. *Write:* CEEM, Box 536, Fairfax, VA 22030

November 17–19 Austin, TX
December 1–3 Atlanta, GA
December 8–10 Chicago, IL
Hazardous Waste Engineering. Vanderbilt University School of Engineering

Fee: $475. *Write:* Janet Vance, Vanderbilt University, Box 1525, Sta. B, Nashville, TN 37235

November 17–21 Charlotte, NC
Industrial Hygiene Monitoring and Control. University of North Carolina

Fee: $215. *Write:* Office of Continuing Education, Univ. of North Carolina School of Public Health 251H, Chapel Hill, NC 27514

November 19–20 Madison, WI
Passive Solar Building Design. University of Wisconsin–Extension, Engineering

Fee: $175. *Write:* Donald Schramm, Dept. of Engineering, Univ. of Wisconsin-Extension, 432 N. Lake St., Madison, WI 53706

November 24–25 Washington, DC
Understanding and Controlling Particulate Emissions. George Washington University

Fee: $375. *Write:* Director, Continuing Engineering Education Program, George Washington University, Washington, DC 20052

November 24–25 New York, NY
The Energy Revolution: Its Impact on Industry and Society. Energy Magazine

Fee: $325. *Write:* Energy Magazine, Dept. C8, Box 2070C, Stamford, CT 06906

November 24–25 University Park, PA
Visible Emissions Training Program. Pennsylvania State University

Fee: $100. *Write:* Norman Lathbury, Keller Conference Center, Penn State, University Park, PA 16802

December 1–2 Washington, DC
Toxic Control Seminar. Government Institutes, Inc.

Fee: $345. *Write:* Government Institutes, Box 5918, Washington, DC 20014

December 1–5 Phoenix, AZ
Practical Aspects of Industrial Hygiene. American Industrial Hygiene Association

Fee: $450. *Write:* ATHA, 475 Wolf Ledges Pkwy., Akron, OH 44311

December 8–12 Asheville, NC
Basic Industrial Hygiene. University of North Carolina

Fee: $245. *Write:* Registrar, Office of Continuing Education, Univ. of North Carolina School of Public Health 251H, Chapel Hill, NC 27514

International

December 15–18 Miami Beach, FL
3rd Miami International Conference on Alternative Energy Sources. Clean Energy Research Institute and the University of Miami

Write: Clean Energy Research Institute, Univ. of Miami, Box 248294, Coral Gables, FL 33124

Call for Papers

January 31 deadline
12th Annual Pittsburgh Conference on Modeling and Simulation. School of Engineering, University of Pittsburgh

The conference will be held April 30–May 1, 1981. *Write:* William Vogt, 348 Benedum Engineering Hall, Univ. of Pittsburgh, Pittsburgh, PA 15261

professional consulting services directory

CLASSIFIED SECTION ■ POSITIONS OPEN

ENVIRONMENTAL SCIENTIST

Ecology and Environment, Inc., with offices in 16 U.S. cities and 9 countries, offers outstanding growth opportunities for experienced environmental scientists and engineers. Our consulting projects range from environmental monitoring of the Trans-Alaska Pipeline to studies for the new industrial complex at Yanbu on the Red Sea. Founded in 1970, E & E is expanding rapidly in all areas of environmental consulting.

Currently, we are seeking environmental generalists with master's degrees in related fields and 4–7 years experience in industry or government. Available career positions will be based at our Buffalo headquarters to manage and support E & E projects in alternate energy development (synfuels) and other critical environmental problems facing the nation in the '80s.

Interested candidates should send a current resume and salary requirements to Joan Collins at:

ecology and environment, inc.
International Specialists in the Environmental Sciences

P.O. Box D,
Buffalo, New York 14225
AN EQUAL OPPORTUNITY EMPLOYER

FACULTY POSITION (ENVIRONMENTAL ENGINEERING) FACULTY POSITION UNIVERSITY OF MIAMI

The Department of Civil Engineering is soliciting applications for a tenure track position in Environmental Engineering at the Assistant or Associate Professor level. The applicant should have a Ph.D. in Environmental Engineering, Civil Engineering or Chemical Engineering with emphasis in Water Pollution Control. Preference will be given to those applicants with a background in Environmental Chemistry, Water Treatment, or Physicochemical processes. The successful candidate should have a demonstrated ability to teach effectively and develop meaningful research. An equal opportunity/affirmative action employer.

Send resume, and references to:

Dr. Thomas Waite,
Environmental Engineering
Dept. Civil Engineering
University of Miami
Coral Gables, Florida 33124

INDUSTRIAL POSITIONS AVAILABLE

Various U.S. locations. Minimum requirements are a BS degree and two years U.S. experience in design and use of equipment and systems for environmental control and assessment. Client companies pay agency fee plus interview and relocation. Send resume and current salary or call collect (215) 735-4908 for confidential application.

ATOMIC PERSONNEL, INC., Box J-1
1518 Walnut St., Philadelphia, Pa. 19102

SENIOR ENVIRONMENTAL ENGINEERS

WAPORA, Inc., a leading environmental contract research company, is looking for senior environmental engineers for its offices in New York City; suburban Philadelphia; Chevy Chase, Maryland; Atlanta; Cincinnati; Dallas and Chicago. Environmental impact experience highly desirable. Project management positions, as well as administrative openings exist for personnel who can manage programs, write well, and help in marketing.

Send resume, including salary history, in confidence to:

WAPORA, Inc.
6900 Wisconsin Avenue
Chevy Chase, MD 20015
Attn: Dr. J. I. Bregman, President

EOE M/F Principals Only

ENVIRONMENTAL HEALTH SCIENTIST

Full time teaching with opportunity for program directorship. B.S. Environmental Health Program Graduate degree required. Field experience essential. Rank and salary dependent upon education and experience. Send resumes to Chairman, Biological Sciences, Quinnipiac College, Hamden, Connecticut 06518. Equal Opportunity Affirmative Action Employer.

TERRESTRIAL ECOLOGIST

Position available for Terrestrial Ecologist on Community Environmental Planning Staff of international transportation engineering firm. Position requires a master's degree and 2–4 years experience in wild life management, botany, terrestrial ecology or a directly related field. Candidate must have superior writing skills and be able to integrate technical input with a variety of professional disciplines. Knowledge and/or experience in environmental impact assessment, environmental planning, natural resource management and federal environmental regulations valuable.

Successful candidate will participate in interdisciplinary planning and design assignments related to land use, transportation systems, and natural resource development. Responsibilities will include public/agency coordination, environmental analysis and documentation and report preparation.

We offer a full range of benefits including 100% tuition reimbursement. Send resume to:

David M. Kennedy
Manager of Recruiting
DeLeuw, Cather & Co.
165 W. Wacker Dr.
Chicago, IL. 60601

An Equal Opportunity Employer M/F

DeLEUW CATHER

SANITARY ENGINEER ENVIRONMENTAL ENGINEER

Permanent position available for:

- **Registered Engineer with M.S. in Sanitary/Environmental Engineering.**

Must have 2 to 5 years experience in wastewater treatment facilities planning and design or hazardous toxic waste disposal and solid waste resource recovery.

Send qualifications to:

Mr. L. R. Collins, Director of Personnel
Burk and Associates, Inc.
4176 Canal St., New Orleans, La. 70119

Equal Opportunity Employer

Tenure-track faculty position in a four-year Engineering Technology curriculum which emphasizes environmental pollution control. The program stresses hands-on experience as well as an understanding of basic theory. To fill the position an individual should hold a Master of Science and have at least 3 years of experience in one or more of the following areas: air, water, solid or hazardous waste, or nuclear and radiation pollution control. Registration or the ability to become registered as a professional engineer is desirable. A strong commitment to undergraduate teaching is essential. Norwich University is located in an area of Central Vermont that offers small town or rural living, with good schools and outstanding recreational opportunities. The position will be available 15 January 1981, and will be filled at the Assistant Professor level. Send resume and references to: Dr. John F. Van Domelen, Head, Engineering & Technology Department, Norwich University, Northfield, Vermont 05663. Norwich University is an equal opportunity/affirmative action employer.

FACULTY POSITION

DEPARTMENT OF ENVIRONMENTAL SCIENCES AND ENGINEERING. A senior faculty position will be available in summer or fall 1981 for an environmental chemist with demonstrated excellence and current research interests in cycling and fate of elements in the aquatic environment, emphasizing major systems or the biosphere. Teaching and research will contribute to the Environmental Chemistry and Biology Program Area which aims to integrate basic principles of chemistry and biology with problems of aquatic pollution and environmental deterioration. Rank and salary commensurate with experience. Send resumé and names of at least three references to **Dr. Edward J. Kuenzler, Department of Environmental Sciences and Engineering, University of North Carolina, Chapel Hill, N.C. 27514** before December 15, 1980. An equal opportunity/affirmative action employer.

Environmental Engineers for Israel

The Environmental Protection Service, Ministry of the Interior, Jerusalem, Israel, is the government agency charged with the responsibility for protection of the environment in the State of Israel. It is a small interdisciplinary group that establishes environmental policies, develops new legislation and standards, reviews impact statements of large development projects, enforces environmental laws and consults with land-use planning authorities.

We have immediate positions for qualified chemical and/or process engineers. Successful candidates will be involved with a wide range of environmental problems related to industrial, transportation and agricultural development. Experience should include a MS/Ph.D. and a minimum of three years experience in related fields. Positions will be offered to candidates who consider immigrating to Israel. Please contact or send resume in complete confidence to Dr. Uri Marinov, Director, Environmental Protection Service, c/o Tennessee Valley Authority, Norris, Tennessee 37828. Work telephone 615-494-9800; home telephone 615-691-1088.

Engineering Office looking for engineer to provide specialty consulting services in the construction industry in the area of environmental control and energy conservation. Must have intimate knowledge of construction industry, marketing and sales experience and be able to work independently. 40 hours per week—$12.00 per hour. Send resumes to Missouri Division of Employment Security, Attention: Mr. Hurley, 8671 Olive Boulevard, St. Louis County, Missouri 63132.

INDEX TO THE ADVERTISERS IN THIS ISSUE

Advertising Management for the
American Chemical Society Publications

CENTCOM, LTD.

Thomas N. J. Koerwer, President; James A. Byrne, Vice President; Alfred L. Gregory, Vice President; Clay S. Holden, Vice President; Benjamin W. Jones, Vice President; Robert L. Voepel, Vice President; 25 Sylvan Rd. South, Westport, Connecticut 06881 (Area Code 203) 226-7131

ADVERTISING SALES MANAGER
Alfred L. Gregory

SALES REPRESENTATIVES

Atlanta, Ga. . . . Donald B. Davis, CENTCOM, LTD., Phone (Area Code 203) 226-7131
Boston, Ma. . . . Thomas Carey, CENTCOM, LTD., (Area Code 212) 972-9660
Chicago, Ill. . . . Bruce Poorman, CENTCOM, LTD., 540 Frontage Rd., Northfield, Ill 60093 (Area Code 312) 441-6383
Cleveland, Oh. . . . Bruce Poorman, CENTCOM, LTD., 17 Church St., Berea, OH 44017 (Area Code 216) 234-1333
Denver, Co. . . . Clay S. Holden, CENTCOM, LTD., (Area Code 213) 325-1903
Houston, Tx. . . . Robert E. LaPointe, CENTCOM, LTD., (Area Code 415) 781-3430
Los Angeles, Ca. . . . Clay S. Holden, Robert E. LaPointe, CENTCOM, 3142 Pacific Coast Highway, Suite 200, Torrance, CA 90505, (Area Code 213) 325-1903
New York, N.Y. . . . Thomas Carey, CENTCOM, LTD., 60 E. 42nd Street, New York 10165 (Area Code 212) 972-9660
Philadelphia, Pa. . . . Thomas Carey, CENTCOM, LTD., GSB Building, Suite 510, 1 Belmont Ave., Bala Cynwyd, Pa 19004 (Area Code 215) 667-9666
San Francisco, Ca. . . . Robert E. LaPointe, CENTCOM, LTD., Suite 303, 211 Sutter Street, San Francisco, CA 94108. Telephone: 415-781-3430
Westport, Ct. . . . Thomas Carey, CENTCOM, LTD., 25 Sylvan Rd. South, Westport, Ct. 06881, (Area Code 203) 226-7131
United Kingdom
Reading, England . . . Malcolm Thiele, Technomedia Ltd., Wood Cottage, Shurlock Row, Reading RG10 OQE. Telephone: 073-581-302
Continental Europe . . . Andre Jamar, Rue Mallar 1, 4800 Verviers, Belgium. Telephone: (087) 22-53-85. Telex No. 49263
Tokyo, Japan . . . Shigeo Aoki, International Media Representatives Ltd., 2-29 Toranomon 1-chrome, Minato-Ku, Tokyo 105 Japan. Telephone: 502-0656

PRODUCTION DEPARTMENT

PRODUCTION DIRECTOR
Joseph P. Stenza

PRODUCTION MANAGER
Donna C. Bifano

CLASSIFIED SECTION

POSITIONS OPEN

CLASSIFIED ADVERTISING RATES

Rate based on number of insertions used within 12 months from date of first insertion and not on the number of inches used. Space in classified advertising cannot be combined for frequency with ROP advertising. Classified advertising accepted in inch multiples only.

Unit	1-T	3-T	6-T	12-T	24-T
1 inch	$70	$67	$64	$62	$60

(Check Classified Advertising Department for rates if advertisement is larger than 10".)
SHIPPING INSTRUCTIONS: Send all material to

Environmental Science & Technology
Classified Advertising Department
25 Sylvan Rd. South
Westport, CT. 06880
(203) 226-7131

ES&T RESEARCH

Sorption of Copper and Lead by Hydrous Ferric Oxide

Kathleen C. Swallow,[*†] **David N. Hume, and François M. M. Morel**[‡]

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

■ Sorption of Cu^{2+} or Pb^{2+} on amorphous hydrous ferric oxide was unaffected by aging of the solid over several days, by variations in ionic strength from 0.005 to 0.5, or by changes in the nature of the background electrolyte from $NaClO_4$ to a complex artificial seawater mix. (Only Pb^{2+} sorption decreased because of complexation by Cl^- at high concentration.) Competition between Cu^{2+} and Pb^{2+} was difficult to demonstrate because saturation of the surface was not achieved with either metal before precipitation of the corresponding metal hydroxide. Competition was demonstrated between Cu^{2+} and Fe^{2+} in an oxygen-free system with a large excess of Fe^{2+}, providing an estimate of total adsorption sites of ca. one site per Fe atom. Systematic variations in sorbing metal and hydrous ferric oxide concentrations showed that the sorption process can be approximately described as a simple mass action law. The corresponding adsorption constant which increases with pH with a slope of ca. 1.5 (pK vs. pH) appears applicable over a wide range of pH and metal and oxide concentrations. The high capacity of the iron oxide for metals is inconsistent with a purely surface phenomenon and suggests an open, permeable structure for the hydrous ferric oxide.

The objective of this study is to investigate the sorptive properties of hydrous ferric oxide (by using copper and lead as model sorbates) in laboratory systems mimicking the complexity of natural waters. Although the sorption of metals on hydrous ferric oxide has been investigated previously (*1*, *2*, *13*), the data exist mainly for simple, carefully controlled systems designed to allow for maximum insight into the process of sorption at the microscopic level. Sorption in natural waters, on the other hand, involves many metals interacting with an ill-defined, possibly largely amorphous surface in the presence of a complex background electrolyte. Any or all of these factors may make it unfeasible to extrapolate data from the simpler laboratory systems to natural waters—particularly seawater. A reductionist approach is taken to compare sorption of copper and lead on amorphous ferric oxide in seawater to sorption in simpler systems. The effects of aging of the solid, ionic strength, and nature of the background electrolyte, and relative concentrations of metals and hydrous ferric oxide are isolated and studied.

Background

The formation of crystalline ferric oxides requires elevated temperature, high pressure, or long aging periods. At room temperature and atmospheric pressure amorphous ferric oxides are formed and are stable for periods of months (*4–7*). In a study of Fe(III) speciation in seawater, it was noted that the X-ray amorphous solid phase formed initially in solutions supersaturated with respect to $Fe(OH)_3$ was slowly transformed to a more stable crystalline form (*8*). This transformation was extremely slow, however, and after several months of aging a substantial portion of the solid phase still existed as the amorphous oxide. Previous workers had also noted this slow transformation but found that when the X-ray amorphous solid initially formed in nitrate solution was studied by infrared techniques, the presence of α-FeOOH (geothite) was suggested (*4*). It has been proposed that the iron oxide found in seawater, while X-ray amorphous, actually has a largely geothite nature (*9*).

It is difficult to assess whether coprecipitation with, and sorption on, hydrous ferric oxides are actually different processes. Kolthoff and Moskovitz (*5*) found that if the oxide was formed at room temperature, leading to an amorphous precipitate, there was only slightly more copper carried down if it was present during the precipitation of ferric oxide than if it were added immediately or soon afterward. With precipitate formed at 98 °C, however (crystalline), the differences were more pronounced. Gadde and Laitinen (*10*) found more removal of lead by hydrous ferric oxide if the lead was present in the solution during the precipitation than if it was added immediately after. Fresh hydrous ferric oxide sorbed more lead than aged, and lead sorbed on the fresh oxide was less efficiently recovered, suggesting that some occlusion occurs in the coprecipitation process. In a later paper (*11*), however, the same authors reported that this effect was not pronounced.

Sorption isotherms on hydrous oxides show little effect of competition from the major cations in natural waters. For example, McNaughton and James (*12*) found no competition between Hg^{2+} and either Na^+ or Mg^{2+} for sorption sites on α-quartz. By contrast, a competition for metal ions between the surface and soluble ligands has been observed in several instances. The sorption of Hg^{2+} by several substrates is depressed by complexation of Hg^{2+} by Cl^- (*1*, *12*), and the sorption of Cu^{2+} by hydrous ferric oxide is depressed by the formation of $Cu\text{–}NH_3$ complexes (*5*). On the contrary, an enhancement of Zn^{2+} sorption on amorphous iron and aluminum oxides in the presence of phosphate has been observed (*13*). This effect has been explained as a bridging between metal ions and surface sites. A similar explanation has been given (*14*) for the enhancement of sorption in the presence of some organic ligands. Other organic ligands either had no effect or depressed sorption depending on the functionalities. It should be noted that sorption on clays such as illite, which has been interpreted as an ion exchange process rather than

---

[†] Present address: Department of Chemistry, Wellesley College, Wellesley, MA.

[‡] Department of Civil Engineering, Massachusetts Institute of Technology, Cambridge, MA.

0013-936X/80/0914-1326$01.00/0

surface sorption, seems to be much more affected by the composition of the background electrolyte than sorption on hydrous oxides (*15*).

Experimental Section

All chemicals used were analytical reagent grade. Sodium hydroxide solutions free from carbonate were prepared from 50% NaOH solution and stored in polyethylene dispenser bottles. The 6 N HCl was distilled in quartz. Synthetic ocean water (SOW) was prepared according to the FWPCA formulation (*16*).

Glassware was soaked in 3 N HCl at least 12 h before use. All tubing and other equipment which contacted sample solutions was either glass or Teflon. Experiments were performed in an airtight system purged with N_2 to exclude CO_2. Measurement of pH was made with an Orion Model 91-01 glass electrode and an Orion Model 90-02 double junction reference electrode connected to an Orion Model 701 or 801A digital pH meter. Equilibrium was defined as a drift of less than 0.002 pH units/min.

Hydrous ferric oxide sols were prepared by adding a stoichiometric amount of CO_2-free NaOH to solutions of $Fe(NO_3)_3$ in the appropriate background electrolyte. When hydrous ferric oxide was prepared fresh for each experiment in the various background electrolyte solutions, a nonsystematic variability, presumably due to differences among the batches of ferric oxide, obscured the effects of the parameter being studied. To eliminate batch-to-batch variations in the oxide, for each set of isotherms to be compared to each other, we prepared a large batch of hydrous ferric oxide in 0.01 M $NaClO_4$. The various ionic strength and background electrolyte compositions were obtained by appropriate dilution with concentrated $NaClO_4$, NaCl, SOW, or deionized, distilled water. Samples of the stirred sol were pipetted directly into the reaction vessel for each experiment. The stock sols were never used longer than 1 month. There were no significant differences in the nature of isotherms obtained with hydrous ferric oxide prepared this way and those obtained with freshly prepared hydrous ferric oxide.

Isotherms were generated by adjusting the pH of a portion of the sol to ca. 3.5, purging the CO_2, and then incrementally raising the pH with additions of 0.05 N NaOH. After pH equilibrium was reached for each increment, a sample was withdrawn and filtered through a 0.025-μm cellulose acetate filter. The filtrate was analyzed for Cu^{2+} or Pb^{2+} by flame atomic absorption spectrophotometry using a Perkin-Elmer Model 360.

Results

Acid–Base Titrations. To avoid possible changes in the nature of the precipitate due to filtration, we performed the acid–base titrations in the same medium from which the hydrous ferric oxide had been precipitated. Reproducible titrations of the amorphous hydrous ferric oxide were very difficult to obtain. Similar difficulties were encountered by Davis (*14*).

Because the methods available for determining surface area are unsatisfactory for use with suspensions in the medium in which they have been precipitated, excess surface charge in equiv/mol has been substituted here for surface charge density. If a constant specific surface area is assumed, the two differ only by a constant. The excess surface charge is calculated from the difference in acid or base required to reach the same pH in a sample of hydrous ferric oxide sol and in the filtrate from a filtered sample used as a blank.

Excess surface charge as a function of pH is the same within experimental error for 0.1, 0.25, and 0.5 M $NaClO_4$. The nearly linear curves do not exhibit the sigmoid characteristics obtained for other oxides (*2, 17, 18*), and, therfore, a precise value for maximum reactive sites cannot be obtained, although it can be calculated to be in excess of 0.15 site/Fe. The pH_{PZC} appears to be in the range of 7.9–8.5. This is in agreement with data reported for various crystalline and amorphous iron oxides (*1, 2, 6, 19*).

Aging. Titration curves obtained as soon as possible after preparation of the oxide (*ca.* 2 h due to pH equilibration time) required more acid than curves obtained for the same oxide after 24 h. No further change occurred after 24 h. This shift in the titration curves, shown in Figure 1, can be interpreted as a release of acid (or a consumption of base) by the aging oxide. The two curves are roughly parallel, 1.3×10^{-4} equiv apart for 1×10^{-4} M Fe. Copper isotherms obtained simultaneously with the same batch of oxide showed no effect of aging. This is shown in Figure 2, which also illustrates that the same isotherm was obtained when copper was coprecipitated with the iron.

Ionic Strength and Background Electrolyte Composition. As shown in Figure 3, variations in the ionic strength and composition of the background electrolyte solution had no measurable effect on the Cu^{2+} sorption isotherm. The ionic strength was varied from 0.005 to 0.5 M $NaClO_4$. The complexity of the background electrolyte was increased gradually from the indifferent electrolyte $NaClO_4$ to include the more

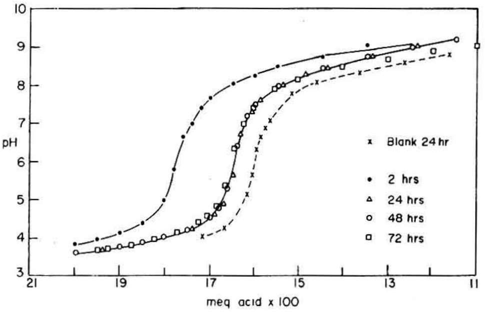


Figure 1. Changes in the titration curve with aging for 1.0×10^{-4} M hydrous ferric oxide in SOW.

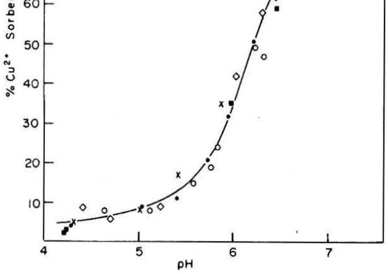


Figure 2. Effect of aging of the oxide on the Cu^{2+} isotherm for 1.0×10^{-5} M Cu^{2+} on 1.0×10^{-4} M hydrous ferric oxide in SOW.

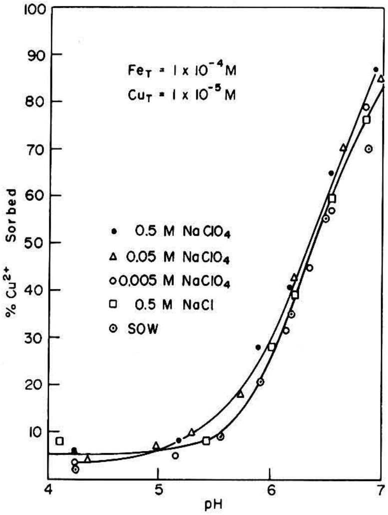


Figure 3. Effect of ionic strength and background electrolyte composition on the Cu^{2+} isotherm for 1.0×10^{-5} M Cu^{2+} on 1.0×10^{-4} M hydrous ferric oxide.

reactive Cl^- ligand and finally to include all of the major ions of seawater.

The Pb^{2+} sorption isotherm was similarly unaffected by changes in ionic strength (Figure 4). However, the presence of Cl^-, which is known to form important di- and trichloro complexes at $[Cl^-] = 0.5$ M, decreased dramatically the percentage of Pb^{2+} sorbed at any given pH. Apparently Cl^- competed successfully with the surface for Pb^{2+} coordination. With experimental error the isotherms were identical in 0.5 M NaCl and SOW demonstrating no competition effect for sorption sites by the major divalent cations, Ca^{2+} and Mg^{2+}.

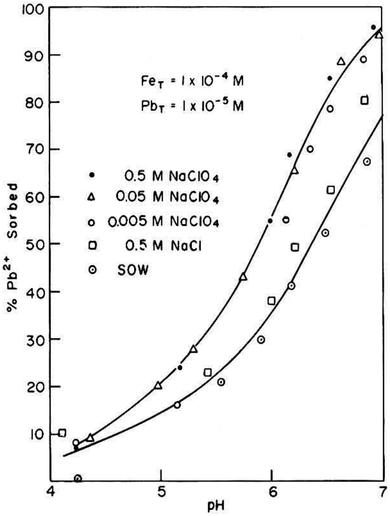


Figure 4. Effect of ionic strength and background electrolyte composition on the Pb^{2+} isotherm for 1.0×10^{-5} M Pb^{2+} on 1.0×10^{-4} M hydrous ferric oxide.

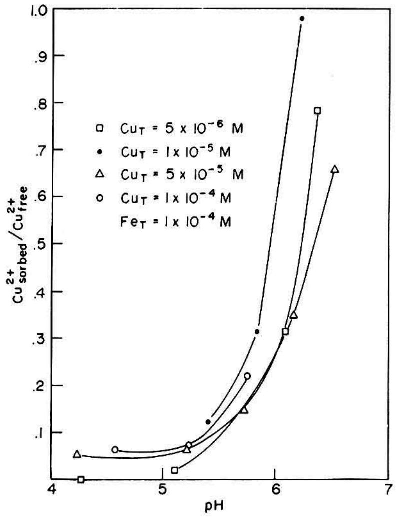


Figure 5. The ratio $Cu^{2+}{}_{sorbed}/Cu^{2+}{}_{free}$ as a function of pH for variable Cu_T on 1.0×10^{-4} M hydrous ferric oxide.

Concentration of Sorbent and Metal Ions. To elucidate the nature of the reaction, we systematically varied metal and oxide concentrations. The precipitation of the Cu^{2+} and Pb^{2+} hydroxides limited the metal concentrations that could be used to ca. 1×10^{-4} M Cu^{2+} and 4×10^{-4} M Pb^{2+}. The minimum oxide concentration yielding measurable uptake of metals was 5×10^{-5} M. As a first hypothesis, one may consider a simple mass action expression for the sorption reaction at fixed pH

$$\equiv M{-}O^- + Me^{2+} \rightleftarrows \equiv M{-}O{-}Me^+$$

$$K = \frac{\{\equiv M{-}O{-}Me^+\}}{\{\equiv M{-}O^-\}[Me^{2+}]} \qquad (1)$$

where { } and [ ] indicate concentrations of species (mol/L) in the solid and aqueous phases, respectively. One would then expect that below saturation the ratio of sorbed to free metal should remain constant while the total moles of metal sorbed increases (as long as the available reaction sites are in large excess). As saturation is approached, the ratio of sorbed to free metal should begin to decrease as the available reaction sites decrease.

Experimentally, the ratio $Cu^{2+}{}_{sorbed}/Cu^{2+}{}_{free}$ remained approximately constant (Figure 5) at a given pH while the moles of Cu^{2+} sorbed increased with increasing Cu^{2+} up to 1×10^{-4} M Cu_T. Although the data may suggest a slight saturation effect (decrease in $Cu^{2+}{}_{sorbed}/Cu^{2+}{}_{free}$ at a given pH as Cu_T is increased), this trend is within the scatter of the data and is probably fortuitous. It appears that under these conditions, an approach to saturation cannot be reached before the precipitation of $Cu(OH)_2$ begins. The distinction between sorption and precipitation of Cu^{2+} in these experiments was very clear. Before the onset of precipitation, a gradual decrease in free Cu^{2+} accompanied a gradual increase in pH as base was added. When precipitation of $Cu(OH)_2$ began, a rapid decrease in free Cu^{2+} occurred while the pH remained constant with the addition of base. Reduction of the hydrous ferric oxide concentration to 1.0×10^{-5} M resulted in negligible Cu^{2+} sorption in the pH range 4–7.

Since the Cu^{2+} hydrolysis and precipitation made it impossible to demonstrate saturation of the hydrous ferric oxide with Cu^{2+}, the experiments were repeated with Pb^{2+}, which precipitates (as $Pb(OH)_2$) at a slightly higher pH than Cu^{2+} but gives a similar isotherm on hydrous ferric oxide. The results shown in Figure 6 are not as straightforward as those for

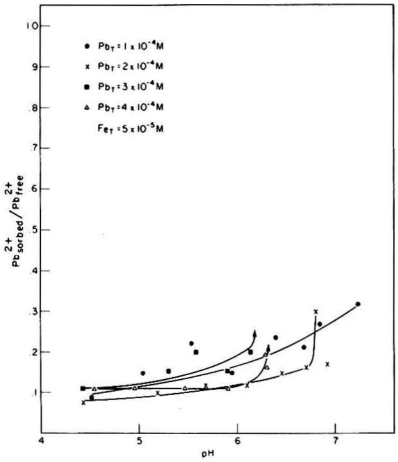


Figure 6. The ratio $Pb^{2+}{}_{sorbed}/Pb^{2+}{}_{free}$ as a function of pH for variable Pb_T on 5.0×10^{-5} M hydrous ferric oxide.

Cu^{2+}. During the generation of the isotherms, the Pb^{2+} solutions apparently became supersaturated with respect to $Pb(OH)_2$ and an addition of base actually lowered the pH when precipitation commenced. The complex and variable hydrolysis of Pb^{2+} in these solutions reflects the known polynuclear behavior of Pb^{2+} hydrolysis products. Britton (*20*), in a study of the precipitation of trace metal hydroxides, found that the K_{sp} for $Pb(OH)_2$ increased with the amount of alkali added, ranging from 3×10^{-19} to 1.35×10^{-15}. A phenomenon of this kind is indicated in the data presented here. At high Pb^{2+} concentration (4.0×10^{-4} M) the precipitation of $Pb(OH)_2$ caused the hydrous ferric oxide to coagulate, and a white solid was carried down with the brick red ferric oxide. Before the appearance of the white solid, however, the distinction between sorption and precipitation of the hydroxide was not as clear for Pb^{2+} as it was for Cu^{2+}. Despite these difficulties, an approach to saturation may be suggested by the constancy of the concentration of lead sorbed as a function of pH at the highest Pb^{2+} concentration.

The expected proportional increase in Cu^{2+} and Pb^{2+} sorption with increasing Fe_T at a given pH is shown in Figures 7 and 8. $Cu^{2+}{}_{sorbed}/Cu^{2+}{}_{free}Fe_T$ and $Pb^{2+}{}_{sorbed}/Pb^{2+}{}_{free}Fe_T$ are roughly constant for a given pH with variable Fe_T. (The high points in the Cu^{2+} plot at low pH and the low points in the Pb^{2+} plot at high pH reflect the large indeterminant errors in the isotherms in these regions.)

Competition between Sorbates. It was impossible to demonstrate competition between Pb^{2+} and Cu^{2+} for the iron. This was consistent with the difficulties encountered in demonstrating saturation for either of the metals. An apparent competition was demonstrated between Cu^{2+} and Fe^{2+} when 1.0×10^{-5} M Cu^{2+} and 6.0×10^{-4} M Fe^{2+} were present with 4.0×10^{-4} hydrous ferric oxide in an O_2-free system. This result is shown in Figure 9 as a large depression in the isotherm compared to the same system in the absence of Fe(II).

Discussion

As the data reduction in Figures 5–8 demonstrates, the reaction of Cu^{2+} and Pb^{2+} with amorphous ferric oxide is, to a first approximation, proportional to the free metal concentration in solution and to the amount of oxide over the range 5×10^{-6}–4×10^{-4} M metal and 5×10^{-5}–1×10^{-3} M oxide.

To reduce the data further and test eq 1 requires an estimate of the total number of reactive sites on the oxide in order

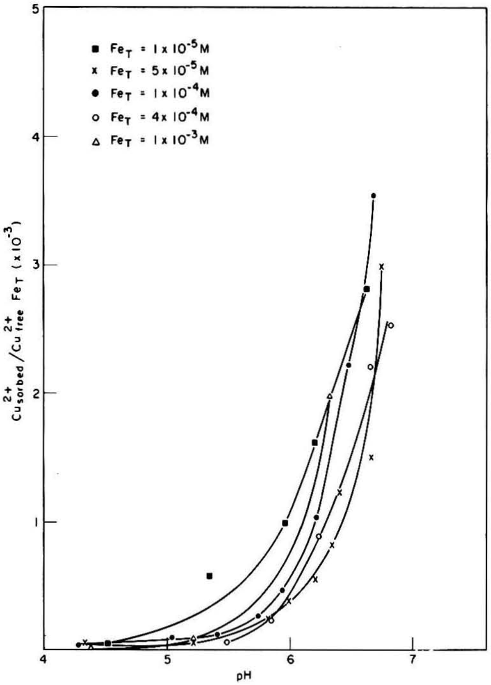


Figure 7. Reduction of data from isotherms for 1.0×10^{-5} M Cu^{2+} on various concentrations of hydrous ferric oxide in SOW to $Cu^{2+}{}_{sorbed}/Cu^{2+}{}_{free}Fe_T$ as a function of pH.

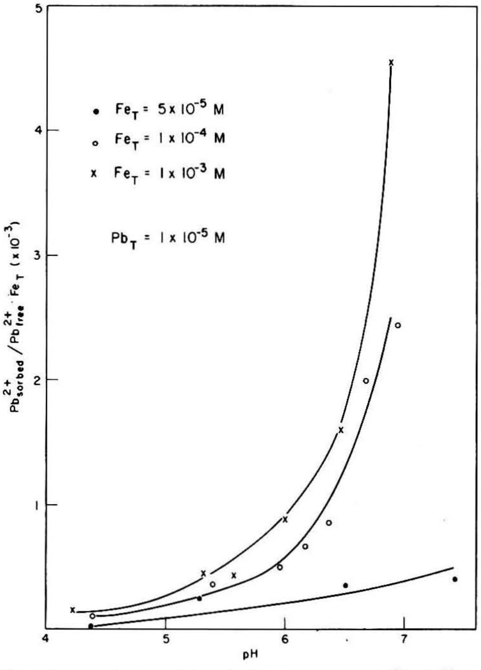


Figure 8. Reduction of data from isotherms for 1.0×10^{-5} M Pb^{2+} on various concentrations of hydrous ferric oxide in SOW to $Pb^{2+}{}_{sorbed}/Pb^{2+}{}_{free}Fe_T$ as a function of pH.

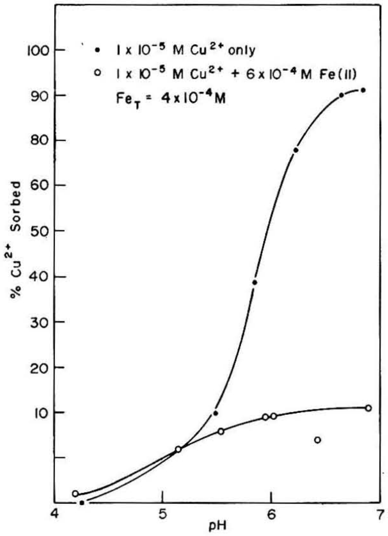


Figure 9. Depression of the isotherm for 1.0×10^{-5} M Cu^{2+} on 4.0×10^{-4} M hydrous ferric oxide in SOW in the presence of 6.0×10^{-4} M Fe^{2+}.

to calculate $\{\equiv M—O^-\}$. The acid–base titration data are of little help for this purpose as not all of the acid–base sites appear to be titrated in the pH range of interest. An estimate of total reactive sites based on such data would result in orders of magnitude underestimation of the removal of Cu^{2+} and Pb^{2+} by the iron. Upper and lower limits for the number of reactive sites can be obtained directly from the metal sorption data. The Pb^{2+} data provide the lower limit of 0.8 site/Fe, while an upper limit of 1.5 site/Fe is implied from the Fe(II)–Cu competition experiment (Figure 9). This is consistent with the estimate obtained by Davis (*14*) of 0.87 site/Fe on the basis of Yates' (*21*) data obtained from rapid tritium exchange experiments. Figure 10 shows the reduction of the data using a value of 1 site/Fe for the Cu^{2+} isotherms in seawater for all values of Cu and Fe_T. It should be noted both that the data are consistent with the mass law expression and that, since all the isotherms were below saturation, this is not a sensitive test of the value chosen for total reactive sites. Although the Pb^{2+} data would provide a more sensitive test, their scatter renders such reduction meaningless.

Above pH 5.5 the points on Figure 10 cluster about a straight line with a slope of ~1.5. There is no simple theoretical reason that the apparent sorption constant should become independent of pH at lower pH values. Experimentally these points represent measurements of between 1 and 10% metal removed from solution measured by difference in solution concentrations. Adsorption by the glassware could well account for removal of micromolar concentrations of Cu^{2+}. In fact it is interesting to note that extrapolation of the line to lower pH yields a log *K* of ~1.2 for pH 4.4. This is the pH found by Kinniburgh et al. to have yielded 50% Cu^{2+} sorption by slightly less than 0.1 M Fe_T (thus log *K* slightly above 1; see Figure 10). This agreement among data from experiments performed by different experimenters under different conditions bolsters the interpretation of the sorption process as simple mass action. Figure 10 provides then a convenient means to predict Cu^{2+} removal (within a factor of 2) by iron oxide under a wide variety of conditions.

The very complex system of amorphous ferric oxide in seawater behaves in a remarkably simple way with respect to Cu^{2+} and Pb^{2+} removal. There is no effect of ionic strength, no effect of background electrolyte (except for the expected Cl^- effect on Pb^{2+}), no effect of aging, and no difference whether iron is precipitated in the presence or the absence of the metal. (Note that the absence of an ionic strength effect on the sorption of metals by hydrous ferric oxide does not extend to other iron oxide substrates. O'Connor and Kester (*15*) found significant ionic strength effects on the removal of Cu^{2+} and Co^{2+} by various solids, especially illite. This suggests different sorption mechanisms for different substrates.)

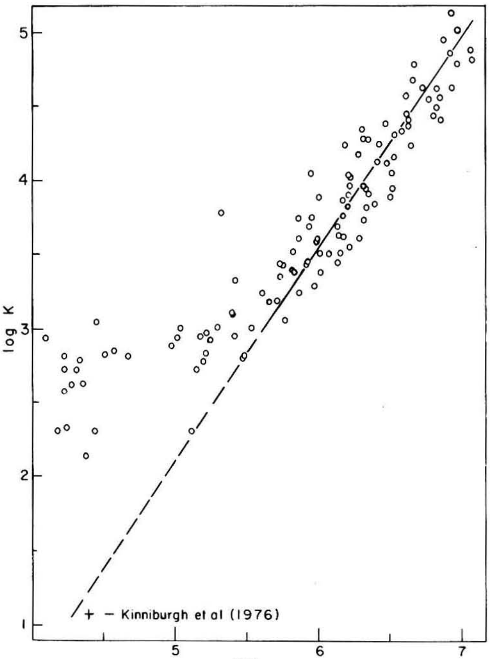


Figure 10. log *K* as a function of pH for all Cu^{2+} data where $K = Cu^{2+}_{sorbed}/(Cu_T - Cu^{2+}_{sorbed})(Fe_T - Cu^{2+}_{sorbed})$.

The expected effect of ionic strength depends to some extent on the model being considered. The ionic strength enters into electrical double layer calculations and affects the Coulombic interactions between the charged surface and the sorbing ions by changing the thickness of the double layer. What effect this has on sorption of trace metal cations, which are specifically sorbed against the electrostatic repulsion of a positively charged surface, is unclear. In all cases, however, the Coulombic interactions in the sorption process can only play a role for reactions resulting in a net change of charge. The remarkable consistency of the isotherms for various ionic strengths invites a speculation that the reaction of iron oxide with Cu^{2+} and Pb^{2+} results in no net change in charge in the pH range of interest. For example, two protons may exchange for one metal ion. This is reinforced by the aging study which demonstrates a clear change in charge (evidenced by a change in uptake of acid by the solid) with no concomitant change in the isotherm.

It is puzzling that the release of 1.3 equiv/mol of H^+/Fe over 24 h of aging is not accompanied by any change in the Cu^{2+} isotherms. There is a strong implication that the protons lost in aging are not the exchangeable protons on the reactive sites. This may be a consequence of different coordination of the oxygen atoms or of geometrical inaccessability of some of the oxygen atoms. The oxo bridges formed during oxolation of an iron oxide react very slowly with acid (*4*). Oxolation would explain the release of acid over the first 24 h of aging. The oxygen atoms involved in oxolation are already bound to two iron atoms and are not likely to be the reactive sites. That the acid–base sites with rapidly exchangeable protons and the coordination sites for Cu^{2+} are indeed the same is supported by the dependence of the apparent sorption constant (K) on pH.

The capacity of amorphous hydrous ferric oxide for metal ions makes the meaning of the terms "surface" and "adsorption" somewhat arbitrary. It becomes necessary to provide a more satisfactory image of the system than that of an interface separating two phases. One is clearly not concerned with the interface between the visible precipitate and the bulk solution, but rather the interface between some microstructure and its immediately surrounding water. Amorphous hydrous ferric oxide has been described as "amorphous, randomly cross-linked aggregates containing large and indefinite amounts of water" (*22*). This description calls to mind the structure of a swollen ion-exchange resin which is permeable to hydrated ions. The ions are free to diffuse throughout the structure and are not restricted to external "surface" sites. The loose, highly hydrated structure of the ferric oxide used in this work readily accommodates foreign ions which become incorporated into the solid as they hydrolyze. The observed effect of chloride is a consequence of the formation of complexes with the lead ion which are not incorporated into the solid.

In addition to accounting for the high capacity of the iron for metals, this image also provides an explanation for the similarity between isotherms obtained by precipitation of the iron in the presence and the absence of Cu^{2+}. It is also consistent with what is known regarding the formation of metal ferrites (*23*). The amorphous complex oxides, such as those obtained in this work, are precursors of the crystalline ferrites. Adamovich et al. (*24*) examined the solid resulting from the coprecipitation of Fe and Cu by X-ray diffraction and thermogravimetry and found evidence for a single solid phase rather than a mixture of iron and copper oxides. Heating the solid produced a compound whose X-ray diffraction pattern was suggestive of copper ferrite. Gmelin (*25*) documents the preparation of copper ferrite by heating a coprecipitated iron and copper oxide. When the oxides are precipitated separately, mixed, and heated, only CuO and Fe_2O_3 are formed.

The results of this study show that despite its complexity, sorption by amorphous iron oxide may be described rather simply. The removal of a metal can be approximately predicted under all concentration and electrolyte conditions by a constant which is only a function of pH. This pH dependence can presumably be accounted for in a numerical model by adjusting the acid–base chemistry of the solid which is difficult to quantitate experimentally (*26*). Although the mathematics appears to be similar to the surface complexation model for sorption on crystalline metal oxides, the reaction between amorphous iron oxide and metals should not be viewed as a macroscopic surface phenomenon. In many ways, amorphous ferric oxide can be viewed as more closely analogous to polyelectrolytes than to crystalline solids such as quartz.

Acknowledgment

We thank Dr. Earl Davey, EPA, Narragansett, RI, for his invaluable assistance with this project.

Literature Cited

(1) Forbes, E. A.; Posner, A.; Quirk, J. P. *J. Colloid Interface Sci.* **1974** *49*.

(2) Yates, D. E.; Healy, T. W. *J. Colloid Interface Sci.* **1975,** *52,* 222.

(3) Kinniburgh, D. G.; Jackson, M. L.; Syers, J. K. *Soil. Sci. Soc. Am. J.* **1976,** *40,* 796.

(4) Dousma, J.; deBruyn, P. L. *J. Colloid Interface Sci.* **1976,** *56,* 527.

(5) Kolthoff, I. M.; Moskovitz, B. *J. Phys. Chem.* **1937,** *41,* 629.

(6) Parks, G. A.; deBruyn, P. L. *J. Phys. Chem.* **1962,** *66,* 967.

(7) Atkinson, R. J.; Posner, A. M.; Quirk, J. P. *J Phys. Chem.* **1967,** *71,* 550.

(8) Byrne, R. H.; Kester, D. R. *Mar. Chem.* **1976,** *4,* 255.

(9) Stumm, W., Eidgenoissische Technische Hochschulen, personal communication, 1976.

(10) Gadde, R. R.; Laitinen, H. A. *Environ. Lett.* **1973,** *5,* 223.

(11) Gadde, R. R.; Laitinen, H. A. *Anal. Chem.* **1974,** *46,* 2022.

(12) McNaughton, M. G.; James, R. O. *J. Colloid Interface Sci.* **1974,** *47,* 431.

(13) Stanton, D. A.; Burger, R. duT, *Geoderma* **1967,** *1,* 13.

(14) Davis, J. A.; Ph.D Thesis, Stanford University, Stanford, CA, 1977.

(15) O'Connor, T. P.; Kester, D. R. *Geochim. Cosmochim. Acta* **1975,** *39,* 1531.

(16) "FWPCA Methods for Chemical Analysis of Water and Wastes", U.S. Department of the Interior, Nov 1969, p 240.

(17) Berube, Y. G.; deBruyn, P. L. *J. Colloid Interface Sci.* **1968,** *27,* 305.

(18) Breeuwsma, A.; Lyklema, J. *Discuss. Faraday Soc.* **1971,** *52,* 324.

(19) Lyklema, J. *Croat. Chem. Acta* **1971,** *43,* 249.

(20) Britton, H. T. S. "Hydrogen Ions"; Van Nostrand: Princeton, NJ, 1956; Vol. II.

(21) Yates, D. E. Ph.D Thesis, University of Melbourne, Melbourne, Australia, 1975.

(22) Walton, H. F. "Principles and Methods of Chemical Analysis"; Prentice-Hall: Englewood Cliffs, NJ, 1964; Chapter 2, p 28.

(23) Hilpert, S.; Wille, A. *Z. Phys. Chem., Abt. B18,* **1932,** 291.

(24) Adamovich, T. P.; Sviridov, V. V.; Lobanok, A. D. *Dokl. Akad. Nauk. BSSR* **1964,** *8,* 312.

(25) Gmelin's "Handbuch der Anorganischen Chemie", Kupfer Teil B, Lief. 3, System Num. 60; Verlag Chemie: Weinheim, 1965; p 1276.

(26) Morel, F. M. M.; Yeasted, J. G.; Westall, J. C. In "Absorption of Inorganics at the Solid–Liquid Interface", Anderson, M. A., Rubin, A., Eds.; Ann Arbor Science: Ann Arbor, MI, 1979.

Received for review August 27, 1979. Accepted July 22, 1980. This work was supported in part by U.S. Environmental Protection Agency Grant No. R-803738.

Prediction of the Volatilization Rates of High-Volatility Chemicals from Natural Water Bodies

James H. Smith,* David C. Bomberger, Jr., and Daniel L. Haynes

SRI International, Menlo Park, California 94025

■ A simple laboratory procedure has been used to obtain volatilization rate data for compounds of environmental interest. The measured parameter is the ratio of the evaporation rate constant of the chemical to the oxygen reaeration rate constant, k_v^C/k_v^O, which has been shown to be constant for volatile substances over a wide range of conditions. If the oxygen reaeration rate constant, k_v^O, can be estimated or measured in a natural water body or in a wastewater treatment unit, then the volatilization rate constant of the chemical under those same conditions can be estimated by multiplying the value of the ratio by the environmental value of k_v^O. The results suggest that the major environmental fate of many low-molecular-weight, nonpolar compounds will be volatilization.

Introduction

Transport of chemicals from water bodies to the atmosphere (volatilization or evaporation) can be an important environmental pathway for certain chemicals. Compounds of low molecular weight and high vapor pressure, such as vinyl chloride, have been shown to volatilize rapidly (*1*). However, some high-molecular-weight, low-solubility compounds such as DDT may also volatilize at an appreciable rate (2) because they have a high activity coefficient in aqueous solution. Thus, volatilization may be an important environmental fate for compounds introduced into both freshwater and marine environments by inadvertent spills, by agricultural runoff, and by industrial effluents or introduced directly into the air from industrial unit processes such as a biotreator or a cooling tower.

A convenient expression for the volatilization rate of a chemical C from water is

$$-\,d[C]/dt = k_v^C[C] \tag{1}$$

where k_v^C is the volatilization rate constant of chemical C. Several groups have reported various methods for estimating volatilization rates of organic chemicals from natural water bodies (*1–12*). These workers have used the classical two-film mass-transfer model developed by Whitman (*13*). The volatilization rate constant k_v is expressed in terms of the mass-transfer rates of the substance across liquid- and gas-phase boundary layers. The general expression for k_v is

$$k_v = \frac{1}{L}\left[\frac{1}{k_l} + \frac{RT}{H_c k_g}\right]^{-1} \tag{2}$$

where k_v is the volatilization rate constant (h^{-1}); L is the depth (cm), which equals the interfacial area, A, divided by the liquid volume, V; k_l is the liquid-film mass-transfer coefficient (cm h^{-1}); R is the gas constant (L torr K^{-1} mol^{-1}); T is the temperature (K); H_c is the Henry's law constant (torr L mol^{-1}); and k_g is the gas-film mass-transfer coefficient (cm h^{-1}). Liss and Slater (*8*) and Mackay and Leinonen (*4*) have recently reviewed the two-film theory and applied it to environmental problems.

To use eq 2 to estimate k_v^C, it is necessary to measure or estimate the mass-transfer coefficients and the Henry's law constant. Although Mackay and Cohen (*5*) have described several methods for measuring these values in the laboratory, their methods require a special apparatus and some experimental care. A major problem with their approach is that it is difficult to measure or estimate the mass-transfer coefficients in real water bodies. Therefore, prediction of volatilization rate constants for environmental conditions is difficult.

The overall mass-transport rate of a substance may depend on liquid-phase or gas-phase resistance or both, depending on the relative magnitude of k_l and $H_c k_g$. Liss and Slater (*8*) estimated values of k_l for CO_2 (20 cm h^{-1}) and of k_g for water (1000–3000 cm h^{-1}). These values were assumed to be typical and substituted into eq 2. Then, the ratio of the first term to the sum of the two terms is set equal to the fraction of liquid-phase control, and the equation is solved for H_c. The calculation shows that mass transfer in the liquid phase controls about 95% of the volatilization rate constant when the value of H_c is greater than ~3500 torr L mol^{-1}. We have called chemicals that meet this requirement high-volatility compounds. A similar calculation shows that, if H_c is less than 10 torr L mol^{-1}, mass transfer in the gas phase is rate controlling. These are low-volatility compounds. If H_c is between ~10 and 3500 torr L mol^{-1}, then both terms in eq 2 are significant. A similar procedure has been described by Dilling (7).

In this paper we will consider a technique for predicting volatilization rates of high-volatility compounds in natural water bodies and wastewater treatment facilities that avoids the requirement for measuring or estimating values of k_l and k_g. The procedure is based on Tsivoglou's observation (*9,10*) that for high volatility compounds the ratio of k_v^C and the oxygen reaeration rate constant, k_v^O, can be measured simultaneously in the laboratory and k_v^C/k_v^O can then be calculated. The theoretical justification for the constancy of the ratio of the volatilization rate constants of two high-volatility chemicals is given in a later section of this paper.

The value of H_c for oxygen is ~1.2×10^5 torr L mol^{-1} at 25 °C. This value was calculated from the solubility of oxygen in water (*14*). Therefore, oxygen is a high-volatility compound, and k_v^O is limited only by mass transport in the liquid phase.

Several researchers have shown that the ratio measured in the laboratory, $(k_v^C/k_v^O)_{lab}$, is a constant for high-volatility compounds for a range of turbulence levels readily achieved in the laboratory (*1,9–11*). If the ratio can be measured in the laboratory and if the oxygen reaeration rate constant in a real water body, $(k_v^O)_{env}$, is known, then the volatilization rate constant of the chemical in the environment, $(k_v^C)_{env}$, can be estimated:

$$(k_v^C)_{env} = (k_v^C/k_v^O)_{lab}(k_v^O)_{env} \tag{3}$$

Also

$$(k_v^O)_{env} = (k_l^O)_{env}/L_{env} \tag{4}$$

since the second term in eq 2 is small compared with the first. The effects of environmental parameters such as temperature, turbulence, and the presence of a surface-active organic layer are all included in $(k_l^O)_{env}$.

This paper reports measurements of $(k_v^C/k_v^O)_{lab}$ for benzene and several chlorinated hydrocarbons, considers various theoretical approaches to estimating k_v^C/k_v^O, and extends the applicability of the approach to natural water bodies.

0013-936X/80/0914-1332$01.00/0

Table I. Solubilities and Analytical Methods of Chemicals Studied

chemical	solubility, mg L^{-1}	initial concn, mg L^{-1}	sample workup method	detection [a]
benzene	1780 [b]	300	none	UV absorption
carbon tetrachloride	800 [c]	50	DAI [d]	GC/CECD
chloroform	7840 [c]	15	DAI	GC/CECD
1,1-dichloroethane	5100 [c]	20	DAI	GC/CECD
dicyclopentadiene	40 [e]	19	[f]	GC/FID
tetrachloroethylene	140 [c]	15	DAI	GC/CECD
trichloroethylene	1100 [c]	30	DAI	GC/CECD

[a] GC = gas chromatography; CECD = Coulson electrolytic conductivity detector; FID = flame ionization detector. [b] Reference *15*. [c] Reference *7*. [d] DAI = direct aqueous injection. [e] Estimated from the solubility of diolefins of similar molecular weight, using data in ref *15*. [f] Aliquot was mixed with an equal volume of acetone containing naphthalene as an internal standard.

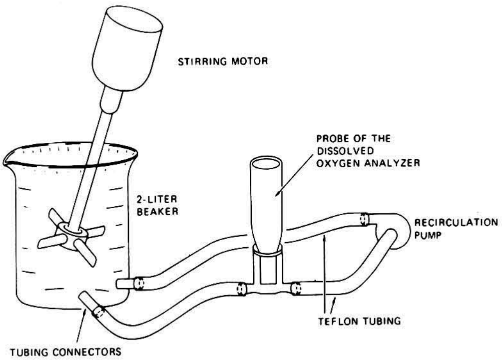


Figure 1. Volatilization rate apparatus for high-volatility compounds.

Experimental Section

The volatilization rate constant ratios, k_v^C/k_v^O, were measured by using the method described by Hill et al. (*1*). A sample of deionized water was purged with nitrogen to strip the dissolved oxygen. Then an aliquot of the compound, usually dissolved in methanol or water, was added and allowed to dissolve in the water. At the start of the experiment the concentration of the substance was measured by gas chromatography or ultraviolet spectrometry (see Table I). The data for carbon tetrachloride, chloroform, and 1,1-dichloroethane were obtained by using solutions containing the three halogenated organics plus 2-chloroethanol, a nonvolatile compound that was used as an internal standard. In a typical experiment, the average concentration of 2-chloroethanol was 28 ± 4 ppm during a 1-h experiment. Some of the data for chloroform and carbon tetrachloride and all of the data for trichloroethylene and tetrachloroethylene were obtained by using 3-chloro-1-propanol as the internal standard. In a typical experiment, the average concentration of 3-chloro-1-propanol was 50 ± 2 ppm during a 2-h experiment.

The oxygen concentration was measured with a Delta Model 2110 dissolved-oxygen analyzer. Successive chemical and oxygen-concentration measurements were made at regular intervals.

The initial experiments were conducted in 1-L beakers suspended in a water bath. At slower stirring rates, the measurement of the dissolved-oxygen concentration was erratic and not reproducible, presumably because the flow of water past the sensor face was slow and the probe consumed the oxygen faster than it was replenished. To correct this problem, we used the apparatus shown in Figure 1. The dissolved-oxygen probe was mounted in a side arm, and the solution pumped past the probe with a Valcor Model 104A44B Teflon diaphragm pump at a linear flow rate of more than 10 cm s^{-1}. The beaker was suspended in a constant-temperature water bath and stirred with a three-bladed propeller and a constant-speed stirring motor. Oxygen reaeration rate constants below 0.3 h^{-1} were readily obtained and accurately measured with the side-arm apparatus. The data for benzene, trichloroethylene, and tetrachloroethylene and some of the data for chloroform and carbon tetrachloride were obtained in the modified apparatus.

Special precautions were taken for the volatilization experiments on benzene with a surfactant, 0.003% Triton X-100. The apparatus was washed with methanol and then water before each experiment. The last water wash overflowed the beaker. The benzene solution contained about 300 mg L^{-1} of benzene. The surface tensions were measured with a Fischer Model 21 surface tensiomat.

The artificial seawater solutions were prepared according to the formula recommended by the EPA (*16*) for approximating estuarian conditions. The sample of natural water was obtained from Searsville Pond, Portola Valley, CA, and was tested within 4 h of collection.

The substance concentrations as a function of time were fitted to the integrated form of eq 1 by using linear least-squares routines of a hand-held calculator. The oxygen-concentration data were fitted to the exponential expression for oxygen reaeration

$$\ln([O_2]_s - [O_2]_t) = -k_v^O t + \ln([O_2]_s - [O_2]_0) \qquad (5)$$

where $[O_2]_s$ is the saturation oxygen concentration at the temperature of the solution and $[O_2]_0$ and $[O_2]_t$ are the oxygen concentrations at times 0 and t, respectively.

Results and Discussion

Table II summarizes k_v^C/k_v^O values for a number of chemicals of environmental interest that were found in the literature or were measured in our laboratory. The experimental data for benzene and chloroform are shown in Figures 2 and 3. The experimental data for the other compounds listed in Table II were similar. These data confirm the literature reports that, for high-volatility compounds ($H_c > 3500$ torr M^{-1}), the ratio k_v^C/k_v^O is independent of k_v^O over a wide range (0.05–15 h^{-1}) and, therefore, independent of the turbulence level (*1,9–12,17*). The data for benzene (Figure 2) also show that within experimental error the ratio is independent of temperature between 4 and 50 °C and of the presence of a surface film, a salt mixture approximating seawater, and the components of a natural pond water.

Mass-Transport Theory. Classical two-film theory (*4,8,13*) is based on the assumption that transport through a boundary layer is by molecular diffusion, because the fluid in the boundary layer is stagnant. Then the diffusion process can be described by Fick's law in one dimension, where the flux of the chemical N (g cm^{-2} h^{-1}) is

$$N = -D\frac{\partial C}{\partial z} \qquad (6)$$

where D is the diffusion coefficient and z is the vertical distance. If the concentration gradient $\partial C/\partial z$ is constant within the boundary layer, eq 6 can be rewritten as

$$N = k\Delta C \qquad (7)$$

The mass-transport coefficient k has the units of velocity and is

Table II. Comparison of Predicted and Measured Values of k_v^C/k_v^O

compd	D_l^C/D_l^O predicted [a]	D_l^C/D_l^O measured	$(m^O/m^C)^{1/2}$ [b]	measured k_v^C/k_v^O	range of k_v^O, h^{-1}
benzene	0.45	0.52	0.64	0.56 ± 0.03	0.4–15.5
carbon dioxide	0.84		0.85	0.89 ± 0.03[c]	0.07–0.6
carbon tetrachloride	0.43		0.47	0.63 ± 0.07	0.4–10.7
chloroform	0.47		0.52	0.57 ± 0.05	0.4+10.7
1,1-dichloroethane	0.47		0.57	0.71 ± 0.11	0.3–12.0
dicyclopentadiene	0.31		0.49	0.54 ± 0.02	1.6–10.4
ethylene	0.70	0.77	1.06	0.87 ± 0.02[d]	0.1–2.2
krypton	0.78		0.62	0.82 ± 0.08[c,e]	0.06–2.9
propane	0.53	0.77	0.85	0.72 ± 0.01[d]	0.2–1.6
radon	0.66		0.38	0.70 ± 0.08[c,e]	0.08–0.5
tetrachloroethylene	0.40		0.44	0.52 ± 0.09	1.6–10.7
trichloroethylene	0.44		0.49	0.57 ± 0.15	1.6–10.7

[a] See text for discussion of estimation methods. [b] m = molecular weight. [c] Reference *16*. [d] Reference *17*. [e] Reference *13*.

$$k = D/\delta \qquad (8)$$

where δ is the boundary-layer thickness.

A diffusion coefficient is dependent on the temperature and the viscosity of the solution (*18*). However, when the ratio of two diffusion coefficients is calculated, the effect of temperature and viscosity cancel and the ratio depends only on the physical properties of the solutes. Thus, the ratio of two diffusion coefficients measured in the same solution should be a constant and should be independent of solvent viscosity and temperature. Therefore, the ratio k_v^C/k_v^O for high-volatility compounds, where liquid-phase mass-transport resistance determines the volatilization rate, should be a constant, since

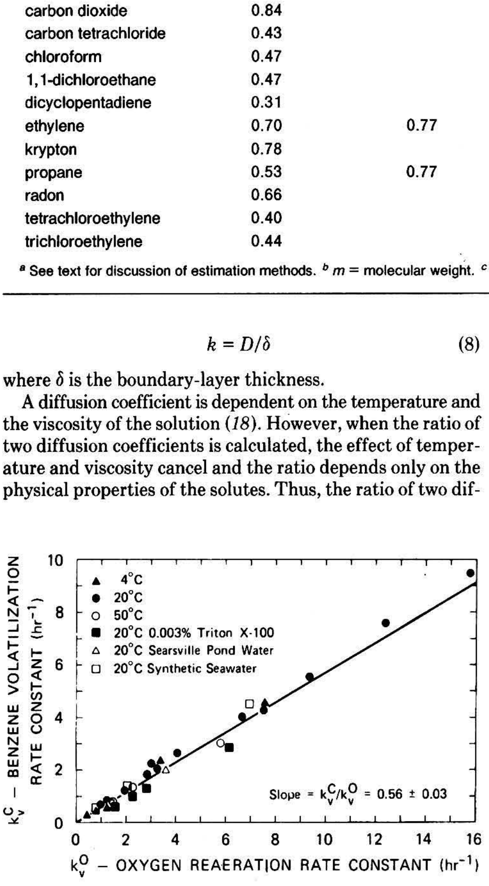


Figure 2. k_v^C vs. k_v^O data for benzene.

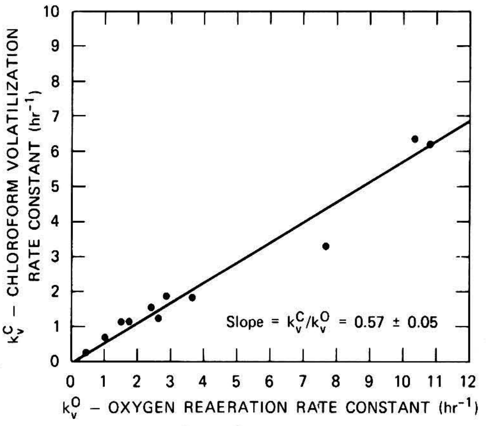


Figure 3. k_v^C vs. k_v^O data for chloroform.

$$k_v^C/k_v^O = k_l^C/k_l^O = f(D_l^C/D_l^O) \qquad (9)$$

where D_l^C and D_l^O are the liquid-phase diffusion coefficients of the chemical and of oxygen. If the classical two-film theory is valid, then $f(D_l^C/D_l^O) = D_l^C/D_l^O$.

The modern theories of mass transport have been reviewed by Treybal (*19*) and Brtko and Kabel (*20*). Penetration (*21*) and surface-renewal (*22*) theories of mass transfer across an air–water interface assume that packets of bulk liquid are transported to the interface, where they remain for a period of time and are then displaced by other packets from the bulk liquid. While the packet is at the interface, material diffuses across the interface; when displaced, the packet is mixed into the bulk liquid and loses its identity. Penetration theory assumes that all of the packets reside at the interface for the same time. Surface-renewal theory assumes that the probability of a packet being displaced is independent of its previous time history. In both cases, it is assumed that the liquid packets do not remain at the interface long enough for the materials to diffuse completely through them.

The results of both theories are similar. Penetration theory yields

$$k_l = 2(D_l/\pi\theta)^{1/2} \qquad (10)$$

where θ is the fixed time period that packets reside at the surface. Surface renewal theory yields

$$k_l = (D_l s)^{1/2} \qquad (11)$$

where s is the fractional rate of packet displacement. The important aspect of these two theories is that they both show k_l to be proportional to the square root of the diffusion coefficient, whereas classical film theory shows k_l to be directly proportional to D_l.

Dobbins (*23*) proposed a modification of surface-renewal theory that allows some packets to remain at the surface long enough for material to diffuse completely through the packet. Then k_l is given by

$$k_l = (D_l s)^{1/2} \coth (sL^2/D_l)^{1/2} \qquad (12)$$

where s is again the fractional rate of packet displacement and L is the actual packet thickness. L is very similar to the film thickness parameter δ. This expression has two limiting forms:

(1) When L is small or D is large, $k_l = D_l/L$ (since coth (x) = $1/x$ as $x \rightarrow 0$), which corresponds to the expression derived from film theory. (2) When L is large or D is small, $k_l = (D_l s)^{1/2}$ (since coth (x) = 1 as $x \rightarrow \infty$), which corresponds to the form of eq 10 and 11 from penetration and surface-renewal theory. Therefore, in the combined theory, under different extreme circumstances either film theory or surface-renewal theory obtains, and under other circumstances the dependence of k_l on D_l is intermediate.

Dobbins (*23*) showed by experiments that highly agitated conditions yielded $k_l \propto D_l^n$, where $n \rightarrow 1/2$, meaning that surface renewal dominated mass transport. Under less agitated conditions, $k_l \propto D_l^n$, where $n \rightarrow 1$, meaning that diffusion across a film dominated mass transport. Lee (*24*) used a capillary microelectrode to measure oxygen concentrations in a stirred liquid a few millimeters below the gas–liquid interface. Regular concentration fluctuations were detected and were interpreted in terms of surface-renewal theory. With this interpretation, a value of the diffusion coefficient of oxygen in water of 2.3×10^{-6} cm^2 s^{-1} was estimated, which Lee compared with a literature value of 2.2×10^{-5} cm^2 s^{-1}. Dobbins and Lee's work raises some questions about Tsivoglou's conjecture (*9,10*) that the ratio of mass-transport rates of gases into lakes and streams is the same as the ratio of their diffusion coefficients. Their studies suggest that eq 9 should be rewritten

$$k_v^C/k_v^O = k_l^C/k_l^O = (D_l^C/D_l^O)^n \qquad 0.5 \leq n \leq 1 \qquad (13)$$

reflecting a combination of film and surface-renewal theory.

There are numerous ways to estimate or measure diffusion coefficients. When eq 9 is used, some investigators have used the Einstein equation for diffusion of particles in water and have estimated the ratio of diffusion coefficients, D^1/D^2, as d^2/d^1 where d is the molecular diameter of the compound being considered (*9,10,12*). Other investigators have followed Liss and Slater's suggestions (*8*) and estimated D^1/D^2 as $(m^2/m^1)^{1/2}$ for gas- and liquid-phase mass-transport-limited chemicals, where m is the molecular weight of the compound (*4,7*). This approximation is based on Graham's law of effusion.

Neither of these approaches is correct. Reid and Sherwood (*18*) have thoroughly reviewed the literature on predicting diffusion coefficients and have discussed the limitations of these approaches. Diffusion coefficients in solution are inversely proportional to molecular diameter only for large spherical molecules. Gas molecules and most lower-molecular-weight organics are too small for the approximation to be correct. Graham's law is valid only for molecules effusing in a vacuum where there is no resistance to diffusion. It is true, however, that for most compounds the estimates of the ratio of mass-transport coefficients based on molecular diameters or the square root of the molecular weights are within a factor of 2 of the ratio of diffusion coefficients, as shown by the data in Table II.

Most methods for estimating diffusion coefficients in solution use the solute molar volume at its normal boiling point, V_b (cm^3 mol^{-1}). When the solvent is water, the Othmer–Thakar relation is the most convenient (*18*)

$$D_l^C = \frac{14.0 \times 10^{-5}}{\mu_w^{1.1} V_b^{0.6}} \text{ (cm}^2\text{ s}^{-1}) \qquad (14)$$

where μ_w is the viscosity of water (cP). The values of D_l^C calculated using eq 14 have been compared with measured diffusion coefficients and found to be accurate within ±11%. Equation 14 also suggests that D_l should be nearly inversely related to the viscosity of the solvent.

When the molar volume is not known, it can be estimated by using the molar volume increments proposed by LeBas (*18*). For many light gases, molar volumes for use in eq 14 have been calculated from diffusion coefficients (*18*). The estimates of diffusion coefficients in water should be accurate within ±15%.

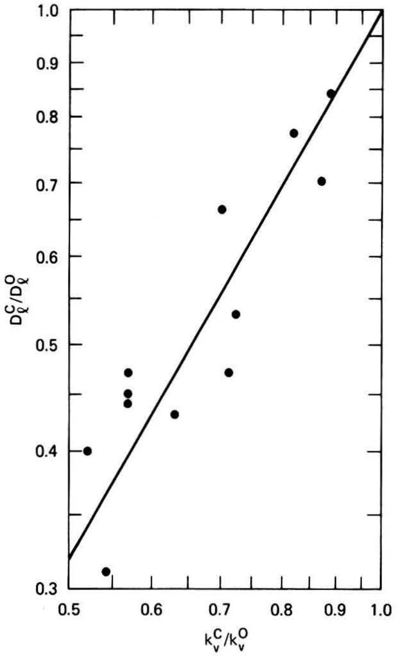


Figure 4. Plot of $-\log(D_l^C/D_l^O)$ vs. $-\log(k_v^C/k_v^O)$.

Table II contains estimates of D_l as well as a summary of the few available literature measurements of the diffusion coefficients for the chemicals in water. In all cases, the measured value of k_v^C/k_v^O is greater than the measured or estimated values of D_l^C/D_l^O. This apparent discrepancy is probably because the classical two-film theory, which assumes stagnant boundary layers, is not a suitable theoretical description of mass transport. However, the data are consistent with eq 13. A plot of the measured values of $-\log(k_v^C/k_v^O)$ vs. the estimated values of $-\log(D_l^C/D_l^O)$ is shown in Figure 4. The slope of the line, n, using a linear least-squares plot forced through the origin, is $n = 0.61$ with a 95% confidence interval of ±0.07.

Estimated diffusion coefficients were used for this correlation for two principal reasons. First, in cases where one diffusion coefficient was known and the other had to be estimated, forming a mixed ratio might bias the results. Second, in cases where both diffusion coefficients had been measured, there was still a large potential error. Rathbun (*17*) assumed that film theory obtained ($n = 1$) and calculated a D_l^C/D_l^O ratio for ethylene by using diffusion coefficients for oxygen and ethylene that were measured by several investigators. When data for oxygen and ethylene measured by the same investigator were used, the ratio was 0.77. If diffusion coefficients measured by different investigators were used, the ratio varied from 0.57 to 0.96. This is a wider range than the range predicted by using the estimated values of the diffusion coefficients and varying n from 0.5 to 1.

Effect of Surfactants. Several workers have shown that the presence of a surface-active agent reduces the volatilization or oxygen reaeration rate constant, even though the stirring rate remains constant (*25–27*). For instance, Goodridge and Robb (*25*) found that an amount of C_{14} to C_{20} alcohols corresponding to twice the amount required to form

Table III. Benzene Volatilization in the Presence of a Surfactant (0.003% Triton X-100)[a]

	no surfactant			with surfactant		
rev min^{-1}	k_v^C, h^{-1}	k_v^O, h^{-1}	k_v^C/k_v^O	k_v^C, h^{-1}	k_v^O, h^{-1}	k_v^C/k_v^O
0	1.11 ± 0.06	2.02 ± 0.22	0.55			
127	2.16 ± 0.06	3.23 ± 0.03	0.67	0.74 ± 0.02	1.39 ± 0.01	0.53
176	2.03 ± 0.03	3.29 ± 0.08	0.62	1.11 ± 0.01	2.15 ± 0.02	0.52
270	3.97 ± 0.10	6.69 ± 0.11	0.59	1.39 ± 0.06	2.69 ± 0.03	0.52
360				2.87 ± 0.20	6.10 ± 0.19	0.47
270[b]	2.06 ± 0.05	3.55 ± 0.41	0.58			
av ± std dev			0.60 ± 0.04			0.51 ± 0.02

[a] Measurements were at 20 °C; surface tension of the solution containing the surfactant was 45 dyn cm^{-1}. [b] Measured in water from Searsville Pond at 23 °C; surface tension was 71.4 dyn cm^{-1}.

Table IV. Oxygen Reaeration Rate Constants in Representative Water Bodies

	lit. values	values used in ref *29*		
	k_v^O, day^{-1}	k_v^O, day^{-1}	k_v^O, h^{-1}	L, cm
pond	0.11–0.23[a]	0.19	0.0080	200
river	0.2,[b] 0.1–9.3[c]	0.96	0.040	300
lake	0.10–0.30[a]	0.24	0.010	500

[a] Reference *30*. [b] Reference *31*. [c] Reference *28*.

a monomolecular layer reduced the value of k_v^C for carbon dioxide by factors of 1.5–4. Bull and Kemp (*27*) found similar effects for oxygen reaeration. These results suggest that several modifications to the mass-transport theory are required (*25,26*). First, a third term due to mass-transport resistance at the interface must be added to eq 2. In the general case, for a solute obeying Henry's law

$$k_v = \frac{1}{L}\left[\frac{1}{k_l} + \frac{RT}{H_c k_s} + \frac{RT}{H_c k_g}\right]^{-1} \qquad (15)$$

where k_s is the mass-transport coefficient at the interface, which from the kinetic theory of gases is

$$k_s = \alpha\left(\frac{RT}{2\pi m}\right)^{1/2} \qquad (16)$$

where α is the accommodation coefficient or the fraction of molecules of the chemical striking the surface that condense on the surface, R is the gas constant in erg mol^{-1} K^{-1}, and m is the molecular weight. Equation 16 suggests there may be an energy of activation to cross the interface (*25*). The effect of k_s is most clearly seen in the reduction of the evaporation rate of water (which is gas-phase mass-transport limited) by the addition of a long-chain alcohol.

Davies and Rideal (*26*) also suggest that the presence of a surfactant can also affect k_l by increasing the viscosity of the surface. In terms of the classical two-film theory, this is equivalent to decreasing the value of D_l in the boundary layer or increasing the thickness of the boundary layer. In terms of penetration or surface-renewal theory, either D_l or the residence time of a packet at the surface can be reduced.

It is difficult to separate the two interfacial effects. Goodridge and Robb concluded that both the energy barrier (e.g., k_s as defined in eq 16 is significant) and the hydrodynamic effect are operative at the same time (*25*).

The purpose of the foregoing discussion was to indicate the complexities in the effect of surfactants on volatilization rate. The volatilization rate constants for benzene at 20 °C in the absence and the presence of 0.003% Triton X-100 are summarized in Table III. The values of k_v^C/k_v^O are plotted in Figure 2. The concentration of the surfactant equals the critical micelle concentration reported by the manufacturer. The data show that, while the values of k_v^C and k_v^O are reduced by the surfactant by about a factor of 2, the value of k_v^C/k_v^O is independent of the presence of the surfactant, within experimental error.

Prediction of Environmental Volatilization Rates

Equation 3 is useful for extrapolating laboratory measurements to predict environmental volatilization rate constants. The volatilization rate constant ratio, k_v^C/k_v^O, is constant over a wide range of laboratory conditions. Several problems may arise, however. The conditions of mixing and flow in the natural environment (streams, ponds, and lakes) will probably be different from conditions in the laboratory where k_v^C/k_v^O was measured. Under laboratory conditions, n is ~0.61 because the turbulence is relatively high. In the environment where the turbulence is lower, n may be >0.61. Some error then results in the prediction of k_v^C under environmental conditions.

If the view is correct that $n = 1$ in the environment because the turbulence is low, then it may be appropriate to raise the value of $(k_v^C/k_v^O)_{lab}$ to the 1/0.61 = 1.6 power to improve the accuracy of predictions in lakes and ponds. Thus

$$(k_v^C)_{env} = (k_v^C/k_v^O)_{lab}^{1.6}(k_v^O)_{env} \qquad (17)$$

may be correct for lakes and ponds.

If laboratory experiments are not conducted, but instead k_l^C/k_l^O is estimated by using diffusion coefficients, the same kind of error can occur if the wrong value of n is used. The error can be ca. ±30% if the compound of interest is similar to those shown in Table I where $k_v^C/k_v^O \approx 0.6$. Thus, eq 18 may give the best estimate of $(k_v^C)_{env}$ for lakes and ponds

$$(k_v^C)_{env} = (D_l^C/D_l^O)_{est}(k_v^O)_{env} \qquad (18)$$

while eq 19 may give the best estimate of $(k_v^C)_{env}$ for rivers

$$(k_v^C)_{env} = (D_l^C/D_l^O)_{est}^{0.6}(k_v^O)_{env} \qquad (19)$$

Clearly, the success of the method depends on the value of $(k_v^O)_{env}$ used. Typical values of $(k_v^O)_{env}$ are given in Table IV. Excellent procedures are available for estimating $(k_v^O)_{env}$ for streams and rivers, where the volatilization rate of a given high-volatility compound will be highest (*10,28*). Equivalent procedures for estimating $(k_v^O)_{env}$ for lakes are not available. The values reported in Table IV are based on data obtained before ca. 1920, and additional research is clearly necessary.

Acknowledgment

We thank G. L. Baughman, D. S. Brown, and S. W. Karickhoff of the Environmental Research Laboratory, U.S. Environmental Protection Agency, Athens, GA, for many helpful discussions in the early phases of this work.

Literature Cited

(1) Hill, J., IV; Kollig, H. P.; Paris, D. F.; Wolfe, N. L.; Zepp, R. G. "Dynamic Behavior of Vinyl Chloride in Aquatic Ecosystems"; U.S. Environmental Protection Agency, EPA-600/3-76-001, Jan 1976.
(2) Acree, F.; Beroza, M.; Bowman, M. C. *J. Agric. Food Chem.* **1963,** *11,* 278.
(3) Mackay, D.; Wolkolf, A. W. *Environ. Sci. Technol.* **1973,** *7,* 611.
(4) Mackay, D.; Leinonen, P. J. *Environ. Sci. Technol.* **1975,** *9,* 1178.
(5) Mackay, D.; Cohen, Y. "Prediction of Volatilization Rate of Pollutants in Aqueous Systems", presented at the Symposium on Nonbiological Transport and Transformation of Pollutants on Land and Water, National Bureau of Standards, Gaithersburg, MD, May 11, 1976.
(6) Dilling, W. L.; Tefertiller, N. B.; Kallos, G. J. *Environ. Sci. Technol.* **1975,** *9,* 833.
(7) Dilling, W. L. *Environ. Sci. Technol.* **1977,** *11,* 405.
(8) Liss, P. S.; Slater, P. G. *Nature (London)* **1974,** *247,* 181.
(9) Tsivoglou, E. C.; O'Connell, R. L.; Walter, C. M.; Godsil, P. J.; Logsdon, G. S. *J. Water Pollut. Control Fed.* **1965,** *37,* 1343.
(10) Tsivoglou, E. C. "Tracer Measurement of Stream Reaeration"; Federal Water Pollution Control Administration: Washington, D.C., 1967.
(11) Smith, J. H.; Bomberger, D. C. "Water, 1978"; Bennet, G. F., Ed.; American Institute of Chemical Engineers: New York, 1979; p 375.
(12) Paris, D. F.; Steen, W. C.; Baughman, G. L. *Chemosphere* **1978,** 319.
(13) Whitman, W. G. *Chem. Metall. Eng.* **1923,** *29,* 146.
(14) "Handbook of Chemistry and Physics", 54th ed.; Weast, R. C., Ed.; CRC Press: Cleveland, OH, 1973; p B-116.
(15) McAuliffe, C. *J. Phys. Chem.* **1966,** *70,* 1267.
(16) McCarthy, L. T., Jr.; Wilder, I.; Dorrler, J. S. May 1973, U.S. Environmental Protection Agency Report No. EPA-R2-73-201.
(17) Rathbun, R. E.; Stephens, D. W.; Shultz, D. J.; Tai, D. Y. *J. Environ. Eng. Div. (Am. Soc. Civ. Eng.)* **1978,** *104,* 215.
(18) Reid, R. C.; Sherwood, T. K. "The Properties of Gases and Liquids", 2nd ed.; McGraw-Hill: New York, 1966.
(19) Treybal, R. E. "Mass-Transfer Operations", 2nd ed.; McGraw-Hill: New York, 1968.
(20) Brtko, W. J.; Kabel, R. L. *J. Phys. Ocean.* **1978,** *8,* 543.
(21) Higbie, R. *Trans. Am. Inst. Chem. Eng.* **1935,** *31,* 365.
(22) Danckwerts, P. V. *AIChE J.* **1955,** *1,* 456.
(23) Dobbins, W. E. In "Advances in Water Pollution Research"; Macmillan: New York, 1964; Vol. 2, p 61.
(24) Lee, D. D. Masters Thesis, Iowa State University, Ames, IA, 1973.
(25) Goodridge, F.; Robb, I. D. *Ind. Eng. Chem. Fundam.* **1965,** *4,* 49.
(26) Davies, J. T.; Rideal, E. K. "Interfacial Phenomena"; Academic Press: New York, 1961.
(27) Bull, D. N.; Kempe, L. L. *Biotechnol. Bioeng.* **1971,** *13,* 529.
(28) Langbein, W. B.; Durum, W. H. *Geol. Surv. Circ. (U.S.)* **1967,** *no. 542.*
(29) Smith, J. H.; Mabey, W. R.; Bohonos, N.; Holt, B. R.; Lee, S. S.; Chou, T.-W.; Bomberger, D. C.; Mill, T. "Environmental Pathways of Selected Chemicals in Freshwater Systems, Part I: Background and Experimental Procedures"; EPA Report No. 600/7-78-074, May 1978.
(30) Metcalf and Eddy, Inc. "Wastewater Engineering: Collection Treatment, Disposal"; McGraw-Hill: New York, 1972; p 681.
(31) Grenney, W. D.; Porcella, D. B.; Cleave, M. L. In "Methodologies for the Determination of Stream Resource Flow Requirements: An Assessment"; Stalnaker, C. B., Arnette, J. L., Eds.; Utah State University: Logan, UT, 1976.

Received for review October 12, 1979. Accepted June 16, 1980. Portions of this work were supported by the U.S. Environmental Protection Agency, Contract No. 68-03-2227; the National Science Foundation, Grant No. PFR 78-10691; and the U.S. Army Medical Research and Development Command, Contract No. DAMD-17-78-C-8063.

Seasonal and Episodic Trends in Sulfate Concentrations (1963–1978) in the Eastern United States

A. P. Altshuller

Environmental Protection Agency, MD-59, Research Triangle Park, North Carolina 27711

■ The ambient air quality data for sulfates and sulfur dioxide available through 1978 have been analyzed for seasonal trends and episodic characteristics. The monitoring sites available were grouped into five sets: Northeast urban, Southeast urban, East nonurban, Midwest urban, and Midwest nonurban. Each group of sites showed unique aspects with respect to seasonal trends. Winter quarter sulfate trends at urban sites trended downward between 1963 and 1978, particularly at Northeast urban sites. At the Northeast sites, local scale primary sulfate emissions accounted for most of the excess in urban sulfate concentrations above regional background. In contrast, in all groups of sites during the summer months regional-scale processes contributed substantially to sulfate concentration levels. Summertime sulfate levels were strongly influenced by episodes of elevated sulfates. The trends in urban excess sulfate concentration followed the trends in sulfur oxide concentrations at urban sites. The trends in sulfate also can be related to sulfur oxide emission trends. Significant relationships between sulfate and visibility trends are noted, particularly for the summer months of the year.

Sulfates constitute a substantial fraction of total suspended particulate matter and an even larger fraction of inhalable particles and fine particulate matter (*1*). Much of the sulfate has been demonstrated to be finely divided (*1*) and to undergo long-range transport across the North American and European continents (*2–7*). Visibility effects show substantial correlations with sulfate concentrations (*8–10*). A varying portion of the total sulfate has been shown to be present as acid sulfate species (*1, 11–13*). Acid forms of sulfate have been identified as a major contributor to the acidity of precipitation impacting aquatic and terrestrial ecosystems (*6, 14, 15*). The concurrent formation of sulfate along with ozone and other photochemical smog products has been considered (*16–18*).

Because of the importance of sulfates as atmospheric pollutants, all available approaches to better understanding the origins and distribution of sulfates in the atmosphere need to be utilized. One of these approaches uses trend analyses to investigate historical changes in sulfate distributions. Several previous studies of this sort have been reported considering such trends, regional differences, and urban-to-nonurban ratios (*2, 3*). Some seasonality trends have been examined between 1965 and 1972 (*19*). Episodic behavior of sulfates has been discussed by several investigators using results from the 1974–76 period (*4, 17, 18, 20*).

In the current investigation the 1963–78 NASN data base has been used. The measurements have been stratified geographically in more detail than that reported previously (*19*). Possible quantitative relationships between sulfate trends and

Published 1980 American Chemical Society

SO_x emissions in the northeastern United States have been considered. In addition, the frequency with year and season of episodes has been determined for the 1965–78 period. The consistencies between sulfate trends and previous reported visibility trends have been examined.

The eastern United States was selected for emphasis because the sulfate concentrations have been the highest in this area of the country. Also substantial changes in sulfur oxide emissions have occurred during the 1963–78 period in the northeastern United States.

Procedures. The computations were made by using the 24-h average total water-soluble sulfate and sulfur dioxide concentrations reported by site from 1963 through 1978 as available in computer printouts. Some suspicious values were discarded. Most of these were concentrations reported at zero. The individual values were used to compute quarterly averages. Although some of the earlier monitoring results are available in reports as annual averages by site or as frequency distributions, the source for individual measurements is the National Aerometric Data Bank (NADB).

Although sampling was carried out at a large number of eastern sites, the length and the completeness of the collection and analysis of samples proved highly variable. In this work, results from 1963 through 1978 were sought for urban sites and from 1965 through 1978 at nonurban sites. The number of sites where results were complete over the entire period was limited. Therefore, where results were available at urban sites starting in 1964 rather than 1963 or ending in 1977 rather than 1978, these sites also are included.

Five groupings of monitoring sites are utilized: Northeast urban, Southeast urban, Midwest urban, East nonurban, and Midwest nonurban. The Appalachian Mountains are used as the boundary between Northeast urban and Midwest urban as well as between East nonurban and Midwest nonurban. The 3-yr quarterly averages by site are also averaged over all of the sites in each grouping to obtain a "regional average". The number of monitoring sites over which the measurements are averaged to obtain regional trends for sulfates are as follows: Northeast urban, 10; Southeast urban, 6; Midwest urban, 18; East nonurban, 6; Midwest nonurban, 5.

Potential for Artifact Formation of Sulfate. Laboratory results have indicated a sulfate artifact because of collection and conversion of a portion of the sulfur dioxide present to sulfate on glass-fiber filters. This artifact, although recognized some years ago (*21*), has been the subject of recent laboratory (*22, 23*) and field investigations (*1, 24, 25*). The laboratory results indicate that such an artifact should be influenced by sulfur dioxide concentration air volume per unit area, temperature, humidity, and other parameters. Artifact sulfate formation was reported to show a low dependency on humidity but a substantial dependence on sulfur dioxide concentration and temperature (*22, 23*). Artifact sulfate values ranged from ~1 $\mu g/m^3$ in the presence of 20 $\mu g/m^3$ of sulfur dioxide at a high temperature to 6 $\mu g/m^3$ or more in the presence of 120 $\mu g/m^3$ of sulfur dioxide and a low temperature (*23*). However, these results on uncoated filters are confounded by the further result that a loading of ambient air particulates on similar filters at 120 $\mu g/m^3$ and low temperatures reduced the artifact sulfate from 6 to 2 $\mu g/m^3$ (*23*). Coutant (*22*) concluded that sulfate loading errors from the use of common glass-fiber filters under normal Hi-Vol sampling conditions would be in the range of 0.3–3 $\mu g/m^3$.

Appel et al. (*24*) could find no clear evidence of artifact sulfate by using a group of particulate samples collected on glass fiber, quartz, and fluoropore in St. Louis and subjected to analysis by several different analytical techniques. The differences observed could be explained by estimated interference effects, analytical efforts at low concentrations, and differences in particle collection efficiencies (*24*). Stevens et al. (*1*) observed excess sulfate concentrations for samples collected from September to December, 1975, in St. Louis on glass-fiber filters over those collected on cellulose ester filters at eight sampling sites ranging from 1.4 to 3.3 $\mu g/m^3$. However, the samplers as well as the analytical methods used were different with the two filter media.

Pierson et al. (*25*) reported on spurious sulfate found on two samples collected in a tunnel and two rural samples. The "excess sulfate" ranged from 0.18 out of 13.2 $\mu g/m^3$ in a tunnel sample with a concurrent SO_2 concentration of 125 $\mu g/m^3$ to 2.46 out of 8.7 $\mu g/m^3$ in a rural sample with a concurrent SO_2

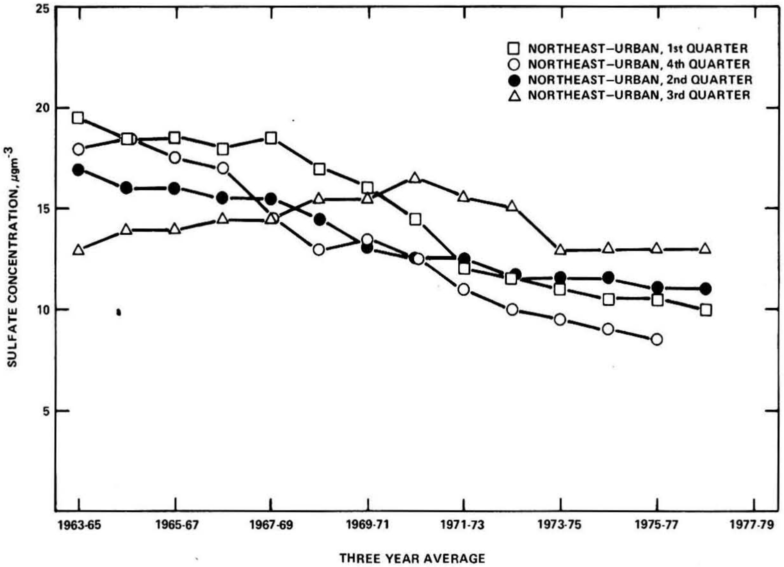


Figure 1. Three-year running average sulfate concentrations by quarter of the year for urban sites in northeastern United States.

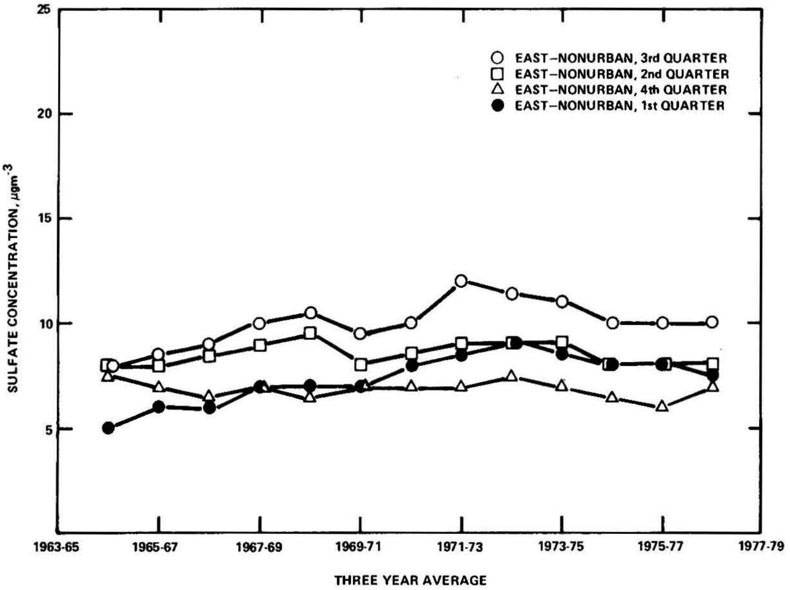


Figure 2. Three-year running average sulfate concentrations by quarter of the year for nonurban sites in eastern United States.

concentration of 16 $\mu g/m^3$. The authors concluded that they observed an incoherent pattern of spurious sulfate formation (*25*).

It has to be assumed in the discussion that follows that the sulfate artifact, if present, was small enough not to substantially influence the interpretation of results on trends in sulfate concentrations.

Results on Seasonal Trends in Sulfate Concentrations

At the urban sites in the northeastern United States, the averaged trends for three quarters of the year show that overall decreases occurred in sulfate concentrations between 1963–65 and 1976–78 (Figure 1). However, the third-quarter trend was definitely upward during the late 1960s and early 1970s with a subsequent decline in sulfate concentrations in the 1970s. No overall change in sulfate concentration occurred between 1963–65 and 1976–78 (Figure 1). In the other three quarters, the overall downward trends show a number of changes in slope, plateaus, and even one brief increase in sulfate concentration (first quarter). The overall decreases in sulfate concentration between 1963–65 and 1976–78 were substantial and as follows: first quarter, 10 $\mu g/m^3$; second quarter, 6 $\mu g/m^3$; fourth quarter, 10 $\mu g/m^3$. As a result of these shifts in sulfate concentration with time the ordering of concentrations by quarter of the year reversed between the 1960s and 1970s. In earlier years the sulfate concentrations often were in the relationship first and fourth quarters ≧ second quarter > third quarter, whereas by the 1970s the relationship had become third quarter ≧ second quarter > first and fourth quarters.

The third-quarter trend at the nonurban sites is clearly upward during the 1960s and early 1970s (Figure 2). A moderate downward trend occurs subsequently, but the sulfate concentrations in 1976–78 still averaged 2 $\mu g/m^3$ higher than in 1965–67. The first quarter shows a small upward trend of 2 $\mu g/m^3$ overall (Figure 2). The second quarter after a small upward trend declines by 1976–78 to the same average sulfate concentration, 8 $\mu g/m^3$, occurring in 1965–67. The fourth quarter shows little variation, the overall change being a decrease of 1 $\mu g/m^3$ in the sulfate concentration between 1965–67 and 1976–78.

The averaged trends in sulfate concentrations for the winter quarters at the urban sites in the southeastern United States show only small variations (Figure 3). The net changes in sulfate concentrations between 1965–67 and 1976–78 for the first and fourth quarters, respectively, were decreases of 2 and 3 $\mu g/m^3$. The second-quarter trend increased, reached a plateau, then decreased in the early 1970s, but then increased again through 1975–77 (Figure 3). The third-quarter sulfate concentrations showed a continuing upward trend with several plateaus, but with a net increase of 4 $\mu g/m^3$ between 1966–67 and 1976–78. The first-, second-, and fourth-quarter trends at the urban sites in the southeastern United States have little or no resemblance to the trends at urban sites in the northeastern United States. Although by no means identical, the trends in the urban sites in the Southeast are closer to the nonurban trends in the East than the urban trends in the Northeast.

The averaged trends in sulfate concentrations for the winter quarters at the urban sites in the midwestern United States, as in the Southeast, show only small variations (Figure 4). The net changes in the sulfate concentration between 1964–66 and 1975–77 for the first and fourth quarters, respectively, were decreases of 3 and 4 $\mu g/m^3$. As in the Southeast, the concentration of sulfate increased in the second quarter during the 1960s. Somewhat similar to the trend in the Southeast, after a subsequent decrease, the sulfate concentration leveled off then increased again (Figures 3 and 4). The net result was no change in sulfate concentration during the second quarter between 1964–66 and 1976–78 (Figure 4). The trend in sulfate concentration in the third quarter in the Midwest was upward well into the 1970s followed by a small decrease. The net increase between 1964–66 and 1976–78 was 2 $\mu g/m^3$ (Figure 4). The third-quarter trend line, although higher overall, had similarities to the trend at nonurban sites in the eastern United States (Figures 2 and 4).

The averaged trends in sulfate concentrations for the winter quarters at the nonurban sites in the midwestern United States show only small variations (Figure 5). The net changes in the sulfate concentration between 1965–67 and 1976–78 in the first quarter was an increase of 1 $\mu g/m^3$, whereas no net change occurred in the fourth quarter. The second-quarter

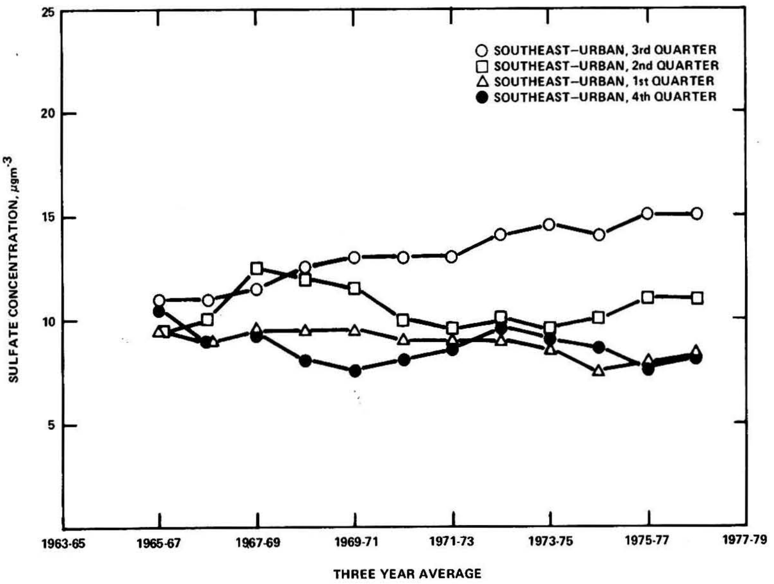


Figure 3. Three-year running average sulfate concentrations by quarter of the year for urban sites in southeastern United States.

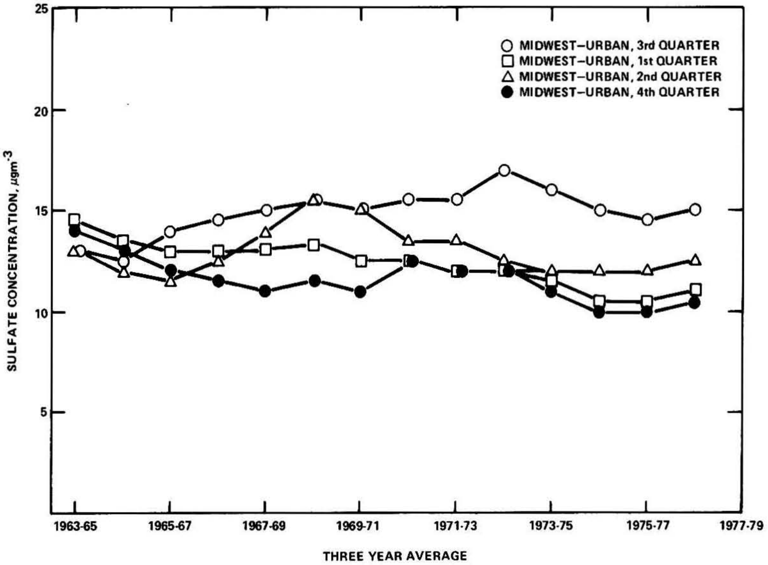


Figure 4. Three-year running average sulfate concentrations by quarter of the year for urban sites in midwestern United States.

trend in sulfate concentration also showed small variations up and down with a net increase between 1965–67 and 1975–77 of 2 $\mu g/m^3$. The sulfate concentrations during the third quarter showed a substantial upward trend in the 1960s into the 1970s followed by a rapid decrease in the mid-1970s. The net change in sulfate concentration in the third quarter between 1965–67 and 1975–77 was an increase of 4 $\mu g/m^3$.

Comparisons of the trends in urban compared to nonurban sulfate concentrations are of interest. The change in patterns observed appear to relate to changes in local vs. regional influences. In Table I the urban excesses, the average differences between concentrations of sulfates at groupings of urban sites and nonurban sites in the same geographical region, are computed for 1976–78 compared to 1965–67.

Urban excesses decrease markedly between 1965–67 and 1976–78 in the northeastern United States for all quarters of the year although the largest changes are in the winter quarters. Much smaller decreases in the urban excesses occur between 1965–67 and 1976–78 (Table I) in the midwestern United States. In the Southeast the urban excesses decreased somewhat for the winter quarters between 1965–67 and 1975–77, whereas the urban excesses increased during the second and third quarters of the year.

In Tables II and III (see paragraph at end of text regarding

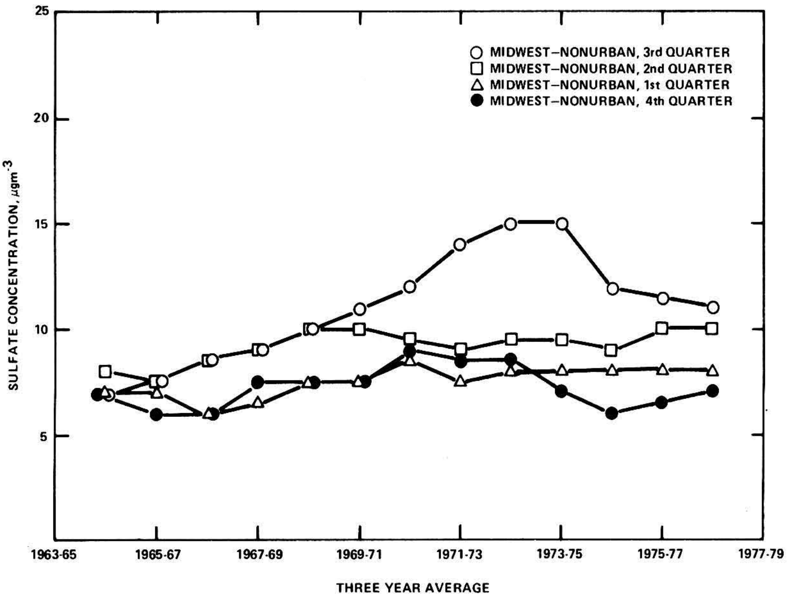


Figure 5. Three-year running average sulfate concentrations by quarter of the year for nonurban sites in midwestern United States.

Table I. Urban Excesses over Nonurban Sulfate Concentrations in 1976–78 Compared with 1966–67

differences between groupings of sites	sulfate concn							
	1st quarter		2nd quarter		3rd quarter		4th quarter	
	1965–67	1976–78	1965–67	1976–78	1965–67	1976–78	1965–67	1976–78
$U_{NE}{}^{a} - NU_{E}{}^{b}$	12	3	8	3	6	3	11	1
$U_{SE}{}^{c} - NU_{E}{}^{b}$	3	1	2	4	3	5	3	1
$U_{MW}{}^{d} - NU_{MW}{}^{e}$	6	3	4	2	6	4	6	4

[a] Urban Northeast. [b] Nonurban East. [c] Urban Southeast. [d] Urban Midwest. [e] Nonurban Midwest.

supplementary material) are tabulated by site and quarter of the year the 3-yr average sulfate concentrations for (a) 1965–67 compared to 1976–78 and (b) the highest concentrations during the 1963–78 period along with the corresponding time period.

The trends at individual sites can differ significantly from the averaged regional trends. For example, while the average second-quarter trend in sulfate concentrations at the urban sites in the northeastern United States was downward, the trend at a site in the Washington, DC area on the southern edge of the region was upwards. At a site in Charleston, WV, the trends in sulfates *for all* quarters was *sharply* downward unlike the trends at other urban sites in the Midwest. With respect to peaking of sulfate concentrations in the third quarter, the sites in Charleston, WV, and Roanoke, VA, showed maximum sulfate concentrations in the late 1960s, whereas at other sites in the same regions the sulfate concentrations peaked in the 1970s or showed no peaking through 1977.

Elevated Sulfate Concentrations and Regional Sulfate Episodes

Other features of the sulfate concentration distributions are the characteristics of the higher range of sulfate concentrations particularly those associated with large region episodes of elevated pollution levels. Locally high sulfate concentration in an urban area may result from higher than usual local emission rates combined with less than favorable local meteorological conditions for dispersion of pollutants. Therefore, evaluation of elevated sulfate concentrations at nonurban sites appears to represent a possibly better approach to identifying regional scale phenomena.

It was decided to survey the data between 1965 and 1977 at 11 nonurban sites located from North to South from Maine to Virginia and as far west as Indiana. (Date were missing at a number of these sites in 1978.) Preliminary scanning of the data indicated that selection of a sulfate concentration level of ≧15 $\mu g/m^3$ as elevated would provide a useful higher frequency range of values. Sulfate concentration measurements were available for a total of 2825 24-h periods between 1965 and 1977 at the 11 sites. The sulfate concentration of 15 $\mu g/m^3$ was equalled or exceeded during 12% of the total measurement periods of 332 24-h periods. The frequency with which 15 $\mu g/m^3$ was equalled or exceeded varied from 4% at the Acadia National Park site in Maine to 18% at the Parke County site in Indiana. For the 332 24-h periods with concentrations ≧15 $\mu g/m^3$ the distribution by month of year of the 24-h periods by percent is as follows: January, 3%; February, 4%; March, 3%; April, 4%; May, 6%; June, 18%; July, 20%; August, 22%; September, 11%; October, 5%; November, 2%; December, 2%. Therefore, 28% of the elevated sulfate concentrations measured occur in the second quarter of the year and 53% in the third quarter of the year, whereas 9–10% of the elevated concentrations occur in either the first or fourth quarter. A similar evaluation of the distribution of sulfate concentrations at nonurban sites ≧20 $\mu g/m^3$ and 30 $\mu g/m^3$ indicated that 75 and 88% of such elevated concentrations occurred during June through August.

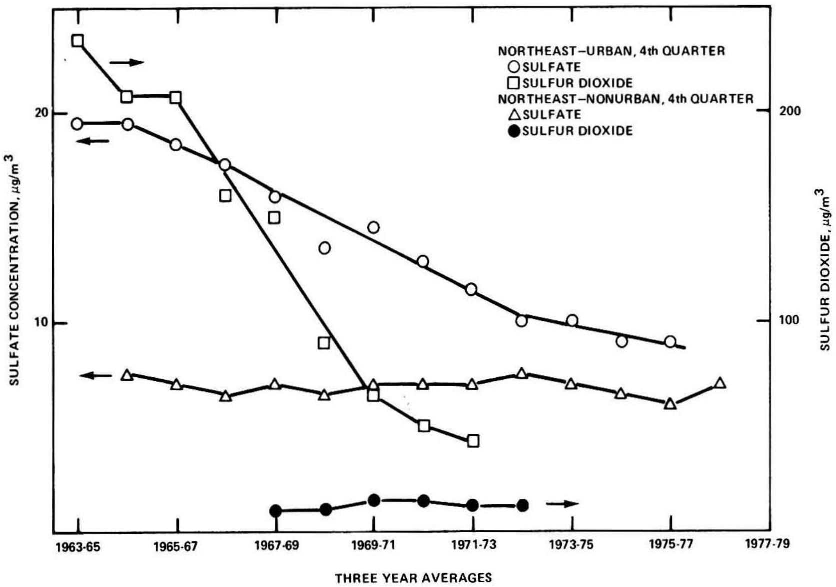


Figure 6. Three-year running average sulfur dioxide and sulfate concentrations during fourth quarter of year for urban and nonurban sites in the northeastern United States.

To investigate the influence of time interval on the number of 24-h elevated sulfate concentrations, we divided the total 1965–77 period into three subintervals: 1965–68, 1969–72, and 1974–77. The measurements at 9 of the 11 sites was extensive enough throughout the entire period to utilize in the computations. These sites were as follows: Acadia National Park, MA; Orange County, VT; Coos County, NH; Washington County, RI; Shenandoah National Park, VA; Jefferson County, NY; and in the Midwest, Clarion County, PA; Monroe County; IN; and Park County, IN. While the number of 24-h sulfate concentrations greater than or equal to 15 $\mu g/m^3$ was much larger during the 1969–72 period than during the earlier or later periods, the number of 24-h sulfate concentrations greater than or equal to 20 $\mu g/m^3$ was only moderately larger in the 1969–72 interval. The largest number of 24-h sulfate concentrations greater than or equal to 30 $\mu g/m^3$ occurred in the 1974–77 period. Therefore, the very highest sulfate concentrations did not peak out, but instead increased into the 1974–77 period.

Using the data base of 332 24-h average sulfate measurements during which sulfate concentrations were greater than or equal to 15 $\mu g/m^3$, the subgroup of 24-h periods was identified when elevated sulfate concentrations occurred concurrently at several of the nonurban sites. For this survey, data from a total of 14 nonurban sites was examined. Measurements frequently were missing on any particular day at several of these sites. In a few instances, the measurements were available over several successive dates rather than a single date. On the basis of such intercomparisons, a total of 55 *potential* episodes of elevated sulfate concentrations were identified. The distribution of these potential elevated sulfate episodes by time interval was as follows: 1965–68, 9; 1969–72, 23; 1974–77, 17. In addition, six potential episodes were identified during 1973. The distribution of potential episodes by month was as follows: January, 0%; February, 4%; March, 2%; April, 4%; May, 9%; June, 22%; July, 23%; August, 27%; September, 7%; October, 0%; November, 2%; December 0%. Again, the June–August period dominated with 72% of potential episodes during these three months at nonurban sites.

The geographical distribution of sulfate concentrations during six of the episodes (June 1966, August 1977, June 1968, August 1970 (2), August 1972) with strong regional aspects have been evaluated. Elevated sulfate concentrations were measured over the midwestern states east of the Mississippi River and in the mid-Atlantic states during each of the six episodes. Lower New England also had elevated sulfate concentrations during several of these episodes while upper New England did during a few of the episodes. In only one of the six episodes did elevated sulfate concentrations extend into states west of the Mississippi River.

Discussion

Since sulfur dioxide emissions from combustion sources are the dominant precursor to formation of particulate sulfate in the eastern United States, it is important to compare the trends in sulfate with those for sulfur dioxide. Because 24-h sulfur dioxide concentration data were not available on a consistent basis at all of the sites at which sulfate data were available, the averaged sulfate concentrations were recomputed for the smaller set of sites. The sulfur dioxide measurements available at southeastern urban and nonurban locations were too limited to permit detailed comparisons. Comparisons are shown in Figures 6–12 for northeastern and midwestern urban sites of sulfur dioxide (through 1973) and sulfate concentrations for several seasons of the year.

The fourth-quarter sulfur dioxide concentrations at Northeast urban sites (Figure 6) averaged 235 $\mu g/m^3$ in 1963–65 but had decreased to 43 $\mu g/m^3$ by 1971–73, an 82% reduction. The third-quarter sulfur dioxide concentrations at these sites (Figure 7) which averaged 77 $\mu g/m^3$ in 1962–65 and 16 $\mu g/m^3$ by 1971–73 decreased by 79%. The ambient air levels in the summer were only one-third the levels in the winter. At these sites during the second quarter the decrease in sulfur dioxide concentrations again averaged near 80%, and the concentrations measured were intermediate between first- and fourth- and the third-quarter average sulfur dioxide concentration levels (Figure 8).

At the Midwestern urban sites the average sulfur dioxide ambient air concentrations in the mid-1960s were only one-

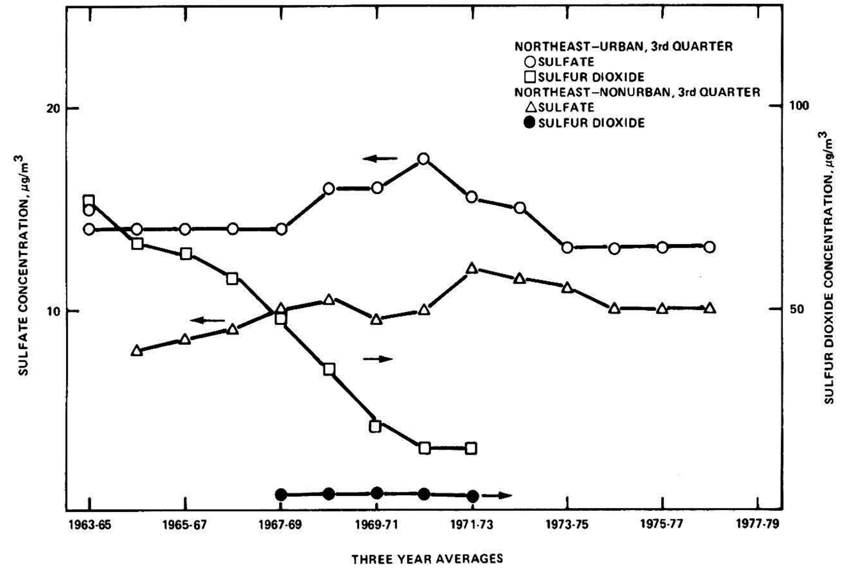


Figure 7. Three-year running average sulfur dioxide and sulfate concentrations during third quarter of year for urban and nonurban sites in the northeastern United States.

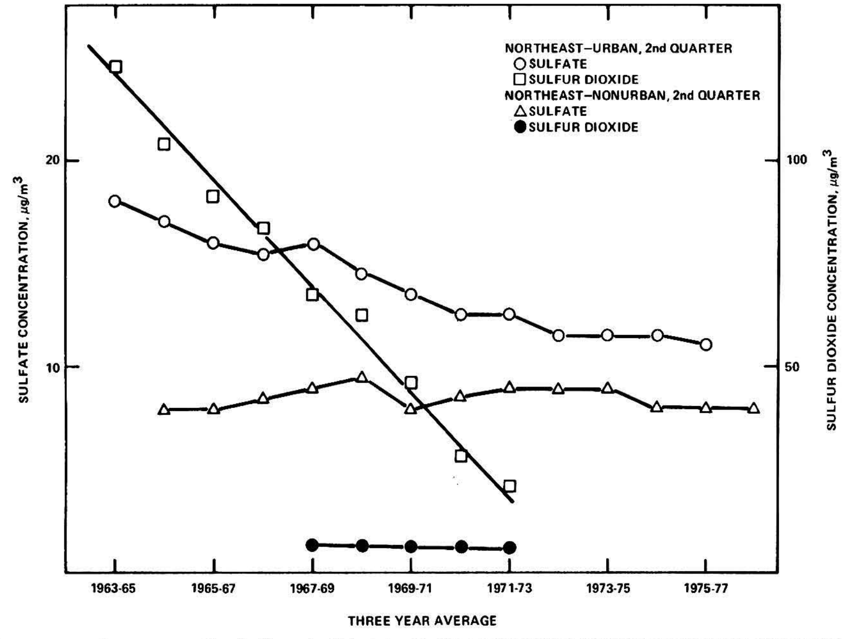


Figure 8. Three-year running average sulfur dioxide and sulfate concentrations during second quarter of year for urban and nonurban sites in the northeastern United States.

third to one-half of the sulfur dioxide concentrations in the Northeast (Figures 10–12). Sulfur dioxide concentrations at these sites during the winter quarters did not exceed those measured during the summer at Northeastern urban sites (Figure 10). The sulfur dioxide decreased between 1963–65 and 1972–74 during the first and fourth quarters by ~50%. During the second quarter (Figure 11) at these sites, the sulfur dioxide concentration in 1965–67 averaged 40 μg/m³ and decreased by about one-third by 1972–74. During the third quarter (Figure 12) at the Midwestern urban sites, sulfur dioxide concentrations averaged ~40 μg/m³ in 1965–67 and decreased ca. 50% by 1972–74. Therefore, both the concentration levels and the percent reductions of sulfur dioxide with time in the Midwest were substantially less than in the Northeast for all quarters of the year.

Sulfates measured in the atmosphere might be associated with a number of primary sources and secondary atmospheric formation. Several of the mechanisms associated with secondary formation will be briefly discussed.

Contribution of Primary Sources of Sulfates. The contributions from primary emissions will be considered first. Sulfur dioxide in flue gases appears to be proportional to the sulfur content of the fuel (*26*). Increasing sulfur content (*27, 28*), increasing vanadium in oil (*30*) content, and increasing oxygen in the furnace (*26, 27, 29, 30*) all can result in increasing primary sulfur trioxide/sulfate emissions. Of particular consequence is the result that at least a three-to-one higher conversion of sulfur dioxide to sulfates has been found from oil-fired boilers (6%) compared to coal-fired boilers (1–2%) *27, 28*).

In New York–New Jersey, Philadelphia, and certain other urban areas, regulations limiting the percentage of sulfur in coal and in fuel oil were implemented in the latter part of the 1960s with subsequent increasingly restrictive limits on the sulfur content of fuels (*31*). Although the earlier regulations allowed 2% sulfur in coal, the sulfur content in all fuels by the early 1970s was reduced depending on fuel type and urban area (*31, 32*). These low sulfur in fuel regulations greatly restricted or eliminated the use of coal as a fuel within urban areas of the northeastern U.S.

For example, in New York City the sulfur content of the utility coal was reduced between 1965 and 1967 from 1.6 to 1.2% and the utility oil from 2.3 to 1.9% (*32*). The sulfur content of the utility coal was reduced to 0.9–1.0% by 1968 and stayed in that range subsequently. The sulfur content of the utility oil used decreased to the 0.8–0.9% range in 1968–70 and decreased by 1972 to 0.4% for No. 6 fuel oil and less than 0.2% for No. 2 fuel oil (*32*). With increasing restrictions on sulfur content of fuels, the use of coal was reduced drastically between 1967 and 1971, and utility coal was eliminated as a fuel in New York City by 1972 (*32*). Similar shifts to lower sulfur content coal and from coal to oil occurred in other cities as well (*31*).

How significant a contribution is made by sulfates directly emitted from coal- and oil-fired sources to local/urban ambient air sulfate levels? Most investigators agree that sulfur emissions from coal in the form of SO_3 and particulate sulfate range from less than 1% to ca. 2% (F_{1C}) (*27, 28*). Homolya and Cheney (*27*) report an average of 6–7% from oil-fired sources (F_{1O}). In 1965–67 in New York–New Jersey a significant part of sulfur oxide emissions was associated with coal. In a 1965 sulfur oxides emission inventory 38% of sulfur oxides were computed as emitted by power plants (*33*). When 1964 sulfur oxide emissions were estimated for the same area (*34*), 327 000 tons of sulfur dioxide were computed to be released by coal-fired power plants compared to 234 000 tons from use of residue oil in other power plants in the New York–New Jersey area. Multiplying these emissions by 4/3 to include all coal-fired emission sources results in 436 000 tons out of a total of 1.55 million tons (*33*) or ca. 28% of sulfur dioxide being associated with combustion of coal. The 1972 emission inventory report (*35*) lists ca. 20% of the sulfur oxide emissions in the Hartford–New Haven area and 40% of the sulfur oxides in the Washington area as associated with coal burning. It will be assumed that 30% of the SO_2 emissions were associated with coal (F_{2C}) and 70% with oil (F_{2O}) on the average in the Northeast in 1965–67 in the winter months. The urban excess of sulfate emissions was 11–12 μg/m^3 in the first and fourth quarters (Table I, Figure 6). The sulfur dioxide excess was 230 − 10 μg/m^3 (regional) or 220 μg/m^3 (Figure 6). The contribution from primary sulfate emissions can be estimated from the relationship $C(SO_4) = [F_{1C}F_{2C} + F_{1O}F_{2O}]C(SO_2)$. When F_{1C} is 0.015, the midrange emission factor, F_{2C}, is 0.30, F_{1O} is 0.065, and F_{2O} is 0.70, $C(SO_4) = [0.0045 + 0.045] \times 220$ μg/m^3 equalling 11 μg/m^3. For the second quarter a similar calculation results in 4 μg/m^3 of sulfate derived from primary emissions. On the basis of these estimates, essentially all of the excess sulfate can be associated with primary emissions in the first and fourth quarters and ca. 50% of the excess in the second quarter (Table I, Figure 8).

One of the reasons that these results can only be considered as estimates is the lack of data on what fraction of the sulfur dioxide measured at ground level sites was associated with emissions from stacks or chimneys at various heights. Simon and Ferrand (*33*) discussed the relative contributions at increasing distances from point and area sources. Local oil-fired, near surface sources appeared to contribute most of the sulfur oxides measured.

The decrease in excess sulfate (over regional background) between 1965–67 and 1975–77 during the first and fourth quarters at urban sites in the Northeast corresponded to a 70–83% overall decrease in sulfate (Table I). Such a percentage decrease in excess sulfate in the winter months is very close to the 80% decrease in sulfur dioxide already discussed. These results also are consistent with the reductions in sulfate emitted from the burning of oil being approximately proportional to the decrease in sulfur content in oil.

In the early part of the period when oil was being substituted for coal, leveling off or even increases in sulfate emissions might be expected as a result of higher sulfate emissions from the substitution of high-sulfur fuel oil used. Such effects appear to be consistent with the plateau in atmospheric sulfate concentrations occurring for some of the years during the 1960's in the first, second, and fourth quarters in the Northeast (Figure 1). In the 1970s the trend in atmospheric sulfates was downward. This later behavior is consistent with the switch to much lower sulfur content fuels by the 1970s with resulting lower primary sulfate emissions.

The sulfur dioxide and to a lesser extent the sulfate concentrations during the third quarter were lower than they were during the other quarters of the year during most of the 1960s (compare Figures 6–8). The lower ambient sulfate concentrations can be associated with the much reduced levels of both sulfur dioxide and sulfate emissions as a result of minimal usage of fuel oil for space heating in the summer months. During the third-quarter sulfur emissions from utility sources were of particular significance. The change in fuel mix with time was even more pronounced for utility usage than for overall fuel usage. In New York City there was a slow switch between 1965 and 1969 from coal to oil in utility usage. The sulfur content of the oil was about as high as or higher than the sulfur content of the coal at least through 1971. Either no decrease or some increase in directly emitted sulfates from utility sources would be expected because of the higher emissions from oil compared with coal or equivalent sulfur content. Making an estimate similar to that made above from the sulfur dioxide ambient air concentrations and the primary sulfate emissions factors, one would predict an urban excess primary sulfate contributions of 3–4 μg/m^3 in the third quarter during the middle 1960s. The observed excess was from 5 to 6 μg/m^3 (Table I, Figure 7). By the middle 1970s the third-quarter observed urban excess was reduced to 2 μg/m^3 (Table I, Figure 7). The predicted primary contribution in the middle 1970s would be $\sim$1 μg/m^3. During intermediate periods of the early 1970s, the third-quarter urban sulfate peaked with the urban excess reaching 5–7 μg/m^3, while the predicted contribution from primary emissions was from 1 to 2 μg/m^3. Therefore, a substantial portion of the urban excess of sulfate in the third quarter throughout the entire 1968–75 period ranging from 1–2 μg/m^3 to as much as 4–6 μg/m^3 cannot be accounted for by primary sulfate emissions.

Ambient air vanadium concentrations tended to peak at the various urban sites in the Northeast in the late 1960s or early 1970s and drop rapidly in concentration subsequently (*36*).

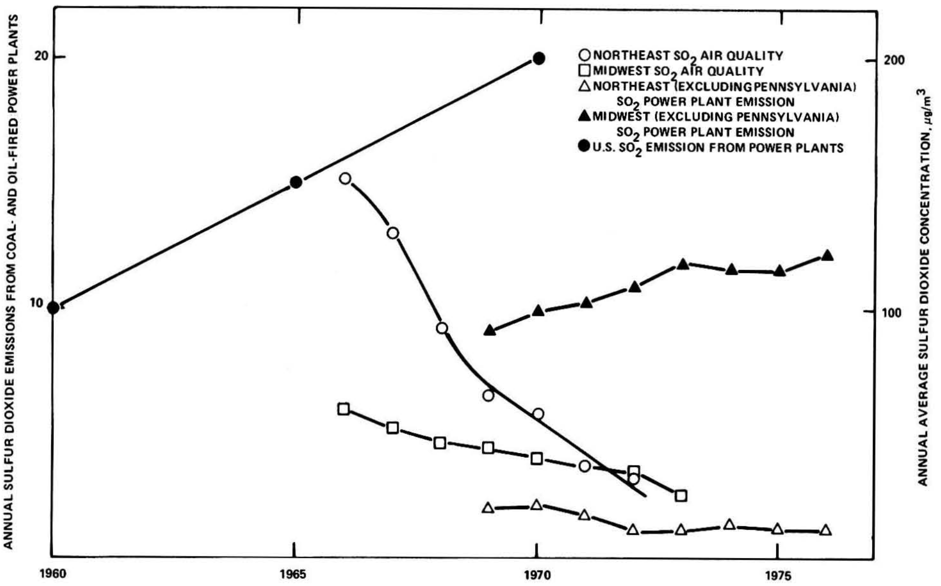


Figure 9. Annual average ambient air concentrations and emissions of sulfur dioxide in northeastern and midwestern United States.

The increase in vanadium measured in the 1960s reflected the increased use of higher-sulfur-content fuel oils. As the regulations on sulfur contents of fuels became increasingly stringent in the last 1960s and early 1970s, desulfurized fuel oils were substituted along with low-sulfur fuel oils derived from North African crudes (*33*). These fuels contained much less vanadium because vanadium was removed along with the sulfur in the desulfurization process and because of the low vanadium contents of the crudes used. Since vanadium can have a direct positive catalytic effect on the flue gases (*30*), to some extent the rapid decrease in vanadium in the 1970s could have been associated with the decrease in primary sulfate emissions along with the decrease associated with the reduction of sulfur content of the fuel.

As noted earlier, the nonurban sulfate concentration trends in the eastern United States bear little or no relationship to the urban trends in the northeastern United States. During the 1960s, except for the third-quarter trend, the trends at these nonurban sites were slightly upward, or no trend at all was evident. A small downward trend occurs during the 1970s (Figure 2). Vanadium has been used as a surrogate for dispersion of primary sulfur emissions out of urban sources in the northeastern United States (*3*). The estimate made was that the amount of primary sulfate transported to nonurban areas could range from 1.2 to 2.6 $\mu g/m^3$. Therefore, it would appear that use of low-sulfur fuel oil might have contributed by the 1970s to a reduction in the nonurban sulfate concentrations of 1–2 $\mu g/m^3$.

While local sulfur dioxide emissions were being reduced within urban areas in the northeastern United States, statewide coal and oil-fired utility sulfur emissions for the area from Maine to Washington, DC did not decrease substantially until the 1970s (*37*) (Figure 9). Between 1970 and 1976 sulfur oxide utility emissions decreased from 2.06 to 1.14 million tons, a percentage decrease of 45%. About 70% of this reduction was associated with coal-fired power plant operations in the northeastern U.S. (*37*). The small decline observed in eastern nonurban sulfate emissions in the early 1970s (Figures 6–8) could also be associated with the decrease in northeastern regional scale utility emissions in the 1970s. Similarly, some part of the decrease in urban sulfate concentrations in the Northeast in the 1970s may be associated with this decrease in regional utility emissions in the Northeast.

The large source emissions of sulfur oxides from Midwestern utility sources increased by over a factor of 2 through the 1960s into the 1970s (*37*) (Figure 9). Long-range transport of a portion of primary emissions from these sources into the Northeast could have some counterbalancing effect on changes in ambient air sulfate concentrations within the Northeast.

At Midwestern urban sites, where coal-fired sources dominate, the contribution of primary sulfate emissions do not account for much of the excess urban sulfate observed. During the fourth quarter (Figure 10), if a 10% oil-fired combustion contribution is assumed in 1965–67 at Midwestern urban sites, $C(SO_4) = (0.015 \times 0.9 + 0.065 \times 0.1) \times 60\ \mu g/m^3$ or $1.2\ \mu g/m^3$ compared to a 6 $\mu g/m^3$ excess in sulfate. For the second and third quarters (Figures 11 and 12) the local primary sulfate contribution would account for less than 1 $\mu g/m^3$ of the observed excesses of 4 and 6 $\mu g/m^3$, respectively.

The contribution from the increasing emissions from nonurban utility sources in the Midwest may have made a contribution of a few $\mu g/m^3$ of primary sulfates to urban and nonurban Midwestern sulfate concentrations. This contribution also may account for the small increases observed during the 1960s into the 1970s in first- and second-quarter sulfate concentrations (Figure 5) at Midwestern nonurban sites. Similarly, such a regional increment may have resulted in sulfates at urban sites undergoing a smaller decrease with time in the winter months than would have otherwise occurred.

There also was a shift from coal to oil in steam plants in some southeastern states. In particular, there was an appreciable shift in Virginia towards the use of oil instead of coal in the late 1960s into the 1970s (*37*). The net result was about a 25% increase in utility emissions (*37*). This local increase as well as sulfate transported from west of the Appalachians may account for the increases in sulfate during the third quarter at these urban sites between 1965–67 and 1976–78.

Although a small increment in sulfates in the eastern United

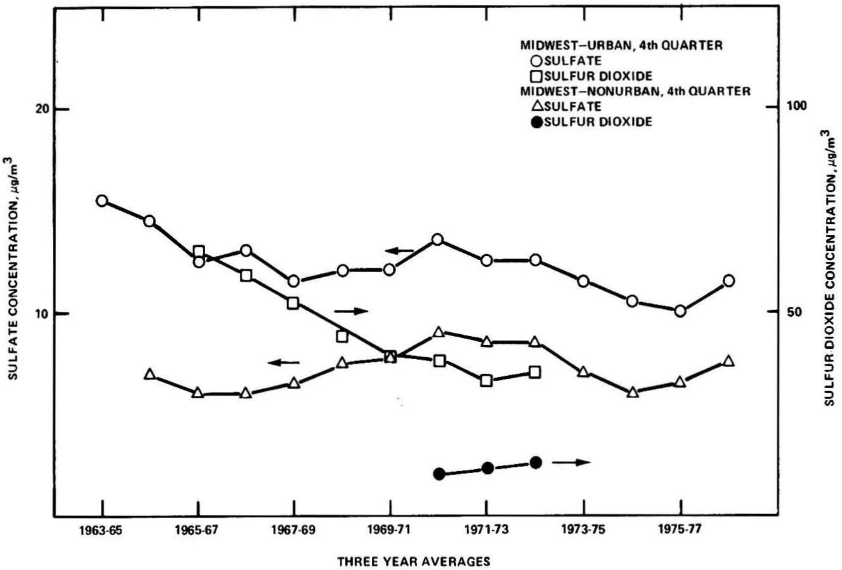


Figure 10. Three-year running average sulfur dioxide and sulfate concentrations during fourth quarter of the year for urban and nonurban sites in midwestern United States.

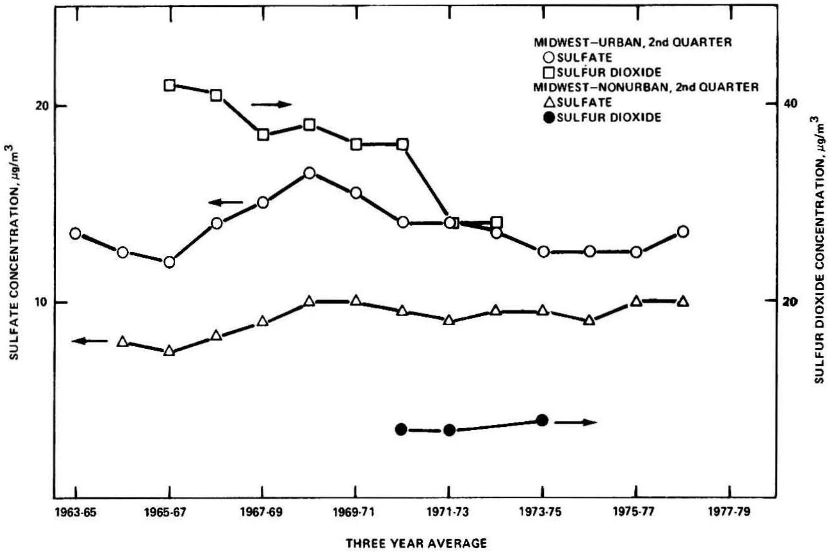


Figure 11. Three-year running average sulfur dioxide and sulfate concentrations during second quarter of the year for urban and nonurban sites in midwestern United States.

States may be associated with increases in coal-fired utility emissions in the Midwest, the increment is by no means proportional to the large increase in emissions. This result is consistent with much of these emissions moving aloft in plumes separated from the surface layer where the air quality measurements are made.

Contribution of Secondary Processes of Sulfate Formation. In the discussion thus far no consideration has been given to secondary formation of sulfates from sulfur dioxide. Such atmospheric conversions can occur by either photochemically initiated homogeneous processes or a variety of heterogeneous mechanisms. The homogeneous processes are better defined at present in terms of their atmospheric contributions to sulfate formation than are heterogeneous mechanisms.

For the winter at the latitude of cities in the Northeast or Midwest considered (37–47° N latitude), the tropospheric photochemical conversion rates on a diurnal average would be less than 0.1% h^{-1} (*38*). The total conversions in 24 h periods would be 0.5–1.5%. Such low winter rates would not be likely to contribute substantially to atmospheric sulfate loadings. In contrast, at these latitudes in the summer months

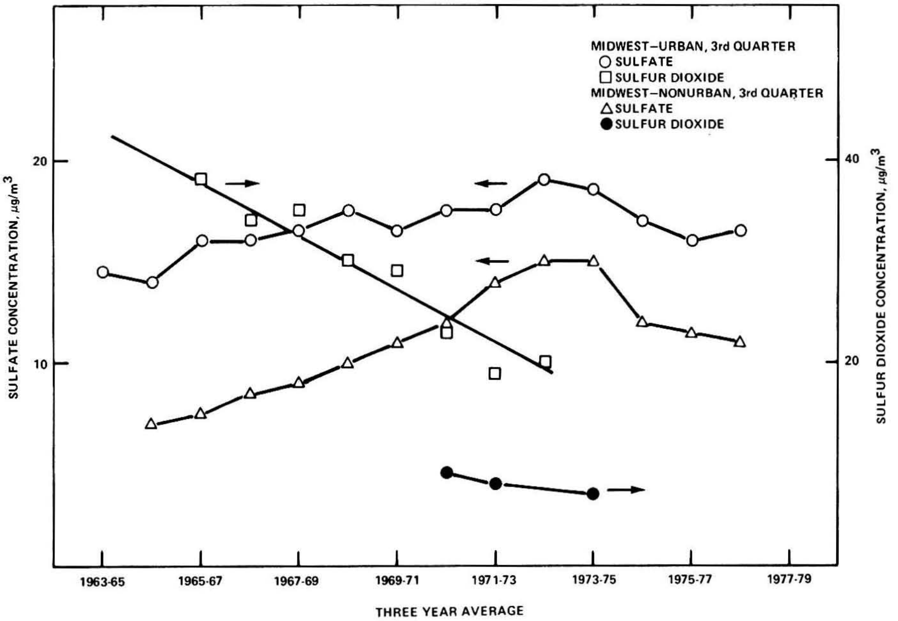


Figure 12. Three-year running average sulfur dioxide and sulfate concentrations during third quarter of the year for urban and nonurban site in the midwestern United States.

diurnal tropospheric rates would be 0.25–0.4% h^{-1} total resulting in conversion in 24-h periods of 6–10% of the sulfur dioxide to sulfate (*38*).

The background tropospheric rates discussed above are the homogeneous oxidation rates in "clean" atmospheres. Polluted-to-clean atmosphere conversion rate ratios of 2–3:1 have been estimated (*38*). Therefore, if the air remained within an urban plume during the daylight hours in the summer months, it is estimated that from 12 to 30% of the sulfur dioxide present could be converted to sulfate. In support of this estimate, Isaksen (*39*) predicted from an urban plume model with a homogeneous chemical kinetic module that ~25% conversion of sulfur dioxide to sulfate should occur during the daylight hours on a specific summer day. The model prediction was ~30% lower than the observed rates reported for that day (*39, 40*).

The high frequency of episodes during the summer months along with the concurrent elevation of oxidants and sulfate in these summertime episodes are consistent with the homogeneous photochemically induced processes being an important mechanism for the production of sulfates in the summer. The oxidant data base used in an evaluation of the role of stagnating anticyclones on regional scale oxidant episodes can be used to make intercomparisons (*41, 42*). For three high regional sulfate episodes in June 1966, August 1967, and June 1968, discussed earlier, elevated oxidant concentrations measurements were observed at sites in Philadelphia, PA, Washington, DC, Cincinnati, OH, and St. Louis, MO, on a number of days during these episodes.

The highest frequency of summertime sulfate episodes coincides in time with the peaking in third-quarter sulfate concentrations in the late 1960s for most groups of sites through the eastern United States (Figures 1, 2, 4, and 5). The higher frequency of episodes in 1969–72 compared to 1965–68 is consistent with Midwestern regional emission trends (Figure 9). On the other hand, no increase in frequency of stagnation cases in the eastern United States occurred in 1969–72 compared to 1965–68 based on Korshover's criteria (*43*). Therefore, the frequency of episodes cannot be explained by a difference in the two time intervals in frequency of stagnation cases.

Another mechanism involving oxidation of sulfur dioxide in aqueous droplets requires oxidizing agents such as ozone and hydrogen peroxide (*44*), manganese, or mixed salts (*45*). These types of mechanisms along with olefin–O_3–SO_2 reaction processes (*46*) could explain the formation of sulfate in fogs. The contributions from cloud processes can be important for acid-precipitation phenomenon but not for ground-level, suspended-sulfate concentrations. Therefore, some contribution to sulfate formation can occur through these mechanisms depending on the frequency of fogs as well as the assumptions as to the size distribution and solubility of catalytic particles present.

Several regional scale sulfate models also assume faster chemical conversion rates for sulfur dioxide within source regions than outside of these regions (*47–49*). Such models suggest some urban excess in sulfate owing to faster reaction rates in more contaminated atmospheres as is observed (Table I), even if primary sulfate emissions were reduced to low levels.

Sulfate/Visibility Relationships. Trijonis and Yuan (*10*) investigated trends in airport visual range measurements reported averaging over the sites that 49% of the extinction budget was contributed by sulfates. A clear relationship between third-quarter trends in visibility and in sulfates was noted (*10*).

The sulfate was increasing in concentration into the 1970s during the third quarter. This result appears to be consistent with a dominant role of sulfates in causing haziness at least for the third quarter. An improvement in third-quarter haziness would be predicted late in the 1970s for most urban and nonurban sites in the Northeast and Midwest on the basis of the third-quarter trend analyses presented in this paper. On the other hand, in the Southeast and in some sites in the Ohio Valley a continuing increase in third-quarter haziness would be predicted.

A long trend toward improved visibility during the first and fourth quarters in the mid-Atlantic states and lower New England has been demonstrated (*50*). This trend is consistent with the decreasing sulfate concentrations but may also be associated with reductions in soot particles in the atmosphere.

Conclusions

1. Control of sulfur oxide emissions on a local scale has resulted in a substantial reduction of sulfate concentrations in the first, second, and fourth quarters of the year in cities in the northeastern United States over the 1963–77 period. Similar, but much smaller, decreases in sulfate concentrations occurred during the first and fourth quarters in cities in the midwestern and southeastern United States. These trends can be accounted for, particularly in the Northeast, by changes in primary sulfate emissions with shift in fuel usage. The *urban excess* of sulfate over regional sulfate levels decreased during the first, second, and fourth quarters approximately in proportion to decreases in sulfur oxides on a local scale at Northeastern urban sites.

2. The sulfate concentrations during the third quarter of the year increased for a number of years into the 1970s, then decreased at urban sites in the Northeast, but continued to increase in cities in the Southeast as well as at some urban sites within the Ohio Valley region of the midwestern United States.

3. In nonurban areas of the eastern and midwestern United States, sulfate concentrations not only did not generally decrease during the winter and spring quarters, but instead increased slightly. Comparison of these trends with those in cities indicates a decoupling of processes between urban and rural areas for these portions of the year.

4. The increases in third-quarter sulfate concentrations at both urban and nonurban sites into the 1970s appeared to be related to increases in regional scale emissions of sulfur oxides and sulfates and to photochemically induced reaction processes. The third-quarter sulfate concentrations also were associated with a higher frequency of summer regional scale sulfate episodes.

5. Sulfate and visibility trends appear to correlate during the 1960s and early 1970s. The more recent sulfate trends for the third quarter of the year compared with recent trends in visibility.

Literature Cited

(1) Stevens, R. K.; Dzubay, T. B.; Russwurm, G.; Rickel, D. *Atmos. Environ.* **1978,** *12,* 55–68.
(2) Altshuller, A. P. *Environ. Sci. Technol.* **1973,** *7,* 709–12.
(3) Altshuller, A. P. *J. Air Pollut. Control Assoc.* **1976,** *26,* 318–24.
(4) Hidy, G. M.; Mueller, P. K.; Tong, E. Y. *Atmos. Environ.* **1978,** *12,* 735–52.
(5) Johnson, W. B.; Wolf, D. E.; Mancuso, R. L. *Atmos. Environ.* **1978,** *12,* 511–28.
(6) Ottar, B. *Atmos. Environ.* **1978,** *12,* 445–54.
(7) Whelpdale, D. M. *Atmos. Environ.* **1978,** *12,* 661–70.
(8) Barnes, R. A.; Lee, D. O. *Atmos. Environ.* **1978,** *12,* 791–4.
(9) Waggoner, A. P.; Vanderpol, A. J.; Charlson, R. J.; Larson, S.; Granat, L.; Trägardh, C. *Nature (London)* **1976,** *261,* 120–2.
(10) Trijonis, J.; Yuan, K. Washington, D.C., Aug 1978, EPA Report 600/3-78-075.
(11) Brosset, C. *Atmos. Environ.* **1978,** *12,* 25–38.
(12) Cobourn, W. G.; Husar, R. B.; Husar, J. D. *Atmos. Environ.* **1978,** *12,* 89–98.
(13) Elshout, A. J.; Viljeer, J. W.; Duuren, Van H. *Atmos. Environ.* **1978,** *12,* 785–90.
(14) Galloway, J. N.; Galloway, J. N.; Likens, G. E. *Geophys. Res. Lett.* **1978,** *5,* 757–60.
(15) Miller, J. M.; Galloway, J. N.; Likens, G. E. *Geophys. Res. Lett.* **1978,** *5,* 757–60.
(16) Altshuller, A. P. "Formation and Removal of SO_2 and Oxidants from the Atmosphere in Fate of Pollutants in the Air and Water Environment", part II; Suffet, I. M., Ed.; Wiley: New York, 1977.
(17) Husar, R. B.; Patterson, D. E.; Paley, C. C.; Gillani, N. V. "Ozone in Hazy Air Masses", presented at the International Conference on Photochemical Oxidant Pollution and Its Control, Raleigh, NC, Sept 12–17, 1976.
(18) DeMarrais, G. A. Washington, DC, Feb 1979, EPA Report 600/4-79-009.
(19) Frank, N. H.; Possiel, N. H., Jr. "Seasonality and Regional Trends in Atmospheric Sulfates", presented before the Division of Environmental Chemistry, American Chemical Society, San Francisco, CA, Aug–Sept 1976.
(20) Tong, E. Y.; Batchelder, X. *Proc. Int. Tech. Meet. Air Pollut. Model. Its. Appl., 9th,* **1978,** 407–16.
(21) Lee, R. E., Jr.; Wagman, J. *J. Am. Ind. Hyg. Assoc.* **1966,** *27,* 266–71.
(22) Coutant, R W. *Environ. Sci. Technol.* **1977,** *11,* 873–8.
(23) Meserole, F. B.; Schwitzgebel, K.; Jones, B. F.; Thompson, C. M.; Mesich, F. G. "Sulfur Dioxide Interferences in the Measurement of Ambient Particulate Sulfates"; Research Project 262, Final Report, Vol. I, Jan. 1976; prepared for the Electric Power Research Institute.
(24) Appel, B. R.; Kothny, E. L.; Hoffer, E. M.; Wesolowski, X. Washington, DC, Nov 1977, EPA Report 600/7-77-128.
(25) Pierson, W. R.; Hammerle, W. H.; Brachaczek, W. W. *Anal. Chem.* **1976,** *48,* 1808–11.
(26) Hunter, S. C.; Engel, P. K. Washington, DC, Aug 1978, EPA Report 600/9-78-020b, Vol. 2, pp 13–51.
(27) Homolya, J. B.; Cheney, J. L. Washington, DC, Aug 1978, EPA Report 600/9-78-020b, Vol. 2, pp 3–11.
(28) Howes, J. E., Jr. Washington, DC, Aug 1978, EPA Report 600/9-78-020b, Vol. 2, pp 87–97.
(29) Doyle, B. W.; Booth, R. C. Washington, DC, Aug. 1978, EPA Report 600/9-78-020b, Vol. 2, pp 53–65.
(30) Dietz, R. N.; Wieser, R. F.; Newman, L. Washington, DC, Aug. 1978, EPA Report 600/9-78-020b, Vol. 2, pp 239–70.
(31) Environmental Protection Agency, Monitoring and Air Quality Trends Annual Report, 1972, pp 4-4–4-8, EPA Report 450/1-73-004, Dec 1973.
(32) The City of New York, Department of Air Resources, "Consolidated Edison Fuel Use 1966–74", Jan 1974, Report TS1.
(33) Simoi, C.; Ferrand, E. F. *Proc. Int. Clean Air Congr., 2nd, 1970* **1971.**
(34) Rohrman, F. A.; Ludwig, J. H.; Steigerwald, B. J. *Oil Gas J.* **1966,** *64,* 154–6.
(35) Environmental Protection Agency, 1972 National Emissions Report, National Emissions Data System (NEDS) of the Aerometric and Emissions Reporting System (AEROS) Office of Air Quality Planning and Standards, Research Triangle Park, NC, EPA Report-450/2-74-012, June 1974.
(36) Faoro, R. B.; McMullen, T. B. Washington, DC, Feb 1977, EPA Report 450/1-77-003.
(37) Holland, T. C.; Short, R. L.; Wehe, A. H. "SO_2 Emissions from Power Plants over the 1969–1985 Period"; U.S. Environmental Protection Agency: Research Triangle Park, NC, Oct 27, 1977.
(38) Altshuller, A. P. *Atmos. Environ.* **1979,** *13,* 1653–61.
(39) Isaksen, I. S. A.; Hesstradt, E.; Hov, Ö. *Atmos. Environ.* **1978,** *12,* 599–604.
(40) White, W. H.; Anderson, J. A.; Blumenthal, D. L.; Husar, R. B.; Gillani, N. V.; Husar, J. D. *Science* **1976,** *194,* 187–9.
(41) Altshuller, A. P. *J. Air Pollut. Control Assoc.* **1975,** *25,* 19–24.
(42) Altshuller, A. P. *J. Air Pollut. Control Assoc.* **1978,** *28,* 152–5.
(43) Korshover, J. "Climatology of Stagnating Anticyclones East of the Rocky Mountains, 1936–1975", NOAA Technical Memorandum ERL ARL-55, July 1975.
(44) Penkett, S. A.; Jones, B. M. R.; Brice, K. A.; Eggleton, A. E. J. *Atmos. Environ.* **1979,** *13,* 123–37.
(45) Penkett, S. A.; Jones, B. M. R.; Eggleton, A. E. J. *Atmos. Environ.* **1979,** *13,* 139–47.
(46) Wolf, G. T.; Monson, P. R.; Ferman, M. A. *Environ. Sci. Technol.* **1979,** *13,* 1271–6.
(47) Eliassen, A. *Atmos. Environ.* **1978,** *12,* 479–89.
(48) Fisher, B. E. A. *Atmos. Environ.* **1978,** *12,* 489–501.
(49) Szepesi, D. J. *Atmos. Environ.* **1978** *12,* 529–35.
(50) Husar, R. B.; Patterson, E. E.; Holloway, J. M.; Wilson, W. E.; Ellestad, T. G. *Symp. Atmos. Turbul., Diffus., Air Qual., 4th, 1979.*

Received for Review January 14, 1980. Accepted June 30, 1980. Presented at the Environmental Chemistry Division, 178th Meeting of the American Chemical Society, Washington, DC, Sept 10–14, 1979.

Supplementary Material Available: Table II providing the 3-yr average sulfate concentrations for the 1965–67 and 1976–78 and Table III providing the highest 3-yr average sulfate concentrations between 1965–67 and 1975–77 (5 pages) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper or microfiche (105 × 148 mm, 24× reduction, negatives) may be obtained from Business Operations, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, DC 20036. Full bibliographic citation (journal, title of article, author) and prepayment, check or money order for \$5.50 for photocopy (\$7.00 foreign) or \$3.00 for microfiche (\$4.00 foreign), are required.

Retention of Radionuclides by Mobile Humic Compounds and Soil Particles

John C. Sheppard,*[1] Malcolm J. Campbell,[1] Todd Cheng,[1] and James A. Kittrick[2]

Department of Chemical Engineering and Department of Agronomy and Soils, Washington State University, Pullman, Washington 99164

■ Particles of colloidal dimensions are shown to be important potential vehicles for the transport of radionuclide elements in soils and ground water. For the soils studied, the distribution of radionuclides between the soil and aqueous phases is determined by a characteristic spectrum of radionuclide-bearing particles. These spectra, which are related to the physical and chemical composition of the soils, include uncomplexed ions, complexes of fulvic and humic acid polymers, and larger radionuclide-bearing particles, such as clay. This contrasts with the earlier observation that there are two components to distribution ratios, one particulate and another ionic. Thus, distribution ratios of radionuclides are functions of the soils studied and the particle size resolution of the techniques used. For this set of soils and experimental techniques, three broad classes of particles determine the observed distribution ratios: (1) ionic ones, that is, particles containing radionuclides which have radii less than 1 mm, (2) complexes of humic matter, possibly humic acid polymers with molecular weights between 8000 and 50 000 (2–3-mm radii), and (3) larger soil particles bearing radionuclides and with radii in the 10–60-nm range.

Introduction

Radionuclides can be transported in soils by both diffusion and mass flow, with the latter the more important process. The apparent diffusion coefficient of Am^{3+} in U.S. soils is 3.2 $\times 10^{-11}$ $cm^2\ s^{-1}$ (*1*), suggesting that Am can, by diffusion, move ~1 cm in 1000 yr. Mass flow is likely to be a much more rapid process for the transport of Am and other radionuclides. Hajek (*2*) found that the apparent diffusion velocities of Pu and Am in moist soils were ~10^{-4} of the transporting solution velocity. Such a low mobility cannot be attributed simply to the distribution of ions between the aqueous and soil phases. Consequently, much of the observed mobility of radionuclides may reflect the mass-flow mobility of small soil colloids such as clay particles and humic compounds. Recent research (*3*) has supported this hypothesis since it was demonstrated that distribution ratios can be represented by $R^* = R^*_{\mathrm{p}} + R_{\mathrm{I}}$, where R^*, R^*_{p}, and R_{I} are respectively the observed, particulate, and ionic distribution ratios. The objective of this research was to further evaluate the importance of contributions of the ionic species, humic acid complexes of radionuclides, and radionuclide-bearing soil colloids to R^*_{p} and R_{I}. As a step in this direction, distribution ratios have been determined as a function of particle size for particles having radii less than 60 nm.

Experimental Section

Materials. Five U.S. soils, shown in Table I, were chosen for study because of their widely different physical and chemical properties and their proximity to nuclear processing installations. Distribution ratios, as defined in ref 3, were measured by the batch equilibration method at a solution-to-soil ratio of 10 mL g^{-1}. Solutions containing 10 mL of deionized water and less than 25 μL of tracer were equilibrated in a 50-mL polycarbonate centrifuge bottle for approximately 10 min. Subsequently, a 100-μL aliquot was withdrawn and counted as the initial assay. One gram of the air-dried soil was then added to the solution and equilibrated on a rotary shaker at 200 rpm for 2 weeks. Distribution ratios were calculated from

$$R = \frac{\text{cpm per cm}^3\text{ of aqueous phase}}{\text{cpm per g of soil before equilibration}}$$

Note that the distribution ratio is approximately equal to the reciprocal of the K_{d} used by soil scientists when $R < 10^{-2}$.

Distribution Ratios of Particles with Radii Smaller than 1 nm. An aliquot of 250 μL obtained from the supernatant of the solution centrifuged at 12 000 rpm was passed through Pharmacia PD-10 columns containing Sephadex G-25. Columns were eluted with at least 40 mL of 0.5 M NaCl and counted with the Ge(Li) detector. This fraction contains the ions with possible contributions from small complexes.

Distribution Ratios of Particles with Radii from 1 to 10 nm. Soils investigated by the gel filtration method were Ritzville with Am, Fuquay with Am, and Burbank with Sr. The solution-to-soil ratio was 10 mL g^{-1}, and the tubes were centrifuged at 4000 rpm for 30 min to sediment large soil particles. A 250-μL aliquot of supernatant was withdrawn and passed through the Bio-Gel A-1.5m column by using 0.5 M NaCl as the eluant. Fractions were collected and counted with a Ge(Li) detector. Lanthanum oxalate was used to coprecipitate Am when the fraction volume was larger than 1 mL.

Distribution Ratio of Particles with Radii from 10 to 60 nm. To reproduce conditions, each 100-μL assay was removed from the top 4 mm of supernatant after centrifuging in an International 856 centrifuge at different angular velocities ranging from 2000 to 12 000 rpm for 30 min. Aliquots were counted with a Ge(Li) detector connected to a 1024-multichannel analyzer. Counts were accumulated until the error was less than 3%, except for the samples with very low count rates.

Particle Size Distribution of Soils. Ritzville and Idaho Falls soils were double sealed in polyethylene vials and irradiated at a neutron flux of 2 × 10^{12} n $cm^{-2}\ s^{-1}$ for 8 h in the Washington State University Triga reactor. After 160 h of cooling, the vials were monitored with the Ge(Li) detector for induced radionuclides. After the short-lived and water-soluble

---

[1] Department of Chemical Engineering.

[2] Department of Agronomy and Soils.

Table I. Physical and Chemical Properties of Soils Studied

soil code	sand, %	silt, %	clay, %	soil class	pH	CEC, mequiv/100 g	org material, %
MUS[a]	12.6	65.8	21.6	silt loam	5.3	16.88	3.61
BUR[b]	76.0	21.2	2.8	loamy sand	8.1	5.94	0.43
RITZ[c]	32.0	56.0	12.0	silt loam	6.5	10.76	0.84
FQ-1[d]	91.2	7.8	1.0	sand	4.0	2.01	1.19
ID-B[e]	60.4	19.4	20.2	sandy clay loam	8.4	10.44	0.18

[a] Muscatine silt loam obtained from R. C. Dahlman, Oak Ridge National Laboratory, Oak Ridge, TN. [b] Burbank loamy sand obtained from R. C. Dahlman, Oak Ridge National Laboratory, Oak Ridge, TN. [c] Ritzville silt loam obtained from R. C. Dahlman, Oak Ridge National Laboratory, Oak Ridge, TN. [d] Fuquay sand obtained from F. W. Boone, Allied Chemical Co., Barnwell, SC. [e] "Idaho" soil obtained from F. J. Miner, Dow Chemical Co., Rocky Flats, CO.

radionuclides, such as ^{24}Na and ^{42}K, had decayed to undetectable levels, the centrifugation method was used to determine the size distribution of soil particles with radii from 10 to 60 nm by counting the ^{46}Sc produced from the titanium-bearing minerals. Only the Ritzville soil produced sufficient ^{46}Sc to perform the subsequent analysis.

Effect of Humic Acid on the Distribution Ratios of Kaolinite. Humic acid was extracted from a lake sediment with 0.1 N NaOH and precipitated with 0.5 N HCl. A stock humate solution was prepared by dissolving 2 g of a wet humate precipitate in 40 mL of 0.1 N NaOH, followed by titration with 0.1 N HCl to pH 7.0 and dilution to 100 mL. Solutions containing 0–6 mL of this humate stock solution and 10 μL of ^{241}Am tracer were diluted to 10 mL with deionized water and equilibrated with 0.5 g of kaolinite. Distribution ratios were determined by the centifugation method described above.

Results and Discussion

Ion, Complex, and Particle Contributions to Solubility. An objective of this study is to determine the contribution of both ions and larger complexes and particles to the measured distribution of nuclides between the soil and aqueous phases. As noted earlier (*3*), when phase separation is accomplished by centrifugation, distribution ratios depend on the cutoff size of dispersed soil particles remaining in the aqueous phase. This implies that particles or complexes of sizes much larger than ionic make significant contributions to the distribution ratio.

We compare the contributions of colloids of different sizes (radii) by plotting the "size-dependent distribution ratio" $r(a)$. Specifically, we define $r(a)\,da$ to be the fraction of the nuclide on particles with radii in the range a–$(a + da)$, multiplied by M/V, where M is the mass of the soil and V the volume of the aqueous phase. Then the distribution ratio, determined by a technique which retains all particles smaller than $a_{\max}$ in the aqueous phase, while separating all larger soil particles, will be

$$R(a_{\max}) = \int_0^{a_{\max}} r(a)\,da \tag{1}$$

Evaluation of $r(a)$ is accomplished by using the centrifuge data for sizes between 10 and 60 nm and the gel filtration data for smaller sizes. Contributions to the distribution ratio from particles smaller than 1 nm (mol wt $\sim$ 2500) will be collectively classed as ionic, although small complexes may contribute.

Reduction of Gel Filtration Data. For particle sizes smaller than 10 nm equivalent radius (mol wt = 2.5×10^6), we have determined $r(a)$ from the gel filtration data. Each fraction of the eluate is assigned size limits (a_n, a_{n+1}) by means of blue dextran and the gel manufacturer's calibration curve, and $r(a)$ is then calculated by dividing the proportion of the total counts in that fraction by $(a_{n+1} - a_n)$ and then multiplying by the distribution ratio applicable to the added sample as a whole. The distribution ratio is determined at a standard centrifuge condition, usually 4500 rpm.

When the fraction size limits were calculated from the calibration molecular weights, it was assumed that the complexes/particles were spherical and had a density of 1 g cm^{-3}. No attempt was made to determine the relationship of $r(a)$ with particle size for sizes below 1.3 nm (mol wt = 5000). By classifying all of these materials not excluded by Sephadex G-25 as the "ionic component", we have included not only all of the ionic radionuclides but also their soluble hydrolysis products and complexes. Examination of the particle size dependent distribution ratios indicates that an area of overlap exists between the ionic component and the size range between 1 and 10 nm. The magnitude of the actual ionic components must, in practice, be smaller than the Sephadex G-25 measurements would suggest. However, the difference should not be too large for Am since its solubilization by fulvic acid has been shown to be unimportant (*4*).

Reduction of Centrifuge Data. In practice, the centrifugation procedure does not perfectly separate particles at a boundary size $a_{\max}$. It does exclude particles larger than $a_{\max}$ from the aqueous samples but retains only a proportion of smaller particles. In our previous paper (*3*), $S(a)$ was defined as the fraction of particles of size a retained in the sample after centrifugation. It can be shown (*3*) that

$$\begin{aligned} S(a) &= 1 - (a/a_{\max})^2 \quad \text{for } a < a_{\max} \\ &= 0 \quad \text{for } a > a_{\max} \end{aligned} \tag{2}$$

where $a_{\max}$ is a function of the centrifuge speed and sampling parameters.

Under these conditions the measured distribution ratios $R(a_{\max})$ are related to $r(a)$ by a slightly more complex relationship than eq 1

$$R(a_{\max}) = \int_0^{a_{\max}} S(a) r(a)\,da \tag{3}$$

where, by differentiation

$$\frac{dR}{da_{\max}} = \int_0^{a_{\max}} \frac{\partial S}{\partial a_{\max}} r(a)\,da$$

since $S(a_{\max}) = 0$. Substituting for $S(a)$

$$\tfrac{1}{2} a_{\max}{}^3 \frac{dR}{da_{\max}} = \int_0^{a_{\max}} a^2 r(a)\,da$$

The integral can now be again differentiated by $a_{\max}$, to yield

$$a_{\max}{}^2 r(a_{\max}) = \frac{d}{da_{\max}} \left| \tfrac{1}{2} a_{\max}{}^2 \frac{dR}{da_{\max}} \right|$$

or

$$r(a{=}a_{\max}) = a_{\max}{}^{-2} \frac{d}{da_{\max}} \left| \tfrac{1}{2} a_{\max}{}^3 \frac{dR}{da_{\max}} \right| \tag{4}$$

The distribution ratios of several representative radionuclides (^{241}Am, ^{233}U, ^{137}Cs, and ^{85}Sr) between the Fuquay, Idaho, Burbank, Ritzville, and Muscatine soils and the aqueous phase have been determined as a function of $a_{\max}$. The variations of R with $a_{\max}$ have been fitted by least squares to an expression

$$R(a_{\max}) = Ba^{\beta}$$

with B and β adjustable parameters and a in nanometers.

Values of B and β were transformed to C and γ by using eq 4. In the resulting equation

$$r(a) = Ca^{\gamma} \tag{5}$$

where $C = \frac{1}{2}\beta(\beta + 2)B$, $\gamma = \beta - 1$, and a is in nanometers. Values of C and γ are shown in Table II. Also included in this table are correlation coefficients for each least-squares fit of $R(a_{\max}) = Ba^{\beta}$. Averages and standard deviations of constant distribution ratios are also shown.

Discussion

Curves of $r(a)$ vs. a for Fuquay, Ritzville, and Burbank soils are shown in Figures 1–3. The physical area under the curve between two particle sizes represents the distribution ratio attributable to complexes or soil particles with sizes in this range.

For the soils studied, a maximum in radionuclide capacity occurs at sizes corresponding to molecular weights of 8000–50 000 (particle sizes 2–3 nm). This is essentially the range of mean molecular weights of soil humic acid determined by Schnitzer (*5*). Knonova (*6*) also reported that humic acid has molecular weights between 30 000 and 50 000. These high-molecular weight compounds apparently result from polycondensation of 30–50 single humic acid monomers which have an average molecular weight of 1400 (*7*). The similarity of the molecular weight distribution for actinide, Sr, and Cs complexes determined in these experiments to that found by Schnitzer (*5*) and Knonova (*6*) for soil humic acids is strong evidence for humic acid being the complexing agent since other major soil components in this size range have not been noted.

Strontium is known (*8*) to be strongly bound by humic matter, and the gel permeation measurements on the distribution of ^{85}Sr among soil particle sizes were indeed exceptional. The distribution ratios of strontium were almost independent of the centrifuge speeds, and, in addition, the ionic component was much smaller than the distribution ratios at 12 000 rpm for all of the five soils studied. For example, the ionic component of Fuquay soil was only 0.3% of the distribution ratio at 12 000 rpm. These data are summarized in Figure 3, which shows that almost all of the strontium is carried by particles of ~3 nm size. In view of the affinity of Sr for humates and the lack of other complexing agents of suitable abundance in this size range, the Sr-carrying capacity is attributed to the formation of Sr–humate complexes.

The fact that the distribution ratio of Sr at 3 nm is three orders of magnitude larger than its ionic component can be taken to reflect its ability to form exceptionally strong complexes with humic acid. Juo (*9*) has commented on this behavior.

Confirmation of the role of humic acid in complexing of the actinides was obtained by direct measurements of the effect of humic acid concentration on the distribution of Am(III) between kaolinite and the aqueous phase. Kaolinite is free of humic acid as supplied. These experiments clearly showed

Table II. Particle Size Dependent Distribution Ratios for Selected U.S. Soils [a]

soil	radionuclide				
	^{85}Sr	^{137}Cs	^{233}U	^{237}Np	^{241}Am
ID-B					
r^2 [b]	0.83	0.95	0.84	*b*	0.84
C	5.31×10^{-4}	7.1×10^{-5}	6.64×10^{-2}	0.39 ± 0.03	3.28×10^{-6}
γ	−0.931	−0.949	0.293		−0.061
R_I [c]	$(7.00 \pm 0.93) \times 10^{-5}$	$(2.74 \pm 0.07) \times 10^{-4}$	*d*	(8.00 ± 0.016) mult 10^{-2}	$(6.16 \pm 0.06) \times 10^{-5}$
BUR					
r^2	0.28	0.99	0.90	*b*	0.71
C	$(3.90 \pm 0.11) \times 10^{-2}$	1.54×10^{-5}	1.61×10^{-3}	0.101 ± 0.006	4.89×10^{-4}
γ	−0.022	0.440	−0.731		−0.861
R_I	$(6.92 \pm 0.20) \times 10^{-5}$	$(5.98 \pm 3.50) \times 10^{-5}$	*d*	$(6.34 \pm 0.03) \times 10^{-2}$	$(2.64 \pm 0.03) \times 10^{-3}$
RITZ					
r^2	0.99	0.86	0.99	*b*	0.87
C	5.46×10^{-4}	2.54×10^{-4}	2.60×10^{-5}	0.262 ± 0.034	2.96×10^{-5}
γ	−0.568	−0.214	0.71		−0.861
R_I	$(5.33 \pm 0.24) \times 10^{-5}$	$(6.80 \pm 1.35) \times 10^{-4}$	*d*	$(5.57 \pm 0.08) \times 10^{-2}$	$(1.71 \pm 0.03) \times 10^{-4}$
MUS					
r^2	0.82	0.93	0.92	*b*	0.85
C	1.21×10^{-4}	2.73×10^{-5}	2.09×10^{-5}	0.678 ± 0.162	1.51×10^{-5}
γ	−0.648	0.640	0.284		−0.597
R_I	$(3.14 \pm 0.45) \times 10^{-4}$	$(6.10 \pm 4.10) \times 10^{-5}$	*d*	$(4.46 \pm 0.06) \times 10^{-1}$	$(5.02 \pm 0.15) \times 10^{-5}$
FQ-3					
c [f]	$(7.10 \pm 0.02) \times 10^{-2}$	$(6.20 \pm 1.40) \times 10^{-3}$	$(3.37 \pm 0.95) \times 10^{-2}$	$(2.62 \pm 0.34) \times 10^{-1}$	$(9.78 \pm 0.83) \times 10^{-3}$
R_I	$(1.53 \pm 1.12) \times 10^{-4}$	$(6.32 \pm 1.14) \times 10^{-4}$		$(5.57 \pm 0.08) \times 10^{-2}$	$(7.06 \pm 0.50) \times 10^{-3}$

[a] These particle size dependent distribution ratio data cover the 10–60-nm soil particle size range. Each $r(a)$ determination represents six distribution ratios, covering centrifuge angular velocities between 2000 and 12 000 rpm. [b] The coefficients of determination are reported to give indications of goodness of fit to a power curve; that is, $R(a_{\max}) = Ba^{\beta}$. [c] Ionic distribution ratios, defined by a particle size cutoff of 1 nm, must contain radionuclide-bearing soil particles, small humic and fulvic acid complexes, as well as ions and hydrolytic products of these radionuclides. [d] The "ionic" distribution ratio of ^{233}U was not measured. [e] The ^{237}Np distribution ratios were independent of centrifuge speed and were not fit to eq 7. [f] Distribution ratios of the Fuquay sand independent of centrifuge speed for all radionuclides studied. These data were not fit to eq 5.

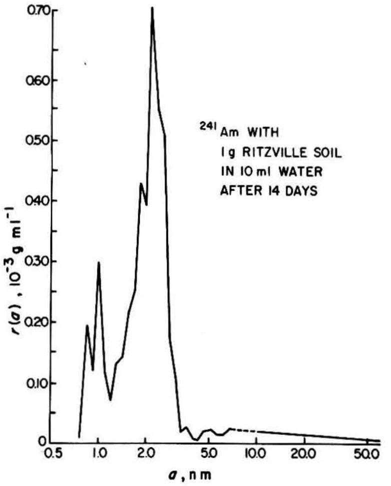


Figure 1. A plot of the particle size dependent distribution ratio of ^{241}Am for the Ritzville soil. Note the large particle tail.

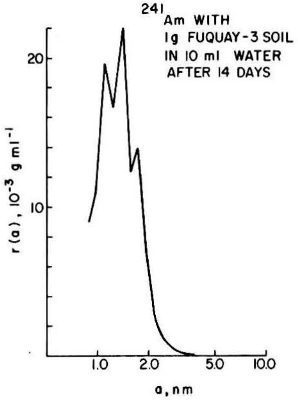


Figure 2. A plot of the particle size dependent distribution ratio of ^{241}Am for Fuquay sand. Note tack of large particle tail.

that the distribution ratio increased with increasing humic acid concentrations. The distribution ratios were found to fit an equation of the type

$$R_c/R_0 = 1 + 4.18C + 0.58C^2 \tag{6}$$

where R_c = the distribution ratio with relative humic acid concentration C, and R_0 = the distribution ratio in the absence of humic acid. The coefficients may represent Am(III)–humic acid formation constants; however, the uncertainty in the humic acid concentration and the added uncertainty of the actual nature of the Am(III)–humic acid bonding would suggest caution in interpretation of the coefficients at this time, even though Bertha and Choppin (*10*) have demonstrated the existence of strong, but poorly understood, interactions of Am(III) with humic acid.

Attachment to Smaller Soil Particles. We have studied the affinity of nuclides for the larger soil particles by using neutron activation to determine the particle size distribution of Ritzville soil in the 10–60-nm range. We assume that titanium, the precursor of the scandium produced by neutron activation, is a constant proportion by mass of the soil particles, independent of particle size. Hence the scandium activity in particles of radii in the range a–(a + da) should be proportional to

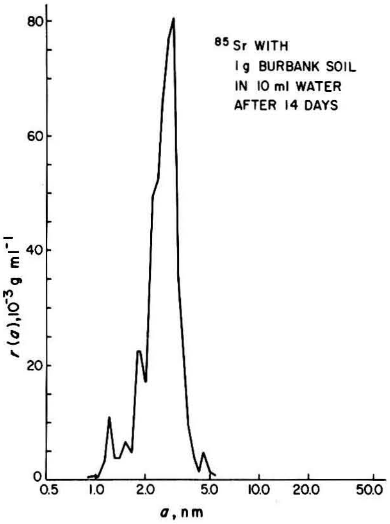


Figure 3. A plot of the particle size dependent distribution ratio of ^{85}Sr for the Burbank loamy sand.

$$q(a)\,da = n(a)a^3\,da \tag{7}$$

where $n(a)$ is the particle size distribution function; that is, $n(a)\,da$ is the number of particles, per unit mass of soil, with radii between a and $(a + da)$. The factor a^3 arises from the proportionality of the activity of a particle to its volume.

Provided the soil particles are completely dispersed in the suspension, the function $q(a)$ can be determined from centrifugation of the suspended, activated soil in exactly the same manner as $r(a)$ was determined for the actinide-doped soils. The results are shown in Table III. As with the distribution ratio data, a good fit was found to a power law expression, yielding

$$n(a) = Aa^{\gamma} \tag{8}$$

with A a constant and $\gamma = -3.26 \pm 0.38$ for the size range 10–60 nm.

Assume that the mean number of nuclide atoms attached to a soil particle in this size range is proportional to a^{δ}. A value of $\delta = 2$ corresponds to a nuclide whose attachment probability is proportional to the *surface area* of the soil particle, while $\delta = 3$ corresponds to a nuclide whose attachment probability is proportional to the *volume* of the particle. Since the size-dependent distribution ratio $r(a)$ is a measure of the number of nuclide atoms carried by *all* particles of size a, we can write

$$r(a) = Dn(a)\,a^{\delta} \tag{9}$$

where D is a constant. Using the power-law fitted forms of $r(a)$ and $n(a)$ we have

$$\delta = \alpha - \gamma \tag{10}$$

permitting δ to be evaluated from the distribution ratio and neutron activation data. The results for Cs, Sr, Am, and U in Ritzville soil are shown in Table III. Within the rather large limits of error, it appears that Am is surface distributed on soil particles in the 10–60-nm range, while Cs is attached in quantities proportional to the particle volume. The results for

Table III. Parameters of $r(a)$ and Data for Cs, Sr, and Am in Ritzville Soil[b]

nuclide	nonhydrated cation radius, nm	hydrated radium, nm	$10^{-6}r(a = 20\text{ nm})$, g mL^{-1} nm^{-1}	$10^{-6}C$ (eq 6), g mL^{-1} nm^{-1}	α	δ
^{137}Cs(I)	0.165	0.505	134	250 ± 160	−0.21 ± 0.16	3.0 ± 0.4
^{85}Sr(II)	0.127	0.960	98.5	543 ± 37	−0.57 ± 0.02	2.7 ± 0.4
^{241}Am(III)	0.099	1.0–2.0[a]	2.3	29.8 ± 2.5	−0.86 ± 0.03	2.4 ± 0.4
^{233}U(VI)	0.093		218	26 ± 2	+0.71 ± 0.10	4.0 ± 0.4

[a] Estimated radius of $Am(OH)_3$. [b] Errors are estimated standard deviations.

Sr lie between surface and volume attachment, while the uranium results show an excess preference for large particles over volume attachment.

Magnitude of Retention. Table III also shows the magnitude of $r(a)$ for particles of 20-nm radius. This can be taken as a measure of the retention affinity for the finer soil particles. It will be seen that this varies inversely with the hydrated radius of the ion and directly as the charge density of the hydrated ion.

Conclusion

For the soils studied, the distribution of radionuclides between the soil and aqueous phases is determined by a characteristic spectrum of radionuclide-bearing particles. These spectra, which are related to the physical and chemical composition of the soils, include uncomplexed ions, complexes of fulvic and humic acid polymers, and larger radionuclide-bearing particles, such as clay. This contrasts with the earlier observation that there are two components to distribution ratios, one particulate and another ionic (*3*). Thus, distribution ratios of radionuclides are functions of the soils studied and the particle size resolution of the techniques used. For this particular set of soils and experimental techniques, three broad classes of particles determine the observed distribution ratios: (1) ionic ones, that is, particles containing radionuclides which have radii less than 1 mm, (2) complexes of humic matter, possibly humic acid polymers with molecular weights between 8000 and 50 000 (2–3 mm radii), and (3) larger soil particles bearing radionuclides and with radii in the 10–60-mm range.

Gel filtration data, as shown in Figures 1–3, clearly show that humate complexes dominate distribution ratios for the soil systems studied. It is likely that these colloidal particles in the 2–3-mm range are humic acid polymer complexes of radionuclides, although the evidence is inconclusive. Evidence that humic acid complexing of radionuclides may be significant was obtained from kaolinite experiments in which the Am distribution ratio increased with increasing humic acid concentration. Thus, much of the mobility of radionuclides in the soil-aquatic environment is probably due to soil particles in the 2–3-mm range. This component apparently dominates the strontium and americium distribution ratios.

Experiments suggest that the "ionic" component still contributes a small, but significant, amount to the observed distribution ratios of these radionuclides, especially neptunium. The exact contribution of the pure ionic components of the distribution ratio remains uncertain, but it is very likely to be much smaller than the values reported in Table III.

The relatively large and constant neptunium distribution ratios may be attributed to its low charge density.

Radionuclide-bearing soil particles in the 10–60-mm range make up the third component of the observed distribution ratio. With the soils studied, the "particle" component is small and varied from soil to soil. Sorption sites for radionuclides appear to be on the surfaces of soil particles. Adsorption tendencies of these cations vary with the charge density of the hydrated ion. As estimated for distribution ratios at a = 20 mm, the order is U > Cs > Sr > Am.

If this investigation is correct, even partially, use of distribution ratios (or K_d values) for the estimation of relative rates of radionuclide transport in the soil-aquatic environment should be used cautiously. Most estimates (*11*) of radionuclide migration rates in the soil-aquatic environment use the relation

$$V_i = V_w \Big/ \left(1 + \frac{\rho}{\theta R}\right) \tag{11a}$$

or

$$V_i = V_w/(1 + K_d/\theta) \tag{11b}$$

where V_w and V_i are respectively the velocity of water and radionuclides, ρ is soil density, and θ is the soil porosity. Implied in the use of this equation is the assumption that uncomplexed ions are distributed between the two phases, that is, the use of R_I's. Any radionuclide humic complexing, as suggested by this research and demonstrated by Bertha and Choppin (*10*), has the effect of increasing apparentg ρ and K_d values and, consequently, will increase V_i. Inclusion of the transport of radionuclide-bearing soil particles, as noted by Seitz et al. (*12*) and suggested by this and earlier research (*3*), complicates the use of eq 11 since this amounts to the transport of a small fraction of the soil phase. Use of particle size dependent distribution ratios might resolve this problem but requires the determination of this quantity for each soil, complicating the modeling of radionuclide transport.

Literature Cited

(1) Sheppard, J. C.; Kittrick, J. A.; Hardt, T. L. Pullman, WA, 1976, Washington State University, Department of Chemical Engineering, Research Report No. 76/13-33.

(2) Hajek, B. F. Richland, WA, 1966, Battelle Pacific Northwest Laboratories, BNWL-CC-925.

(3) Sheppard, J. C.; Campbell, M. J.; Kittrick, J. A.; Hardt, T. L. *Environ. Sci. Technol.* **1979,** *13*, 680.

(4) Cleveland, J. M.; Rees, T. F. *Environ. Sci. Technol.* **1976,** *10*, 802.

(5) Schnitzer, M.; Khan, S. U. "Soil Organic Matter"; Elsevier: New York, 1978; p 24.

(6) Knonova, M. M. "Soil Organic Matter"; Pergamon Press: Oxford, 1966; p 103.

(7) Ermolenko, N. F. "Trace Element and Colloids in Soils"; Keter Press: Jerusalem, 1972; p 89.

(8) Stumm, W.; Morgan, J. J. "Aquatic Chemistry"; Wiley-Interscience: New York, 1970; p 283.

(9) Juo, A. S.; Barber, S. A. *Soil Sci.* **1969,** *108*, 89.

(10) Bertha, E. L.; Choppin, G. R. *J. Inorg. Nucl. Chem.* **1978,** *40*, 655.

(11) Baetsle, L. H.; Souffiau. "Isotopes in Hydrology"; Proceedings of International Atomic Energy Agency Symposium, Vienna, 1966; p 617.

(12) Seitz, M. G.; Rickert, P. G.; Fried, S.; Friedman, A. M.; Steindler. *Nucl. Technol.* **1979,** *44*, 284.

Received for review January 24, 1980. Accepted June 30, 1980. This research was supported by Department of Energy Contract No. EY-76-S-06-2221, Task 12, Modification 2.

Gas-Chromatographic/Mass-Spectrometric Analysis of Derivatized Amino Acids in Municipal Wastewater Products

Jimmie L. Burleson, Gary R. Peyton, and William H. Glaze*

Department of Chemistry and Institute of Applied Sciences, North Texas State University, Denton, Texas 76203

■ Amino acids were purified by a combination of cation and ligand exchange and derivatized to *N*(*O*)-heptafluorobutyrylisoamyl and *N*(*O*)-heptafluorobutyryl-*n*-propyl esters for GC/MS analysis. Overall recoveries for 20 common amino acids averaged 90% with a range of 69–101%. The procedure was applied to the analysis of wastewaters and municipal waste sludges before and after chlorination and yielded results which correlated well with those obtained by a standard amino acid analyzer.

This work is part of a broader study to determine the chemical byproducts from the chlorination of municipal water sources, wastewaters and sludges (*1–3*). In the context of this study the chlorination of amino acids has been examined (*4*), necessitating an analytical method which would determine amino acids at the μg/L level in complex matrices. Because of the need to identify possible chlorinated amino acids or their byproducts, a GC/MS-based method was required.

Several methods for derivatizing amino acids for GC work have been reported including silylation (*5*) and combined acylation/esterification (*6–8*). Silylation methods produce more than one derivative for many of the amino acids and were not used for this reason. Because of the success of investigators using heptafluorobutyric anhydride (HFBA) as an acylating agent of esterified amino acids, it was judged that this method would be well suited for this work.

For purification of the analytes from complex wastewater matrices, a combined cation/ligand exchange procedure was adopted (*9–11*). This method has been used successfully by Gardner and Lee (*12*) for the isolation of amino acids from surface water sources.

As shown below, the combination of the cation/ligand exchange procedure with GC/MS analysis of the derivatized amino acids offers an efficient method for the determination of these substances in complex matrices at concentrations below 1 μmol/L.

Experimental Section

Materials. The reagent water used in this work was prepared from the tap by passage through a Continental deionizer unit (Model 200), a Calgon Filtrasorb 400 activated carbon column, and then a Whatman qualitative filter. Amino acid standards were obtained from Jack Graff Associates, Santa Clara, CA. Heptafluorobutyric anhydride was purchased from Pierce Chemical Co., Rockford, IL. Anhydrous sodium sulfite (analytical reagent grade, Mallinckrodt) was heated for 2 h at 130 °C in an oven. The *o*-tolidine and arsenite (OTA) reagents for the residual chlorine determinations were prepared according to standard methods (*13*). Chlorine gas used to prepare hypochlorous acid was purchased from Dixie Chemical Co., Houston, TX, and was claimed by the manufacturer to contain 100% active chlorine. All alcohols were redistilled in all glass apparatus after refluxing 2 h over magnesium turnings and then stored under dry conditions at low temperature. The cation exchange resin, Dowex 50W-X8 (sodium ion form, 100–200 mesh) and Chelex 100 resin (200–400 mesh) were obtained from Bio-Rad Laboratories, Richmond, CA. All glassware was well cleaned with chromic acid cleaning solution and then rinsed with tap water, deionized water, and finally redistilled acetone. The glassware was then placed in an oven at 130–150 °C for 8–10 h.

Gas Chromatography/Mass Spectrometry. The Finnigan Model 3200 gas-chromatograph/mass-spectrometer system with a Model 6100 digital data system was used to separate, detect, and identify the amino acid derivatives. All test mixtures and extracts were chromatographed by using a 5 ft × 2 mm i.d. glass column packed with 10% SP-2100 on 100/120 Supelcoport (Supelco, Inc., Bellefonte, PA). The GC/MS conditions used were as follows: MS sensitivity, 10^{-7} A/V; electron impact energy, 70 eV; GC injector temperature, 240 °C; column temperature program, 50–280 °C at 4 °C/min; carrier gas, helium at 20 mL/min. Identification of the amino acids was confirmed by using known fragmentation mechanisms (*14*). Quantification was accomplished by comparing the samples against a standard mixture of 20 amino acids of known weight. Any unresolved peaks were quantified by limited mass search to determine peak areas.

Amino Acid Analyzer. A Beckman Model 120-C amino acid analyzer, which is located in the Chemistry Department of North Texas State University, was used in this work. It was operated under standard conditions.

Procedure for Isolation of Amino Acids. A procedure similar to that used by Gardner and Lee (*12*) was used in this work. The procedure consists of isolation and purification of amino acids from water by a combined ion exchange/ligand exchange method (Figure 1).

A glass column (36 × 1.5 cm i.d.) with a standard taper ground-glass joint at the top was slurry packed with 30 cm of Dowex 50W-X8 (hydrogen ion form, 200–400 mesh) (*9, 10, 12*). Glass wool plugs of 1-cm length were used at both ends of the Dowex resin.

The ligand exchange column is a modification of that used by Siegol and Degens (*10*). A glass column (36 × 1.5 cm i.d.) with a standard taper ground-glass joint at the top and glass wool plugs was slurry packed with 3 cm of Chelex-100-NH_3 resin. Chelex-100-Cu-NH_3 resin (27 cm) was slurried on top of the Chelex-100-NH_3 resin and capped with a 1-cm glass wool plug.

Three-liter separatory funnels with standard taper ground-glass joints at the effluent end were used to hold the samples. Nitrogen pressure applied at the top of the separatory funnel was used to control the flow rate at 10 mL/min. Wastewater samples were treated with excess sodium sulfite to quench any chlorine residual, and then the samples were centrifuged, filtered, adjusted to pH 2.2, and passed through the Dowex column. The amino acids were eluted with 100 mL of 2 N ammonia solution, and ammonia was removed from the eluate by rotary evaporation at 60 °C. The residue was transferred to a 5-mL reaction vial where the drying continued at 60 °C under a gentle stream of nitrogen.

Derivatization of Amino Acids. The amino acid derivatives used in this study are the *N*(*O*)-heptafluorobutyrylisoamyl and the *N*(*O*)-heptafluorobutyryl-*n*-propyl esters (*6, 15*).

The *N*(*O*)-heptafluorobutyrylisoamyl esters were prepared by using the method of Zanetta and Vincedon (*15*) with some major variations. The esterification reagent was triisoamoxymethane which was prepared in the laboratory according to the procedure of Gilman (*16*). One milliliter of the esterification reagent was added for each 10 μmol of dried amino

0013-936X/80/0914-1354$01.00/0

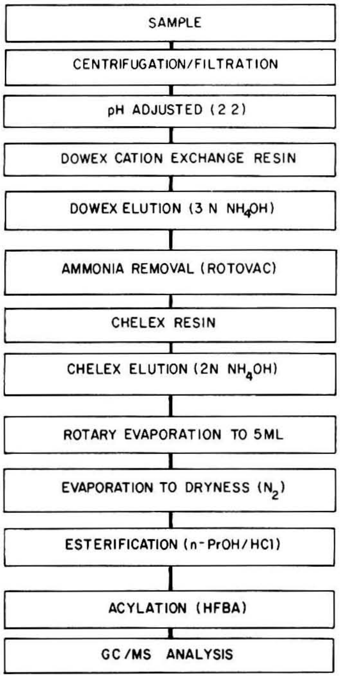


Figure 1. Scheme for separation of amino acids from wastewater products.

acids in a reaction vial. Concentrated HCl (50 μL) was added, and the vial capped and heated in a sand bath at 110 °C for 1 h. The esterification reagent was then evaporated under a stream of nitrogen at 60 °C. Acetonitrile (0.5 mL) was then added along with 100 μL of HFBA for each 10 μmol of amino acid. The vial was capped and heated in a sand bath for 10 min at 150 °C. The derivatized amino acids were dried under a gentle stream of nitrogen at room temperature and dissolved in an appropriate volume of ethyl acetate for GC/MS analysis.

The *N*(*O*)-heptafluorobutyryl-*n*-propyl esters of the amino acids were prepared in a reaction vial by adding 3 mL of 8 M HCl in 1-propanol (*6*). The reaction vial was capped and heated in a sand bath for 10 min at 100 °C. The esterification reagent was evaporated under a gentle stream of nitrogen. The propylation procedure was repeated and the *n*-propyl esters were dried under a gentle stream of nitrogen at 60 °C. After drying, 1 mL of acetonitrile was added with 1 mL of HFBA. The vial was capped and heated at 150 °C for 10 min in a sand bath and then cooled to room temperature. The derivatized amino acids were then dried under a gentle stream of nitrogen. After drying, the remainder of the procedure was the same as for the isoamyl derivatives.

Reaction of Some Amino Acids with Hypochlorous Acid. Serine, threonine, alanine, valine, tyrosine, and tryptophan were chosen to test the reaction of amino acids and HOCl. The HOCl solutions were prepared by bubbling chlorine gas into organic-free water and checking the HOCl concentration by the OTA method (*13*). One milliliter of a 20 μmol/mL solution of each of the above amino acids except tryptophan was placed in separate 5-mL reaction vials and adjusted to pH 1–2 with 6 N HCl. One milliliter of 2000 mg/L (28 μmol of Cl_2/mL) aqueous chlorine was added to each vial. The vials were capped, shaken, and allowed to stand for 30 min at room temperature. Controls were also run on each of the amino acids. The control consisted of 1 mL of the amino acid solution and 1 mL of the water used to make the HOCl solution. After 30 min, each vial was extracted with 1 mL of ether by shaking vigorously for 1 min. The ether extract was analyzed by GC/MS for identification of any ether-soluble reaction products with the only change in GC/MS conditions being the initial temperature of the column (30 °C). The remainder of the aqueous solution was dried under a stream of nitrogen, and the volatile derivatives were prepared and analyzed by GC/MS as described above.

Table I. Minimum Detection Limits and Cation/Ligand Exchange Recoveries of 20 Amino Acids[a]

amino acid	minimum detectable limit,[b] ng *n*-propyl ester[c]	minimum detectable limit,[b] ng isoamyl ester	recovery,[d] %
alanine	4.0 ± 0.3	10.8	88.9 ± 0.2
glycine	2.6 ± 0.2	13.5	101 ± 2
valine	3.4 ± 0.5	10.8	95 ± 1
threonine	1.4 ± 0.2	2.6	94 ± 1
serine	1.2 ± 0.1	4.0	93.4 ± 0.4
leucine	3.8 ± 0.1	3.1	94.7 ± 0.3
isoleucine	3.7 ± 0.2	5.6	91 ± 2
proline	4.3 ± 0.3	2.1	92 ± 1
cysteine	3.5 ± 0.3	18.9	92 ± 2
tryptophan	18.8 ± 1.2	*e*	82 ± 3
hydroxyproline	3.8 ± 0.3	2.8	95 ± 2
methionine	6.9 ± 0.2	6.3	94 ± 2
histidine	167 ± 10	*e*	99 ± 6
phenylalanine	1.5 ± 0.1	8.9	93 ± 2
ornithine	3.8 ± 0.1	7.9	83 ± 3
lysine	4.1 ± 0.2	8.5	91 ± 1
tyrosine	5.0 ± 0.4	7.7	81 ± 2
aspartic acid	4.0 ± 0.3	6.5	89 ± 1
arginine[d]	7.7 ± 0.7	*f*	81 ± 2
glutamic acid	6.2 ± 0.5	9.5	69 ± 2

[a] GC/MS conditions in text. [b] MDL measured at S/N = 2. [c] Average of three determinations. [d] Average of two determinations. [e] Not detected. [f] Not included in standard.

A solution which contained 76.8 mg (376 μmol) of tryptophan was reacted with 3.3 mL of a HOCl solution which contained 13.3 mg (188 μmol) of chlorine for 30 min at room temperature. The reaction mixture was then extracted with ether by using the same procedure as above. The ether extract which contained a red-colored product was analyzed by GC/MS under the same conditions as previous ether extracts. The ether material did not yield any gas-chromatograph peaks. The amino acid derivatization procedure was carried out on the red-colored product, and the derivative mixture analyzed by GC/MS. The aqueous portion of the reaction mixture was dried under a stream of nitrogen and derivatized by using the procedure described above.

Analysis of Wastewater Samples. Sewage product samples from four cities were analyzed for amino acids. The cation and ligand exchange procedure was used to concentrate the amino acids as described in Figure 1. Derivatives were prepared by using the acylation and esterification procedures as previously described. City A sample consisted of 100 mL of raw sewage which was quenched for residual chlorine by using sodium sulfite. The sample from city B was 25 L of anaerobic digestor supernate which had been chlorinated at ca. 2000 mg/L at the city plant. This "superchlorinated" sample was quenched on site with sodium sulfite to remove residual chlorine. The sample from city C consisted of combined primary and secondary sludges which were also "superchlorinated" at the city's plant. Two liters of the supernatant of this sample was quenched with sodium sulfite after 2 h. Another

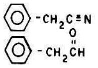
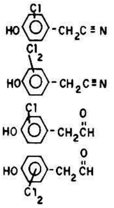
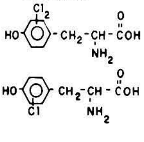
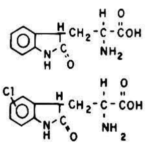
2 L of the sample from city C was quenched with sodium sulfite after 4 days. Samples from city D were 1 L of "superchlorinated" septage which was chlorinated at the city's plant and 1 L of raw septage. The samples were quenched on site with sodium sulfite. Any particulate matter was removed from the sample by filtering through Whatman 50-cm prefolded filter paper or by centrifugation and filtering.

Results and Discussion

Gas Chromatography/Mass Spectrometry. Minimum detectable GC/MS limits for the derivatized amino acids are shown in Table I. Values for the isoamyl ester are compared with those for the *n*-propyl ester, the latter being the average of three separate runs. A signal-to-noise ratio of 2:1 was used as the criterion for the minimum detectable limit, and the procedure consisted of injection of increasingly dilute solutions of the acids of equal volume. As noted by others, histidine has a high minimum detection limit (MDL) (*17, 18*), presumably due to decomposition of acyl derivatives during gas chromatography. The isoamyl ester of histidine is not seen at all, nor is the ester of tryptophan. On the other hand, the rather severe conditions required for preparation of the propyl esters causes the oxidation of cysteine to cystine, and quantification of the former must be taken with reservation. For the majority of amino acids, the GC/MS MDL values in Table I represent a detection limit of ~5 ppb (μg/L) in environmental samples, assuming a concentration factor of 1000:1 in the procedure shown in Figure 1.

Cation/Ligand Exchange Recovery Studies. To determine the recoveries of 20 standard amino acids by the combined cation/ligand exchange procedure, we used a solution containing 0.50 μmol of each amino acid in 2 L of water. The eluate from the Chelex column was dried and derivatized to *N*(*O*)-heptafluorobutyryl-*n*-propyl esters as described above. Fifty micromoles of the same amino acid mixture was derivatized as a control. The recovery efficiencies listed in Table I vary from 100% for glycine to 69% for histidine with an average of 90%.

Table II. Reaction Products Identified from the Reaction of Amino Acids with HOCl

amino acid	products in ether extract	products in aqueous solution
SERINE	NONE	SERINE
ALANINE	$CH_3C\equiv N$ $CH_3\overset{O}{\overset{\|}{C}}H$	ALANINE
VALINE	$(CH_3)_2CHC\equiv N$ $(CH_3)_2\,CH\overset{O}{\overset{\|}{C}}-N$	VALINE
THREONINE	NONE	THREONINE
LEUCINE	$(CH_3)_2\;CHCH_2C\equiv N$ $(CH_3)_2CH-CH_2\overset{O}{\overset{\|}{C}}H$	LEUCINE
PHENYLANINE		PHENYLANINE
TRYOSINE		TRYOSINE 
TRYPTOPHAN	NONE	

Reaction of Some Amino Acids with Hypochlorous Acid. The neutral reaction products from serine, threonine, alanine, valine, leucine, phenylalanine, tyrosine, and tryptophan and those obtained by the HFBA-*n*-C_3H_7 derivatization procedure are listed in Table II.

The reaction products of HOCl and amino acids in general were a confirmation of previous work (*19–30*), but in general this work represents the first confirmatory data on their structures. Of particular interest are chlorotyrosine and the dichlorotyrosine which had not been confirmed before by spectroscopic evidence (*29–30*). The oxindole derivatives of tryptophan were also very unusual since these compounds have not been reported by other workers and show further carbon–chlorine bonding.

The mass spectra of *N*(*O*)-heptafluorobutyryl-*n*-propyl esters of mono- and dichlorotyrosine are shown in Figures 2 and 3, respectively. Figures 4 and 5 rationalize the major peaks in terms of a plausible fragmentation pattern. The spectra in Figures 2 and 3 actually were obtained on compounds found in the sludge sample from site C after 4 days of "superchlorination" but are identical with those of products found in the laboratory chlorination of tyrosine. Peaks at *m/e* 436, 394, 377, 349, and 337 for chlorotyrosine and *m/e* 470, 429, 411, 383, and 371 for dichlorotyrosine indicate that chlorination is on the aromatic ring, presumably at the 3- and 5-positions, but the precise position cannot be ascertained from mass spectrometry alone.

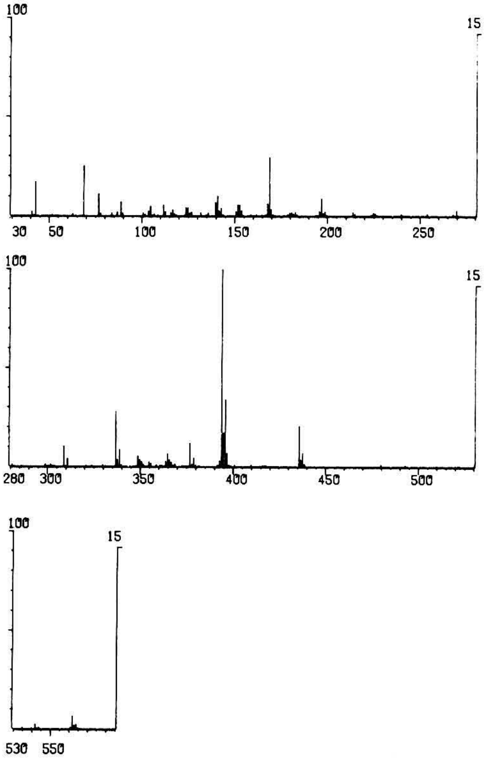


Figure 2. 70-eV mass spectrum of chlorotyrosine (*N*(*O*)-heptafluorobutyryl-*n*-propyl ester).

Comparison of GC/MS and Beckman 120-C Amino

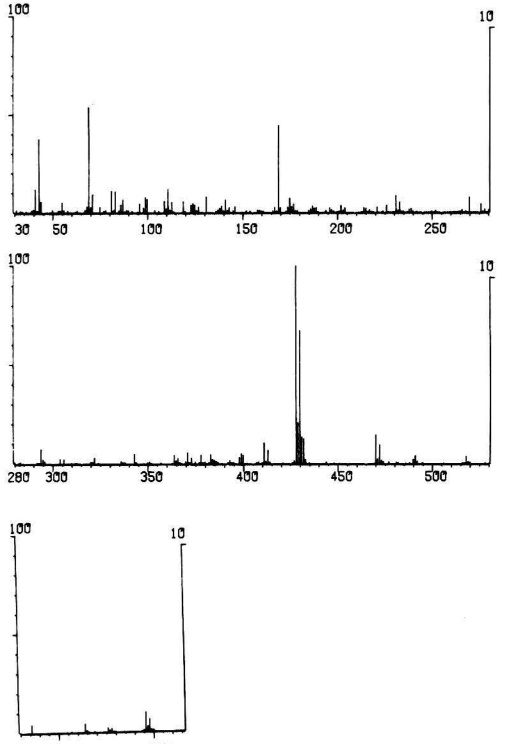


Figure 3. 70-eV mass spectrum of dichlorotyrosine (*N*,*O*)-heptafluorobutyryl-*n*-propyl ester).

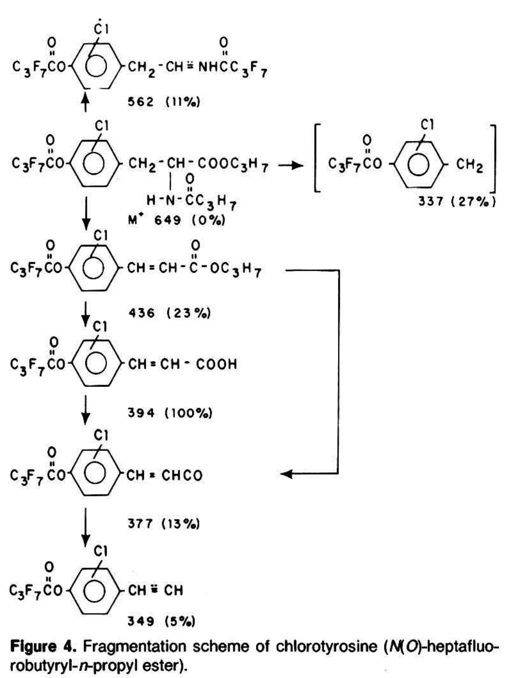


Figure 4. Fragmentation scheme of chlorotyrosine (*N*,*O*)-heptafluorobutyryl-*n*-propyl ester).

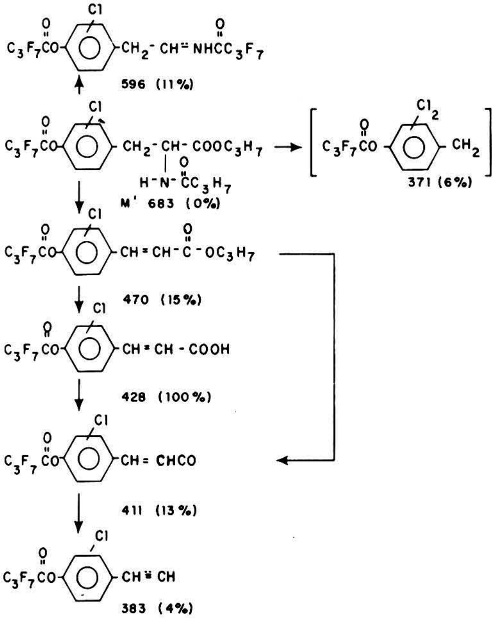


Figure 5. Fragmentation scheme of dichlorotyrosine (*N*,*O*)-heptafluorobutyryl-*n*-propyl ester).

Acid Analyzer. To compare the two methods, using a wastewater matrix, we obtained 2 L of the final effluent from a city sewage plant. The final effluent was quenched with excess sodium sulfite to remove residual chlorine and then filtered. The 2-L sample was spiked with a standard mixture of 20 amino acids at the 5 μmol/L level. Two 1-mL samples of this solution were run on the Beckman Model 120-C amino acid analyzer, and the remainder of the sample was split into two equal parts and analyzed by the GC/MS procedure. The cation and ligand exchange procedure for cleanup and concentration of the amino acids, and the *n*-propyl esterification and HFBA acylation procedures described earlier in this section, were used.

In general, both methods gave good accuracy and precision, as can be seen in Table III. The amino acid analyzer had a low value with cysteine while the GC/MS system obtained a relatively high value; also, the amino acid analyzer would not elute hydroxyproline. No explanation is offered for the large GC/MS value for histidine. Overall, the comparison was very good with both methods having ~90% efficiency. The average difference between the two methods was 12.8% with a maximum and minimum of 48.8 and 1.40%, respectively. Most

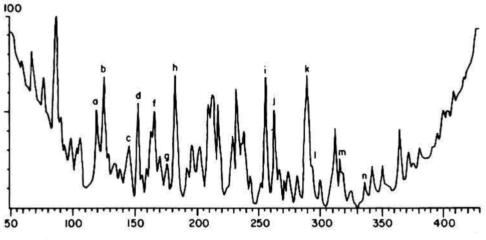


Figure 6. Reconstructed gas chromatogram of amino acids in combined sludge after superchlorination (*N*,*O*)-heptafluorobutyryl-*n*-propyl esters): (a) alanine; (b) glycine; (c) valine; (d) threonine; (f) serine; (g) leucine; (h) isoleucine; (i) phenylalanine; (j) glutamic acid; (k) lysine; (l) tyrosine; (m) chlorotyrosine; (n) dichlorotyrosine.

Table III. Comparison of GC/MS Analysis of Free Amino Acids with a Beckman Amino Acid Analyzer Using a Wastewater Matrix

amino acid	spiked concn, μm/l	amino acid analyzer concn found, μm/l			GC/MS concn found, μm/l		
		1	2	av	1	2	av
alanine	5.08	5.29	5.29	5.29 ± 0.01	4.98	4.83	4.91 ± 0.08
glycine	5.00	5.02	4.58	4.80 ± 0.22	4.51	4.33	4.42 ± 0.09
valine	5.00	4.20	5.01	4.61 ± 0.41	4.59	4.89	4.74 ± 0.15
threonine	5.18	5.04	4.70	4.87 ± 0.17	4.73	4.66	4.70 ± 0.03
serine	5.00	4.43	4.51	4.47 ± 0.04	4.74	4.58	4.66 ± 0.08
leucine	5.00	4.43	4.38	4.41 ± 0.02	4.57	4.54	4.56 ± 0.01
isoleucine	5.19	5.12	4.81	4.97 ± 0.15	5.07	5.02	5.04 ± 0.03
proline	5.00	5.18	5.11	5.15 ± 0.03	4.72	4.70	4.71 ± 0.01
cysteine	5.00	2.70	2.13	2.42 ± 0.28	5.24	5.38	5.31 ± 0.07
hydroxyproline[a]	5.00				4.64	4.56	4.60 ± 0.04
methionine	5.00	4.11	3.67	3.89 ± 0.22	4.57	4.51	4.54 ± 0.03
aspartic acid	5.00	5.29	5.16	5.23 ± 0.06	4.45	4.38	4.41 ± 0.04
phenylalanine	5.00	4.52	4.25	4.39 ± 0.13	4.64	4.54	4.59 ± 0.05
glutamic acid	5.00	5.55	5.38	5.47 ± 0.08	4.95	5.28	5.12 ± 0.16
ornithine[b]	5.00				4.52	4.58	4.55 ± 0.03
lysine	5.00	5.19	4.88	5.04 ± 0.15	5.02	4.91	4.96 ± 0.01
tyrosine	5.00	4.41	3.89	4.15 ± 0.26	4.76	4.65	4.71 ± 0.05
arginine	5.00	4.94	4.72	4.83 ± 0.11	4.80	4.68	4.74 ± 0.06
histidine	5.11	4.47	4.32	4.40 ± 0.07	6.84	7.65	7.24 ± 0.41
tryptophan	5.00	5.06	5.43	5.25 ± 0.18	4.67	4.55	4.61 ± 0.06

[a] Hydroxyproline not eluted from amino acid analyzer column. [b] Ornithine not in standard used on amino acid analyzer.

Table IV. Amino Acids Present in Municipal Wastes (μg/L)

	typical[a] domestic sewage	city A raw sewage	city B super chlorinated anaerobic digestor supernatant	city C combined sludge		city D septage	
				2-h super-chlorination	4-day super-chlorination	raw	super-chlorinated
alanine	20–90	250	4.0	3.1	3.2	1220	8.3
glycine	20–130	44	24.0	8.9	5.1	1410	5.6
valine	50–240	200	0.9	11.1	3.2	780	4.0
threonine	10–180	120	3.0	0.9	tr	450	0.9
serine	20–130	37	36.9	2.4	1.2	400	1.2
leucine	60–280	380	tr	7.9	tr	960	2.7
isoleucine		130	8.0	7.1	5.8	580	1.3
proline	0	42	3.0	<0.11	<0.04	100	<0.07
cysteine		<7	<0.07	<0.09	0.03	60	<0.05
hydroxyproline		52	<0.08	<0.10	<0.04	100	<0.06
methionine	50–240	19	<0.14	<0.17	<0.07	110	<0.10
aspartic acid	20–130	82	<0.08	<0.10	<0.04	130	<0.06
phenylalanine	20–330	88	5.0	10.5	3.6	300	2.1
glutamic acid	10–180	52	3.0	15.1	4.5	150	0.4
lysine	tr	110	5.0	3.5	3.6	130	1.9
arginine	tr	<15	<0.15	<0.19	<0.07	750	<0.12
histidine	tr	130	<3.3	<4.2	<1.6	370	<2.5
tyrosine	60–90	150	3.0	1.4	1.1	450	0.4
chlorotyrosine		<10[b]	3.0[b]	1.0[b]	1.3[b]	<5[b]	0.2
dichlorotyrosine		<10[b]	<0.10[b]	<0.12[b]	0.5[b]	<5[b]	<0.8

[a] Reference *32*. [b] Based on detector response to tyrosine.

significantly, the results show that free amino acids are at quite low levels in the final effluent before spiking, confirming the work of Subrahmanyam (*31*).

Analysis of Municipal Waste Products for Amino Acids. Wastewater samples from four cities were analyzed for free amino acids. The cation and ligand exchange procedure was used for cleanup and concentration as described in Figure 1. Figure 6 is a typical GC/MS reconstructed gas chromatogram of the amino acid extract. Derivatives were prepared by using the HFBA acylation and 1-propanol esterification procedure. The results of these analyses are shown in Table IV. The sample from city A consisted of 100 mL of raw sewage which had been chlorinated at a high dose (ca. 2000 mg/L HOCl) and was quenched for residual chlorine by using sodium sulfite. The sample from city B consisted of anaerobic digestor supernate which also had been "superchlorinated". Samples from city C consisted of combined primary and secondary sludges which were also "superchlorinated" and quenched after 4 days of contact with HOCl. The sample from city D consisted of both raw and "superchlorinated" septage.

These samples were quenched with sodium sulfite at the plant.

Table IV shows the concentrations of amino acids found in these samples. It is interesting to note that the levels found in raw sewage of city A differ in a few cases from those reported in the literature (*32*). Presumably, this is due to the nature of the plant influents. As expected, amino acid levels are higher in septage; however, it can be seen that "superchlorination" is an effective method for destroying the amino acids. Since chlorine doses used in this method are typically in the 0.2–0.4% range, one would expect these conditions to cause extensive oxidation of organic materials. In addition, one would expect to observe considerable formation of chlorinated organic products, which has been confirmed by Glaze and Henderson (*1*). Parallel work on the samples listed in Table IV by other members of the North Texas State University research team has shown that numerous chloroorganics are present in "superchlorinated" samples from cities B, C, and D.

Table IV shows that these samples also contain chlorotyrosine, and in one case dichlorotyrosine. This observation represents the first confirmation of a chlorinated amino acid in a wastewater product (*4*).

The significance of these chlorinated products in wastewater plant products cannot be stated at this time. The fate of the compounds in the receiving environment undoubtedly will depend on the choice of disposal method, as well as the stability of the particular compound. In the case of "superchlorinated" sludge or septage products, there may be some concern for the leaching of compounds into receiving streams or ground water if sludge beds are not adequately sealed. In any case, these data and the results of earlier works point out the need for caution in the disposal of "superchlorinated" waste products to avoid possible contamination of the environment.

Toxic effects of chlorinated amino acids have not been reported. However, Fortunato (*33*) has shown that 3,5-dibromotyrosine inhibits the synthesis of thyroid hormones from inorganic iodine with consequent effects on hormone concentrations in both the thyroid and the vascular spaces in rats. A similar effect may be postulated for the chlorinated analogues, but more work on the toxicology of these and other chlorinated compounds is needed.

Literature Cited

(1) Glaze, W. H.; Henderson, J. E. *J. Water Pollut. Control Fed.* **1975**, *10*, 2511–5.

(2) Glaze, W. H.; Peyton, G. R.; Rawley, R. *Environ. Sci. Technol.* **1977**, *11*, 685–90.

(3) Glaze, W. H.; Peyton, G. R.; Saleh, F. Y.; Huang, F. Y. *Int. J. Environ. Anal. Chem.* **1979**, *7*, 143–60.

(4) Glaze, W. H.; Burleson, J. L.; Peyton, G. R. *Bull. Environ. Contam. Toxicol.* **1978**, *19*, 724–8.

(5) Gerke, C. W.; Lumin, K. *J. Chromatogr.* **1971**, *57*, 219–38.

(6) Moss, C. W.; Lambert, M. A. *J. Chromatogr.* **1971**, *50*, 134–6.

(7) Hardy, J. P.; Kerrin, S. L. *Anal. Chem.* **1972**, *44*, 1497–9.

(8) Jonsson, J.; Eyem, J.; Sjoquist, J. *Anal. Biochem.* **1973**, *51*, 204–19.

(9) Harris, C. K.; Tigane, E.; Hanes, C. S. *Can. J. Biochem.* **1961**, *39*, 439–50.

(10) Seigol, A.; Degens, E. T. *Science* **1966**, *151*, 1098–101.

(11) Zumwolt, R. W.; Roach, D.; Gehrke, C. W. *J. Chromatogr.* **1970**, *53*, 171–94.

(12) Gardner, W. S.; Lee, G. F. *Environ. Sci. Technol.* **1973**, *7*, 719–24.

(13) American Public Health Association "Standard Methods for the Examination of Water and Wastewater", 13th ed.; New York, 1971; pp 17–24.

(14) Gelpi, E.; Koenig, W. A.; Gilbert, J.; Oro, J. *J. Chromatogr. Sci.* **1969**, *7*, 604–13.

(15) Zanetta, J. P.; Vincedon, G. *J. Chromatogr.* **1973**, *76*, 91–9.

(16) Gilman, H. E. "Organic Synthesis," Collective Vol. I; Wiley: New York, 1941; p. 258.

(17) Blau, K, Szymanski, H. G., Eds. "Biomedical Applications of Gas Chromatography"; Plenum Press: New York, 1968; Vol. 2, p. 1.

(18) Moodie, J. M. *J. Chromatogr.* **1974**, *99*, 495–505.

(19) Langheld, K. *Chem. Ber.* **1909**, *42*, 2360–74.

(20) Dakin, H. D.; Coehn, J. B.; Daufresne, M.; Kenyon, J. *Proc. R. Soc. London, Ser. B* **1916**, *89*, 232–51.

(21) Milroy, T. H. *Biochem. J.* **1916**, *10*, 453–65.

(22) Dakin, H. D. *Biochem. J.* **1917**, *2*, 79–95.

(23) Wright, N. C. *Biochem. J.* **1926**, *20*, 524–32.

(24) Norman, M. F. *Biochem. J.* **1936**, *30*, 484–96.

(25) Wright, N. C. *Biochem. J.* **1936**, *30*, 1661–7.

(26) Ingols, R. S.; Wyckoff, H. A.; Kethley, T. W.; Hodgden, H. W.; Fincher, E. L.; Hildebrand, J. C.; Mandel, J. E. *Ind. Eng. Chem.* **1953**, *45*, 996–1000.

(27) Ingols, R. S.; Jacogs, G. M. *Sewage Ind. Wastes* **1957**, *29*, 258–62.

(28) Poroshin, K. T.; Chuvaeva, T. P.; Shibnev, V. A. *Dokl. Bolg. Akad. Nauk* **1969**, *22*, 1265–8; *Chem. Abstr.* **1970**, *72*, 90866a.

(29) Kantouch, A.; Abdel-Fattah, S. H. *Chem. Zvesti* **1971**, *25*, 222–30.

(30) Pereira, W. E.; Hoyano, Y.; Summons, R. E.; Bacon, V. A.; Duffield, A. M., *Biochim. Biophys. Acta* **1973**, *313*, 181–9.

(31) Subrahmanyam, P. V. R., Sastry, A. C., Rao, P., Pillai, S. C. *J. Water Pollut. Control Fed.* **1965**, *37*, 1142–63.

(32) Hunter, J. V. In "Organic Compounds in Aquatic Environments," Faust, S. D., Hunter, J. V., Eds.; Marcel Dekker: New York, 1965; pp 51–94.

(33) Soares, Fortunato, J. *Omnia Med. Ther.* **1976**, *3*, 121–33; *Chem. Abstr.* **1977**, *86*, 84019z.

Received for review February 25, 1980. Accepted July 18, 1980. This work was supported by a grant from the U.S. Environmental Protection Agency R-805822-010 and by assistance from the North Texas State University Faculty Research Committee.

Computer Modeling Studies of the Impact of Vehicle Exhaust Emission Controls on Photochemical Air Pollution Formation in the United Kingdom

Richard G. Derwent* and Øystein Hov†

Environmental and Medical Sciences Division, Atomic Energy Research Establishment, Harwell, Oxfordshire, England

■ Numerical simulation techniques are applied to the formation of photochemical air pollutants in the London region from emissions of NO, CO, SO_2, CH_4, and 35 organic hydrocarbon and oxygenated species. The model gives a realistic simulation of the observed production of ozone, peroxyacetyl nitrate (PAN), peroxyproprionyl nitrate (PPN), and sulfate aerosol during photochemical episodes. The relative effects of reducing hydrocarbon and nitrogen oxide emissions have been investigated, and hydrocarbon control appears to offer much greater potential for reducing secondary pollution formation in the London region. The controls of vehicle exhaust emissions required or proposed in the United Nations Economic Commission for Europe (ECE) Regulations should markedly reduce ozone and PAN formation in the London region.

Introduction

It is now well established through extensive monitoring programs both in the United Kingdom and in Europe that the concentrations of ozone (*1–3*), peroxyacetyl nitrate (*4, 5*), and visibility-reducing aerosols (*6*) may increase significantly during sunny summer periods. Simultaneous measurements of CCl_3F have demonstrated that these elevated concentrations have been formed in air masses heavily polluted by emission, from man's activities (*6, 7*).

With the increasing awareness of photochemical air pollution, despite its appreciable year-to-year variability, the question remains as to what control strategies might be realistically available to ameliorate the situation. Present evidence appears to show that the potential for the production of photochemical air pollution is available throughout western Europe (*1*). Furthermore, long-range transport appears to advect photochemically reacted air masses to remote areas of northwest Europe (*6, 7*). Consequently, any controls which might be required must be international, if they are to be successful.

Any approach to the control of photochemical air pollution must be firmly based on an adequate understanding of the phenomenon. Much of this understanding has been accumulated from laboratory investigations using smog chambers and from observations of the behavior of pollutants in photochemical episodes. The secondary pollutants, ozone and peroxyacetyl nitrate (PAN), arise by reactions involving hydrocarbons and oxides of nitrogen driven by sunlight (*8, 9*). The secondary pollutants may have both chemical (photolysis and thermal decomposition) and physical sinks (dry deposition and aerosol scavenging). Their overall behavior in the atmosphere, leading to characteristic diurnal variations, represents a subtle interplay between photoproduction and removal by chemistry and deposition (*10, 11*). The atmospheric degradation of hydrocarbons by OH radicals plays a central role in the oxidation of NO to NO_2 and hence in ozone and other secondary pollutant formation (*12*).

Computer modeling techniques have been employed to evaluate the potential for photochemical air pollution formation in southern England. A fixed-point urban model has been employed to study the first day's photochemistry. The behavior of subsequent days in photochemical episodes is much more complex because of the effects of emissions elsewhere in the UK and continental Europe. The potential effect of uniform controls on precursor emissions from all sources in general, and of vehicle exhaust emission controls in particular, have been evaluated.

Description of the Model

The detailed formulation of the photochemical model of the London conurbation is described elsewhere (*13*), and only a brief description is given here.

The horizontal dimensions of the box model are 32 × 50 km. The vertical dimension extends from the ground to the mean inversion height. Data from the Balthum ascents at Cardington, Bedfordshire, give a mean inversion height during the summer months at midday of 1300 m (*14*). This value was taken as the mixing height, H, in the present study. No horizontal or vertical grid is included, and all emissions are assumed to be well mixed throughout the model volume. The intention is to study the generation of secondary pollutants over time scales from several hours to several tens of hours, and, within these time scales, the assumption of instantaneous mixing can be justified because turbulent mixing during photochemical episodes is usually vigorous.

Each model species, of which there are 180 or so in all, satisfies the continuity equation

$$dc/dt = P_e + P_{ch} - c(L_{ch} + L_d + L_v) \tag{1}$$

where c is the species concentration. The terms P_e and P_{ch} represent the production terms due to emission and chemistry, respectively. The terms cL_{ch}, cL_v, and cL_d represent the loss terms due to chemistry, dilution, and deposition on the ground, respectively.

The emission term, P_e, is defined as follows:

$$P_e = E/H \tag{2}$$

where E is the emission flux. Nitric oxide, sulfur dioxide, carbon monoxide, and 36 individual volatile organic compounds are emitted into the model volume. These 36 volatile organic compounds include the C_1–C_5 alkanes, C_2–C_5 alkenes, C_1+C_5 aldehydes, C_3–C_5 ketones, C_7–C_8 aromatic compounds, C_1–C_2 alcohols, and acetylene. These emissions are split up into contributions from eight source categories which comprise petrol-engined motor vehicle exhaust, diesel-engined motor vehicle exhaust, petrol-engined motor vehicle evaporative emissions, stationary fuel combustion, solvent usage, industrial processes, petroleum distribution, and natural gas leakage. The emissions were calculated on an annual basis for 1974/1975 by using a combination of emission factors, statistics of fuel comsumption, and other relevant data (*13*). The split into individual species as well as source categories enables an evaluation of the relative contribution to secondary pollutant formation from single hydrocarbons as well as from each source category. The organic species specifically included in the model comprised over 80% by volume of the hydrocarbon emissions from the major source category, motor-vehicle exhaust. The remainder of the emissions which included higher alkanes and aromatics were redistributed among the 36 model species. If, subsequently, OH-rate data and chemical degradation schemes become available for some of these im-

---

† On leave from Institute of Geophysics, University of Oslo, Norway.

0013-936X/80/0914-1360$01.00/0

Table I. Deposition Velocities Employed in the Photochemical Model

species	deposition velocity, mm s^{-1}	ref
ozone	6	(*11, 45*)
sulfur dioxide	8	(*46*)
nitrogen dioxide	1	(*47*)
PAN and its homologues	2	(*11, 48*)

portant hydrocarbons, they could be specifically treated in our model.

The chemical formulation of the model includes the 40 emitted species, 25 inorganic species (including O_3, NO_2, aerosol components, and free radicals such as OH and HO_2), and 120 organic intermediates required to describe the atmospheric degradation of the volatile organic species emitted into the model. The degradation pathways have been constructed from the available laboratory studies and reviews (*4, 15–17*). The P_{ch} and cL_{ch} terms have been constructed from over 40 reactions involving the inorganic species alone and over 200 reactions describing the atmospheric degradation of the organic constituents. A further 41 photochemical processes are included to describe the behavior of the 20 photochemically labile organic and inorganic species. These photochemical processes are given diurnally dependent rate coefficients calculated by using a method which allows treatment of the atmospheric scattering processes (*18*).

Deposition on the ground is included through the term cL_d in eq 1. The deposition flux is calculated as follows:

$$cL_d = (c/H)v_g \tag{3}$$

from the deposition velocity, v_g, the values of which are given in Table I.

Many of the chemical processes occurring in photochemical air pollution have rate coefficients which are temperature dependent. In particular, the thermal decomposition of PAN (*19*) is highly sensitive to temperature variations in the ambient range. To give an adequate simulation of the life cycle of PAN and its homologues, a diurnally dependent temperature was specified based on the observed behavior for a typical photochemical episode, June 16, 1973. The midafternoon peak temperature reached 25 °C, and the early morning minimum was 8 °C. The diurnal dependence of relative humidity (RH) for that day was taken and converted into absolute water vapor concentrations (in molecule cm^{-3}) by using an expression taken for the water vapor saturation pressure over a plain surface (*20*).

The prevailing horizontal visibility (*21*) was calculated by using eq 4 for the visual range in kilometers and the extinction coefficient, σ, in km^{-1}.

$$\text{visual range} = 3.91/\sigma \tag{4}$$

The extinction coefficient was estimated from the model sulfate aerosol concentrations in $\mu g\ m^{-3}$ by using eq 5 obtained by Garland (22).

$$\sigma = [\text{aerosol}]/\exp\{0.465 \ln (100 - \text{RH}) + 3.129\} \tag{5}$$

Nitrate aerosol was assumed to have a similar effect on visibility on a molar basis.

The effect of dilution by the prevailing easterly wind during the first day of a photochemical episode was accounted for by using eq 6

$$cL_v = cu/x \tag{6}$$

where x is the downwind dimension of the model box, 50 km for greater London, and u is the wind speed. From an analysis of the photochemical episodes during 1973–74, u was found to be 2.4 m s^{-1} (*11*). This dilution term was applied only to the precursor pollutants and not to the secondary pollutants in order to simulate the "worse case". However the effect of the transport of secondary pollutants into the model has been studied and is reported elsewhere (*13*). Models using more complete treatments of transport and mixing layer depths give quite similar secondary pollutant concentrations to the calculations described here which aim to study the effects of changing only small parts of the model input, e.g., the vehicle exhaust emission factors.

The system of differential equations describing the time evolution of the photochemical air pollution system were integrated by using the Harwell computer program FACSIMILE (*23*), which employs a variable order Gear's method. About 1 min of CPU was required on the Harwell IBM 3033 computer per night and about 2 min per day's simulation.

Numerical Simulation of Photochemical Air Pollution Formation in Southeast England

A photochemical box model was assembled from the emissions and chemistry occurring in the atmosphere over the London conurbation. The model was integrated starting from tropospheric background concentrations of methane, carbon monoxide, and hydrogen, through one day and night. The results described here are taken from the second day's simulation. All concentrations were generated by the model,

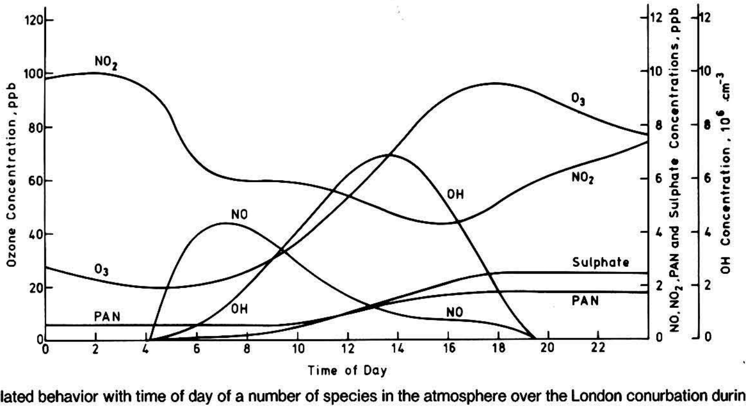


Figure 1. The calculated behavior with time of day of a number of species in the atmosphere over the London conurbation during a photochemical episode.

thereby removing any bias caused by choice of initial conditions. Only external input data are specified: precursor emissions, meteorological conditions, atmospheric chemistry, and photodissociation rates, etc.

Figure 1 shows the calculated behavior for a number of pollutants of interest. Ozone rises from its early morning minimum of 19 ppb, reaching a maximum of 96 ppb at 18:00 before its decrease during the night. From a study of the ozone monitoring data at five locations in southeast England (*2*), over 250 days have been recorded with maximum hourly mean over 80 ppb, 136 days over 100 ppb, and 29 days over 150 ppb. The median maximum ozone concentration is accordingly estimated as 97 ppb in agreement with the model result.

PAN rises to a peak concentration of 1.8 ppb at about the same time that the ozone maximum is reached. The typical PAN concentrations observed during photochemical episodes in southeast England are from 2.0 to 8.9 ppb (*24*). The model value is slightly below the lower limit of the observations in rural areas. The calculated ozone/PAN ratio of 53 is in excellent agreement with the 50:1 ratio observed in Oxfordshire, UK (*25*), and with the ratio of 59 measured at Delft, Netherlands (*5*).

Peroxyproprionyl nitrate (PPN) follows a very similar behavior in the model to PAN. The calculated PPN/PAN ratio is 0.18, which is in reasonable accord with the observed ratio of their peak heights, 0.14 ± 0.02 (*25*).

Sulfate and nitrate aerosols are shown to be produced by photochemical oxidation of sulfur dioxide and nitrogen dioxide. These aerosol species reach concentrations of 2.5 and 1.6 ppb, respectively, by the end of the day. The sulfate and nitrate aerosol concentrations have been monitored in Oxfordshire, England, since 1954 (*26*). The highest summertime 2-week mean concentrations have averaged 3.2 ppb (12.6 $\mu g\ m^{-3}$) and 2.0 ppb (5.7 $\mu g\ m^{-3}$) over the period 1968–74 for sulfate and nitrate aerosols, respectively. Peak hourly concentrations, particularly of sulfate aerosol, have been much higher during photochemical episodes, reaching 17 ppb (*27*).

It therefore appears that the concentrations of the main secondary pollutants predicted in the photochemical box model are about the correct magnitude when compared with the available observational data. Further details of model validation, particularly for the precursors, are given elsewhere (*13*).

Effect of "HC Control" and "NO_x Control" Strategies on Photochemical Air Pollution Formation

Two techniques for the control of photochemical air pollution formation have been given considerable attention. These involve selective control of the atmospheric emissions of organic compounds—"HC control"—or of the oxides of nitrogen—"NO_x control". Since present understanding of photochemical air pollution formation assigns to these difference classes of compounds, HC and NO_x, quite different roles, it is anticipated that they will not have equal potential as control strategies.

The effect of NO_x and HC control has been studied for the London conurbation by using the photochemical box model. Firstly, both NO_x and HC control were applied with equal severity to all sources whether this was considered practical or not. All hydrocarbons from all sources were controlled to an equal extent.

Figures 2–5 show the effect of HC and NO_x controls on the ozone, peroxyacetyl nitrate, sulfate aerosol, and visibility reached at the end of the second day's photochemistry. With increasing reductions of hydrocarbon emissions, ozone, PAN, and sulfate aerosol concentrations all steadily decline. Furthermore, the assumption that the reductions in concentrations are proportional to the reduction in emission is not generally applicable to HC control of any of the secondary pollutants.

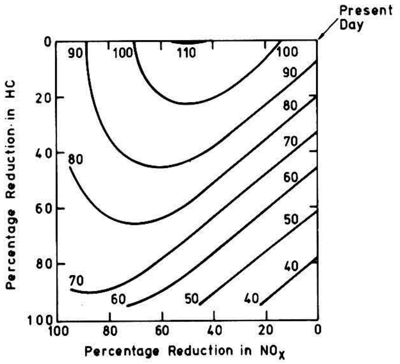


Figure 2. The effect of reducing HC and NO_x emissions on the ozone concentration in ppb at 18:00 h.

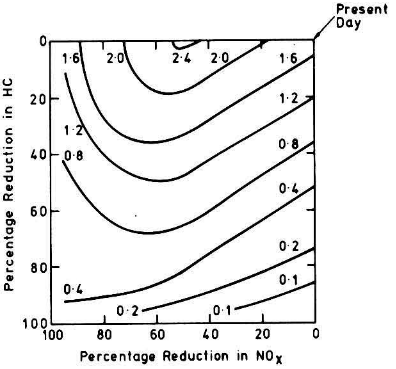


Figure 3. The effect of reducing HC and NO_x emissions on the PAN concentration in ppb at 18:00 h.

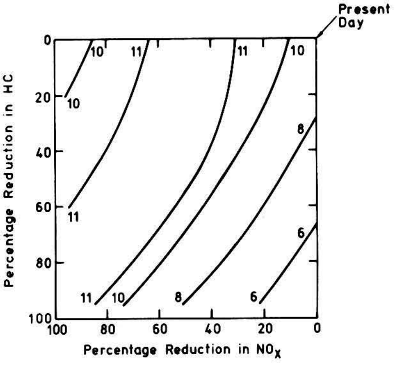


Figure 4. The effect of reducing HC and NO_x emissions on the sulfate aerosol concentration in $\mu g\ m^{-3}$ at 18:00 h.

With increasing reductions of NO_x emissions, ozone, PAN and sulfate aerosol start to increase above the uncontrolled values before they decline. This illustrates the very different effects that these two classes of pollutants exert on the photochemical system. The oxides of nitrogen exert an inhibiting influence on secondary pollutant formation in the London conurbation, whereas the hydrocarbons exert a promoting influence. It is readily obvious from Figures 2–4 that the concentrations of ozone, PAN, and sulfate aerosol do not decline linearly with the amount of NO_x control.

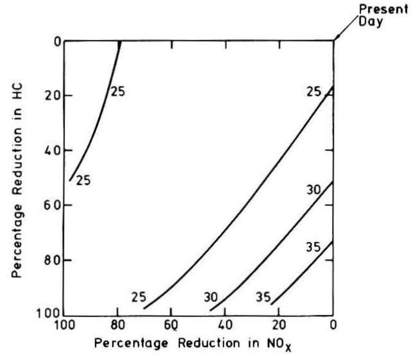


Figure 5. The effect of reducing HC and NO_x emissions on the prevailing visibility in kilometers at 18:00 h.

Both HC and NO_x controls offer some potential amelioration of the effects of photochemical air pollution. However, for a given reduction in secondary pollutant concentration, HC control appears much more efficient than either NO_x control alone or a combination of both HC and NO_x control. Arguing solely on the basis of the generation of photochemically generated secondary pollutants, there does not seem to be any merit in NO_x control for the United Kingdom. NO_x control, however, may help alleviate other potential pollution problems due to urban NO_2 exposure and the long-range transport of acidic species, so that it should not necessarily be dismissed altogether.

It is readily apparent from Figures 4 and 5 that, even when HC and NO_x emissions are strictly controlled, significant oxidation of sulfur dioxide (SO_2) to sulfate aerosol with attendant visibility reduction is still predicted. The amount of sulfate aerosol produced depends on both the OH and SO_2 concentrations. When HC and NO_x emissions are both strictly controlled, the OH chemistry is controlled largely by the tropospheric background species, CH_4, CO, H_2, and O_3, and also by SO_2 itself. Under these conditions slightly more SO_2 oxidation is predicted than without HC or NO_x controls. Reduction of SO_2 emissions would however reduce sulfate aerosol formation directly.

It is difficult to extend the time scale of our calculations to ascertain the effect of HC and NO_x control strategies on the long-range transport of photochemical oxidants. Although we have studied the behaviour of UK air masses on subsequent days, we would require the corresponding emissions data for other European countries before a complete picture could be assembled. Our evidence is that the situation revealed in the urban model is not significantly different from that obtained from a study of multiday irradiations (*28*). The production of secondary pollutants is determined essentially by hydrocarbon oxidation.

Other evaluations of photochemical air pollution control strategies have focused attention on the relationship between precursor concentrations measured in urban areas to the secondary pollutants generated in downwind areas. To place the present evaluation in a similar context, the model precursor concentrations have been converted into central London mean values from a consideration of the observed geographical distribution of sulfur dioxide monitored throughout the survey region during June 1976 (*29*). This month was chosen because it contained the photochemical episode with the highest ozone concentrations, 250 ppb: yet recorded in the UK (*30*). Accordingly, the uncontrolled NO_x and nonmethane hydrocarbon concentrations appropriate to Figures 2–5 are estimated to be ~25 ppb and 300 ppbC in central London.

In the USA, HC emission control requirements were originally estimated by using an upper limit curve relating maximum oxidant concentrations to nonmethane hydrocarbon (NMHC) concentrations measured in the center of urban areas (*31*). In order to achieve the then desired oxidant air quality of 0.08 ppm maximum 1-h concentration, NMHC concentrations were to be reduced to 0.24 ppmC. The present modeling study would suggest that this NMHC concentration should be lower by a factor of 2 or so to keep ozone below 80 ppb in the London conurbation. Subsequently, the upper limit curve method has been replaced by the isopleths method (*32*). This method would indicate that about a 25% reduction in NMHC emissions would be required to keep ozone concentrations below 80 ppb, in quantitative accord with our conclusions in Figure 2.

In Sydney, Australia, the optimum oxidant control strategy has been shown to be control of NMHC emissions, whereas NO_x emission reductions applied in conjunction with substantial NMHC emission controls could have a detrimental effect on ozone concentrations (*33*). Our conclusions would support those from the Sydney Oxidant Study and would show furthermore that they would apply with equal force to other secondary pollutants. The observed isopleths in Sydney (*33*) are shifted somewhat toward higher precursor concentrations when compared with our model calculations; viz., ozone $= 0.39 \times (0.025 \times 0.3)^{0.36} = 0.067$ ppm, whereas the model gives 0.096 ppm. It may well be therefore that the differences between the regions preclude the quantitative transfer of control strategies between one region and another.

Such an argument must be invoked in comparing our results for London with those for New York. Cleveland and Graedel (*34*), using chemical kinetic modeling techniques, show that only small decreases in ozone, PAN, and sulfate aerosol result from HC control and that NO_x control would markedly reduce PAN and sulfate and increase ozone. Only the latter result, that NO_x control increases ozone, is confirmed by our study of the London region. The marked difference in the predicted success of HC control between the two studies is most striking. Unfortunately the models are not comparable since the New York model uses propylene to describe all reactive hydrocarbon species (*35*) and does not appear to treat dry deposition of ozone and PAN and the thermal decomposition of PAN. On the other hand, the London model employs only one box, whereas the New York model contains six boxes along the direction of an advecting wind. It is therefore not possible to judge whether the contrasting proposed control strategies reflect real differences in the emissions of the regions or differences stemming from our limited ability to model the respective regions.

In the paragraphs which follow, attention is directed further from the effect of blanket controls on precursor emissions to the effects of controls upon emissions from a single source category, vehicle exhaust emissions. These are given particular attention because they are already the subject of control regulations and not because of their contributions to total emissions. Indeed, vehicle exhausts are by no means the sole source of precursors in the London region (*13*).

Effect of Vehicle Exhaust Emission Controls on Photochemical Air Pollution Formation

The gaseous exhaust emission from motor vehicles in the United Kingdom are controlled through the construction and use regulations (*36*) which in turn refer to internationally agreed standards prescribed under United Nations Economic Commission for Europe (ECE) regulation 15 and the European Economic Community (EEC) directive 70/220/EEC. European vehicle gaseous emission standards have and are being progressively tightened. Although the main aim of the legislation has been to reduce the amounts of pollutants

Table II. Emission Factors for UK Vehicles

comment	emission factor, g km^{-1} CO	HC	NO_x	source
model estimates for 1974–1975	36	2.8	1.3	this work
Pre-1970 vehicles	56	3.6	1.1	(*37*)
ECE 15-00	39	2.5	—	(*38, 49*)

Table III. Percentage Reduction in Emissions Required by Present ECE Regulations

ECE regulation	percentage control relative to ECE 15-00 CO	HC	NO_x
15-00	0	0	0
15-01 and 15-02	20	15	−60
15-03	35	25	−40

Table IV. Percentage Reductions below ECE 15-00 Implied by Proposed ECE 15-04 Regulations

	percentage control relative to ECE 15-00				
	CO	HC Control		NO_x Control	
origin of ECE 15-04 proposal		HC	NO_x	HC	NO_x
West Germany[a]	73	96	−16	48	93
Switzerland (1982)[a]	76	96	25	72	93
East Germany[b]	37	73	−40	27	93
Italy[b]	39	26	−40	25	−38
Netherlands[b]	39	61	−40	25	50

[a] Reference *37*. [b] Reference *50*.

emitted, particularly in urban areas, the standards have not been based on a requirement to achieve specific ambient air quality for the protection of health. Largely, the standards have been designed so that as the vehicle population and mileage increase, total emissions remain roughly constant.

It is therefore apparent that the evaluation of health effects data and ambient air quality for carbon monoxide (CO), hydrocarbons (HC), and oxides of nitrogen (NO_x) has not played an important role in setting vehicle exhaust emission standards. Nevertheless it is of interest to understand the likely impact of vehicle legislation on ambient air quality. The present study describes one particular aspect of this complex problem.

The starting point for this evaluation of the effect of vehicle exhaust legislation on photochemical air pollution formation in the UK is the emissions from vehicles during 1974–75. Table II gives the emission factors for CO, HC, and NO_x used in the standard photochemical model. These are compared with an assessment of the emission factors for precontrol (pre-1970) UK vehicles taken from Larbey (*37*). In estimating these emissions, we have employed conversion factors of 4 km $test^{-1}$ and 1.5 g of NO_2 per g of NO. Table II also shows the emission standards for vehicles meeting the original ECE 15 type 1 (type approval) regulation using an average over the reference weight distribution. These regulations were to be met by all UK vehicles manufactured after November 1973 (*38*).

The main effect of the original ECE 15 regulation (ECE 15-00) was to reduce the emissions of CO and HC through limits on emissions at idle and from the crankcase. Table II shows that the model estimates are in good agreement with the type approval standards implied by ECE 15-00 particularly bearing in mind that the production conformity standards are higher by 20% for CO and 30% for HC.

In order to assess the effects of the subsequent ECE regulations, we have expressed each proposal relative to ECE 15-00 in Table III. In the case of NO_x, since ECE regulation 15-00 does not cover this pollutant, the model estimate is taken as the base figure. It is then readily apparent that developments made by motor manufacturers to meet the ECE 15-01 standards (EEC directive 74/290/EEC) (*36*) led to engines running at leaner air–fuel ratios than previously. Although this had the desired effect of reducing HC and CO emissions, there was a consequential increase in NO_x emissions which were not the subject of control (*37*). Our estimates point to there being an increase of ~60% in NO_x emissions as a direct result of ECE 15-01 (see Table III). These regulations were to be met by vehicles manufactured after April 1977 (*38*).

As far as vehicle exhaust emission standards are concerned, ECE regulation 15-02 (EEC directive 77/102/EEC) (*36*) is of little significance since it is merely a statement of existing emissions. The next set of regulations of significance are the ECE 15-03 amendments which are proposed for ECE and EEC adoption in 1979 and will be applied to vehicles manufactured after April 1981 (*38*). Table III shows that the ECE 15/03 regulations imply a limited amount of NO_x control which will be met by unsophisticated techniques without the use of catalyst technology.

The proposals for ECE 15-04 are more difficult to quantify since they contain not only reduction in emissions but also changes in the testing procedure and in the method of reporting emissions of HC and NO_x. The proposal to combine the HC and NO_x emissions into a single standard is of particular relevance in the present context, since these two pollutants have completely different effects on photochemical air pollution formation. Within the HC plus NO_x linking, therefore, two options represent the extremes of overall behavior, and these are the HC-control and NO_x-control options. In evaluating the proposals for ECE 15-04 in Table IV, we have included the effects of the changes in the test procedure and have calculated the standards for both HC-control and NO_x-control options. In all cases, it has been assumed that no deterioration of the individual HC or NO_x emissions below ECE 15-03 would be tolerated and that emissions could not be reduced by more than 95% below the ECE 15-03 values.

The photochemical model was rerun for each of the ECE regulations and proposals, while all other input data were unchanged excepting the vehicle exhaust emission factors. Among the many parameters kept constant were the exhaust hydrocarbon composition, fuel consumption, fuel quality, exhaust NO_x composition, UK vehicle mileage, and emissions from all other source categories. Since the ECE regulations up to ECE 15-03 and some of the milder ECE 15-04 proposals have been or could be met with existing technology, the assumptions of constant exhaust hydrocarbon composition (*39, 40*) fuel quality and exhaust NO_x composition are probably quite reasonable. However for the stringent ECE 15-04 proposals, particularly those involving strict NO_x control, there is no way of assessing changes in exhaust components or fuel composition that will result. Clearly if the data become available, these computer simulations could readily be made more realistic.

In modeling each of the scenarios of exhaust emission controls, we have assumed the same density of UK motor spirit, 0.7497 kg L^{-1} (*41*). The fuel consumption of an average UK vehicle in 1974–75 was estimated as follows: in 1974, 16.484×10^9 kg of motor spirit (*42*) were consumed by 12.7×10^6 motor vehicles, each covering an average of 14 300 km (*43*). On this basis, an average fuel consumption of 8.3 km L^{-1} is estimated for the UK as a whole. This estimate can be compared with published fuel consumption statistics for the 676 new vehicle models on sale in 1978 (*44*). The median fuel consumptions for the urban, 56-mph, and 75-mph tests are 8.5, 14.7, and 9.7 km L^{-1}, confirming that overall motor vehicle usage is well simulated by the urban test.

Table V shows the predicted concentrations of ozone, PAN, and sulfate aerosol together with the prevailing visibility in the London region at 18.00 calculated in the photochemical box model using the different vehicle exhaust emission factors.

Table V. Effect of Changing the Vehicle Exhaust Emission Factors on Photochemically Generated Pollutant Concentrations and Visibility at 18:00 h in the London Region[a]

	secondary pollutant concentration			
origin of exhaust emission factor	ozone, ppb	PAN, ppb	sulfate aerosol, $\mu g\ m^{-3}$	visual range, km
ECE 15-00	96	1.8	9.4	23
ECE 15-01 and ECE 15-02	65	0.8	6.6	29
ECE 15-03	68	0.8	7.1	28
ECE 15-04 Proposals				
HC control—West Germany	51	0.4	6.4	31
—Switzerland	65	0.7	8.3	26
—East Germany	52	0.4	6.1	31
—Italy	68	0.8	7.1	28
—Netherlands	56	0.5	6.4	30
NO_x control—West Germany	98	2.1	12.6	21
—Switzerland	93	1.8	12.7	20
—East Germany	103	2.2	12.6	21
—Italy	69	0.9	7.2	27
—Netherlands	102	2.1	11.5	21

[a]: 1 ppb sulfate aerosol = 3.9 $\mu g\ m^{-3}$.

The calculations show that some improvement in photochemical pollutant concentrations and visibility in the London region should result as the fraction of vehicles meeting ECE regulation 15-01 increases from 1977 onward. Several years will be required, however, before a substantial fraction of the UK vehicle fleet meets ECE 15-01. Over this time period, vehicle usage may well have expanded from the constant 1975 figures assumed here. Nevertheless, the improvement brought about by ECE 15-01 could be readily discernible by 1983, or thereabouts.

The effect of ECE 15-03 will be to increase, slightly, photochemical pollutant concentrations with an insignificant worsening in visibility. These effects result from the significant amount of NO_x control implied by ECE 15-03. In fact, the beneficial effects of ECE 15-01 are postulated to result largely from the increase in NO_x emissions caused by the leaner air–fuel ratios. ECE 15-03 attempts to reduce the NO_x emissions somewhat and thus sacrifices some of the advantage gained by ECE 15-01.

The various proposals for ECE 15-04 have widely differing effects on secondary pollutant concentrations and visibility. Those proposals which require stringent HC control (without significant NO_x control) can make remarkable reductions in ozone and PAN concentrations, reducing them much below present levels. Proposals which require both HC and NO_x control are not generally quite so effective as those involving HC control alone. However, the proposals which imply significant NO_x control are generally very much less effective at reducing ozone and PAN concentrations. In fact, the application of a combination of moderate HC and NO_x controls could lead to increases of ozone and PAN even above those produced when vehicles met ECE 15-00.

As far as visibility and sulfate aerosol concentrations are concerned, a slightly different picture emerges. The effect of ECE 15-01 and ECE 15-03 will be to produce substantial reductions in sulfate aerosol and improvements in visibility. The application of HC control would certainly continue this trend, whereas NO_x control would not. However the dramatic improvements potentially available for ozone and PAN would not apparently be evident with sulfate aerosol. Clearly, alternative measures on other sources such as fuel desulfurization or flue gas desulfurization would be required if substantial improvements in visibility should be called for.

Conclusions

(a) In principle, it is possible to evaluate the effects of various vehicle exhaust emission control strategies on photochemically generated secondary pollutants by using computer simulation techniques. The models have many underlying approximations which can be readily improved as more detailed information becomes available.

(b) HC and NOx emissions have quite different effects on the production of photochemical pollutants in the London region. Increasing HC emissions promote their formation, whereas increasing NO_x emissions inhibit their formation.

(c) The progressive "leaning" of UK vehicle operating conditions may have led to an increase in exhaust emissions of NO_x from ECE 15-00 to ECE 15-01. When the increased inhibition of photochemical pollution formation resulting from the increased NO_x emission is coupled with the inhibition resulting from the decreased HC emissions, a dramatic drop in ozone, PAN, and sulfate aerosol is predicted.

(d) The summation procedure adopted for HC plus NO_x in ECE 15-04 lumps together with different classes of species which have different effects on photochemical air pollution in the London region. Within this summation HC control offers more advantages than either NO_x control or a combination of both.

(e) These conclusions require investigation over a wider geographical context which would include the remainder of southeast England and the other countries of northwest Europe.

Acknowledgment

We thank Dr. A. Eggleton, A. Curtis (AERE, Harwell), Dr. A. Apling (Warren Spring Laboratory), and Dr. R. Larbey (Associated Octel) for useful discussions.

Literature Cited

(1) Guicherit, R.; van Dop, H. *Atmos. Environ.* **1977,** *11,* 145–55.
(2) Derwent, R. G.; McInnes, G.; Stewart, H. N. M.; Williams, M. L. Stevenage, UK, 1976, Warren Spring Laboratory Report LR 227(AP).
(3) Schjoldager, J.; Sivertsen, B.; Hanssen, J. E. *Atmos. Environ.* **1978,** *12,* 2461–8.
(4) Sandalls, F. J.; Penkett, S. A.; Jones, B. M. R. AERE Report-R 7807, H. M. Stationery Office, London, 1974.
(5) Niebohr, H.; van Ham, J. *Atmos. Environ.* **1976,** *10,* 115–20.
(6) Lovelock, J. E. *Atmos. Environ.* **1972,** *6,* 917–25.
(7) Cox, R. A.; Eggleton, A. E. J.; Derwent, R. G.; Lovelock, J. E.; Pack, D. H. *Nature (London)* **1975,** *225,* 118–21.
(8) Leighton, P. A. "Photochemistry of Air Pollution"; Academic Press: London, 1961.
(9) Demerjian, K. L.; Kerr, J. A.; Calvert, J. G. *Adv. Environ. Sci. Technol.* **1974,** *4,* 1–262.
(10) Hov, O.; Hesstvedt, E.; Isaksen, I. S. A. *Nature (London)* **1978,** *273,* 341–4.

(11) Garland, J. A.; Derwent, R. G. *Q. J. R. Meteorol. Soc.* **1979,** *105,* 169–83.
(12) Calvert, J. G. *Environ. Sci. Technol.* **1976,** *10,* 256–62.
(13) Derwent, R. G.; Hov, O. AERE Report-R 9434, H. M. Stationery Office, London, 1979.
(14) Smith, F. B.; Hunt, R. D. *Atmos. Environ.* **1978,** *12,* 461–78.
(15) Niki, H.; Maker, P. D.; Savage, C. M.; Breitenbach, L. P. *J. Phys. Chem.* **1978,** *82,* 135.
(16) Atkinson, R.; Darnall, K. R.; Lloyd, A. C.; Winer, A. M.; Pitts, J. N. *Adv. Photochem.* **1979,** *11,* 375.
(17) Cox, R. A.; Derwent, R. G.; Williams, M. R. *Environ. Sci. Technol.* **1980,** *14,* 57–61.
(18) Isaksen, I. S. A.; Midtbo, K.; Sunde, J.; Crutzen, P. J. Oslo, Norway, 1976, Institute for Geofysik, University of Oslo, Institute Report No. 20.
(19) Cox, R. A.; Roffey, M. J. *Environ. Sci. Technol.* **1977,** *11,* 900–6.
(20) McDonald, J. E. *J. Geophys. Res.* **1965,** *70,* 1553–4.
(21) Middleton, W. E. K. "Vision through the Atmosphere"; University of Toronto Press: Toronto, 1952.
(22) Garland, J. A. *Atmos. Environ.* **1969,** *3,* 347–54.
(23) Chance, E. M.; Curtis, A. R.; Jones, I. P.; Kirby, C. R. "FACSIMILE: A Computer Program for Flow and Chemistry Simulation, and General Initial Value Problems"; AERE Report-R 8775, H. M. Stationery Office, London, 1977.
(24) Penkett, S. A. *Environ. Pollut. Manage.* **1978,** Jan/Feb. 8–12.
(25) Penkett, S. A.; Sandalls, F. J.; Lovelock, J. E. *Atmos. Environ.* **1975,** *9,* 139–40.
(26) Salmon, L.; Atkins, D. H. F.; Fisher, E. M. R.; Healy, C.; Law, D. V. *Sci. Total Environ.* **1978,** *9,* 161–200.
(27) Atkins, D. H. F.; Cox, R. A.; Eggleton, A. E. J. *Nature (London)* **1972,** *235,* 372–6.
(28) Hov, O. WMO Symposium No. 538, 173–180, (1979).
(29) Department of Industry "The Investigation of Air Pollution. National Survey Smoke and Sulphur Dioxide, April 1976–March 1977"; H. M. Stationery Office, London, 1978.
(30) Apling. A. J.; Sullivan, E. J.; Williams, M. L.; Ball, D. J.; Bernard, R. E.; Derwent, R. G.; Eggleton, A. E. J.; Hampton, L.; Waller, R. E. *Nature (London)* **1977,** *269,* 569–73.
(31) "US HEW, Air Quality Criteria for Hydrocarbons"; US Department of Health Education and Welfare, Washington, D.C. 1970.
(32) Dimitriades, B. International Conference on Photochemical Oxidant Pollution and Its Control, Proceeding Volume II, 871-879 EPA-600/3-77-00-6 US Environmental Protection Agency Research Triangle Park, NC, 1977.
(33) Post, K. *Atmos. Environ.* **1979,** *13,* 783–90.
(34) Cleveland, W. S.; Graedel, T. E. *Science* **1979,** *204,* 1273–8.
(35) Graedel, T. E.; Farrow, L. A.; Weber, T. A. *Atmos. Environ.* **1976,** *10,* 1095–116.
(36) The Motor Vehicles (Construction and Use) Regulations 1978. Statutory Instruments, 1978, No. 1017, H. M. Stationery Office, London, 1978.
(37) Larbey, R. J. "Trends in the Control of Exhaust Emissions from European and American Vehicles"; The Associated Octel Co. Ltd.; London, 1979.
(38) Ellis, M. V. "Legislative Control of Motor Vehicle Emissions, Workshop on Pollution from Road Vehicles"; National Society for Clean Air: Brighton, 1979.
(39) Papa, L. J. "Measuring Exhaust Hydrocarbons Down to Parts per Billion, Vehicle Emissions Part III", (Selected SAE papers 1967/1970) Progress in Technology, Society of Automotive Engineers: New York, 1971; Vol. 14, pp 43–65.
(40) Guicherit, R.; Hoogeven, A. "Sources of Primary (Precursor) Pollutants. Photochemical Smog Formation in the Netherlands"; TNOs Gravenage: Netherlands, 1978.
(41) "Associated Octel, Octel Group Gasoline Survey—Europe and a Review of European Gasoline Quality 1977"; The Associated Octel Co. Ltd.: London, 1978.
(42) "Department of Energy, Energy Trends. A Statistical Bulletin. March 1977"; H. M. Stationery Office, London, 1977.
(43) Tanner, J. C. "Forecasts of Vehicles and Traffic in Great Britain: 1974 Revision"; Crowthorne, Berkshire, 1974, Transport and Road Research Laboratory Report 650.
(44) "Department of Energy, Official List of Results of Fuel Consumption Tests on Passenger Cars"; H. M. Stationery Office, London, 1978.
(45) Galbally, I. E. *Q. J. R. Meteorol. Soc.* **1971,** *97,* 18–29.
(46) Garland, J. A. *Proc. R. Soc. London, Ser. A* **1977,** *354,* 245–68.
(47) Bottger, A.; Ehhalt, D. H.; Gravenhorst, G. "Atmospharishhe kreislauf von Stickoxiden and ammoniak. Jul-1558 Kernforschungsanlage"; Julich GmbH, Julich, West Germany, 1978.
(48) Garland, J. A.; Penkett, S. A. *Atmos. Environ.* **1976,** *10,* 1127–31.
(49) Weaving, J. H. "The Technology of Controlling Exhaust Emissions. Workshop on Pollution from Road Vehicles"; National Society for Clean Air: Brighton, 1979.
(50) ECE 19th GRPA meeting, Sept. 1978, Economic Commission for Europe, Geneva, 1978.

Received for review March 3, 1980. Accepted July 14, 1980. This work was partly sponsored by the Royal Norwegian Research Council for Science and Technology through a NATO Science Fellowship and was performed as part of an air pollution research program funded by the UK Department of Environment.

Supplementary Material Available: *Table VI showing the inorganic chemistry, Table VII, the sulphur chemistry, Table VIII, the methane and PAN chemistry, Table IX, the rate coefficients for OH radical attack on the organic molecules, Table X, the photochemical processes occurring in the photochemical model, and Figures 6–18, illustrating the atmospheric degradation schemes used for the 36 volatile organic compounds and 120 organic intermediates (24 pages), will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper or microfiche (105 × 148 mm, 24× reduction, negatives) may be obtained from Business Operations, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Full bibliographic citation (journal, title of article, author) and prepayment, check or money order for $8.00 for photocopy (9.50 foreign) or $3.00 for microfiche ($4.00 foreign), are required.*

Sampling Effectiveness of the Inlet to the Dichotomous Sampler

James B. Wedding* and Michael Weigand
Aerosol Science Laboratory, Engineering Research Center, Colorado State University, Fort Collins, Colorado 80523
Walter John and Stephen Wall
Air and Industrial Hygiene Laboratory, California Department of Health Services,
2151 Berkeley Way, Berkeley, California 94704

■ The sampling effectiveness of the inlet to the dichotomous virtual impactor has been measured in a wind tunnel at speeds from 5 to 40 km/h by using monodisperse oleic acid particles of 5–30 μm aerodynamic diameter. A static test was performed at near-zero wind speed. Over this range of wind speeds the 50% cut point varied from 10 to 22 μm, with a maximum near 2.5 km/h. At a given wind speed the cutoff curve (effectiveness vs. particle diameter) is not sharp. Flow visualization studies revealed strong channeling of the flow inside the inlet. A simple theoretical model based on this flow pattern including inertial and gravitational forces on the particles accounts well for the observations. It is concluded that a better inlet is required for the dichotomous sampler. The present experience indicates the need for rigorous experimental validation of new inlet designs.

Background

The inlet is a vital component of a sampler; unfortunately, this aspect of sampler design has not received adequate attention. Furthermore, few samplers are equipped with inlets which have been rigorously tested. The Hi-volume sampler (*1*) is typical of many samplers in that the inlet determines the upper particle size cutoff. The accuracy of measurements of suspended particulate with the standard Hi-Vol can be questioned because of the large variation in sampling effectiveness as a function of wind speed and direction as shown by Wedding (*2, 3*).

Several investigators have studied the particle and fluid mechanics related to the sampler inlet problem. Davies (*4, 5*) investigated sampling biases of various sized tubes as a function of particle size, sampling rate, and wind velocity. Agarwal (*6*) performed a theoretical study of a cylindrical tube. May (*5*) looked at a variety of samplers in a field study using a portable wind tunnel. Errors in sampling at nonisokinetic conditions as well as probe design limitations were studied by the researchers in ref *7–14*. Steen and co-workers (*15–17*) characterized those samplers used in Europe to collect aerosols. These results confirmed that it is difficult to design an inlet that has an efficiency independent of sampling conditions.

The present study involved the determination of the variation with wind speed of the sampling effectiveness (transmission efficiency) of the inlet of the commercially available Sierra 244E dichotomous sampler (Figure 1a). This type of dichotomous virtual impactor has been developed by Loo et al. (*18, 19*) in support of programs of the U.S. Environmental Protection Agency. The dichotomous samplers are being deployed in a trial network by the EPA as part of a project directed toward the establishment of an inhalable particle standard based on a particle size cutoff at 15 μm (*20*). Since the cutoff is determined by the inlet, it was important to assess the effect of wind speed on the cutoff. It was unnecessary to study the effect of wind direction because of the cylindrical symmetry of the inlet. Studies were carried out in a wind tunnel. The results motivated additional testing near zero wind speed. A theoretical model was then developed to explain the observations.

Experimental Section

Wind Tunnel Tests. The Sierra Model 244E ambient aerosol sampling inlet was tested in the closed-loop Aerosol Science Laboratory Wind Tunnel at Colorado State University (shown schematically in Figure 2). The tunnel has cross-sectional dimensions of 1.22 m square at the test section. The longitudinal component of turbulence intensity at the test location was found by hot wire anemometer measurements to be 4%. The tests utilized monodisperse aerosols with nominal aerodynamic diameters of 5–30 μm generated by a vibrating orifice atomizer operating in an inverted manner. Aerosol from the atomizer was injected through a 15.24-cm diameter pipe containing a Kr-85 charge neutralizer. The pipe diverged into the annular region between two cones. Six pipes spaced around the annular region led the aerosol into the tunnel. This injection system produced a particle concentration profile across the test section which was found to be independent of wind speed. Variation of the concentration across the width of the inlet was less than 10%.

The sampling inlet was tested at wind speeds of 5, 15, and 40 km/h, as measured upstream of the test section with a calibrated hot wire anemometer (Andersen air velocity meter). To determine the inlet effectiveness, the aerosol concentration was measured before and after each test by using a sampling manifold 0.90 m wide with six isokinetic sampling nozzles spaced at equal intervals (~15 cm) in the same horizontal plane as the inlet opening. Each nozzle led to a 47-mm Gelman AE glass fiber filter. The dichotomous sampler inlet was mounted on a vertical tube ~1 m long sealed to a Milipore filter holder on the bottom. The sampling effectiveness of the inlet was determined by comparing the quantity of aerosol passed by the inlet and deposited on the filter to that collected by the isokinetic sampling system with appropriate corrections for differences in sampling volume and pressure drops as monitored in the lines. Particles utilized in the study were made from an oleic acid–ethanol mixture tagged with uranine. Collection substrates were washed in 50 mL of pure ethanol and then diluted 1:1 with distilled deionized water. A 4-mL aliquot of each sample solution was measured for uranine content with a fluorometer (Turner Model 111).

Other commercial models of the inlet differ in design slightly from the Sierra 244E (see Figure 1a). The Sierra 244 inlet has no holes in the center pipe but instead ends ~1 cm from the top. The Beckman inlet (Figure 1b) in contrast to the Sierra inlets has rain grooves in the bottom cone and minor differences in pipe dimensions. A check of several examples of each inlet showed that in each case the dimensions agreed closely with manufacturer's specifications.

Static Tests. In order to completely characterize the inlet, it is necessary to determine the sampling effectiveness at near-zero wind speed where impaction is absent and sedimentation is the only particle deposition mechanism. The arrangement used for the static measurements is shown in Figure 3. This work was carrried out at the Air and Industrial

0013-936X/80/0914-1367$01.00/0 © 1980 American Chemical Society

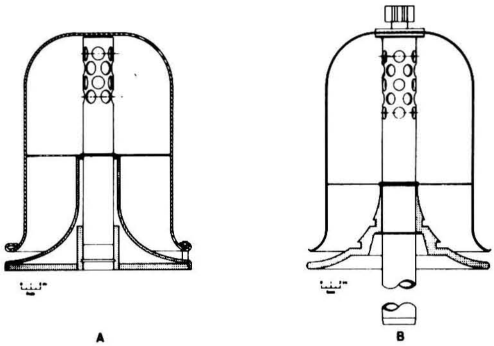


Figure 1. Inlets for the dichotomous virtual impactor: (a) Sierra Model 244E, (b) Beckman automated dichotomous particulate sampling system.

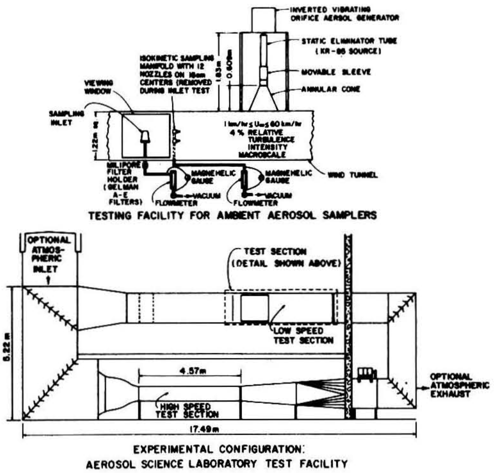


Figure 2. Schematic drawing of the wind tunnel test facility.

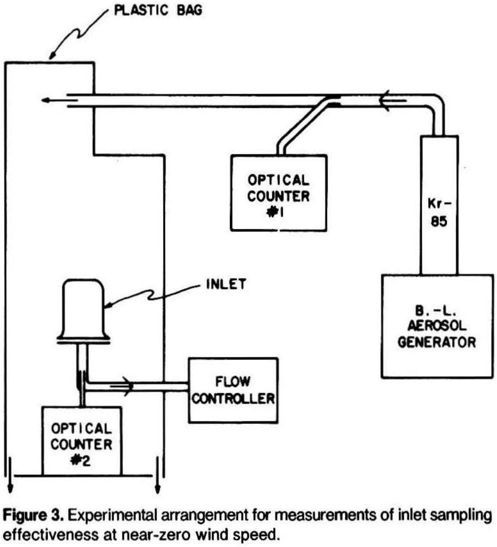


Figure 3. Experimental arrangement for measurements of inlet sampling effectiveness at near-zero wind speed.

Hygiene Laboratory in Berkeley. Monodisperse particles of oleic acid containing 1% uranine by volume were produced by a vibrating orifice aerosol generator (Berglund-Liu) and passed through a Kr-85 charge neutralizer. Optical particle counter No. 1 (Climet Model 201) continuously monitored the size and concentration of the particles. The aerosol entered the top of a plastic bag, flowed downward at an average velocity approximately $1/10$ of the flow velocity into the inlet, and exited at the bottom. Anemometer measurements showed a fairly uniform downward flow of less than 1 cm/s with occasional gusts up to several times the average velocity.

The inlet was pumped by an electronically stabilized flow controller with 5.7 L/min of the flow split isokinetically into optical counter No. 2 (Climet Model 208). The total flow was the standard 16.7 L/min sampling rate of the inlet. The particle counting rate in optical counter No. 2 was first determined by sampling for 1 min with the inlet removed from the sampling tube. Under these conditions, the sampling criteria of Davies (*21*) which consider the effects of impaction and sedimentation are satisfied. Then the inlet was replaced, and, after a delay of 1 min to allow the flow to stabilize, another 1-min count was taken. The sampling effectiveness was calculated from the ratio of inlet off to inlet on counts. The error was less than 1–2% from counting statistics. The optical counter data were taken only from the main particle peak in a multichannel analyzer so that multiplets from particle coagulation, etc., were automatically excluded. For each particle size the inlet was cycled through several on and off counts to obtain averages.

As a reference method, aerosol from the inlet pipe was collected directly onto a Teflon membrane filter. The uranine was then extracted from the filter by sonication in alcohol–water (90%/10%) and quantitation on a fluorometer (Aminco Model J4-7439). Successive 20-min filter samples were taken with the inlet on and off the pipe.

Flow Visualization. Understanding of the data on the sampling effectiveness is aided by knowledge of the airflow pattern within the inlet. To this end, the metal top of the inlet was replaced with one of transparent Lucite and smoke introduced to make the airflow visible. A fog of glycerol particles from an ultrasonic nebulizer was also used. Because the airflow was extremely sensitive to ambient air currents, consistent results were obtained only when the aerosol was injected at a speed exceeding ~20 cm/s (0.7 km/h).

Theory of the Sampling Effectiveness

At zero wind speed the airflow is directed toward the axis of the inlet because of the cylindrical symmetry (refer to Figure 1a). For any appreciable (~1 km/h or greater) wind speed, the flow entered the inlet channels, following the vertical radius closely, as observed in the visualization tests. The horizontal width of the air parcel sampled is small compared to the inlet diameter as air enters virtually along the stagnation point streamline. The width can be calculated from the known volumetric flow rate (16.7 L/min), the 1-cm height of the inlet slit, and the assumed wind speed. The air not sampled simply flows around the inlet, entering and exiting the inlet slit.

The above considerations lead to a simplified model of the sampling effectiveness. As illustrated in Figure 4, air enters the slit and flows in a channel of constant width along the vertical arc of the lower surface of the inlet. A particle traveling in the flow will drift outward along the radius under the influence of centrifugal and gravitational forces. The sum of these forces may be equated to the Stokes drag force

$$\left(\frac{3\pi D\mu}{C}\right)\frac{\mathrm{d}r}{\mathrm{d}t} = \frac{mv^2}{R} + mg\cos\theta \qquad (1)$$

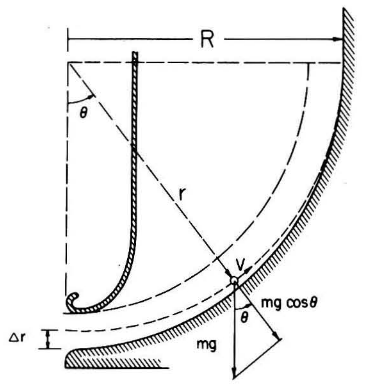


Figure 4. Vertical cross section of inlet showing particle trajectory for theoretical calculation of the sampling effectiveness.

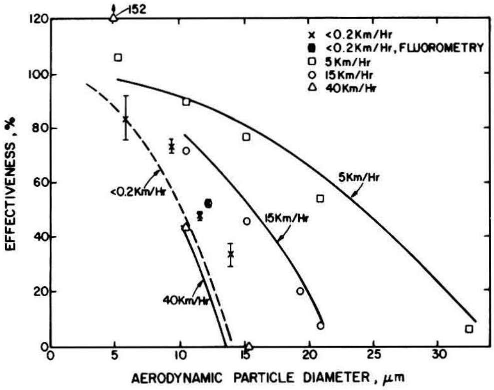


Figure 6. Sampling effectiveness data for Sierra 244E inlet including that for near-zero wind speed (crosses). The lines are from the theory presented in the text. The zero wind speed line is dashed for clarity.

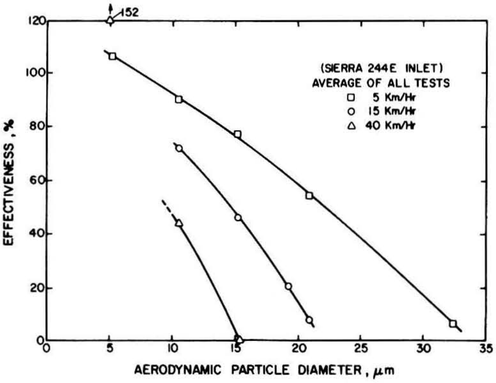


Figure 5. Sampling effectiveness of the Sierra Model 244E inlet vs. particle diameter for three wind speeds. The lines are arbitrary fits.

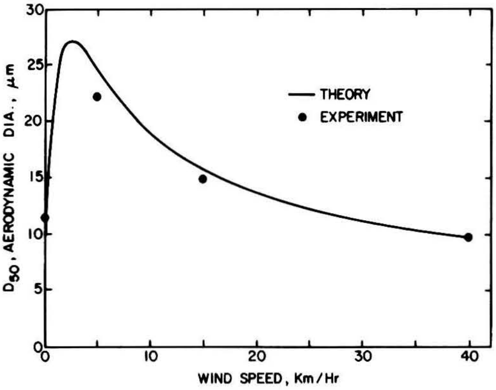


Figure 7. Plot of the 50% cut point of the inlet vs. wind speed.

with D and m the diameter and mass of the particle, respectively, μ the coefficient of viscosity, C the Cunningham slip correction factor, R the radius of the arc, and r and θ the coordinates shown in Figure 4.

The velocity v is the sum of the sampling velocity and the ambient wind velocity; v is taken to be constant along the arc as a first approximation. Then neglecting the small change in radius

$$v = R\,\mathrm{d}\theta/\mathrm{d}t \tag{2}$$

The limiting trajectory, shown as the dashed line in Figure 4, is described by a particle starting at Δr above the bottom of the slit and just touching the wall at $\theta = \pi/2$. Taking a spherical particle of density ρ, we obtain

$$\Delta r = \frac{\rho D^2 CR}{18\mu v}\int_0^{\pi/2}\left(\frac{v^2}{R} + g\cos\theta\right)\mathrm{d}\theta = \frac{\rho D^2 C}{36\mu v}(\pi v^2 + 2Rg) \tag{3}$$

Finally, the effectiveness η can be calculated from Δr and the height, h, of the slit

$$\eta = 1 - \Delta r/h \tag{4}$$

Also, the aerodynamic diameter D_{50} giving $\eta = 50\%$ is

$$D_{50} = 6\left(\frac{\mu v h}{2(\pi v^2 + 2Rg)}\right)^{1/2} \tag{5}$$

Results and Discussion

Results from the wind tunnel tests on the sampling effectiveness of the Sierra 244E are shown in Figure 5. It is evident that the inlet performance is strongly affected by wind velocity. The 50% effectiveness point (D_{50}) varies substantially as a function of wind speed. Results also indicate some enrichment occurring at the higher wind speeds and smaller particle sizes.

The experimental sampling effectiveness for all tests as well as those calculated from eq 4 are shown vs. particle size in Figure 6. The theory adequately reproduces the trends of the experimental data. At any given wind speed, the cutoff is not sharp, particularly for particles smaller than D_{50}. D_{50} at zero wind speed was found to be 11.4 μm. The data point determined by fluorometry (static test) agreed well with the optical particle counter results (the latter requiring an order of magnitude less analysis time).

During the static tests, sampling effectiveness was found to be quite sensitive to subtle wind currents. Whereas for the near quiescent conditions 12-μm particles produced an effectiveness of 45%, a small fan inserted in the top of the bag (see Figure 3), producing a barely detectable increase in vertical wind speed at the inlet, caused an increase in effectiveness to 61%. When the fan speed was increased to produce a vertical air velocity about equal to the inlet intake velocity, the effectiveness increased to 90%.

The D_{50} values calculated from eq 5 are graphed as the solid line in Figure 7 with the solid dots representing the experimental data. The agreement with the data is quite good, considering that the model has no adjustable parameters. The trend can be understood qualitatively as follows: At very low wind speed particle deposition is by sedimentation alone (results from the static tests revealed 90% of the mass was deposited on the lower curved surface of the inlet). As the speed increases, the residence time decreases and consequently D_{50} increases. At higher wind speed impaction becomes important, resulting in decreasing D_{50} with increasing wind speed. The two opposite dependencies on wind speed cross over, producing a maximum in D_{50} near 2.5 km/h.

Measurements on the Beckman inlet in the wind tunnel at 5 km/h showed that the effectiveness vs. particle diameter was similar to that of the Sierra 244E with the curve shifted slightly to smaller size, the 50% point occurring at 20 μm rather than 22 μm.

Conclusions

Wind tunnel and static tests reveal that the D_{50} for the Sierra 244E inlet varies by more than a factor of 2 in the range of wind speeds from 0 to 40 km/h, with a maximum at ~2.5 km/h. Flow visualization studies showed that the flow inside the inlet channels strongly. A simple model based on the observed flow pattern including inertial and gravitational forces fits the data well. The model predicts a maximum in D_{50} at low wind speed due to the oppositely varying effects of sedimentation and impaction with flow velocity.

At a given wind speed, the cutoff curve (effectiveness vs. particle diameter) is not sharp; in fact, it does not satisfy the criteria recommended by a recent EPA workshop group (*22*). When the excessive variation with wind speed is also taken into account, it is concluded that an improved inlet design is required particularly over the range 0–5 km/h. The present work has already stimulated several workers, including the authors, to develop improved inlets for the dichotomous sampler.

The present experience can be generalized to conclude that all inlet designs should be subjected to complete rigorous wind tunnel tests under standardized procedures. The tests should include measurement of the sampling effectiveness at near-zero wind speed. Flow visualization is also useful in analyzing the inlet behavior.

Acknowledgment

We thank J. J. Wesolowski for his interest and support, and Neil Jacquay and Glen Sasaki for their assistance in the laboratory.

Literature Cited

(1) Silverman, L.; Viles, F. J. *J. Ind. Hyg. Toxicol.* **1948,** *30,* 124–32.

(2) Wedding, J. B.; McFarland, A. R.; Cermak, J. E. *Environ. Sci. Technol.* **1977,** *11,* 387–90.

(3) Wedding, J. B.; Carney, T. C.; Stevens, R. K. *Int. J. Environ.* **1979,** *3,* 3–11.

(4) Davies, C. N. *Staub* **1968,** *28,* 1–9.

(5) Davies, C. N. *Br. J. Appl. Phys.* **1968,** *2,* 921–7.

(6) Agarwal, J. K. Minneapolis, MN, May 1975, Particle Technology Laboratory, The University of Minnesota, Publication No. 265.

(7) Raynor, G. S. *Am. Ind. Hyg. Assoc. J.* **1970,** *31,*294–302.

(8) May, K. R.; Pomeroy, N. P.; Hibbs, S. *J. Aerosol Sci.* **1976,** *7,* 53–61.

(9) Watson, H. H. *Am. Ind. Hyg. Assoc. J.* **1954,** *15,* 21–5.

(10) Vitols, V. *J. Air Pollut. Control Assoc.* **1966,** *16,* 79–84.

(11) Sehmel, G. A. *Am. Ind. Hyg. Assoc. J.* **1970,** *31,* 758–63.

(12) Selden, M. G. *Am. Ind. Hyg. Assoc. J.* **1975,** *36,* 549–56.

(13) Parker, G. J. *Atmos. Environ.* **1968,** *2,* 477–90.

(14) Breslin, J. A.; Stein, R. L. *Am. Ind Hyg. Assoc. J.* **1975,** *36,* 576–81.

(15) Steen, B. Ph.D. Thesis, Chalmers Institute of Technology, Goteborg, Sweden, 1975.

(16) Steen, B.; Johansson, B. "The Sampling Efficiency of Two Types of Inlets Commonly Used for the Sampling of Aerosols in Ambient Air"; Swedish Water and Air Pollution Research Labs, B 230, Goteborg, Sweden, 1975.

(17) Steen, G.; Andreasson, K. "Comparative Measurements of Particle Concentrations in Ambient Air Made at Background Station with Different Types of 'Hi-Volume' Samplers"; Swedish Water and Air Pollution Labs, B 190, Goteborg, Sweden, 1974.

(18) Loo, B. W.; Jaklevic, J. M.; Goulding, F. S. In "Fine Particles: Aerosol Generation, Measurement, Sampling and Analysis"; Liu, B. Y. H., Ed.; Academic Press: New York, 1976; 311–50.

(19) Loo, B. W.; Adachi, R. S.; Cork, C. P.; Goulding, F. S.; Jaklevic, J. M.; Landis, D. A.; Searles, W. L. Berkeley, CA, 1979, Lawrence Berkeley Laboratory, LBL-8725.

(20) Miller, F. J.; Gardner, D. E.; Graham, J. A.; Lee, R. E., Jr.; Wilson, W. E.; Bachman, J. D. *J. Air Pollut. Control Assoc.* **1979,** *29,* 610–5.

(21) Davies, C. N. *Staub-Reinhalt. Luft* **1968,** *28,* 1–7.

(22) "Sampling Techniques for Inhalable Particulate Matter," SORI-ESA-79-031, Southern Research Institute, Birmingham, AL, Jan 16, 1979, prepared for the U.S. Environmental Protection Agency, Industrial Environmental Research Laboratory, Research Triangle Park, NC.

Received for review March 3, 1980. Accepted July 8, 1980. This research was sponsored by the U.S. Environmental Protection Agency.

Volatile Halocarbon Production from the Chlorination of Marine Algal Byproducts, Including D-Mannitol

Allan M. Crane*[1]

U.S. Environmental Protection Agency, Bears Bluff Field Station, Gulf Breeze Environmental Research Laboratory, Wadmalaw Island, South Carolina 29487

Peter Kovacic

Department of Chemistry, University of Wisconsin, Milwaukee, Wisconsin 53201

Eric D. Kovacic

Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138

■ The ability of various exudates of marine algae to produce chloroform during solution chlorination was investigated. D-Mannitol generated amounts that increased markedly with increase in pH, whereas glycerol under similar conditions yielded little product. L-Proline exerted an inhibiting effect. The mechanism of the D-mannitol reaction is believed to proceed via formation of a ketolactone which undergoes ring opening by chloride, followed by the classical haloform process.

The generation of volatile halocarbons during chlorination of aqueous environments has been demonstrated for both fresh (*1–3*) and marine waters (*4–6*). Investigations into the chemical nature of the precursors responsible for their generation have disclosed that in addition to the natural humic substances initially proposed by Rook (*7*) and later studied by Stevens et al. (*8*), various other organic compounds may also function as haloform precursors (*9*).

In a previous study (*6*), chlorination of estuarine water containing cultured marine algae revealed that the resulting concentrations of volatile halocarbons were dependent upon the species of algae. For example, in the presence of 10^6 cells/mL of *Isochrysis galbana* (Chrysophyceae), chlorination increased the concentration of volatile halocarbons normally generated in estuarine water by 41%. The presence of *Thalassiosira pseudonana* (Bacillariophyceae) resulted in a 24% decrease, whereas populations of *Carteria* spp. (Chlorophyceae) did not produce a statistically significant difference in the concentration of volatile halocarbons. Further, chlorination of the same estuarine water after removal of algal populations by filtration resulted in volatile halocarbon concentrations similar to those produced when algal cells were present, suggesting that the production of these compounds may be attributed to chlorination of specific metabolic byproducts of the algal species.

Hellebust (*10*) reported that glycerol, mannitol, and proline were excreted singularly or in various combinations by 81% of the marine algal species examined and generally comprised between 50 and 90% of the total identified exudate. Therefore, these three compounds were selected as models for the following study of the chlorination of algal byproducts.

Experimental Section

Chlorination of each model compound was performed in triplicate with molar ratios of compound to chlorine of 1:3, 1:1, and 3:1. Stock solutions (0.1 M) of glycerol, D-mannitol, and L-proline were prepared from "Fisher Certified" grade reagents (Fisher Scientific Co) and carbon-filtered, deionized water (Continental Water Conditioning). Individual aliquots of stock were pipetted into two sets of 12 100-mL glass volumetric flasks. Solutions in two flasks were buffered at pH 7 with a phosphate buffer while the remaining flasks were treated with appropriate volumes of 0.1 M NaOH to furnish the desired concentration of added hydroxide ion. All were then diluted and chlorinated with aqueous NaOCl (Fisher Scientific Co) to give final concentration ratios of model compound to chlorine (Cl^+) of 0.003:0.009, 0.003:0.003, and 0.009:0.003 with added OH^- concentrations of 0.0 (pH 7), 0.003 (pH 10.8), 0.006 (pH 11.2), and 0.009 M (pH 11.4) at each ratio. Both sets of flasks were stoppered with Teflon-lined screw caps and left under overhead fluorescent lighting (2500 lm/m^2) at 20 °C. Aliquots (2 mL) were taken from each flask of one set at 10, 30, 60, and 180 min, then randomly thereafter for 24 h and added to a beaker containing 1 mL of acetate buffer (pH 4) and 2 mL of freshly prepared 20% KI solution (Fisher Scientific Co). The mixture was diluted to 200 mL with carbon-filtered deionized water and amperometrically analyzed for total residual oxidant as given in Standard Methods (*11*). Residual oxidant determinations were performed with a Wallace and Tiernan amperometric titrator. Phenylarsine oxide titrant (0.0056 N) was obtained from Wallace and Tiernan Co.

After 24 h, residual chlorine oxidants in the remaining set of flasks were quenched by adding 5% $Na_2S_2O_3{\cdot}5H_2O$ (1 mL) (Baker Analyzed Reagent). Contents of the flasks were immediately extracted with 2 mL of pesticide grade pentane (Burdick and Jackson Laboratories, Inc). A 1.0-μL aliquot of the organic layer was then removed with a microliter syringe for gas-chromatographic analysis of total volatile halocarbons. Gas chromatograms were obtained with a Hewlett-Packard Model 5710A gas chromatograph with a ^{63}Ni electron capture detector. A 1.8 m × 2 mm i.d. glass column packed with 12% OV-101 on Anakrom Q 101/120 mesh (Analabs, Inc) was used. Injection port and detector temperatures were 100 °C. The column was maintained at 55 °C, and 95:5 argon/methane used as the carrier gas (40 mL/min). Identification of the major chromatographic peaks was made by employing the admixture technique to extracted samples. Quantification was accomplished by direct comparison of sample peak areas to those of authentic standards in pentane.

Results and Discussion

In the absence of added hydroxide ion (pH 7.0), only L-proline demonstrated a chlorine demand significantly different (Student's *t* test, $\alpha = 0.05$) from the deionized water blank (Table I). While volatile halocarbons were not detected from the reaction, molar ratios of L-proline to Cl^+ of 3:1 caused rapid reduction of oxidative Cl^+ from the nominal 110 mg/L to 6 mg/L in 10 min and to a nondetectable residual (<0.01 mg/L) after 180 min. Introducing hydroxide ion to aqueous solutions of L-proline had no effect on the inability of this compound to generate haloforms during chlorination. Even with a nominal excess of Cl^+ of 3:1, chlorine residuals were

---

[1] Present address: Alumax of South Carolina, Technical/Emission Control Department, P.O. Box 1000, Goose Creek, SC 29445.

Table I. Average ($N = 3$) Residual Chlorine Concentration (in mg/L) with Time in the Absence of Hydroxide Ion (pH 7) from Model Compound Solutions (0.009 M) Chlorinated with NaOCl to a Nominal 110 mg Cl$^+$/L (0.003 M)

sample	0 min	10 min	60 min	180 min	1440 min
blank H_2O	110	110	112	108	100
glycerol	110	108	108	107	101
D-mannitol	110	108	108	106	100
L-proline	110	6	1	<0.01	<0.01

Table II. Average ($N = 3$) Total Volatile Halocarbons (in μg/L) Produced in the Absence of Hydroxide Ion (pH 7.0) from Model Compound Solutions Chlorinated with NaOCl

sample	0.003 M sample + 0.009 M Cl$^+$	0.003 M sample + 0.003 M Cl$^+$	0.009 M sample + 0.003 M Cl$^+$
blank H_2O	5 ± 2	3 ± 2	3 ± 2
glycerol	4 ± 3	4 ± 2	8 ± 3
D-mannitol	7 ± 4	10 ± 4	6 ± 3
L-proline	2 ± 1	<1	<1

completely reduced after 24-h contact with L-proline without concurrent production of volatile halocarbons.

Because of its greater reactivity leading to N-chlorination (*12*), proline can, in addition, apparently inhibit the generation of volatile halocarbons during the chlorination of natural waters. Our estuarine water, which normally produces an average of 187 μg/L of bromoform and chlorodibromomethane when chlorinated, generated only 85 μg/L after addition of 0.003 M L-proline. Although we were unable to identify any proline/chlorine reaction products, Smith (*13*) demonstrated, using high-performance liquid chromatography, that the addition of up to a 3:1 molar excess of NaOCl to solutions of proline in seawater from Biscayne Bay, FL, produced an unknown product which he proposed was possibly 2-bromopyrrolidine.

At all three molar ratios of model compound to chlorine employed, the volatile halocarbon concentrations produced during the chlorination of glycerol and D-mannitol solutions buffered to pH 7 were not statistically different (Student's *t* test, $\alpha = 0.05$) from the carbon-filtered deionized water blank (Table II). However, with the addition of hydroxide ion, D-mannitol exhibited a discernible increase in reactivity. Regression analysis showed highly significant linear correlations ($P < 0.001$; 95% confidence level) between increasing nominal hydroxide ion concentrations and the concurrent increases in both chlorine demand (Figure 1) and production of volatile halocarbons (Figure 2). Total halocarbon comprised mainly chloroform with lesser amounts (16–61 μg/L) of one unidentified product and traces (<0.1 μg/L) of a third unidentified compound. Greatest haloform production was observed when D-mannitol was in excess. At the D-mannitol/chlorine ratio of 3:1, the yield of total volatile halocarbons was 557 μg/L following chlorination in the presence of 0.009 M hydroxide ion. This represents an increase of 450% from the mannitol/chlorine ratio of 1:3 in the presence of 0.009 M hydroxide ion. In addition, glycerol exhibited no significant (Student's *t* test, $\alpha = 0.05$) change in halocarbon yield as pH increased (Figure 3). These results correlate nicely with the fact that the presence of *Isochrysis galbana*, whose principal exudate is D-mannitol (*10*), increases the chloroform concentration in surrounding waters during chlorination, whereas *Thalassiosira pseudonana* and *Carteria*, which secrete mainly proline and glycerol (*10*), respectively, have a negative or little effect.

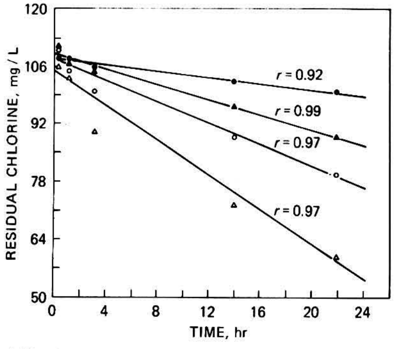


Figure 1. Total residual chlorine as a function of time for solutions of D-mannitol (0.009 M) containing nominal 0.0 (●), 0.003 (▲), 0.006 (○), and 0.009 M (△) OH^- as NaOH. Solutions were chlorinated with aqueous NaOCl to a nominal 0.003 M Cl$^+$ at time zero.

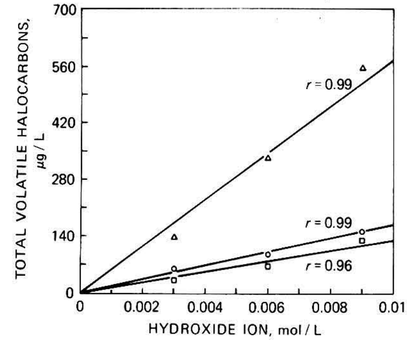


Figure 2. Total volatile halocarbon production as a function of nominal hydroxide ion concentrations as NaOH added to solutions of D-mannitol/Cl of 0.003:0.009 (□), 0.003:0.003 (○), and 0.009:0.003 (△).

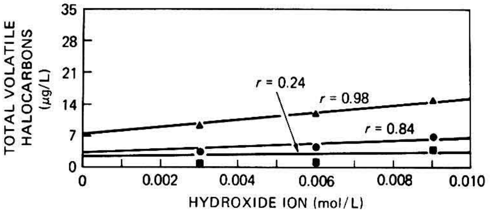


Figure 3. Total volatile halocarbon production as a function of nominal hydroxide ion concentrations as NaOH added to solutions of glycerol/Cl$^+$ of 0.003:0.009 (■), 0.003:0.003 (●), and 0.009:0.003 (▲).

Polysaccharides have been identified as widespread components of natural waters (14–20), but they do not make up the principal category of the organic matter. Fulvic acids represent the bulk of the carbon-containing material (*20, 21*). From a previous study involving certain members of the series, the conclusion was drawn that sugars, in general, do not appear to be significant precursors of chloroform, nor do they contribute to chlorine uptake (*9*). In view of the present results, it appears that in terms of potential for haloform production there is specificity in relation to the type of sugar and the reaction conditions, especially pH.

We present here a mechanistic sequence that serves to rationalize the chloroform product from mannitol, as well as other aspects of our experimental data. The haloform reaction provides a unifying theme, together with other transformations which are reasonably expected to occur under the conditions employed. The structural prerequisite of the haloform reaction is a ketone capable of trihalogenation at the α-carbon, a situation absent from the constitution of all common sugars, including D-mannitol.

The presence of hypohalite, however, readily produces oxidative derivatives of carbohydrates, as appreciable previous work has shown. For example, common oxidation products of polyols in the presence of NaOBr or NaOCl are hydroxyketones and hydroxyketo acids, some of which may exhibit carbon chain shortening via loss of carbon dioxide (*22a–c, 24a,b,e*). (Enzymatic oxidation can also take place in natural waters (*22d*).) By analogy, D-mannitol might reasonably be expected to undergo the oxidative degradation depicted (Scheme I). Because of its structure, however, the oxidation product is incapable of trihalogenation at the α-carbon, owing to the hydroxyl substituent's extremely poor leaving capabilities in nucleophilic reactions. It is, therefore, unlikely that haloform production can occur directly from these hydroxyketone intermediates.

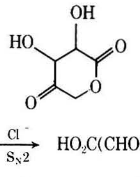
Scheme I

$$\mathrm{HOCH_2(CHOH)_4CH_2OH} \xrightarrow{\mathrm{NaOCl}} \mathrm{HO_2C(CHOH)_2COCHOHCO_2H} \xrightarrow{-\mathrm{CO_2}} \mathrm{HO_2C(CHOH)_2COCH_2OH}$$

Further reactions common to these systems provide a possible key to the production of volatile halocarbons. Since characteristic behavior of oxidized sugars in aqueous solution is lactonization to form 5- or 6-membered rings (*22e*), a structure (Scheme II) in which the methylene α to the ketone is attached to the carboxylate functionality could easily arise, providing a far better leaving group than hydroxyl in S_N2 displacements. We propose that chloride ion (small concentrations of which are generated in chlorinated waters from HCl arising in the oxidation process or from salt normally present in natural water) acts as a nucleophile upon the ketolactone to produce α-chlorinated keto acids, analogous to attack of lactone by cyanide (*23a*).

Scheme II

$\mathrm{HO_2C(CHOH)_2COCH_2OH} \xrightarrow{-\mathrm{H_2O}}$



$\xrightarrow[S_N2]{\mathrm{Cl^-}} \mathrm{HO_2C(CHOH)_2COCH_2Cl}$

Chlorinations of carbohydrates have, in fact, been carried out via S_N2 displacements by chloride on tosylate, phosphate, and nitrate esters (*24f*). In ordinary aliphatic systems, chloride displacement of the nitrate group has an activation energy of 27.5 kcal/mol, whereas the corresponding reaction of carboxylate (≈*F*) requires ~29 kcal/mol (*25, 26a*). This represents a 16-fold decrease in rate of displacement. The ketone α to the methylene, however, lowers the activation energy of the process by at least 6 kcal/mol, and more probably by 7 or 8 kcal/mol. This has been demonstrated in experiments in which S_N2 displacement rates of chloride from chloropropanone and 1-chloropropane were compared (*26b*). Since the present system entails carboxylate displacement by chloride, whereas the system referenced (*26b*) comprises chloride replacement by iodide, the ketone probably enhances the rate here by 1 or 2 kcal/mol more than it does in the cited experiment. This is because the transition state of S_N2 displacement receives greater stabilization from the carbonyl when the nucleophile and leaving groups are poorer, as they are in our system. (Identical *A* values are assumed for the rate calculations.) The presence of the keto moiety allows the transformation to proceed at a minimum of 2100 times (possibly as much as 160 000 times!) the rate of chlorinations of nitrated sugars. Furthermore, steric hindrance to attack is less in the lactonic system than in the open-chain analogue, a situation which should further increase the rate. Theoretically, both γ- and δ-lactones could be involved in this process, although the appropriate γ derivatives are opened with considerably greater difficulty than their δ counterparts (*22e*).

Generation of the α-chloroketo acid is followed by the haloform reaction (Scheme III). It is well-known that the rate-determining step in such a process is formation of the enolate anion (23b).

Scheme III

$$\mathrm{HO_2C(CHOH)_2COCH_2Cl} \xrightarrow[\mathrm{OH^-}]{\mathrm{NaOCl}} \mathrm{HO_2C(CHOH)_2COCCl_3} \xrightarrow{\mathrm{OH^-}} \mathrm{HCCl_3} + \mathrm{HO_2C(CHOH)_2CO_2H}$$

Various correlations can be made between the schematic outline and the following experimental findings with the D-mannitol model system: the rate of chlorine uptake increased appreciably with increases in hydroxide ion concentration, and a threefold drop in the concentration of Cl^+ did not significantly affect the rate of haloform production over a range of hydroxide ion concentrations, whereas a threefold increase in the concentration of D-mannitol did so markedly. For example, the required preliminary oxidations are more rapid and extreme at higher pH (*24b*); the haloform reaction is base catalyzed and is terminated by attack of hydroxide at the carbonyl group. These features of our proposal correlate with previous findings that haloform production during chlorination of drinking water is known to be greatly increased at higher pH values (*27*). It should be noted, however, that other organic components of natural waters, including the major ones, have been shown to yield chloroform upon addition of hypohalite (*20, 21*).

Green's finding (*24c*) that inulin, the polysaccharide of D-fructose, yielded bromoform, oxalic acid, and glycolic acid when treated with bromine water is noteworthy since a sequence similar to the one described above, including lactonization, could be invoked to account for the products. Furthermore, it is significant that our data show that glycerol, which is incapable of forming a γ- or δ-lactone, did not exhibit enhanced chloroform production with increases in hydroxide ion concentration (Figure 3). On the other hand, glycerol can function as a precursor to haloform under acid conditions, as shown by the production of bromoform, glyceric acid, and carbon dioxide on exposure to bromine water (*24d*). Presumably, the sequence in Scheme IV pertains. This pathway may also apply to the D-fructose–Br_2–H_2O system (vide supra).

Scheme IV

$$\mathrm{HOCH_2CHOHCH_2OH} \xrightarrow{\mathrm{(O)}} \mathrm{HOCH_2COCH_2OH} \xrightarrow{\mathrm{H^+}} \mathrm{HOCH_2COCH_2OH_2^+} \xrightarrow[-\mathrm{H_2O}]{\mathrm{Br^-}} \mathrm{HOCH_2COCH_2Br} \xrightarrow[\text{reaction}]{\text{haloform}} \mathrm{HOCH_2CO_2H} + \mathrm{HCBr_3}$$

A number of simpler mechanistic proposals have been made on systems where acetyl, rather than hydroxyacetyl, groups act as precursors for chloroform in the classical haloform reaction during chlorination of natural waters (*9, 28–30*). Evidence in some cases indicates the presence of a trichlorinated intermediate that hydrolyzes to produce chloroform under alkaline conditions (*9*). The polyol precursors that we discuss here require a somewhat different approach because the hydroxyl groups complicate the structural requirements.

Finally, it should be noted that the postulated reactions need not be efficient, high-yield processes since the haloalkanes are formed in extremely small amounts.

Acknowledgment

We are grateful to Dr. Martin Jones and Ms. Colleen Conway for assistance with background material and to Professor E. A. Hill for helpful discussions. Thanks to Barbara Hill for manuscript typing.

Literature Cited

(1) Jolley, R. L.; Jones, G.; Pott, W. W.; Thompson, J. E. In "Water Chlorination: Environmental Impact and Health Effects", Jolley, R. L., Ed.; Ann Arbor Science Publishers: Ann Arbor, MI, 1975; Vol. 1, pp 105–39.

(2) Keith, L. H.; Garrison, A. W.; Allen, T. R.; Carter, M. H.; Floyd, T. L.; Pope, J. D.; Thruston, A. D., Jr. In "Identification and Analysis of Organic Pollutants in Water", Keith, L. H., Ed.; Ann Arbor Science Publishers: Ann Arbor, MI, 1976; pp 329–73.

(3) Kleopfer, R. D. In "Identification and Analysis of Organic Pollutants in Water", Keith, L. D., Ed.; Ann Arbor Science Publishers: Ann Arbor, MI, 1976; pp 399–416.

(4) Bean, R. M.; Riley, R. C.; Ryan, P. W. In "Water Chlorination: Environmental Impact and Health Effects", Jolley, R. L., Ed.; Ann Arbor Science Publishers: Ann Arbor, MI, 1978; Vol. 2, pp 223–33.

(5) Helz, G. R.; Hsu, R. Y. *Limnol. Oceanogr.* **1978,** *23,* 858.

(6) Crane, A. M.; Erickson, S. J.; Hawkins, C. E. *Estuarine Coastal Mar. Sci.,* in press.

(7) Rook, J. J., *Water Treat. Exam.* **1974,** *23,* 234.

(8) Stevens, A. A.; Slocum, C. J.; Robeck, G. G. In "Water Chlorination: Environmental Impact and Health Effects", Jolley, R. L., Ed.; Ann Arbor Science Publishers: Ann Arbor, MI, 1975; Vol. 1, pp 77–104.

(9) Baum, B.; Morris, J. C., presented at the Division of Environmental Chemistry, 175th National Meeting of the American Chemical Society, Anaheim, CA, March 1978, ENVR-47.

(10) Hellebust, J. A. *Limnol. Oceanogr.* **1965,** *10,* 192.

(11) "Standard Methods for the Examination of Water and Wastewater", American Public Health Association, New York, 1971, pp 112–6.

(12) Kovacic, P.; Lowery, M. K.; Field, K. W. *Chem. Rev.* **1970,** *70,* 640 and 657.

(13) Smith, C. A. "Isolation and Study of Chloro-Organics Resulting from Chlorination of Seawater", Rosenstiel School of Marine and Atmospheric Science, University of Miami. 1979, private communication.

(14) Handa, H.; Hama, T. "Abstracts of Papers", ACS/CSJ Chemical Congress, Honolulu, HI, April 1979; ENVR-22.

(15) Walsh, G. E. *Limnol. Oceanogr.* **1965,** *10,* 570 and 577.

(16) Walsh, G. E. *Limnol. Oceanogr.* **1966,** *11,* 249.

(17) Vaccaro, R. F.; Hicks, S. E.; Jannasch, H. W.; Carey, F. G. *Limnol. Oceanogr.* **1968,** *13,* 356.

(18) Lewis, G. J., Jr.; Rakestraw, N. W. *J. Mar. Res.* **1955,** *14,* 253.

(19) Lewis, R. A. *Can. J. Microbiol.* **1956,** 2, 665.

(20) Rook, J. J. *Environ. Sci. Technol.* **1977,** *11,* 478.

(21) Havlicek, S. C.; Reuter, J. D.; Ingols, R. S.; Lupton, J. D.; Ghosal, M.; Ralls, J. W.; El-Barbary, I.; Strattan, L. W.; Cotruro, J. A.; Trichilo, C. "Abstracts of Papers", ACS/CSJ Chemical Congress, Honolulu, HI, April 1979; ENVR-95.

(22) "The Carbohydrates: Chemistry, Biochemistry, Physiology", Pigman, W., Ed.; Academic Press: New York, 1957: (a) Green, J. W. *Ibid.*, p 344; Lohmar, R. L. *Ibid.*, p 264; (b) Green, J. W. *Ibid.*, p 336; (c) Green, J. W. *Ibid.*, p 343; (d) Sowden, J. C. *Ibid.*, p 132; (e) Green, J. W. *Ibid.*, p 304.

(23) (a) March, J. In "Advanced Organic Chemistry: Reactions, Mechanisms, and Structure", 2nd ed.; McGraw-Hill: New York, 1977; p 436. (b) *Ibid.*, p 575.

(24) (a) Verstraeten, L. M. J. *Adv. Carbohydr. Chem.* **1967,** *22,* 233. (b) Green, J. W. *Ibid.* **1948,** *3,* 156–7. (c) Green, J. W. *Ibid.* **1948,** *3,* 149. (d) Green, J. W. *Ibid.* **1948,** *3,* 167. (e) Green, J. W. *Ibid.*, **1948,** *3,* 147 and 162. (f) Barnett, J. E. G. *Ibid.* **1967,** *22,* 178–83.

(25) Albery, W. J.; Kreevoy, M. M. *Adv. Phys. Org. Chem.* **1978,** *16,* 87.

(26) (a) Gould, E. S. In "Mechanism and Structure in Organic Chemistry"; Holt; New York, 1959; p 261. (b) *Ibid.*, p 284.

(27) Rook, J. J. *J. Am. Water Works Assoc.* **1976,** *68,* 168.

(28) Stevens, A. A.; Slocum, C. J.; Seeger, D. R.; Robeck, G. G. *Environ. Impact Water Chlorination, Proc. Conf.* **1975,** 85.

(29) Uden, P. C.; Quimby, B. D.; Delaney, M. F. "Abstracts of Papers", ACS/CSJ Chemical Congress, Honolulu, HI, April 1979; ENVR-94.

(30) Looyenga, R. W., Harms, L. L., Abstracts of Papers, 173rd National Meeting of the American Chemical Society, New Orleans, Louisiana, March 1977, ENVT-6.

Received for review March 21, 1980. Accepted July 18, 1980.

Elemental Partitioning in an Aboveground Oil Shale Retort Pilot Plant

Jonathan S. Fruchter,* Connie L. Wilkerson, John C. Evans, and Ronald W. Sanders

Battelle Pacific Northwest Laboratory, Physical Sciences Department, P.O. Box 999, Richland, Washington 99352

■ Effluent streams from the Paraho semiworks oil shale retort have been analyzed for up to 47 major and trace element constituents. Mass balance analyses show that three partitioning categories may be defined. Category I, in which less than 0.01% of an element is partitioned from the feed shale into the oil, water, and offgas streams, includes nonvolatile mineral phase elements such as Al, Ba, Ca, Cr, Mn, Na, Rb, Si, etc. These elements are redistributed as entrained shale fines or as dissolved ionic species. Category II consists of elements partitioned between 0.01 and $\sim$5%, and it includes As, B, Co, Fe, Ni, Se, and others. These elements are associated with volatile metallic or organometallic compounds which redistribute primarily into the product shale oil. Category III elements are partitioned more than 20%. This category includes the four major elements C, H, N, and S and the volatile heavy metal Hg.

Introduction

The escalating cost of imported oil has renewed the interest in developing U.S. oil shale reserves in the western states of Colorado, Utah, and Wyoming. These reserves represent a significant potential source of precious liquid hydrocarbon fuels; however, their development is complicated by concerns about environmental impact in the local oil shale regions. To help minimize the impact from any future oil shale industry, there is a need for chemical characterization of the effluents from proposed oil shale plants. Since there is no operating oil shale industry in the U.S. at this time, these chemical characterizations must be performed on experimental pilot plant facilities.

This paper presents inorganic source characterization analyses for the process streams of a surface retorting process. The data presented here are related specifically to one process,

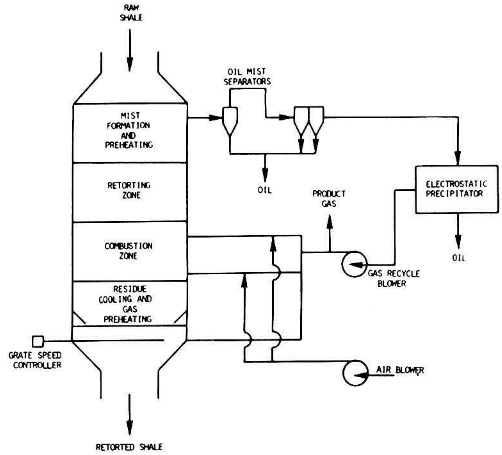


Figure 1. Paraho surface retorting process (direct mode).

the Paraho directly heated semiworks retort at Anvil Points, CO. However, it is probable that many of these data will have considerable general validity for all types of oil shale retorting technologies. The characterization analyses are intended to provide detailed and accurate information on the types and amounts of various substances which may be emitted to the environment from oil shale retorting processes or which may find their way to the environment during subsequent portions of the shale oil cycle. Such information not only is of interest in its own right, but also is vital to related health and environmental fate and effect studies.

The objectives of this initial characterization study were (1) to calculate a representative mass balance for a number of trace and major elements of potential environmental significance and (2) to obtain information on the physical and chemical forms of certain elements emitted from the retort. Although limited elemental mass balance studies have been reported previously on laboratory bench scale retorts (*1*, *2*), this paper represents the first such study that we know of for a large pilot scale plant operating in the field.

Description of the Paraho Retorting Process

The Paraho surface retorting process has been described elsewhere (*3*). It is presently operated by Development Engineers, Inc. (DEI) at Anvil Points, CO, or at the DOE Rifle, CO, oil shale facility. The shale used in the process is obtained from a room and pillar mine in the Mahogany Zone of the Green River Formation. At the processing site the mined shale is crushed and screened to between −7.6 and +0.6 cm. The crushed shale fraction less than 0.6 cm (10–15%) is presently stockpiled.

DEI has recently operated two retorts at Anvil Points, a 0.77 m i.d. × 19 m high pilot plant unit and a 2.6 m i.d. × 23 m high semiworks retort. All of the studies detailed in this report were conducted on the semiworks retort. Both of the retorts can be operated in either a direct or indirect heated mode. Since all of the samples used in this study were obtained during direct heating operation, this mode will be briefly described here.

In direct heated operation, illustrated in Figure 1, controlled combustion within the retort provides the heat necessary for retorting. The process is continuous and flows are countercurrent with the gas phase flowing upwards. The uniform downward flow of shale is controlled by a patented, hydraulically operated grate mechanism. Incoming raw shale is distributed evenly at the top by a rotating distributor and is then preheated by rising hot gases in the mist formation zone. Next, the preheated shale passes through the retorting zone where the organic "kerogen" is decomposed into an oil mist, gas and carbon residue (coke). The retorted shale then enters the combustion zone of the retort where the carbon residue and recycle gas serve as fuel for combustion. Input air is distributed evenly across the bed along with the recycle gas in this retort zone. In the bottom of the retort, the shale is cooled by the incoming bottom recycle gas, giving its heat to this gas; the retorted shale then exits through the bottom of the retort and is conveyed to a storage site. The oil mist produced is carried out the top of the retort through the offgas collector and is separated from the gas by a coalescer and electrostatic precipitator. The product collected is an oil–water emulsion of ~5 wt % water. The emulsion produced is collected in a small gauging tank where it can be sampled. It is then pumped to a settling tank where the water is separated and drained, and "dry" product oil is then pumped to storage.

The Paraho direct mode process produces a maximum temperature of ~750 °C in the combustion zone of the retort. This maximum is significantly lower than that of coal combustion furnaces and is also lower than in situ retorting processes which are believed to produce temperatures in excess of 1100 °C. The lower temperature minimizes the decomposition of the carbonate minerals which are converted to oxides and silicates in the hotter in situ processes. The Paraho direct process operates at pressures slightly above atmospheric, and both oxidation and reducing conditions occur in the retort. The combustion zone is the area where oxidation occurs, whereas reducing conditions predominate in the higher regions of the retort where the oil is volatilized. While the reactions that affect element partitioning in oil shale retorting processes are not fully understood, some general mechanisms have been proposed (*4*). The major reaction classes include (1) mineral decomposition reactions, (2) kerogen conversion reactions, (3) oxidation–reduction reactions, and (4) shale–product interactions.

Sample Collection and Analytical Methods

Sample collection and preparation are critical to a study of this type because meaningful analytical results are dependent on the integrity and representativeness of the samples. To help minimize the difficulties in obtaining representative samples from each important process stream, we arranged a consultation with DEI personnel before the site visit and an appropriate sampling program was developed. The samples were later collected during two field trips, one for 4 days in August, 1977, and one for 3 days in November, 1977. Sample collection and necessary on-site analyses were facilitated by use of a camper-mounted mobile laboratory.

Many of the samples obtained from oil shale retorts are chemically and physically complex, creating the potential for matrix effects as well as other types of interferences in many of the commonly used methods for chemical analysis. Therefore, the techniques employed for inorganic analysis of the samples from the Paraho retort were chosen when possible for their relative freedom from matrix effects as well as their sensitivity and precision. Because no one method can meet these requirements for all elements of interest, a multitechnique analytical approach was adopted. This multitechnique approach to inorganic analysis also provided an opportunity to assess the strengths and weaknesses of the various methods for different samples. The major techniques used included instrumental neutron activation analysis, energy dispersive X-ray fluorescence analysis, dc argon plasma emission spectroscopy, flame atomic absorption spectroscopy, and graphite furnace atomic absorption spectroscopy. Other techniques, including cold vapor atomic absorption spectroscopy, ion se-

Table I. Multielement Analysis of Paraho Feedstock Shale Collected August 24, 1977 (in ppm except as noted)

element	INAA[b]	XRF[c]	PES[d]	FAA[e]	other	error weighted av
Al (%)	3.89 ± 0.14		3.78 ± 0.08	3.69 ± 0.11		3.77 ± 0.06
As	48.0 ± 0.7	41.6 ± 0.5				44.3 ± 0.6
B			94 ± 2			94 ± 2
Ba	483 ± 34		515 ± 8			512 ± 10
Br	0.57 ± 0.13					0.57 ± 0.13
Ca (%)	10.4 ± 0.5	10.7 ± 0.5	9.9 ± 0.1	11.0 ± 0.4[a]		10.1 ± 0.2
Cd					0.64 ± 0.03[f] 0.61 ± 0.08[g]	0.64 ± 0.03
Ce	43.1 ± 0.9					43.1 ± 0.9
Co	9.0 ± 0.1					9.0 ± 0.1
Cr	36.7 ± 1.8	39.7 ± 9.3	33.8 ± 0.6			34.2 ± 0.6
Cs	3.84 ± 0.22					3.84 ± 0.22
Cu		40.3 ± 2.3	40.0 ± 5.5			40.3 ± 2.1
Dy	2.4 ± 0.4					2.4 ± 0.4
Eu	0.60 ± 0.02					0.60 ± 0.02
Fe (%)	2.08 ± 0.04	2.02 ± 0.10	2.01 ± 0.04	2.14 ± 0.04		2.07 ± 0.02
Ga		8.4 ± 0.8				8.4 ± 0.8
Hf	1.75 ± 0.05					1.75 ± 0.05
Hg					0.089 ± 0.005[h]	0.089 ± 0.005
Ho	0.67 ± 0.11					0.67 ± 0.11
v4K (%)	1.69 ± 0.11	1.66 ± 0.02	1.79 ± 0.03	1.55 ± 0.03		1.61 ± 0.02
La	20.6 ± 0.7					20.6 ± 0.7
Lu	0.28 ± 0.03					0.28 ± 0.03
Mg (%)			3.42 ± 0.05	3.59 ± 0.3		3.46 ± 0.06
Mn	312 ± 20	319 ± 20	314 ± 22			315 ± 12
Mo		24 ± 2.5	20.9 ± 1.9			22.0 ± 1.5
Na (%)	1.68 ± 0.01			1.73 ± 0.07		1.69 ± 0.03
Nb		8.0 ± 0.7				8.0 ± 0.7
Nd	20.4 ± 2.1					20.4 ± 2.1
Ni	23.0 ± 5.3	24.2 ± 1.2	27.6 ± 0.6			27.5 ± 0.6
Pb		26.5 ± 2.1				26.5 ± 2.1
Rb	74.9 ± 2.3	74.0 ± 2.7				74.5 ± 1.8
S		5730 ± 500				5730 ± 500
Sb	2.09 ± 0.08					2.09 ± 0.08
Sc	5.77 ± 0.16					5.77 ± 1.6
Se	2.1 ± 0.2	2.7 ± 0.7[a]			2.0 ± 0.1[f]	2.03 ± 0.09
Si (%)		14.1 ± 0.7		15.2 ± 0.1		15.0 ± 0.3
Sm	3.10 ± 0.03					3.10 ± 0.03
Sr	674 ± 24	678 ± 21	712 ± 14			696 ± 11
Ta	0.55 ± 0.02					0.55 ± 0.02
Tb	0.37 ± 0.03					0.37 ± 0.03
Th	6.33 ± 0.13					6.33 ± 0.13
Ti (%)	0.18 ± 0.02	0.17 ± 0.02		0.18 ± 0.01		0.18 ± 0.01
U	4.2 ± 0.3				4.6 ± 0.2[f]	4.5 ± 0.2
V	86 ± 6	95 ± 6	96 ± 3			94.2 ± 2.4
Y		14 ± 1				14 ± 1
Yb	1.26 ± 0.11					1.26 ± 0.11
Zn	67.2 ± 3.7	62.6 ± 2.3	73.2 ± 4.0[a]		63 ± 3[f]	63.6 ± 1.6

[a] Deleted from error weighted average. [b] INAA = instrumental neutron activation analysis. [c] XRF = X-ray fluorescence analysis. [d] PES = plasma emission spectroscopy (sodium carbonate fusion). [e] FAA = conventional flame atomic absorbtion (lithium metaborate fusion). [f] RCAA = radiochemical neutron activation analysis. [g] GFAA = graphite furnace atomic absorbtion. [h] CVAA = cold vapor atomic absorbtion.

lective electrodes, hydride generation, and various gas monitoring devices, were used to supplement these techniques for specific elemental and speciation analysis. A detailed description of the sample collection, preparation, and analytical procedures has been reported elsewhere (5).

Results

Special attention was given to the analysis of samples collected on August 24, 1977, particularly the raw and retorted shale. There were several purposes behind this effort. First, a multitechnique intercomparison was carried out to enable objective assessment of the accuracy of the analytical data. The August 24 raw shale in particular was rigorously characterized for some 47 elements. In addition, a more limited analysis was performed on two splits of the raw shale to verify homogeneity. Finally, the August 24, 1977, samples were chosen as representative samples for a mass balance study for several selected elements of interest.

Tables I and II give the complete analytical results for analysis of the August 24, 1977, raw and retorted shale for 47 elements. For many elements several analytical techniques were employed in the analysis, and it is possible to intercom-

Table II. Multielement Analysis of Paraho Retorted Shale Collected August 24, 1977 (in ppm except as noted)

element	INAA[b]	XRF[c]	PES[d]	FAA[e]	other	error weighted av
Al (%)	4.83 ± 0.05[a]		4.46 ± 0.05	4.56 ± 0.17		4.48 ± 0.08
As	59.2 ± 0.9	59.8 ± 1.9				59.4 ± 1.0
B			107 ± 2			107 ± 2
Ba	593 ± 13		613 ± 12			604 ± 9
Br	0.80 ± 0.18					0.80 ± 0.18
Ca (%)	13.1 ± 0.5	13.9 ± 0.7	13.1 ± 0.2	13.2 ± 0.2		13.3 ± 0.2
Cd					0.90 ± 0.04[f] 0.99 ± 0.13[g]	0.91 ± 0.04
Ce	51.5 ± 1.5					51.5 ± 1.5
Co	11.1 ± 0.2					11.1 ± 0.2
Cr	44.3 ± 0.9	49.6 ± 8.9	41.1 ± 3.8			44.2 ± 0.9
Cs	4.68 ± 0.21					4.68 ± 0.21
Cu		56.3 ± 1.0	46.9 ± 5.3			55.9 ± 1.1
Dy	3.5 ± 0.2					3.5 ± 0.2
Eu	0.73 ± 0.02					0.73 ± 0.02
Fe (%)	2.42 ± 0.04	2.56 ± 0.13	2.35 ± 0.03	2.47 ± 0.08		2.40 ± 0.03
Ga		11.6 ± 1.2				11.6 ± 1.2
Hf	2.11 ± 0.03					2.11 ± 0.03
Hg					0.035 ± 0.003[h]	0.035 ± 0.003
Ho	0.88 ± 0.04					0.88 ± 0.04
K (%)	1.98 ± 0.20	1.94 ± 0.05	2.11 ± 0.05[a]	1.81 ± 0.03		1.86 ± 0.03
La	24.7 ± 0.3					24.7 ± 0.3
Lu	0.35 ± 0.03					0.35 ± 0.03
Mg (%)			3.88 ± 0.03	4.32 ± 0.09		4.07 ± 0.06
Mn	388 ± 23	420 ± 24	374 ± 28			396 ± 14
Mo		32.7 ± 1.4	41.3 ± 3.9			33.7 ± 1.3
Na (%)	2.15 ± 0.03			2.24 ± 0.03		2.19 ± 0.03
Nb		9.2 ± 1.5				9.2 ± 1.5
Nd	22.3 ± 1.1					22.3 ± 1.1
Ni	29.7 ± 4.6	32.1 ± 3.9	32.4 ± 1.8			32.1 ± 1.5
Pb		36.2 ± 2.0				36.2 ± 2.0
Rb	89.9 ± 4.1	88 ± 2				88.4 ± 1.8
S		6780 ± 620				6780 ± 620
Sb	2.63 ± 0.15					2.63 ± 1.5
Sc	6.84 ± 0.15					6.84 ± 0.15
Se		3.4 ± 0.5[a]			2.3 ± 0.1[f]	2.3 ± 0.1
Si (%)		17.8 ± 1.3		18.2 ± 0.3		18.2 ± 0.4
Sm	3.68 ± 0.07					3.68 ± 0.07
Sr	820 ± 26[a]	866 ± 7	892 ± 14			879 ± 12
Ta	0.65 ± 0.02					0.65 ± 0.02
Tb	0.42 ± 0.04					0.42 ± 0.04
Th	7.55 ± 0.10					7.55 ± 0.10
Ti (%)	0.21 ± 0.04	0.24 ± 0.01		0.20 ± 0.03		0.24 ± 0.01
U	5.3 ± 0.2				4.9 ± 0.2[f]	5.10 ± 0.14
V	111 ± 13	139 ± 19	133 ± 7			129 ± 6
Y		16.4 ± 0.9				16.4 ± 0.9
Yb	1.61 ± 0.13					1.61 ± 0.13
Zn	89.2 ± 3.0	86.2 ± 5.5	93.6 ± 5.3[a]		77 ± 4[f]	82.3 ± 2.2

[a] Deleted from error weighted average. [b] INAA = instrumental neutron activation analysis. [c] XRF = X-ray fluorescence analysis. [d] PES = plasma emission spectroscopy (sodium carbonate fusion). [e] FAA = conventional flame atomic absorbtion (lithium metaborate fusion). [f] RCAA = radiochemical neutron activation analysis. [g] GFAA = graphite furnace atomic absorbtion. [h] CVAA = cold vapor atomic absorbtion.

pare results. In general, six replicate samples were analyzed by each analytical technique. The analytical errors for each value in Tables I and II are thus derived from the precision of six analyses. For a few elements only a single determination was made. These include the radiochemical measurement of Cd, Se, U, and Zn, the graphite furnace AA determination of Cd, and the cold vapor AA determination of Hg.

The abundance data in Tables I and II were statistically analyzed by a computer code to obtain an error weighted average value for each element. Each individual determination was assigned a minimum error of 2%, and, where three or more determinations occurred per element, a single application of Chauvenet's criterion was applied to reject outliers. Determinations that were rejected were deleted from the error weighted average and are noted as such in Tables I and II. Once an appropriate error weighted average was determined for each element, the percentage deviation of each individual determination from the average value was computed. Relative to the error weighted average, these deviations are illustrated in Figure 2 for selected elements in the raw shale material. Additionally, a percent root mean squared deviation was computed for each group of data (top of Figure 2).

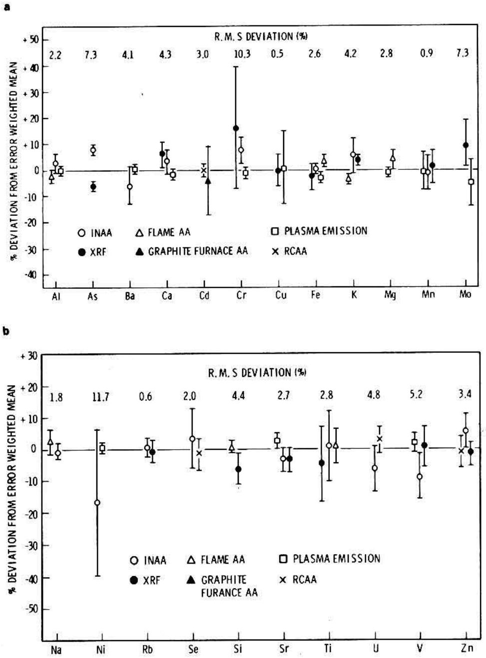


Figure 2. Relative performance of analytical techniques used in the multielement analysis of Paraho raw oil shale (August 24, 1977).

A number of observations can be drawn from Figure 2. Agreement between analytical methods is in general quite good, and in almost all cases the error bars overlap. One notable exception is the determination of As by instrumental neutron activation and X-ray fluorescence. This difference (10–15%) is noticeable since both methods have good precision. The discrepancy in the measurement of raw shale As by instrumental neutron activation and X-ray fluorescence has been noted in work elsewhere (*6*). In addition, a similar As analysis trend is reflected in the results of a multilaboratory round robin characterization for an environmental soil standard (*7*). While the nature of the analytical difference for As in the raw shale matrix is still not understood, various technical reasons have convinced the authors and others that the problem lies with the X-ray fluorescence technique. Therefore, the As mass balance that was computed in this paper was based on the data provided by neutron activation analysis only. For a number of other elements, Figure 2 shows that a wide range of precision is evident and thus illustrates the advantage of using several different analytical techniques for multielement analysis.

Discussion

Mass balances for 31 elements were completed for the Paraho semiworks retort as operated during direct mode retorting. The relative distribution of elements among the products and effluents was determined from (1) accurate, high-precision measurements of each element in the raw shale, retorted shale, product oil, product water, and product gas and (2) the calculated equilibrium material balance between the mass of feedstock and product materials.

The detailed chemical analyses obtained from samples collected on August 24, 1977, were used to compute the elemental mass balances in this paper. In the few cases where chemical characterization data were not available for this date, data from other days were substituted. It is assumed that such substitutions are reasonable and that the computed mass balance of each affected element is valid for the date of interest. This assumption is supported by reported feedstock variation studies (*8*) and by other data (*5*) which suggest that the input and redistribution of elements at the Paraho semiworks retort was rather constant during the time of this study.

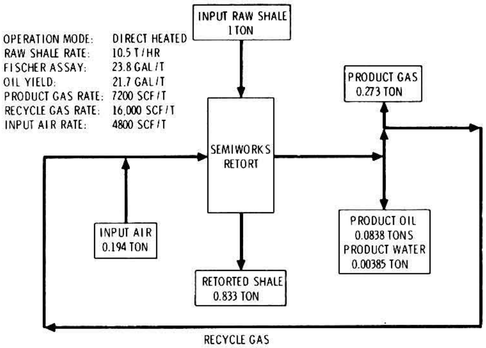


Figure 3. Retorting parameters and material balance flow rates for the Paraho semiworks retort as operated on August 24, 1977.

While the detailed calculations are reported elsewhere (*5*), the completed material balance for the Paraho semiworks retort, normalized to each ton of input raw shale, is shown in Figure 3. Assuming the input of each element to be entirely with the raw shale (process air contribution zero), one may reduce the material balance of Figure 3 to reflect only those terms which relate the mass of the raw shale to the mass of the products. Thus, one ton of input raw shale corresponds to the production of 0.833 ton of retorted shale, 0.0838 ton of product oil, 0.00385 ton of product water, and 0.273 ton of product gas. This relationship and elemental analyses obtained for each process stream were used to determine each element's mass distribution among the products. The resulting mass balances for 31 elements are summarized in Table III.

The elemental mass imbalances in Table III range from −16.0 for Hg to +17.5% for H. The negative (−) and positive (+) signs are defined as observing a deficit or excess of an element in the total products relative to its abundance and input in the incoming shale. The majority of the elements have good mass balance closures, e.g., less than ±10% imbalance. This margin is typical of the imbalances which may result from the propagation of relatively small analytical errors of precision. When the precision of each abundance measurement in a process stream is expected to be small, large mass imbalances (or poor closures) usually result from the inaccurate measurement of an element in one or more of the process streams or from unexplained gains or losses within the system. The larger but still reasonable mass imbalances for six elements, namely, Cu, H, Hg, Mo, N, and Ti, are probably examples of the latter case. This is especially true for the elements H, Hg, and N, which were among the most difficult for us to measure in the various Paraho process streams.

The redistribution of elements from the raw shale may be characterized by three general categories. The first category (I) includes the elements which remain almost totally with the retorted shale and have partitioning coefficients of less than 0.01% for the product oil, product water, and product gas. This group includes the elements Al, Ba, Ca, Cr, K, Mg, Mn, Na, Rb, Si, and Sr. The second category (II) is characterized by elements which have a cumulative partitioning coefficient (products other than retorted shale) of from 0.01% to ~5%. This second category includes the elements As, B, Co, Cu, Fe, Ni, Sb, Se, Th, Ti, V, and Zn. Although they were not detected

Table III. Elemental Mass Balances for the Paraho Semiworks Retort during Direct Mode Retorting

			element redistributed into products and effluents (August 24, 1977), %			
	elemental abundance in raw shale, ppm	retorted shale	product oil	product water	product gas	imbalance, %
Al	37 700	106.7	<0.01	<0.01	<0.01	+6.7
As	49	100.3	5.30	0.04	0.07	+5.7
B	94	94.8	ND[a]	0.18	<0.01	−5.0
Ba	510	98.0	<0.03	<0.01	<0.03	−2.0
C	155 000	32.8	46.5	0.06	21.1	+0.5
Ca	101 000	109.7	<0.01	<0.01	<0.01	+9.7
Co	9.0	102.7	0.87	<0.01	<0.02	+3.6
Cr	34	107.8	<0.01	<0.01	<0.01	+7.8
Cu	40	116.6	0.09	<0.01	<0.01	+16.7
Fe	20 700	96.6	0.02	<0.01	<0.01	−3.4
H	15 000	9.4	65.4	2.7	40.0	+17.5
Hg	0.089	32.8	28.2	0.01	23.0	−16.0
K	16 100	96.2	<0.05	<0.01	<0.01	−3.8
Mg	34 600	104.0	<0.01	<0.01	<0.01	+4.0
Mn	315	104.7	<0.01	<0.01	<0.01	+4.7
Mo	22	117.4	<0.8	<0.01	<0.04	+17.4
N	6 600	37.9	30.3	1.3	17.9	−12.6
Na	16 900	107.9	<0.01	<0.01	<0.01	+7.9
Ni	28	95.2	0.82	<0.01	<0.01	−4.0
Pb	27	108.0	<0.09	<0.01	<0.06	+8.0
Rb	75	97.7	<0.01	<0.01	<0.01	−2.3
S	6 000	80.9	10.4	2.5	12.7	+6.5
Sb	2.1	103.1	0.11	<0.01	<0.03	+3.2
Se	2.0	95.8	3.81	1.88	<0.8	+1.5
Si	150 000	101.1	<0.01	<0.01	<0.01	+1.1
Sr	700	104.7	<0.01	<0.01	<0.01	+4.7
Th	6.3	100.5	0.01	<0.01	<0.01	+0.5
Ti	1 800	111.1	0.01	<0.01	<0.01	+11.1
U	4.5	94.4	<0.06	<0.01	<0.02	−5.5
V	94	101.9	0.02	<0.01	<0.01	+1.9
Zn	64	106.7	0.05	<0.01	<0.01	+6.7

[a] Not determined.

in the product oil, water, or gas, three additional elements, Mo, Pb, and U, cannot be ruled out as members of this group because of their detection limits (see Table III). The third category (III) is characterized by the elements which have greater than 20% of their mass redistributed into products other than the retorted shale. This group includes the major elements C, H, N, and S, and the volatile heavy metal Hg.

The redistribution of category I elements into the product oil is primarily in the form of raw and/or retorted shale fines. This statement is based on data in Table IV, which tabulates the partitioning coefficients for all elements detected in the product oil. The partitioning coefficients for the mineral elements Al, Ca, Mg, Mn, Na, and Si ranged from 0.0021 to 0.0061% with a mean and relative standard deviation of 0.0040 ± 0.0015%. The small but essentially equal fractions of these six elements in the product oil indicate that they are most likely being redistributed together as shale particulate matter. This conclusion was later confirmed by laboratory filtration experiments.

If the base level of elements associated with shale particulates in the product oil is set equal to the mean value calculated above (0.0040%) plus two standard deviations (0.0030%), it is reasonable to conclude that elements with partitioning coefficients exceeding the sum (0.007%) are present in additional chemical forms. Analytical errors or sample contamination may invalidate this statement for a few elements close to the 0.007% limit (e.g., Ti and Th); however, for elements with partitioning coefficients of 0.02% or greater (e.g., Fe), this difference is considered to be real. The elements of category II are probably redistributed as volatile metallic or organo-

Table IV. Percentage of Elements Transferred from Feedstock Raw Shale to Product Oil (August 24, 1977)

element	abundance in raw shale, ppm	abundance in product oil, ppm	element transferred from raw shale to product oil, %
H	15 000	117 000	65.4
C	155 000	860 000	46.5
N	6 600	23 900	30.3
S	6 000	7 400	10.4
Hg	0.089	0.30	28.2
As	49	31	5.3
Se	2.0	0.91	3.8
Co	9.0	0.93	0.87
Ni	28	2.74	0.82
Sb	2.1	0.028	0.11
Cu	40	0.42	0.088
Zn	64	0.41	0.054
V	94	0.25	0.022
Fe	20 700	49	0.020
Th	6.3	0.009	0.012
Ti	1 800	2.6	0.012
Mg	34 600	25	0.0061
Mn	315	0.21	0.0056
Al	37 700	16	0.0036
Ca	101 000	42	0.0035
Si	150 000	55	0.0031
Na	16 900	4.3	0.0021

Table V. Percentage of Elements Transferred from Feedstock Raw Shale to Product Water (August 24, 1977)

element	abundance in raw shale, ppm	abundance in product water, ppm	element transferred from raw shale to product water, %
H	15 000	105 000	2.7
S	6 000	39 000	2.5
Se	2.0	9.8	1.9
N	6 600	23 000	1.3
B	94	43	0.18
C	155 000	25 000	0.062
As	49	5.7	0.045
Hg	0.089	0.0023	0.010
Ni	28	0.54	0.007 4
Cu	40	0.70	0.006 7
Mg	34 600	490	0.005 5
Sb	2.1	0.020	0.003 7
Mo	22	0.15	0.002 6
Na	16 900	111	0.002 5
Zn	64	0.41	0.002 5
Co	9.0	0.03	0.001 3
Ti	1 800	5.1	0.001 1
Rb	75	0.14	0.000 72
Sr	700	0.85	0.000 48
Mn	315	0.18	0.000 22
V	94	0.045	0.000 18
Ca	101 000	38	0.000 15
Si	150 000	41	0.000 11
Fe	20 700	1.5	0.000 028

metallic compounds. This statement is supported by other mass balance studies (*1*, *2*), by studies (*9*) of metalloporphyrins in oil shale, and by investigations (*10*) which report that As and Fe cannot be removed from Paraho shale oil filtered throught 15-μm filters. An additional explanation is that very fine grained and insoluble trace minerals, chemically unlike the shale fines, are being preferentially precipitated or transported into the product oil.

The observed redistribution of category III elements into the product oil ranged from 10.4% for S to 65.4% for H. A significant fraction (30.3%) of the trace element Hg was observed to partition into the product oil. This partitioning coefficient agrees well with others reported for Hg in various oil shale retorting processes (*7*) and in laboratory retorting studies (*11*).

The abundances and partitioning coefficients for elements detected in the product water are summarized in Table V. Because the August 24 water sample was collected from one of the small gauging tanks, it represented product water which had only recently been coproduced by the retorting process. Other more "aged" product waters were collected on August 26 and November 15 and 16 from the large settling tanks used for oil–water separation. The product water obtained from these tanks is typically several days older than water in the gauging tanks.

A comparison between the elemental abundances of each product water type is given in Table VI. Several elements (As, B, Co, Mg, Mo, Na, S, Se, and V) are observed to be two to three times more concentrated in the product waters originating from the large settling tanks. These increased levels are believed to be due to the longer time for separation and

Table VI. Comparison between Elemental Abundances in Gauging Tank and Settling Tank Product Waters

element, ppm unless noted	product water from gauging tanks					product water from settling tanks			
	8/24	8/25	8/26	11/17	av	8/26	11/15	11/16	av
Al	<0.4	0.3	ND[a]	0.4	0.35	0.7	<1	<2	0.7
As	5.7	4.1	4.4	5.9	5.0	10.9	17.4	13.6	14.0
B	43	2.1	13	16	19	41	43	36	40
Ba	ND	ND	<1	<3	<2	ND	<3	<3	<3
C (%)	2.5	ND	ND	ND	2.5	ND	ND	ND	
Ca	38	36	33	41	37	64	43	42	50
Co	0.03	0.13	0.11	0.19	0.12	0.35	0.37	0.30	0.34
Cr	<0.06	<0.04	<0.04	<0.1	<0.04	0.13	<0.1	<0.1	<0.1
Cu	0.7	0.8	0.5	<0.5	0.7	21	6.8	10	12.6
Fe	1.5	2.2	1.8	3.8	2.3	4.2	1.9	1.9	2.7
H (%)	10.5	ND	ND	ND	10.5	ND	ND	ND	
Hg (ppb)	2.3	5.8	ND	<400	4.1	<500	5.6	6.3	6.0
K	<20	<20	<20	<10	<20	65	<30	<30	<30
Mg	490	240	230	320	320	960	870	790	820
Mn	0.18	0.44	0.39	0.46	0.37	0.31	0.12	0.12	0.18
Mo	0.15	0.07	0.07	0.07	0.09	0.53	0.51	0.43	0.50
N (%)	2.3	ND	ND	ND	2.3	ND	ND	ND	
Na	111	107	97	72	97	396	335	316	349
Ni	0.54	0.23	0.22	0.38	0.34	0.41	0.37	0.40	0.39
Pb	<0.4	<0.2	<0.2	<0.3	<0.2	<0.3	<0.3	<0.3	<0.3
Rb	0.14	<0.1	<0.2	0.08	0.1	0.41	0.32	0.34	0.36
S (%)	3.9	1.7	ND	2.2	2.6	5.1	4.8	4.6	4.8
Sb	0.020	0.019	0.010	<0.06	0.016	0.034	<0.02	<0.02	<0.02
Se	9.8	3.7	3.7	4.1	5.3	6.4	6.7	7.1	6.7
Si	41	24	23	39	32	24	35	24	28
Sr	0.85	0.41	0.50	0.43	0.55	1.1	0.80	0.85	0.92
Th	<0.01	ND	<0.01	<0.01	<0.01	ND	<0.01	<0.01	<0.01
Ti	5.1	<1	1.4	2.8	3.1	6.0	<3	10	8.0
U	<0.1	<0.1	<0.1	<0.05	<0.1	<0.1	<0.1	<0.1	<0.1
V	0.045	0.020	<0.01	0.020	0.028	0.094	0.090	0.077	0.087
Zn	0.41	0.31	1.06	0.08	0.47	5.0	0.85	7.5	4.5

[a] Not determined.

Table VII. Percentage of Elements Transferred from Feedstock Raw Shale to Product Gas (August 24, 1977)

element	abundance in raw shale, ppm	abundance in product gas	element transferred from raw shale to product gas, %
H	15 000	26.7 g/m^3	40.0
C	155 000	146 g/m^3	21.1
N	6 600	5.4 g/m^3 [a]	17.9
S	6 000	3.4 g/m^3	12.7
Hg	0.089	75 µg/m^3	23.0
As	49	155 µg/m^3	0.071

[a] N as NH_3.

extraction between the organic and aqueous phases. This explanation is especially fitting when considering the mass differences between the two products (see Figure 3). Even the smallest additional element separation from the product oil will be magnified by ~20–25 times in the product water. The anomalously high values for Cu and Zn in the aged product waters (~10 times the gauging tank abundances) may reflect other factors such as corrosion from the storage tanks.

The partitioning coefficients for S and Se in the August 24 product water are 2.5 and 1.9%, respectively. This rather close agreement may be related to the elements' chemical similarities. The total S measured in the product water was 3.9%; however, the S^{2-} levels were only a few parts per million. About 0.05% of the raw shale As was observed to partition into the product water. The chemical form of the arsenic in the product water is ca. 50% As^{3+} and 50% As^{5+}. No methyl or dimethyl arsenic was detected.

The abundances and partitioning coefficients for elements detected in the product gas are summarized in Table VII. Significant fractions of the elements C, H, Hg, N, and S are released from the raw shale and redistributed into the product gas. In addition, a small fraction of the As (0.07%) was also observed to partition into the gas. The element hydrogen is redistributed in the gas chiefly as water vapor, H_2, CH_4, and other hydrocarbon gases. Carbon is redistributed as hydrocarbon gases, as CO and CO_2 from combustion, and as CO_2 from decomposition of the carbonate minerals. Nitrogen is redistributed chiefly as NH_3 in the gas phase.

The partitioning coefficient for total sulfur redistributed into the product gas was observed to be 12.7%. The partitioning coefficient for Hg in the gas was observed to be 23.0%. The chemical form is assumed to be elemental mercury vapor (Hg^0) as organic forms should be condensed with the product oil. The small fraction of arsenic in the product gas was primarily inorganic As_2O_3 vapor. Only a small quantity of arsine or methylated arsine was detected.

Summary and Conclusions

Inorganic analysis of solid, liquid and gaseous samples from the Paraho semiworks retort was completed by using a multitechnique approach. Most of the techniques used instrumental methods, so that interferences from chemically complex matrices could be minimized.

The data were statistically analyzed both to determine the precision of each method and to see how closely the various techniques compared. The data were also used to construct mass balances for 31 trace and major elements in the various effluents, including the offgas for the Paraho retort operating in the direct mode. The computed mass balances show that ~1% or greater fractions of the As, Co, Hg, N, Ni, S, and Se are released during retorting and redistributed to the product shale oil, retort water, or product offgas. The fraction for these seven elements ranged from almost 1% for Co and Ni to ~50% for Hg and N.

Approximately 20% of the S and 5% of the As and Se are released. The mass balance redistribution during retorting for Al, Fe, Mg, V, and Zn was observed to be no greater than 0.05%. These mass balance figures are generally in agreement with previous mass balance studies made for a limited number of elements on laboratory or smaller scale pilot retorts (*1, 2, 12, 13*). It thus appears that several different retorting technologies exhibit common general patterns with respect to redistribution of inorganic species.

Acknowledgment

We are indebted to C. L. Nelson for technical support, C. M. Smyser for editing and typing, and J. C. Laul, K. H. Abel, and K. K. Nielson for helpful discussions. We are also indebted to R. N. Heistand and the rest of the staff of Development Engineering, Inc., for their help and consideration in both obtaining the samples and reviewing the data. Thanks are due to J. P. Fox of Lawrence Berkeley Laboratory for providing some of the mercury analyses and to LECO Corp. for help with some of the carbon, hydrogen, nitrogen, and sulfur analyses.

Literature Cited

(1) Fox, J. P.; McLaughlin, R. D.; Thomas, J. F.; Poulson, R. E. *Oil Shale Symp. Proc.* **1977,** *10*.

(2) Schendrikar, A. D.; Faudel, G. B. *Environ. Sci. Technol.* **1978,** *12*, 332–4.

(3) Jones, J. B., Jr. *Q. Colo. Sch. Mines* **1976,** *71*, 39–48.

(4) Fox, J. P.; Mason, K. K.; Duvall, J. J. *Oil Shale Symp. Proc.* **1979,** *12*.

(5) Fruchter, J. S.; Wilkerson, C. L.; Evans, J. C.; Sanders, R. W.; Abel, K. H. Richland, WA, 1979, Pacific Northwest Laboratories Report PNL-2945.

(6) Fox, J. P.; Evans, J. C.; Wildeman, T. R.; Fruchter, J. S. Berkeley, CA, 1980, Lawrence Berkeley Laboratory Report LBL-8901.

(7) Dybczynski, R.; Tugsavul, A.; Suschny, O. Vienna, Austria, 1978, International Atomic Energy Agency Report IAEA/RL/46.

(8) Wildeman, T. R.; Heistand, R. N. "Trace Element Variations in an Oil Shale Retorting Operation"; American Chemical Society: Washington, D.C., 1979; Fuel Division Reprints, 24.

(9) Moore, J. W.; Dunning, H. N. *Ind. Eng. Chem.* **1955,** *47*, 1440–4.

(10) Sullivan, R. F.; Frumkin, H. A.; Rudy, C. E.; Chen, H. C. Washington, D.C., 1977, U.S. Department of Energy Report FE-2315-15, p 4.

(11) Donnell, J. R.; Shaw, V. E. *J. Res. U.S. Geol. Surv.* **1977,** *5*, 221–6.

(12) Wildeman, T. "Mass Balance Studies in Oil Shale Retorting" In "Trace Elements in Oil Shale"; Progress Report; June 1, 1975–May 31, 1976. Environmental Trace Substances Research Program, University of Colorado, Colorado State University, and Colorado School of Mines, Feb 1977.

(13) Fruchter, J. S.; Laul, J. C.; Petersen, M. R.; Ryan, P. W.; Turner, M. E. *Adv. Chem. Ser.* **1978,** *No. 170*, 225–89.

Received for review March 31, 1980. Accepted July 1, 1980. This research was supported by the U.S. Department of Energy, Office of the Health and Environmental Research, under Contract EY-76-C-06-1830.

Organic Compounds in an Industrial Wastewater. Their Transport into Sediments

Viorica Lopez-Avila

Midwest Research Institute, 425 Volker Boulevard, Kansas City, Missouri 64110

Ronald A. Hites*

School of Public and Environmental Affairs and Department of Chemistry, Indiana University, 400 East Seventh Street, Bloomington, Indiana 47405

■ The wastewater from a small speciality chemicals manufacturing plant located on the Pawtuxet River (Rhode Island, USA) has contaminated the water and sediment of that river, the Pawtuxet Cove, the Providence River, and (to a lesser extent) the Narragansett Bay. Since the compounds found in this system cover a wide range of functionalities, polarities, and water solubilities, a detailed study of this system has allowed us to assess the environmental behavior of *several* compound types in *one* aquatic system. We find that the aqueous concentrations of the various compounds follow the rules of simple dilution and that those compounds with the highest octanol-water partition coefficients (log P) are strongly associated with the particulate matter in the water and are found in the sediment at the greatest distance from the plant. The sediment concentrations (C) of a given compound can be predicted from its log P value and from its concentration in the wastewater (C_0) by log $(C_0/C) = b_0 + b_2(\text{dist}/\log P)$ where dist is the distance of the sediment sample from the plant and b_0 and b_2 are constants fitted to the data.

The deposition of potentially toxic organic compounds from the wastewaters of chemical processing plants into aquatic sediments is a known phenomenon. Petroleum hydrocarbons (*1*) and Kepone (*2*) are two examples. Our previous study (*3*) on the environmental impact of a small chemical plant is another. In that study, we identified over 120 different organic compounds in the wastewater of a specialty chemicals manufacturing plant and in the nearby river water and sediment. The maximum concentrations of these compounds were 15 ppm in the wastewater, 0.2 ppm in the river water, and 700 ppm in the river sediment. With the exception of some interesting phenol oxidation reactions (which we will report on elsewhere), there were no chemical transformations observed in this system.

Unlike most sediment studies, in which only one or a few compounds have been identified and quantitated, we measured many compounds covering a wide range of functionalities, polarities, and water solubilities (*3*). This was a rare opportunity to study in *one* aquatic system the behavior of *several* compound types. Therefore, we have carried out a detailed study of this system. This paper summarizes the results of our field measurements and presents some useful generalizations by which the sedimentary behavior of industrial organic compounds can be predicted.

Experimental Section

Sampling Area. The plant setting and the receiving water system are described by the maps shown in Figures 1 and 2. The plant wastewater is discharged after some treatment into the Pawtuxet River, Rhode Island (USA). This river, in turn, enters the brackish Providence River through the Pawtuxet Cove. The Providence River flows into Narragansett Bay, an estuarine area of high recreational and commercial activity. Figures 1 and 2 show the locations of the sampling sites in the Pawtuxet River, the Pawtuxet Cove, the Providence River, and Narragansett Bay. Details of the sampling locations, dates, and types are given in Table I.

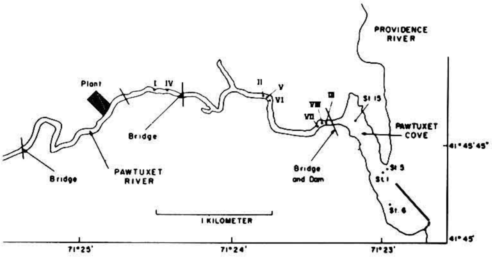


Figure 1. Map of the Pawtuxet River showing the plant location and sediment core sampling sites (I–VIII and stations 1, 5, 6, and 15).

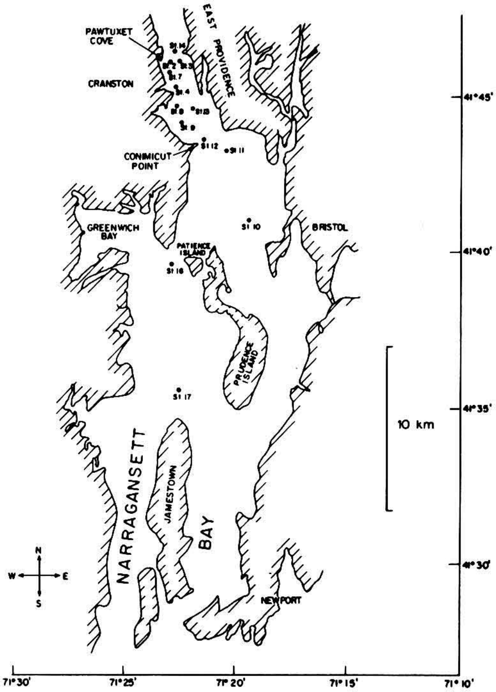


Figure 2. Map of the Providence River and Narragansett Bay showing the sediment core sampling sites (stations 2–17).

Procedures. Wastewater samples were collected in 1-gal, amber glass bottles directly from the clarifier tank. The river water samples were taken 0.5 m below the water surface by divers in 1-gal, amber glass bottles or from bridges with a bucket. Sediment cores were taken by divers with a 6 cm i.d. × 80 cm stainless steel sampler or 24 × 16 × 8 cm bottomless cans. The sediment cores taken with the 6-cm sampler were sectioned into 3- or 4-cm layers at the sampling site and were transferred to 1-qt jars; they were kept frozen until analyzed.

0013-936X/80/0914-1382$01.00/0

The smaller cores taken with the bottomless cans were kept frozen in the can for 3–4 weeks before they were sectioned (6–8-cm layers) and transferred to glass jars. Details about sample preparation and analytical techniques have been given elsewhere (*3, 4*).

Gas chromatography with flame ionization detection, gas-chromatographic mass spectrometry in both electron impact and chemical ionization modes, and high-pressure liquid chromatography with UV detection and mass spectrometric identification were used for the analysis of these samples. Quantitation of the organic compounds was based on peak area measurements relative to external standards. Reported concentrations represent minimum values since they have not been corrected for solvent extraction efficiencies. The extraction recoveries of various compounds spiked into distilled water at ~80 μg/L varied between 85 and 104%. Duplicate analyses had errors of less than ±20% for water samples and less than ±40% for sediment samples, without taking sampling errors into consideration. Under the conditions used, the approximate detection limits for most compounds were 1 ppb for the wastewater, 0.1 ppb for the river water, 0.1 ppm for the river sediment, and 0.05 ppm for the bay sediment.

Aqueous solubilities of the benzotriazoles and the C_{18}–BHT ester (see Figure 3 for structures) were measured by the dynamic coupled column, liquid-chromatographic technique developed by May et al. (*5*). Saturated solutions of the compound to be tested were generated by pumping pure water (high-performance LC distilled water, Baker) at a flow rate of 2 mL/min through a stainless steel column (60 cm × 7.8 mm i.d.) packed with 60/80 mesh silane-treated glass beads coated with the compound to be tested. The coating of the beads with the compound was done by adding 20 g of beads to 200 mL of a 0.1% methylene chloride solution and removing the solvent under vacuum with rotation. Before any measurements were taken, 500–700 mL of water was pumped through the generator column to remove fine particles and equilibrate the column. A known volume of pure water was then passed through the generator column and into the analytical column (3.9 mm i.d. × 30 cm μ-Bondapak-C_{18}, 10 μm, Water Associates) where the compound to be tested was retained. Elution of the test compound from the analytical column was done under gradient elution conditions using a combination of acetonitrile and water.

For the more water soluble compounds (the trichlorodiphenyl ether and the triazine), the method consisted of equilibrating a mixture of the compound to be tested with water until saturation was achieved. The solutions were then filtered through precleaned Whatman GF/F glass fiber filters (0.7 μm), and the filtrates were extracted with methylene chloride at pH 7. This method was also used to measure the solubility of stearyl alcohol. The solubility of phenylbutazone was obtained from the literature (*6*). All solubilities are given in Table II as log *S*.

The *n*-octanol/water partition coefficients (expressed as log *P*) were calculated from the water solubilities by using a correlation published by Chiou et al. (*7*):

$$\log P = 5.00 - 0.670 \log S \qquad r = 0.985 \qquad (1)$$

where *S* is in μmol/L. The regression used to establish this equation extended over a factor of 10^8 for solubility and 10^6 for partition coefficient. The log *P* value of diphenyl ether was taken from the literature (*8*); log *P* values for dibenzoazepine and the phenylnaphthylamine were calculated from a correlation that we established between the high-performance LC

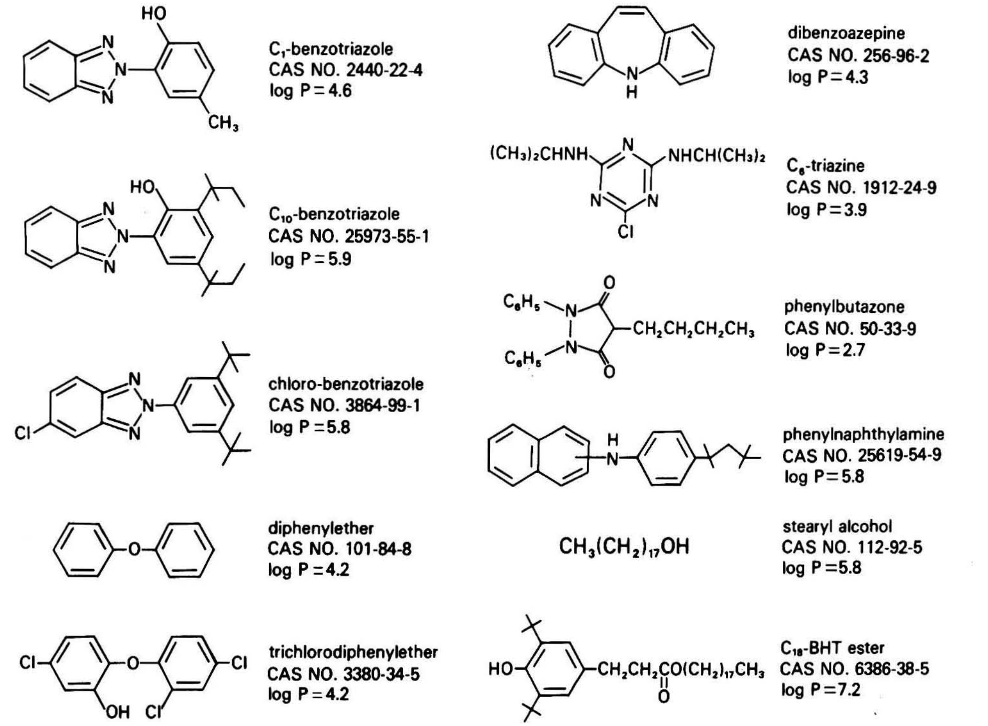


Figure 3. Structures, abbreviated names, Chemical Abstracts Service registry numbers (CAS No.), and octanol–water partition coefficients (log *P*) for the 11 compounds studied.

Table I. Sampling Locations in the Pawtuxet River, the Providence River, and Narragausett Bay

sample no.	date	sample location	type of sample	depth of water, m	station identification
I	9/19/77	71° 24′ 30″ 41° 46′ 10″	sediment core (36 cm) water	1	Pawtuxet River (near plant)
II	9/19/77	71° 23′ 50″ 41° 46′ 07″	sediment core (30 cm) water	2	Pawtuxet River (1 km downstream from the plant)
III	9/19/77	71° 23′ 22″ 41° 45′ 55″	sediment core (12 cm) water	2	Pawtuxet River (near dam)
IV	6/26/78	71° 24′ 25″ 41° 46′ 10″	sediment core (42 cm) water	1	Pawtuxet River (near plant)
V	6/26/78	71° 23″ 45″ 41° 46″ 07″	sediment core (51 cm) water	2	Pawtuxet River (1 km downstream from the plant)
VI	6/26/78	71° 23′ 42″ 41° 46′ 05″	sediment core (54 cm) water	2	Pawtuxet River (1 km downstream from the plant)
VII	6/26/78	71° 23′ 20″ 41° 45′ 53″	sediment core (39 cm) water	2	Pawtuxet River (near dam)
VIII	6/26/78	71° 23′ 17″ 41° 45′ 55″	sediment core (68 cm) water	2	Pawtuxet River (near dam)
1	6/28/77	71° 23′ 13″ 41° 45′ 36″	sediment core (18 cm) water	2.5	Pawtuxet Cove
2	6/28/77	71° 22′ 51″ 41° 45′ 40″	sediment core (21 cm) water	3.5	head of channel, entering Pawtuxet Cove
3	6/28/77	71° 22′ 25″ 41° 45′ 41″	sediment core (21 cm) water	3.5	near Sabin Point, east of Pawtuxet Cove
4	6/28/77	71° 22′ 24″ 41° 41′ 48″	sediment core (21 cm) water	4.5	near Gaspee Point
5	7/29/77	71° 23′ 13″ 41° 45′ 36″	sediment core (35 cm)	3.5	Pawtuxet Cove exit
6	7/29/77	71° 23′ 09″ 41° 45′ 26″	sediment core (18 cm)	2.5	inside Pawtuxet Cove
7	7/29/77	71° 22′ 44″ 41° 45′ 15″	sediment core (16 cm)	3	buoy 31
8	7/29/77	71° 22′ 28″ 41° 44′ 20″	sediment core (19 cm)	4.5	buoy 27
9	7/29/77	71° 21′ 57″ 41° 43′ 23″	sediment core (21 cm)	7.5	buoy 23
10	9/19/77	71° 19′ 20″ 41° 40′ 52″	sediment core (20 cm)	7	Ohio Ledge
11	9/19/77	71° 20′ 12″ 41° 42′ 47″	sediment core (13 cm)	7	buoy N-16
12	9/19/77	71° 21′ 11″ 41° 43′ 10″	sediment core (14 cm)	11	Conimicut Point
13	9/19/77	71° 21′ 57″ 41° 44′ 19″	sediment core (18 cm)	11	buoy N-28
14	9/19/77	71° 22′ 42″ 41° 45′ 55″	sediment core (20 cm)	6	buoy N-2
15	9/19/77	71° 23′ 07″ 41° 45′ 51″	sediment core (9 cm)	3	inside Pawtuxet Cove
16	9/19/77	71° 23′ 00″ 41° 38′ 10″	sediment core (21 cm)	9	Patience Island
17	9/19/77	71° 23′ 40″ 41° 35′ 00″	sediment core (21 cm)	11	north of Jamestown

retention times (expressed as log t_r) and partition coefficients calculated from solubilities:

$$\log P = -0.54 + 4.6 \log t_r \qquad r = 0.980 \qquad (2)$$

Similar correlations have been reported previously (*9*). All of the resulting log *P* values are summarized in Table II.

Results and Discussion

Several hundred quantitative measurements were made on this river and bay system. These data were obtained as a function of specific compound, distance from the chemical plant, depth in core, and date. It would be very difficult to present all of these raw data in a format which makes them comprehensible to the reader. We have, therefore, chosen to present summary data abstracted from the raw information. Furthermore, since only a few of the many compounds found in this environmental system either occur throughout the system or are present at relatively high concentrations, we will limit our attention in this paper to eleven compounds. Figure 3 gives the structures of these compounds and assigns an abbreviated name to them. The reader is referred to our previous paper on this system (*3*) for a discussion of the industrial significance of these particular compounds. Figure 3 also gives the logarithm of the octanol–water partition coefficients of these compounds and their Chemical Abstracts Service registry numbers. All of the individual measurements for these eleven compounds and for many others are available (*4*). For example, anyone interested in the concentration of a specific compound at a particular station as a function of depth in the core may obtain the individual values elsewhere (*4*).

An additional 32 compounds, not reported previously (*3*), were identified in samples taken from the river and estuary system between 1977 and 1978. A list of these compounds; their concentration ranges in the wastewater, river water, and

Table II. Summary of Solubilities, High-Performance LC Retention Times,[a] and Octanol–Water Partition Coefficients of the 11 Compounds

	log S, μmol/L	log t_r, min	log P
C_1-benzotriazole	0.551	1.15	4.6
C_{10}-benzotriazole	−1.37	1.47	5.9
chlorobenzotriazole	−1.21	1.40	5.8
diphenyl ether			4.2[b]
trichlorodiphenyl ether	1.25	1.12	4.2
dibenzoazepine		1.06	4.3[c]
C_6-triazine	1.57	0.92	3.9
phenylbutazone	3.36[d]	0.68	2.7
phenylnaphthylamine		1.38	5.8[c]
stearyl alcohol	−1.26		5.8
C_{18}–BHT ester	−3.33	1.59	7.2

[a] High-performance LC conditions: 3.9 mm i.d. × 30 cm, μ-Bondapak-C_{18}, 10 μm, CH_3CN/H_2O. [b] Reported in ref *8*. [c] Calculated from log t_r − log P correlation. [d] Reported in ref *6*.

sediment samples; and the identification method are given in Table III. Concentration ranges are also reported for several compounds which were identified previously (*3*), but for which no concentration data were available at that time.

Water Analyses. Table IV gives the average water concentrations for the 11 compounds. These are geometric averages of two to five values measured at the specified locations at different times. The geometric average was selected because it is less sensitive to anomalously high or low measurements; but, in almost all cases, the geometric average, the arithmetic average, and the median did not differ from one another by more than 30%. We see that the C_1- and C_{10}-benzotriazoles, the trichlorodiphenyl ether, stearyl alcohol, the C_{18}–BHT ester, and the phenylnaphthylamine were discharged at levels above 1000 ppb. Others appear in the wastewater at lower but consistent levels.

The dilution factor of a wastewater in a river is the ratio of river to wastewater flows. The wastewater discharge rate was regulated at 4.8 × 10^6 L/day (*3*), and the annual average Pawtuxet River flow rate is 1300 × 10^6 L/day (*10*). This is a dilution factor of 270. We calculated river water concentrations from this dilution factor and from the wastewater concentrations; the resulting values are given in Table IV in the last column.

With the exception of the river water sample taken near the plant, the river water and cove water concentrations are all within experimental error of the calculated value. This implies that the water concentrations up to the outlet of the cove (see map, Figure 1) are directly related to the concentrations discharged by the plant. In all cases, the water concentration nearest the plant is somewhat higher than predicted. This is probably because contaminated, suspended material is carried over from the waste treatment system and analyzed as part of the water.

Since the Providence River is a tidal area, no average flows are available. Thus, we cannot predict an expected concentration. In general, the Providence River concentrations are about a factor of 5 lower than the Pawtuxet River and Cove values. Certainly, the dilution effect is at least this large.

In summary, the water data hold no surprises. The aquatic concentrations of the compounds discussed here follow the rules of simple dilution in the Pawtuxet River and Cove and, presumably, in the Providence River.

Sediment Analyses (River). Although analyses of grab sediment samples indicated the accumulation of several organic compounds in the river sediment (*3*), these data could not provide reliable information about this effect. This information could only be obtained from sediment cores. Therefore, eight sediment cores were taken by divers at three locations in the river (see Figure 1). The core sites were selected for an abundance of fine-grained material, since these would be most likely to give information about accumulation of the industrial compounds.

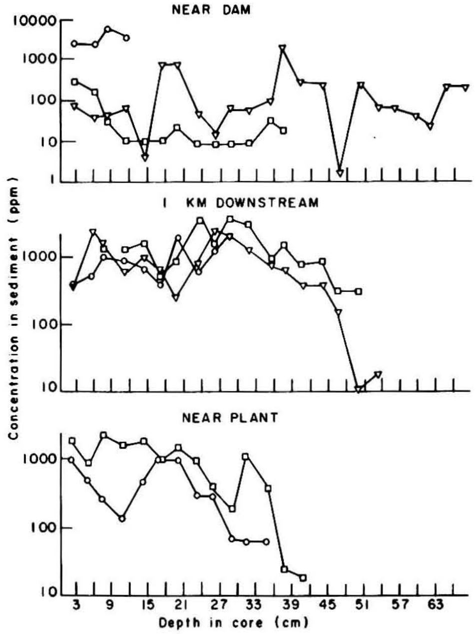


Figure 4. C_1-benzotriazole concentration profiles in Pawtuxet River sediment cores.

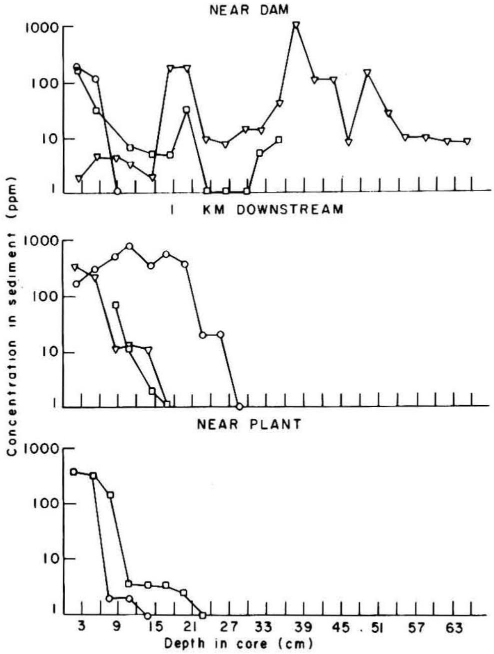


Figure 5. C_{10}-benzotriazole concentration profiles in Pawtuxet River sediment cores.

Table III. Summary of New Compounds Identified in the Pawtuxet River Study

compd	concn range, ppm [d]					identification method [e]
	wastewater	river water	estuary water	river sediment	estuary sediment	
			Nitrogen-Containing Heterocyclics			
5-(2-aminoethyl)dibenzo[*b*,*f*]-azepine	0.01–1.6 (5)	0.002–0.005 (6)	0.001 (1)	ND	ND	GC/MS (EI and CH_4Cl) HRMS
2-(2′-hydroxy-*tert*-amylphenyl)-2*H*-benzotriazole	0.1 (1)	ND	ND	1–5 (5)	ND	GC/MS (EI) HRMS
2-(hydroxy-*tert*-butylmethyl-phenyl)-5-chloro-2*H*-benzotriazole	ND	ND	ND	2–25 (8)	ND	GC/MS (EI) HRMS
2-chloro-4-ethylamino-6-iso-propylamino)-*s*-triazine	ND	ND	ND	3–1400 (20)	ND	GC/MS (EI)
2-chloro-4,6-bis(ethylamino)-*s*-triazine	ND	ND	ND	2–1600 (26)	ND	GC/MS (EI)
methylquinoxaline	0.01–0.03 (4)	<0.001 (7)	0.0001–0.0004 (4)	ND	ND	GC/MS (EI)
dimethylquinoxaline	0.01–0.05 (4)	0.001–0.004 (7)	0.0001–0.004 (4)	ND	ND	GC/MS (EI)
			Amines			
$C_8H_{17}N$ [b]	0.3–50 (2)	0.04 (1)	0.010 (1)	ND	ND	GC/MS (EI and CH_4Cl) HRMS
$C_{12}H_{25}N$ [b]	0.1–2 (2)	0.003–0.010 (4)	0.002 (1)	ND	ND	GC/MS (EI and CH_4Cl) HRMS
N-phenylnaphthylamine [c]	0.04–0.5 (3)	0.002–0.007 (4)	ND	1–5 (3)	ND	GC/MS (EI and CH_4Cl) HRMS
N-(*tert*-butylphenyl)naphthyl-amine	0.01–0.4 (4)	0.001–0.003 (8)	ND	ND	ND	GC/MS HPLC/MS (EI and CH_4Cl) HRMS
N-((2,2,3,3-tetramethybutyl)-phenyl)naphthylamine	0.5–1.7 (5)	0.002–0.030 (8)	0.0002–0.012 (8)	2–260 (53)	0.1–67 (26)	GC/MS HPLC/MS (EI and CH_4Cl) HRMS
N-(C_{12}-phenyl)naphthylamine	*a*	ND	ND	ND	ND	HPLC/MS (EI) HRMS
$C_{10}H_{16}N_4$ [b]	0.07 (1)	0.001–0.003 (8)	ND	ND	ND	GC/MS (EI and CH_4Cl) HRMS
			Sulfur-Containing Compounds			
(toluidinesulfonyl)phenol	ND	ND	ND	1–450 (60)	ND	GC/MS HPLC/MS (EI and CH_4Cl) HRMS
2,4′-sulfonylbis(phenol)	*a*	ND	ND	ND	ND	HPLC/MS (EI) HRMS
(methylthio)benzothiazole	0.01–0.05 (3)	0.001–0.003 (3)	ND	ND	ND	GC/MS (EI) HRMS
benzothiadiazole	0.02 (1)	0.002 (1)	ND	ND	ND	GC/MS (EI)
			Phosphorus Containing Compound			
diphenyl octyl phosphate	ND	ND	ND	2–360 (46)	ND	GC/MS (EI and CH_4Cl) HRMS
			Oxygen-Containing Compounds			
nitrophenol	0.005 (1)	ND	ND	ND	ND	GC/MS (EI)
tert-amylphenol	0.01–0.02 (2)	<0.001 (2)	ND	1–5 (5)	ND	GC/MS (EI)
methoxydi-*tert*-butylphenol [c]	ND	ND	ND	1–5 (5)	ND	GC/MS (EI and CH_4Cl) HRMS
di-*tert*-butylnitrophenol	0.050 (1)	0.001–0.005 (10)	ND	ND	ND	GC/MS (EI and CH_4Cl) HRMS
di-*tert*-butylcyanophenol [c]	ND	ND	ND	1–15 (13)	0.2–6 (6)	GC/MS (EI and CH_4Cl) HRMS
di-*tert*-amylcyanophenol	0.02 (1)	<0.001 (1)	ND	1–10 (15)	0.1–12 (10)	GC/MS (EI and CH_4Cl)
di-*tert*-amyl(cyanomethyl)-phenol	0.02 (1)	<0.001 (1)	ND	1–5 (10)	ND	GC/MS (EI and CH_4Cl)
(2,6-di-*tert*-butyl-*p*-benzoquinonemethide)-acetic acid	0.002 (1)	0.007–0.06 (13)	0.002–0.009 (3)	ND	ND	GC/MS (EI and CH_4Cl) HRMS
n-propyl 1-(carboxymethyl)-3-(3′,5′-di-*tert*-butyl-4′-hydroxyphenyl)propionate	460 (1)	0.002–0.006 (8)	ND	1–660 (42)	<0.1 (4)	GC/MS (EI and CH_4Cl) HRMS
			Halogenated Compounds			
(trifluoromethyl)aniline	0.01 (1)	ND	ND	ND	ND	GC/MS (EI)
chlorophenyl isocyanate [c]	ND	ND	ND	0.1–10 (79)	1–5 (3)	GC/MS (EI and CH_4Cl) HRMS
chloro(trifluoromethyl)-phenyl isocyanate [c]	ND	ND	ND	0.5–50 (79)	0.1–5 (7)	GC/MS (EI and CH_4Cl) HRMS
4,4′-dichlorocarbanilide [c]	ND	ND	ND	*a*, NQ (77)	NQ (3)	HPLC/MS (EI) HRMS
4,4′-dichloro-3-(trifluoromethyl)-carbanilide [c]	ND	ND	ND	*a*, NQ (79)	NQ (8)	HPLC/MS (EI) HRMS

Table III (*Continued*)

compd	concn range, ppm[d] wastewater	river water	estuary water	river sediment	estuary sediment	identification method[e]
4,4′-dichloro-3,3′-bis-(trifluoromethyl)carbanilide[c]	ND	ND	ND	*a*, NQ (79)	NQ (3)	HPLC/MS (EI) HRMS
N-(4-chlorophenyl)-isopropyl carbamate	ND	ND	ND	0.5–10 (79)	0.1–0.2 (14)	GC/MS (EI and CH_4CI) HRMS
N-(4-chloro-3-trifluoromethyl-phenyl)isopropyl carbamate	ND	ND	ND	0.5–20 (79)	0.1–0.2 (14)	GC/MS (EI and CH_4CI) HRMS
trichlorodibenzofuran[c]	a, NQ (6)	NQ (10)	NQ (7)	NQ (9)	NQ (13)	GC/MS (EI)
trichlorodiphenyl ether	0.01–0.02 (2)	ND	ND	ND	ND	GC/MS (EI)
tetrachlorodiphenyl ether	0.01–0.02 (3)	ND	ND	ND	ND	GC/MS (EI)
bis(dichlorophenoxychloro-phenyl) ether[c]	*a* (2)	*a* (1)	ND	ND	ND	HPLC/MS (EI)
2-chloro-4-(2,4-dichlorophen-oxy)phenyl 4-chloro-2-hydroxyphenyl ether	*a* (2)	ND	ND	ND	ND	HPLC/MS (EI)
2-chloro-4-[2-chloro-4-(2,4-dichlorophenoxy)-phenoxy]phenyl 4-chloro-2-hydroxyphenyl ether	*a* (2)	ND	ND	ND	ND	HPLC/MS (EI)

[a] The compound was isolated in a high-performance LC fraction and identified by mass spectrometry. [b] Molecular formula established by high-resolution mass spectrometry (HRMS). [c] Reported in ref *3*. [d] The numbers given in parentheses represent the occurrences in which these compounds were found. The maximum number of occurrences is 6 for the wastewater samples, 18 for river water samples, 9 for estuary waters, 108 for river sediment cores, and 51 for estuary sediment cores. ND = Compound not detected in the sample. NQ = Not quantitated. [e] HRMS = high-resolution mass spectrometry; HPLC = high-performance liquid chromatography.

Table IV. Summary of Water Concentrations (ppb) of the 11 Compounds at the Various Locations[a]

	plant's waste water	Pawtuxet River			Pawtuxet Cove		Providence River			calcd Pawtuxet conc[b]
		near plant	med river	near dam	sta 15	sta 1	sta 2	sta 3	sta 4	
C_1-benzotriazole	4000	80	30	30	40	30	10	2	1	15
C_{10}-benzotriazole	3000	40	10	10	9	8	2	0.5	0.6	10
chlorobenzotriazole	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
diphenyl ether	40	0.3	0.2	0.2	0.2	0.1	0.1	ND	ND	0.15
trichlorodiphenyl ether	4000	40	10	10	10	20	5	2	0.6	15
dibenzoazepine	60	4	1	1	0.2	0.4	0.1	ND	ND	0.2
C_6-triazine	200	5	2	2	1	5	2	1	1	0.7
phenylbutazone	700	10	8	5	2	8	2	0.9	0.9	3
phenylnaphthylamine	1000	10	1	1	0.5	2	0.2	0.2	0.2	4
stearyl alcohol	1000	20	10	10	10	3	3	2	2	4
C_{18}-BHT ester	2000	20	10	10	10	10	2	0.4	0.1	7

[a] All water measurements were made without filtration of sample. ND = not detected. [b] Calculated from the wastewater concentration divided by the dilution factor of 270 (see text).

In the absence of vertical movement of compounds in the sediment, one can use information about the production history of a certain compound to analyze the core measurements and to estimate a net sedimentation rate in the river. For example, information from the chemical plant indicates that the C_1- and C_{10}-benzotriazoles have been manufactured since 1961 and 1970, respectively, and that the chlorobenzotriazole was manufactured between 1963 and 1972. Although there is some scatter, as the depth in the core increases, a sharp decrease in the concentration of the C_1-benzotriazole was found to occur at ~30 cm in the cores taken near the plant (see Figure 4). Since this compound was manufactured at the chemical plant since 1961, the value for the sedimentation rate at this location is 1.8 cm/yr. This value approximately agrees with the core data for the C_{10}-benzotriazole which has been manufactured since 1970 (see Figure 5). If the sedimentation rate of 1.8 cm/yr is correct, we would expect to find none of the chlorobenzotriazole in the top 10 cm of the core. This compound, however, was detected above this level in the core taken near the plant (see Figure 6), implying possible vertical movement of this compound in the bed sediment. There is insufficient environmental data to determine the mechanisms, if any, which cause the vertical movement of this compound in the river sediments. However, vertical mixing of the sediment layers by benthic organisms is possible.

Data for sediment cores taken 1 km downstream from the chemical plant are in good agreement with the production histories of these three compounds and indicate a higher sedimentation rate. For example, the sedimentation rate estimated from the core profile of the C_1-benzotriazole is 3 cm/yr [50 cm/(1978–1961)], and the sedimentation rates estimated from the chloro- and C_{10}-benzotriazole data are 3.4 cm/yr.

The variation in concentration over more than three orders of magnitude for these compounds in the area near the dam

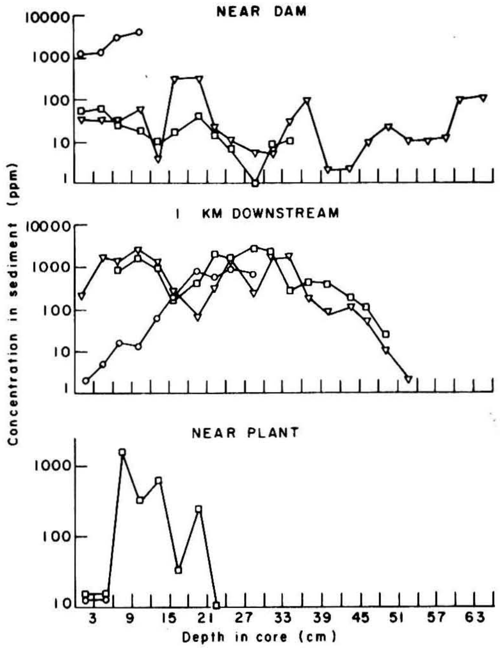


Figure 6. Chlorobenzotriazole concentration profiles in Pawtuxet River sediment cores.

Table V. Particle Size Analysis of Pawtuxet Sediment Cores and Grab Samples[a]

	% particle (by weight)			
particle size µm	core I 9/19/77	core II 9/19/77	core III 9/19/77	grab sample 9/8/76
<53	25	32	18	2.6
53–74	7.6	10	4.5	1.0
74–88	9.5	9.2	4.4	1.4
88–125	20	18	16	4.8
125–150	7.8	6.3	2.9	2.6
150–250	11	8.8	23	5.7
250–300	2.6	2.2	7.3	2.7
300–600	10	9.5	13	0.7
>600	6	4.3	11	78

[a] By dry sieving extracted sediment.

(see Figures 4–6) was mainly due to the presence of "tar balls" which consisted entirely of organic compounds manufactured by the plant (*3*). They were usually extracted along with the sediment, but some were isolated from the sediment and extracted separately. About 25% of such a tar ball is represented by GC volatile material. The abundance of "tar balls" in the sediment was estimated to be 2–3% by weight. This is a very rough estimate based on a particular section of one core. One explanation for the presence of these "tar balls" could be sludge coming from the chemical plant. If these sludges (which consist mostly of organics) entered the river, the water would have transported them downstream to the dam, where they may have agglomerated with sand particles because of turbulence.

Sediment core analyses indicated that most of the compounds were, in fact, accumulated into the bed sediment at higher concentrations than observed in the grab samples. This increase in concentration was attributed to the different type of sediment present in the cores. As indicated, the core sites were specifically selected for abundance of fine-grained material, whereas the grab samples were mostly coarse sand and gravel (see Table V). This particle size analysis indicates that the river sediment in the area under study is dominated by sand-size particles in the center of the river, while finer sediment is deposited into the marginal areas. An inorganic analysis of these sediments (see Table VI) indicates that the concentrations of S, Si, Al, and Fe were uniform. Total carbon concentrations increase downstream from the point of the discharge of the industrial wastewater; this may indicate the effects of the industrial effluent.

Table VI. Inorganic Analysis of the Pawtuxet Sediment (%)[a]

element	core I (0–9 cm) 9/19/77	core II (0–9 cm) 9/19/77	core III (0–9 cm) 9/19/77
total carbon	3.4	5.7	6
inorganic carbon	0.03	0.03	0.03
SiO_2	58	61	64
Al_2O_3	12	12	12
Fe_2O_3	4	3.8	4
S	0.3	0.3	0.5

[a] By Galbraith Laboratories, Knoxville, TN.

The core concentrations of the 11 major compounds in the sediment have been abstracted and are summarized in Table VII. Although there is some uncertainty resulting from condensing core profiles such as shown in Figures 4–6 into a single number, we feel the values given in Table VII are representative of the sediment concentrations in the river and will be very useful in getting an overall picture of this river system.

Sediment Analyses (Estuary). Because of the apparently high environmental concentration and persistence of most of the compounds observed in this river, it was anticipated that many of these industrial organic compounds would be transported to significant distances from the effluent discharge site. Since analyses of water samples taken from the estuary system indicated the presence of many of these compounds, sediments from that area were also analyzed for organic compounds.

Sediment cores were taken by divers at 4 locations in the Pawtuxet Cove and 13 stations in the Providence River and Narragansett Bay. Concentrations of the organic compounds identified in these samples are given elsewhere as a function of depth and location (*4*). There is much less variability in the core profiles in the cove and the bay than in the river. To summarize these concentrations, we have lumped stations 1, 5, 6, and 15 together to get an average cove value; stations 2, 3, 7, and 14 for a "near" Providence River value; stations 4, 8, 9, and 13 for a "far" Providence River value; and stations 10–12, 16, and 17 for a Narragansett Bay value. The summary concentrations for the 11 compounds are reported in the last four columns of Table VII. We emphasize once again that all of the individual values are reported elsewhere (*4*).

Almost all compounds identified in the Pawtuxet River were detected in the sediment core taken at station 15, which was located in the Pawtuxet Cove ~100 m from the dam. Fewer of the plant related organic compounds were detected in the Providence River and Narragansett Bay. Their concentrations decrease both with depth in the sediment and with increasing distance from the discharge. No C_1-benzotriazole was detected in the sediment cores from the Narragansett Bay. The other two benzotriazoles were present in most of these cores at concentrations of less than 1 ppm. The C_{18}–BHT ester was detected at station 17, which is situated north of Jamestown, at a level of 1 ppm.

Filtration Studies. When the mechanism of transport of the organic compounds to the river and estuary sediment was

Table VII. Summary of Sediment Concentrations (ppm) of the 11 Compounds at the Various Locations[d]

	log P	C_0, ppb	Pawtuxet River near plant	Pawtuxet River mid river	Pawtuxet River near dam	Pawtuxet Cove	Providence River near[a]	Providence River far[b]	bay[c]
C_1-benzotriazole	4.6	4000	500	800	40	200	10	0.8	ND
C_{10}-benzotriazole	5.9	3000	300	300	70	100	10	5	0.6
chlorobenzotriazole	5.8	~4000[e]	300	400	20	80	20	2	0.5
diphenyl ether	4.2	40	5	4	3	ND	ND	ND	ND
trichlorodiphenyl ether	4.2	4000	100	80	20	ND	ND	ND	ND
dibenzoazepine	4.3	60	ND	ND	ND	ND	ND	ND	ND
C_6-triazine	3.9	200	100	NQ	2	ND	ND	ND	ND
phenylbutazone	2.7	700	<5	ND	ND	ND	ND	ND	ND
phenylnaphthylamine	5.8	1000	60	80	20	20	NQ	0.1	<0.05
stearyl alcohol	5.8	1000	10	10	5	ND	ND	ND	ND
C_{18}-BHT ester	7.2	2000	200	70	20	100	6	2	1
dist from plant (km)			0	1	2	3	5	9	15

[a] Stations 2, 3, 7, 14. [b] Stations 4, 8, 9, 13. [c] Stations 10–12, 16, 17. [d] ND = not detected; NQ = not quantitated because of high scatter. [e] Calculated from past production information.

Table VIII. Ratio of the Compounds in the Particulate Phase to the Dissolved Phase in River and Cove Waters

	river	cove	av	log A[a]	log P
C_1-benzotriazole	0.44	0.19	0.3	−0.52	4.6
C_{10}-benzotriazole	36	12	20	1.3	5.9
trichlorodiphenyl ether	0.20	0.10	0.15	−0.82	4.2
dibenzoazepine	<0.05		<0.05	−1.3	4.3
phenylbutazone	0.1		0.1	−1.0	2.7
phenylnaphthylamine	60		60	1.8	5.8
stearyl alcohol	40	2.0	9	0.95	5.8
C_{18}-BHT ester	500		500	2.7	7.2

[a] log of average ratio.

considered, it became clear that the amount of an individual compound associated with settlable particulates would determine the extent of incorporation of that compound into the sediment. If the fraction of a compound associated with these particulates could be predicted, then the sediment concentrations might also be predictable.

To study this concept, it was necessary to know the concentrations of the organic compounds which were present on the particulate phase of the river water. Thus, river water samples were filtered through 0.7-μm glass fiber filters (Whatman, GF/F), which were previously cleaned by Soxhlet extraction with methylene chloride. The organic compounds on the filter and in the filtrate were extracted, identified, and quantitated. The concentration of the organic compounds retained on the filter given in μg/L (referring to the volume of solution which was filtered and not to the weight of material retained on the filter) was divided by the concentration in the filtrate to get what could be crudely considered an adsorption coefficient. Similar filtration studies were performed with the cove water samples. These data are shown in Table VIII and indicate that some compounds are highly adsorbed on the particulate matter in the river and cove water. For example, the C_{18}–BHT ester has a concentration ratio of 500.

Examination of Table VIII shows that the most lipophilic compounds (as measured by their octanol–water partition coefficients) are the most highly associated with the particulate or adsorbed phase. In fact, there is a very high correlation between the logarithm of the adsorption ratio (see Table VIII) and log P values; the correlation coefficient is 0.911, which is significant at $p < 0.005$. This suggests that many of these compounds have high affinities for the hydrophobic sites on the particulate matter and that log P values are a useful measure of this behavior.

The utility of log P values for this prediction should not be surprising. These values have been correlated with ecological magnification (*11*), soil–water partitioning (*12*), sediment–water partitioning (*13*), toxic effects (*14*), and bioconcentration (*15*). Because of this utility, log P is now a parameter which might be measured for compounds submitted to the U.S. Environmental Protection Agency under premanufacturing notification regulations of the Toxic Substances Control Act (*16*).

Prediction of Sediment Concentrations from log P Values. Examination of the data in Table VII qualitatively indicates two things: (a) there is a rather rapid falloff in sediment concentration with increasing distance from the plant; (b) those compounds with the highest octanol–water partition coefficients are found at the greatest distance from the plant. For example, the C_{18}–BHT ester and the C_{10}- and chlorobenzotriazoles are the only compounds found in the bay cores; these have log P values of 7.2, 5.9, and 5.8, respectively. Let us address these two qualitative observations separately and see whether a more quantitative interpretation can be developed.

Expanding on point (a) above, we see that at high sediment concentrations near the plant, there is a high concentration gradient vs. distance; but at low concentrations far from the plant, there is little decrease in sediment concentration with increasing distance. Thus, for a given compound, the sediment concentration gradient is proportional to the sediment concentration at that distance

$$-\,\mathrm{d}C/\mathrm{d(dist)} = kC \qquad (3)$$

where C is the sediment concentration (in ppm) and dist is the distance from the wastewater input (in kilometers). Assuming that the sediment concentration at dist = 0 is proportional to the initial concentration of that compound in the wastewater (C_0 in ppb), we integrate eq 3 and get

$$-\ln C = k(\mathrm{dist}) - \ln k'C_0 \qquad (4)$$

Changing to common logarithms and rearranging terms, we get a simple first-order equation of the form

$$\log (C_0/C) = b_0 + b_1(\mathrm{dist}) \qquad (5)$$

where b_0 and b_1 are constants that can be obtained from a least-squares fit of the data.

We carried out such a statistical analysis for the compounds in Table VII and obtained a family of lines with slopes (b_1) which were dependent on the nature of the compound. Highly

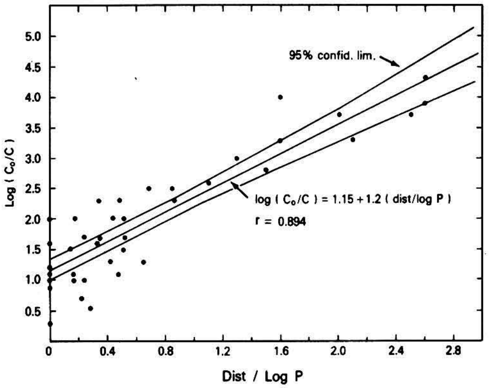


Figure 7. Plot of log (C_0/C) vs. dist/log P. Data were derived from Table VII; the least-squares fitted line and its 95% confidence limits are shown.

lipophilic compounds such as the C_{18}–BHT ester (log $P = 7.2$) had lower slopes ($b_1 \simeq 0.18$) than less lipophilic species such as the trichlorodiphenyl ether (log $P = 4.2$, $b_1 \simeq 0.33$). In fact, the product of the slope and the log P value was almost constant at 1.3 with a relative standard deviation of 13%. Thus, we can say

$$b_1 \log P = b_2 \tag{6}$$

where b_2 is a constant. Substituting this into eq 5, we have

$$\log (C_0/C) = b_0 + b_2(\text{dist}/\log P) \tag{7}$$

We can test the validity of this model by a least-squares fit between log (C_0/C) and dist/log P. All of the data in Table VII were converted to these two variables and are plotted in Figure 7. The fitted line is

$$\log (C_0/C) = 1.15 + 1.2(\text{dist}/\log P) \tag{8}$$

The correlation coefficient is 0.894 which is significant at $p \ll 0.001$ for 42 degrees of freedom. This equation and its 95% confidence limits are also shown in Figure 7.

Equation 8 can be quite useful. For example, we can use it to calculate the maximum distance which compounds discharged from the plant will reach. Let us assume the following: (a) the concentrations in the wastewater (C_0) are at most 5000 ppb; (b) the detection limit of our sediment analyses (C) is 0.05 ppm; (c) the maximum log P value of any discharged compound is 8. Thus, log (C_0/C) = 5.0; therefore, dist/log P = 3.21 and (for log P = 8) dist = 26 km. This distance from the discharge point is still within Naragansett Bay. It would, therefore, be very difficult to detect any sedimentary effect of this chemical plant outside of Narragansett Bay.

We can also use eq 8 to see which compounds should be above our detection limit (C = 0.05 ppm) at our composite Narragansett Bay station (dist = 15 km). Assuming an average discharge concentration of 2000 ppb, we calculate that log (C_0/C) = 4.6; therefore, dist/log P = 2.88 and (for dist = 15) log P = 5.2. Thus, only those compounds with log $P > 5.2$ should be found in the mid to lower Narragansett Bay. This is in agreement with our experimental findings.

Lastly, we would like to suggest that the functional relationship given in eq 8, namely, the linear relationship between log (C_0/C) and dist/log P, is generally applicable. We believe that this type of function can be widely used for the analysis of data on organic compounds in sediments and for the prediction of the sedimentary fate of organic compounds discharged from a point source.

Acknowledgment

The cooperation of the company officials and plant personnel is appreciated. Peter Murphy, Jeff Rosen, and Walt Galloway from the EPA Narragansett Laboratory helped with the sampling; we are grateful to them.

Literature and Notes

(1) National Academy of Sciences, "Petroleum in the Marine Environment," Washington, D.C., 1975.
(2) National Academy of Sciences, "Kepone, Mirex, Hexachlorocyclopentadiene: An Environmental Assessment," Washington, D.C., 1978.
(3) Jungclaus, G. A.; Lopez-Avila, V.; Hites, R. A. *Environ. Sci. Technol.* **1978,** *12,* 88.
(4) Lopez-Avila, V.; Hites, R. A. "Organic Compounds in an Industrial Wastewater: A Case Study of Their Environmental Impact", National Technical Information Service Report No. PB80-124704 (price code A12), 1980.
(5) May, W. E.; Wasik, S. P.; Freeman, D. H. *Anal. Chem.* **1978,** *50,* 175.
(6) "Merck Index", 9th ed., 1976, Article No. 7078.
(7) Chiou, C. T.; Freed, V. H.; Schmedding, D. W.; Kohnert, R. L. *Environ. Sci. Technol.* **1977,** *11,* 475.
(8) Leo, A.; Hansch, C.; Elkins, D. *Chem. Rev.* **1971,** *71,* 525.
(9) Veith, G. D.; Austin, N. M.; Morris, R. T. *Water Res.* **1979,** *13,* 43.
(10) U.S. Department of the Interior, Geological Survey, 1978, Water Data Report MA-RI-78-1.
(11) Coats, J. R.; Metcalf, R. L.; Lu, P.-Y.; Brown, D. D.; Williams, J. F.; Hansen, L. G. *Environ. Health Perspect.* **1976,** *18,* 167.
(12) Chiou, C. T.; Peters, L. J.; Freed, V. H. *Science* **1979,** *206,* 831.
(13) Karickhoff, S. W.; Brown, D. S.; Scott, T. A. *Water Res.* **1979,** *13,* 241.
(14) Hansch, C. *Acc. Chem. Res.* **1969,** *2,* 232.
(15) Neely, W. B.; Branson, D. R.; Blau, G. E. *Environ. Sci. Technol.* **1974,** *8,* 1113.
(16) Bureau National Affairs, *Chemical Regulation Reporter* **1980,** *3,* 1767.

Received for review April 22, 1980. Accepted July 25, 1980. This work has been supported by the U.S. Environmental Protection Agency (Grant No. R806350) and by the National Science Foundation (Grant No. ENV-75-13069).

Factors Influencing the Formation of Haloforms in the Chlorination of Humic Materials

Christopher J. Peters, Robert J. Young, and Roger Perry*

Public Health and Water Resource Engineering Section, Imperial College of Science and Technology, London SW7 2AZ, United Kingdom

■ The reactions with chlorine, under controlled conditions of pH and temperature, of humic and fulvic fractions extracted from the River Thames are described. Chloroform production, monitored by a direct aqueous injection chromatographic technique, indicates that total chloroform is composed of two components: one produced by thermal decomposition of unidentified chlorinated intermediates (residual chloroform) and the other dissolved chloroform. pH is shown to be the dominant factor influencing both the production of total chloroform and the relative proportions of these components. Chloroform production takes place in two phases, the first of which is rapid and strongly pH dependent, whereas the second phase is slower and less dependent on pH. A linear relationship exists between chlorine consumption and total chloroform production. This reaction accounts for only a small proportion of the chlorine consumed. A superficial kinetic treatment is presented with possible reaction pathways.

Introduction

The United States survey on trihalomethanes in potable waters (*1*) stimulated considerable research on this topic, and it is now generally accepted that chlorine reacts with humic materials to form chloroform, with brominated trihalomethanes being produced in addition when bromide is present in the raw water.

Humic material used in this study was extracted from the River Thames. It was composed of ~4% humic acid, 13% hymatomelanic acid, and 83% fulvic acid as opposed to reported studies (*2, 3*) where the humic acid content ranged between 0.1 and 16%. The technique used to extract the humic material from Thames water did not separate the hymatomelanic and humic acid fractions (*2*).

Quantitative comparison of the reactivity of humic and fulvic acids requires material extracted from the same source, as waters from different areas may well contain differing compositions of these acid fractions.

The measurement of the trihalomethanes was carried out by direct aqueous injection (DAI), a method first reported by Nicholson and Meresz (*4*). DAI measures not only the "dissolved" chloroform but also a "residual" chloroform level (see text) which results from the breakdown in the injection port of organochlorine intermediates. Other workers (*5*) in comparing a DAI method of analysis for chloroform in drinking water with head space (*6*) and gas stripping techniques (*7*) have commented on the presence of these intermediates.

The purpose of this paper therefore is to relate the relative contributions of humic and fulvic acid fractions to haloform (principally chloroform) formation and to examine the relationship between residual haloforms and total haloform formation from these acid fractions under conditions generally encountered in water treatment.

Experimental Section

Humic and Fulvic Acids. The humic and fulvic acids isolated from the River Thames by the method of Hall and Packham (*2*) were supplied by the Water Research Centre, UK.

Reaction Vessel and Sampling. A 1-L reaction vessel, illustrated in Figure 1, was used without stirring. Sample withdrawal was organized by injecting nitrogen into the head space, thus displacing the requisite volume of sample for analysis. A high water-to-head space ratio was maintained which minimized evaporative losses of dissolved chloroform (as a percentage of total dissolved chloroform) from solution.

In order to reduce photolytically induced reactions, we enclosed the reaction vessel in a darkened chamber.

Water Chlorination and Chlorine Analysis. Sodium hypochlorite, low in bromine, was used as the chlorinating agent. Chlorine concentration was measured iodometrically by using 25-mL samples as opposed to the 500-mL samples described in the UK standard method (*8*).

Haloform Analysis. Chlorine was quenched before haloform analysis by addition of sodium thiosulfate.

Haloform analysis was carried out with a Hewlett-Packard 5713A gas chromatograph incorporating an electron capture detector, with direct aqueous injection of 5-μL samples. Separation was achieved on a glass column, 4 mm × 1 m, packed with Chromosorb 101 (100–120 mesh) by using 95% argon/5% methane as the carrier gas at a flow rate of 25 mL min^{-1}. The detector temperature was 300 °C and that of the injection port 200 °C. Fine nickel powder (0.3–0.4 g) was introduced before the glass wool packing at the injection end of the analytical column. The column temperature was isothermal at 140 °C for the analysis of chloroform and bromodichloromethane and 180 °C for dibromochloromethane and bromoform.

Dissolved and Residual Chloroform. Total chloroform analysis was evaluated by injection of a 5-μL sample into the chromatograph under the above conditions.

Residual chloroform analysis was carried out by a 5-μL injection of a previously purged water sample (5 mL) under the same conditions. Purging was carried out by using nitrogen at a flow rate of 150 mL min^{-1} for 10 min.

Dissolved chloroform was calculated by difference as total chloroform = residual chloroform + dissolved chloroform.

Results and Discussion

The DAI analytical technique described proved satisfactory for the rapid and reproducible analysis of water samples for chloroform, dichlorobromomethane, dibromochloromethane, and bromoform, with the only sample pretreatment being the addition of a crystal of sodium thiosulfate. The detection limits were as follows: chloroform, 1 μg L^{-1}; bromodichloromethane, 0.5 μg L^{-1}; dibromochloromethane, 1 μg L^{-1}; and bromoform, 2 μg L^{-1}.

Brominated haloforms were not expected to be formed, as sodium hypochlorite, low in bromine, was used as a chlorinating agent. Occasionally, however, relatively high bromodichloromethane (up to 10 μg L^{-1}) levels were detected, and, like chloroform, these were composed of distinct dissolved and residual components. The reduction of the injection port temperature to 140 °C had little effect on the residual chloroform and bromodichloromethane levels. Heating a sample in a digestor for 10 min at 140 °C caused a slight reduction in total chloroform levels, possibly owing to evaporative losses. No residual chloroform was detected, indicating that all the

0013-936X/80/0914-1391$01.00/0 © 1980 American Chemical Society

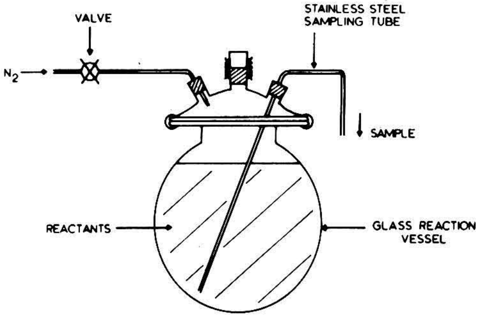


Figure 1. Reaction vessel.

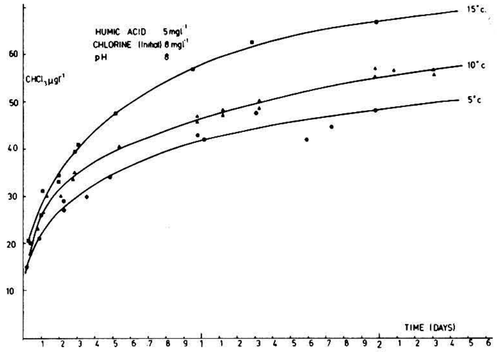


Figure 2. Effect of temperature on dissolved chloroform formation from humic acid at pH 8.

Table I. Ratios of Chloroform Concentrations after 2-Day Reaction

	pH	ratio
$(CHCl_3)_{10\ °C}/(CHCl_3)_{5\ °C}$	6	1.15
	7	1.15
	8	1.15
$(CHCl_3)_{15\ °C}/(CHCl_3)_{10\ °C}$	6	1.29
	7	1.28
	8	1.22

chloroform was removed by purging and that complete breakdown of the dissolved organochlorine intermediate had occurred in the digestor at 140 °C (this temperature being below that normally used in the injection port of the gas chromatograph).

Preliminary studies revealed that a significant loss of haloforms occurred as the reaction progressed. This loss was attributed mainly to evaporation into the head space and subsequent diffusion out of the reaction vessel. Other factors which may have contributed to such losses including adsorption onto the glass walls of the vessel, hydrolytic breakdown, and further reactions of the haloforms could not be experimentally evaluated although it was shown that overall losses of up to 6 $\mu g\ L^{-1}$ for bromodichloromethane and 8 $\mu g\ L^{-1}$ for chloroform per day occurred when using spiked samples in a glass-stoppered flask maintained at 10 °C. Accordingly the reaction vessel and sampling procedure employed were designed so as to minimize evaporative losses.

The presence of nickel powder in the injection port resulted in a "cleaner" chromatogram and more consistent breakdown of intermediates to produce residual chloroform.

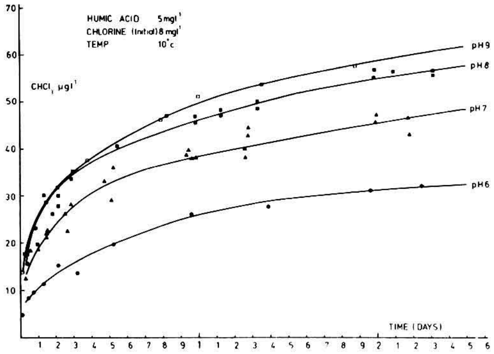


Figure 3. Effect of pH on dissolved chloroform formation from humic acid at 10 °C.

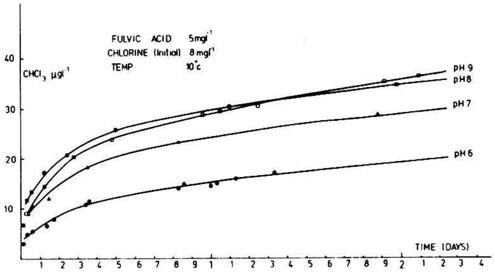


Figure 4. Effect of pH on dissolved chloroform formation from fulvic acid at 10 °C.

It is important to stress that the measurement of dissolved chloroform relied on the nonpurgeability of the organochlorine intermediates and that residual chloroform was formed by breakdown of these intermediates and was not the result of an accelerated reaction with remaining free chlorine as the latter had been quenched by sodium thiosulfate before analysis.

Dissolved Chloroform. Figure 2 shows the relationship between dissolved chloroform formation and temperature, and the appropriate data are summarized in Table I. The activation energy for chloroform production based on these data was calculated to be between 20 and 30 kJ mol^{-1}, a value which compared to the activation energy for the chlorination of polycyclic aromatic hydrocarbons (PAH) (*9*).

The rate of dissolved chloroform production was pH dependent and increased with pH for both the humic and fulvic fractions (Figures 3 and 4).

The trends in chloroform formation from humic and fulvic acids with variations in pH and temperature were similar. There is also a definite relationship between the amounts of chloroform produced on chlorinating humic and fulvic fractions under similar reaction conditions. The mean variation of the ratios of chloroform produced from humic acid to that produced from fulvic acid, under the range of reaction conditions used, were after 1 day 1.68 and after 2 days 1.64. Trussel (*10*) has reported similar findings. Oliver (*11*) found no difference in chloroform formation on chlorinating humic and fulvic acids, although it is not clear whether the acid fractions originated from the same source.

Residual Chloroform. It can be seen from Figures 5 and 6 that reductions occurred in residual chloroform concen-

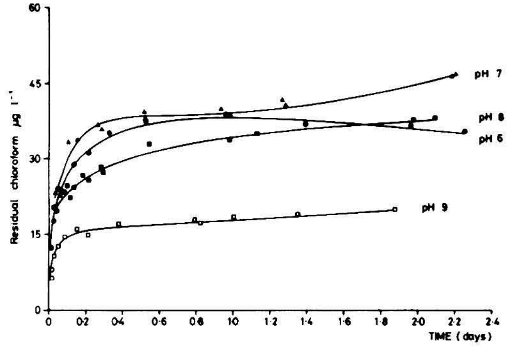


Figure 5. Effect of pH on residual chloroform from humic acid (5 mg L^{-1}) at 10 °C.

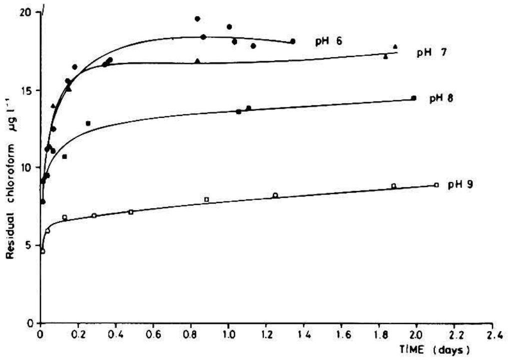


Figure 6. Effect of pH on residual chloroform from fulvic acid (5 mg L^{-1}) at 10 °C.

tration utilizing both humic and fulvic materials when the pH was increased from 7 to 9.

The kinetics of formation of residual chloroform from humic and fulvic acids were similar, both giving characteristic curves between pH 7 and 9.

Residual chloroform formation is considered to involve two stages, an initial rapid phase within the first 5–7 h of the reaction, followed by a slow nearly linear secondary phase. This initial phase of the reaction yielded over 80% of the total residual chloroform intermediates produced over a 2-day period, while over the same time interval only 50% of the chloroform in solution had been formed. This two-stage reaction was compatible with the rate of fall of the chlorine concentration.

Rook (*12*) noted a similar change in the reaction kinetics of chloroform formation (not residual chloroform) on chlorinating fulvic acid although he observed a phase change within the first 15 min of the reaction.

At pH 6 the rate of change of residual chloroform concentration from both acid fractions did not follow the characteristic curves obtained under neutral or alkaline conditions. This could have been the result of a change in mechanism and kinetics of the haloform reaction, or other reactions involving organochlorine intermediates, under acid conditions. At the higher pH levels there was a slow but constant increase in residual chloroform concentration after an initial rapid phase of production (Figures 5 and 6). After 2 days under similar reaction conditions, the ratio of the concentration of residual chloroform produced from humic acid to that produced from fulvic acid was approximately 2.5:1.

For fulvic acid the levels of total chloroform, dissolved chloroform, and residual chloroform after 2 days of reaction at 10 °C are given in Table II. For increasing pH there was a nearly linear decrease in the percentage contribution of residual chloroform to the total chloroform level. A similar dependence on pH has also been reported (*13, 14*) for total organochlorine (TOCl) formation. At a higher fulvic acid concentration (25 mg L^{-1}) the free chlorine was rapidly exhausted, and both residual and dissolved chloroform production were limited by the availability of chlorine.

Residual chloroform, which is a breakdown product of chlorinated compounds heated in the injection port of the gas chromatograph, is considered as an indirect measure of the concentration of chlorinated intermediates of the haloform reaction. The high temperature of the injection port of the gas chromatograph was clearly conducive to a rapid rate of breakdown of these intermediates. It is not known, however, whether all of the intermediates necessarily break down to produce dissolved chloroform at ambient temperature or indeed whether complete breakdown occurs after prolonged storage under normal conditions. Studies on upland waters rich in humic material do indicate that intermediates detected as residual chloroform decompose at ambient temperature to form dissolved chloroform. It is considered that the stability and resistance toward purging of the intermediates might be dependent on the nature and therefore source of the humic material.

Table II. Total, Dissolved, and Residual Chloroform Concentrations (μg L^{-1}) from Fulvic Acid (5 mg L^{-1}) Reaction at 10 °C

pH	total $CHCl_3$	residual $CHCl_3$ (% of total)	dissolved $CHCl_3$ (% of total)
6	37	18 (49)	19 (51)
7	47	18 (38)	29 (62)
8	49	14.5 (29)	34.5 (71)
9	44.5	9 (20)	35.5 (80)

Total Chloroform. A relationship was found between total chloroform formation (residual and dissolved) and chlorine consumption for both humic and fulvic acids over a range of conditions. The relationship illustrated in Figure 7 can be represented by a linear equation

$$(\mathrm{T.Chlor})_t = 0.022[(\mathrm{Cl}_2)_0 - (\mathrm{Cl}_2)_t] \qquad (1)$$

where $(\mathrm{T.Chlor})_t$ = total chloroform concentration (mg L^{-1}) at time t, $(\mathrm{Cl}_2)_t$ = chlorine concentration (mg L^{-1}) at time t, and $(\mathrm{Cl}_2)_0$ = initial chlorine concentration (mg L^{-1}).

The lower yield of dissolved and residual chloroform from fulvic acid compared to humic acid was compensated by a lower overall chlorine consumption.

Total chloroform formation reaches a maximum between pH 7 and 8, consistent with the maximum rate of chlorine consumption. However, it is evident from data presented in Table II that this dependence on pH is much weaker than the marked effect of pH on the relative proportions of dissolved and residual components.

Rate of Reaction. A first-order dependence of the rate of chlorine consumption on chlorine concentration during reaction with humic acid has recently been reported (*10*).

It is doubtful whether the derivation of a general rate equation for both chlorine consumption and haloform formation is possible owing to the complexity of the reactions and the variations in the structure of humic substances present in different waters. A rate equation may, however, be formulated for a specific source of water to predict the effect of changing the chlorination conditions on haloform formation and chlorine consumption.

The data reported here were derived from experiments

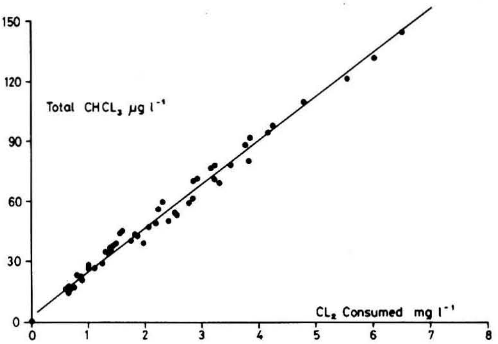


Figure 7. Change in total chloroform formation with chlorine consumption.

designed to examine the variation of chloroform (residual and dissolved) production over a range of reaction conditions. The experimental design was not such as to facilitate rigorous kinetic interpretation. Selection of appropriate groups of data does, however, permit a simple representation of the kinetics involved.

The overall chloroform reaction may be represented by eq 2 and 3, which involve the formation and subsequent breakdown of intermediates detected as residual chloroform (R.Chlor)

$$\mathrm{FA} + n\mathrm{Cl_2} \xrightarrow[\mathrm{OH^-}]{k_1} \mathrm{R.Chlor} \tag{2}$$

$$\mathrm{R.Chlor} \xrightarrow[\mathrm{OH^-}]{k_2} \mathrm{CHCl_3} \tag{3}$$

where R.Chlor = residual chloroform and FA = fulvic acid. The rate of change of residual chloroform concentration and the rate of dissolved chloroform formation are given by eq 4 and 5, respectively

$$\mathrm{d(R.Chlor)}/\mathrm{d}t = k_1(\mathrm{FA})^x(\mathrm{Cl_2})^y(\mathrm{OH^-})^z - k_2(\mathrm{R.Chlor}) \tag{4}$$

$$\mathrm{d(CHCl_3)}/\mathrm{d}t = k_2(\mathrm{R.Chlor}) \tag{5}$$

Equation 6 is the rate of total chloroform formation which is equal to the sum of the rates of formation of residual and dissolved chloroform

$$\frac{\mathrm{d(T.Chlor)}}{\mathrm{d}t} = \frac{\mathrm{d(R.Chlor)}}{\mathrm{d}t} + \frac{\mathrm{d(CHCl_3)}}{\mathrm{d}t} \tag{6}$$

where (T.Chlor) = total chloroform. Thus

$$\mathrm{d(T.Chlor)}/\mathrm{d}t = k_1(\mathrm{FA})^x(\mathrm{Cl_2})^y(\mathrm{OH^-})^z \tag{7}$$

The overall chlorine consumption for fulvic acid after the 2-day reaction was not greater than 25% of the initial chlorine dose. Thus, it may be assumed that, under these conditions, chlorine remains in excess throughout the reaction. At constant pH a pseudo-first-order rate equation may be derived for the rate of total chloroform formation dependent on the fulvic acid concentration (eq 8) or, more correctly, dependent on the number of active sites available for the haloform reaction.

$$\mathrm{d(T.Chlor)}/\mathrm{d}t = k_1'(\mathrm{FA})^x \tag{8}$$

For a first-order rate equation $x = 1$.

For a given quantity of fulvic acid in excess chlorine, the chloroform will reach a limiting value. This maximum chloroform concentration is a measure of the active sites in the acid structure which give the haloform reaction. The effective fulvic acid concentration may therefore be represented in terms of this limiting chloroform concentration by eq 9

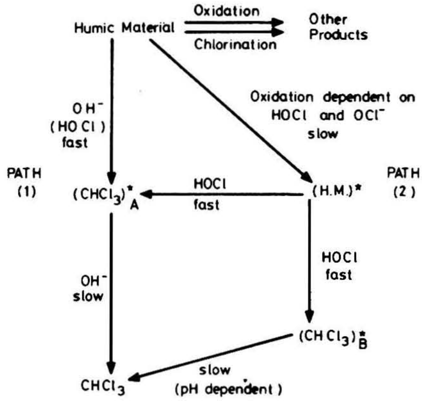


Figure 8. Reaction scheme for chloroform formation.

$$(\mathrm{FA})_t^* \propto (\mathrm{T.Chlor})_{\max} - (\mathrm{T.Chlor})_t \tag{9}$$

where $(\mathrm{FA})_t^*$ = effective fulvic acid concentration at time t. Substituting eq 9 into eq 8 gives

$$\mathrm{d(T.Chlor)}/\mathrm{d}t = k_1''[(\mathrm{T.Chlor})_{\max} - (\mathrm{T.Chlor})_t] \tag{10}$$

and integrating eq 10 gives

$$\ln\left(\frac{(\mathrm{T.Chlor})_{\max} - (\mathrm{T.Chlor})_t}{(\mathrm{T.Chlor})_{\max}}\right) = -k_1''t \tag{11}$$

The two basic assumptions for eq 11 are (a) that chlorine is in excess and (b) that all chloroform is produced via intermediates measured as residual chloroform.

The calculation of the rate constant k_1'' has not been attempted as the value $(\mathrm{T.Chlor})_{\max}$ has not been determined. An arbitrary but realistic value of 100 µg L^{-1} may be assumed for $(\mathrm{T.Chlor})_{\max}$, and straight-line plots were obtained for eq 11 for pH 7, 8, and 9 after 8 h of reaction. These plots also indicated that the initial rate of total chloroform formation is fast and does not follow the first-order rate equation.

If the breakdown of intermediates is rapid ($k_2 \gg k_1$), no residual chloroform would be detected. However, the presence of residual chloroform is a clear indication that the hydrolysis of the organochlorine intermediates (eq 3) is slow and possibly dependent on factors such as steric hindrance and mesomeric and inductive effects. This is comparable to some simple acetyl-containing compounds that produce relatively stable trichloroacetyl derivatives ($\mathrm{CCl_3CO}$–) under acid conditions (*15*) which undergo rapid hydrolytic attack under alkaline conditions to produce chloroform.

A reaction scheme involving a minimum of two possible pathways to chloroform is presented in Figure 8. A fast initial step leads to the formation of an intermediate $(\mathrm{CHCl_3})_A^*$, containing a trichloroacetyl group which is measured as residual chloroform (path 1). The rate-determining step in the formation of this intermediate is proton dissociation consistent with the classical haloform reaction although steric hindrance and other kinetic controlling factors might also involve the chlorinating species HOCl or $\mathrm{H_2OCl^+}$.

The second path (path 2) involves a slow initial oxidation step, which is rate determining, to form an active carbon atom (HM)*. This subsequently undergoes the haloform reaction to produce either intermediate $(\mathrm{CHCl_3})_A^*$ or $(\mathrm{CHCl_3})_B^*$. This secondary phase to total chloroform formation is clearly independent of pH in that both HOCl and $\mathrm{OCl^-}$ are involved in oxidation.

These intermediates are considered to display differences in the ease with which they break down to yield chloroform, the rate being dependent upon pH.

It is implicit from a general consideration of reaction mechanisms that the basic reaction system is complex and that it is further complicated by the presence of such species as bromide, ammonia, and amines.

Summary

It is apparent that more than one route to chloroform formation is available and that the relative rate and extent to which a route is followed depends upon several reaction parameters.

Total chloroform formation is not significantly affected by pH compared to the strong pH dependence of both the dissolved and residual chloroform components.

Several different moieties within the humic structure are capable of undergoing the haloform reaction. The higher molecular weight humic acid fraction, which contains a greater number of active sites than fulvic acid, gives rise to higher chloroform yields.

Chlorinated intermediates detected by DAI as residual chloroform are a potential source of chloroform and must be taken into account when attempting to control trihalomethanes.

The relationship between these laboratory studies and water treatment practice is currently being evaluated, and preliminary indications are that the amount of trihalomethanes detected in tap waters (including the intermediates of the haloform reaction) will depend upon the following: (i) the quality of the source water, (ii) the process conditions during chlorination, (iii) pH with respect to the balance between dissolved and residual chloroform, (iv) bromide concentration with respect to the balance between brominated and chlorinated trihalomethanes involving both residual and dissolved components, and (v) the conditions of water storage and distribution with respect to evaporative losses and breakdown of halogenated organic intermediates of the haloform reaction to yield additional trihalomethanes.

Acknowledgment

We are grateful to the Water Research Centre, UK, for funding this project and to Mr. M. Fielding for valuable discussion, and one of us, C. J. Peters, acknowledges the Science Research Council for a studentship.

Literature Cited

(1) Symons, J. M.; Bellar, T. A.; Carswell, J. K.; De Marco, J.; Kropp, K. C.; Robeck, G. G.; Seeger, D. R.; Slocum, C. J.; Smith, B. L.; Stevens, A. A. *J. Am. Water Works Assoc.* **1975,** *67,* 634–47.
(2) Hall, E. S.; Packham, R. F. *J. Am. Water Works Assoc.* **1965,** *57,* 1149–66.
(3) Black, A. P.; Christman, R. F. *J. Am. Water Works Assoc.* **1963,** *55,* 897–912.
(4) Nicholson, A. A.; Meresz, O. *Bull. Environ. Contam. Toxicol.* **1975,** *14,* 453–6.
(5) Pfaender, F. K.; Jones, R. B.; Stevens, A. A.; Moore, L.; Hass, J. R. *Environ. Sci. Technol.* **1978,** *12,* 438–41.
(6) Rook, J. J. *Water Treat. Exam.* **1974,** *23,* 234–43.
(7) Bellar, T. A.; Lichtenberg, J. J. *J. Am. Water Works Assoc.* **1974,** *66,* 739–44.
(8) "Analysis of Raw, Potable and Waste Waters"; Department of the Environment, U.K., HMSO, 1972, 91-5.
(9) Harrison, R. H.; Perry, R.; Wellings, R. A. *Environ. Sci. Technol.* **1976,** *10,* 1156–60.
(10) Trussell, R. R.; Umphres, H. D. *J. Am. Water Works Assoc.* **1978,** *70,* 604–12.
(11) Oliver, B. G.; Lawrence, J. *J. Am. Water Works Assoc.* **1979,** *71,* 161–3.
(12) Rook, J. J. *Environ. Sci. Technol.* **1977,** *11,* 478–82.
(13) Oliver, B. G. *Can. Res.* **1978,** *11,* 21–2.
(14) Sander, V. R.; Kuhn, W.; Sontheimer, H. *Z. Wasser Abwasser Forsch.* **1977,** *10,* 155–60.
(15) Fuson, R. C.; Bull, B. A. *Chem. Rev.* **1934,** *15,* 275–309.

Received for review June 29, 1979. Accepted June 25, 1980.

NOTES

Development of the FACTS Procedure for Combined Forms of Chlorine and Ozone in Aqueous Solutions

John Liebermann, Jr., and Nina Matheny Roscher
Department of Chemistry, The American University, Washington, D.C. 20016
Eugene P. Meier[1] and William J. Cooper*[2]
U.S. Army Medical Bioengineering Research and Development Laboratory, Fort Detrick, Frederick, Maryland 21701

Chlorine. Specificity is by far the most important characteristic of any analytical procedure for free available chlorine (FAC). However, interferences from impurities such as combined chlorine are common problems in most existing procedures (*1*). An acceptable procedure must also be convenient, rapid, accurate, and precise over a wide range of temperatures, and adaptable to the wide variety of waters encountered in water and waste water treatment. Most of the existing procedures do not meet all of these criteria.

Commercially available colorimetric test procedures have been evaluated (*1, 2*). Of the methods tested, the DPD (*N,N*-diethyl-*p*-phenylenediamine) method was the most accurate and precise while the syringaldazine (liquid) method was the most specific for FAC. A modified syringaldazine (liquid) method called FACTS (free available chlorine test with syringaldazine) was designed for two ranges of FAC concentration (*3*): the FACTS I procedure was designed for lower concentrations of FAC (to 5 mg/L) whereas the FACTS II procedure was developed for a higher concentration range to (10 mg/L).

Early in its development, it was observed that the FACTS method could be modified to measure total available chlorine. This involved the preliminary reaction of both FAC and combined available chlorine with iodide to give iodine, which was then analyzed by the FACTS procedure. The present research was undertaken to exploit these observations by developing a "FACTS" procedure for determining combined and total chlorine.

Ozone. Although ozone is widely used for water treatment in Europe, this is not the case in the United States (*4*). Several factors have prevented its use. These include the high cost of

---

[1] Present address: Methods Development and Analytical Support, U.S. EPA Environmental Monitoring and Support Laboratory, P.O. Box 15027, Las Vegas, NV 89114.

[2] Present address: Drinking Water Research Center, Florida International University, Tamiami Campus, Miami, FL 33199.

■ Most colorimetric procedures for chlorine analysis in treated water and waste water suffer from lack of specificity for free available chlorine. However, the FACTS (free available chlorine test with syringaldazine) procedure is specific for free available chlorine in the presence of the common interferences found in water. This study describes research leading to the modification of FACTS to give a procedure for total and combined available chlorine. The modified FACTS procedure obeys Beer's law through the range of 0–10 mg/L total available chlorine (as Cl_2) with an experimentally determined lower detection limit of 0.2 mg/L (as Cl_2). Ozonation is an alternative method for disinfecting water and waste water. Therefore, the FACTS procedure has also been adapted to determine ozone in aqueous solutions. The ozone method obeys Beer's law through the range of 0–4.5 mg/L O_3 with an experimentally determined lower detection limit of 0.2 mg/L O_3.

ozone generation and the fact that ozone leaves no residual in the treated water. Also of importance for any disinfectant is the need for an analytical procedure to measure low concentrations of the disinfectant in water. The analytical procedures for ozone are hampered by several factors. For example, any method of analysis requiring too much time from sample collection to analysis will result in erroneously low ozone measurements because of the rapid decomposition of ozone in water (*5*).

The current standard method for aqueous ozone analysis involves oxidation of iodide to iodine in the presence of excess iodide (*6*). This reaction is shown by the following equation:

$$O_3 + 3I^- + H_2O \rightarrow I_3^- + O_2 + 2OH^- \qquad (1)$$

The iodine liberated is titrated with standard thiosulfate solution to the starch–iodide end point. It allows little time for loss of ozone to the atmosphere since the sample can be immediately fixed with potassium iodide. The large volumes of sample required for low ozone concentrations (less than 0.1 mg/L) are inconvenient and troublesome but could be tolerated if the method would give reliable and reproducible results.

Schechter analyzed aqueous ozone solutions by the standard volumetric procedure and by a spectrophotometric method (*7*). In every case the standard volumetric method gave the higher results. The higher ozone measurements were attributed to the liberation of additional iodine upon acidification of the sample prior to titration. Equation 1 indicates a stoichiometric ratio of one molecule of iodine liberated per molecule of ozone absorbed in the KI solution. Studies have shown that a stoichiometric ratio of one iodine molecule to one ozone molecule is obtained if the iodine is liberated in a solution buffered at pH 7 (*7–10*). Others have reported data indicating that this volumetric method results in a ratio exceeding 1:1 at low pH (*7, 11–13*). In Schechter's method for ozone, the iodine liberated by ozone in a buffered (pH 7) KI solution (*7*) is determined spectrophotometrically as the triiodide ion, I_3^-, which has an absorption maximum at 352 nm. This method was used as the "referee" method for the determination of ozone in the modification of the FACTS procedure for analysis of ozone in aqueous solutions.

Experimental Section

All spectrophotometric measurements were made on a Beckman ACTA (CV) spectrophotometer. Measurements were made at room temperature and readings normalized for a 1-cm path length.

A Fischer and Porter amperometric titrator (Model 17T1010) was used to standardize all solutions containing chlorine as free available chlorine or combined chlorine. The amperometric procedure has been presented elsewhere (*6, 14, 15*).

A Grace ozone generator manufactured by the W. R. Grace Chemical Division was used to generate ozone for this study. Oxygen (Linde Division, Union Carbide Corp.) was passed without any pretreatment through the generator.

The preparation of chlorine demand-free water and glassware and of syringaldazine indicator solution has been described previously (*3*).

Ozone demand-free glassware was prepared by soaking in strong ozone solutions for at least 15 min. After soaking, the glassware was rinsed in ozone demand-free water and then placed in an oven at ~100 °C for at least 10 min to ensure that the ozone had been dissipated.

The syringaldazine indicator solutions were tested to verify that the response obtained was identical with the response observed during the initial development of the FACTS procedure. This was done by comparing the absorbance obtained with a known FAC concentration to the value calculated from the equations reported in the earlier study (*3*). An indicator solution was judged acceptable if it produced a color within 5% of the calculated value.

Ozone demand-free water was used for all solutions that would come in contact with ozone before analysis. All dilution water and rinse waters were also ozone demand-free. This water was produced by bubbling the ozone–oxygen mixture through doubly distilled water for at least 2 min. The ozonated water was then boiled for at least 15 min to remove any remaining ozone or ozone decomposition products. The water was cooled to room temperature before use. This water was also checked on a spectrophotometer at 260 nm to ensure that all of the ozone had been removed.

Stock buffer solutions of pH 6.6 were made by mixing equal volumes of 0.5 M in KH_2PO_4 (analytical reagent, Mallinckrodt) and 0.5 M in $Na_2HPO_4 \cdot H_2O$ (certified grade, Fisher Scientific); these were prepared in chlorine demand-free water and in ozone demand-free water. Buffers of varying pH (above pH 4) were prepared in chlorine demand-free water by mixing varying proportions of 0.5 M KH_2PO_4 and 0.5 M $Na_2HPO_4 \cdot H_2O$. Buffers for pH values below 4 were made by adding dilute HCl to 0.5 M KH_2PO_4.

Stock solutions of FAC (500 mg/L as Cl_2) were prepared by diluting 10 mL of Clorox to 1 L with demand-free water and standardized by the iodometric method (*6*).

Monochloramine solutions were prepared by the method of Johnson (*16*). The stock monochloramine solutions were diluted with demand-free water to give varying monochloramine concentrations. Solutions were standardized each day by amperometric titration.

Dichloramine solutions were prepared in the same manner (*16*), but the pH of the solution was lowered to approximately 4 by addition of dilute HCl after mixing the NH_4Cl with FAC. The solutions were allowed to stand overnight in a brown glass-stoppered bottle before standardization. The dichloramine solutions were standardized immediately before use.

Ozone demand-free water was ozonated immediately before use as previously described. Spectrophotometric analysis demonstrated that saturated solutions of ozone were produced. These solutions had to be diluted with ozone demand-free water to produce solutions that were reasonably stable over the short period of time needed for analysis. If the more concentrated solutions were not diluted, agitation or pouring caused immediate and drastic changes in ozone concentration.

A sodium thiosulfate solution (anhydrous, certified ACS, Fisher Scientific) was prepared with laboratory distilled water for the iodometric titrations. The solution was standardized several times during the study with 0.025 N Fisher Scientific potassium biiodate solution (*6*).

A 0.02 M $HClO_4$ solution was prepared in ozone demand-free water with Baker reagent grade 70% perchloric acid.

Neutral-buffered potassium iodide solution was prepared for ozone determinations as described by Schechter (*7*).

An iodine solution (ca. 0.01 N) was prepared with distilled water and aged 1 day. Potassium iodide was added to aid dissolution (*7*). This solution was standardized immediately before use by thiosulfate titration using Thyodene (Fisher Scientific starch–iodine indicator) as the indicator. Standard iodine solutions for this study were made by diluting this stock standard solution.

For the FACTS procedure modified for total available chlorine, the pH of each sample was adjusted to ~4 to assure quick and quantitative reaction of iodide with dichloramine. The pH was then adjusted to 7 before addition of indicator to assure maximum color development with syringaldazine indicator.

To obtain calibration curves, the modified procedure was tested against solutions of FAC, monochloramine, and dichloramine by the following steps:

(1) A 5-mL sample was added to a 10-mL test tube.

(2) Two-tenths of a milliliter of pH 4.3 buffer (0.5 M KH_2PO_4) was added.

(3) Four-tenths of a milliliter of KI solution (12.34 g/L) was added, and the tube was capped and inverted to mix.

(4) Two-tenths of a milliliter of pH 6.6 buffer (0.5 M phosphate) was added, and the tube was capped and inverted to mix.

(5) Two milliliters of syringaldazine indicator (118 mg/L in 2-propanol) was added and the tube was capped and inverted to mix.

(6) The absorbance of the solution at 530 nm was determined with a spectrophotometer after 1 min of reaction time.

Two samples of organically polluted water were obtained from the pilot sewage treatment facility of the U.S. Army Medical Bioengineering Research and Development Laboratory, Fort Detrick, Frederick, MD. They had undergone primary settling and secondary activated sludge treatment but had not been chlorinated. A characterization of the samples is given in Table I. The treated sewage effluent was diluted approximately 1:2 with dechlorinated tap water to provide that water for this study. Samples of this water were chlorinated with a stock Clorox solution to produce waters which, after a contact time of at least 2 h, had compositions corresponding to various points along a typical chlorination breakpoint curve.

Table I. Characterization of Organically Polluted Water

characteristic	sample A	sample B
pH	6.9	7.0
conductivity (μmho)	380	420
total carbon (mg/L)	53	50
inorganic carbon (mg/L)	37	34
organic carbon (mg/L)	16	16
ammonia nitrogen (mg/L)	10	7
nitrite nitrogen (mg/L)	0.04	not available
nitrate nitrogen (mg/L)	0.04	not available
iron (mg/L)	0.1	0.1
magnesium (mg/L)	20	29
calcium (mg/L)	143	215

Each of the samples thus prepared was analyzed for total available chlorine by using the modified FACTS procedure. For the organically polluted water, 0.2 mL of 0.1 M HCl was substituted for the buffer to initially lower the pH to 4, and 0.5 mL of pH 6.6 buffer was needed to readjust the pH monitored with a pH meter before adding indicator reagent. Total available chlorine concentrations were calculated by substituting the absorbance readings into the equation for the calibration curve.

In order to check the accuracy of this procedure, we also analyzed each test sample for total available chlorine by amperometric titration.

As previously reported, the spectrophotometric method for ozone was modified slightly and used as the referee method (*7*). The pH was kept at 7 during and after the liberation of iodine. The experimental procedure involved the following sequence of steps:

(1) Five milliliters of 5% KI solution (buffered to pH 7) was added to a 12-mL test tube.

(2) Five milliliters of ozone sample was added by pipette, with the sample permitted to flow down the side of the test tube.

(3) The tube was capped, inverted to mix, and allowed to stand for at least 10 min.

(4) The absorbance of this solution was measured at 352 nm and compared to a standard curve to determine the ozone concentration.

The standard curves for I_3^- were obtained by means of the following procedure:

(1) A 0.10 N iodine solution was prepared and standardized by thiosulfate titration.

(2) The standardized iodine solution was then diluted to 4×10^{-5} N.

(3) The diluted iodine solution (4×10^{-5} N) was mixed with 5% KI solution (buffered to pH 7) to provide samples of known iodine concentration.

(4) The samples were allowed to stand for at least 10 min before measuring their absorbance.

(5) The absorbance of these samples at 352 nm was determined and used to plot the standard curve.

In the modified FACTS procedure for ozone residual, the ozone was first permitted to react with iodide at a neutral pH. The liberated iodine was then allowed to react with syringaldazine, and the resulting color was measured spectrophotometrically. The experimental procedure was the following:

(1) Five milliliters of 5% KI (buffered at pH 7) was added to a 12-mL test tube (tube 1).

(2) Five milliliters of ozone sample was added, and the tube was capped and inverted to mix. The tube was set aside for at least 10 min.

(3) Five-tenths of a milliliter of pH 6.6 buffer (0.5 M phosphate) was added to a 10-mL test tube (tube 2).

(4) Five-tenths of a milliliter of KI solution (12.34 g/L) was added to tube 2. The tube was capped and inverted to mix.

Five milliliters of ozone sample from step 2 was added to tube 2. The tube was capped and inverted to mix.

(6) Two milliliters of syringaldazine indicator solution was added to tube 2. The tube was capped and inverted to mix.

(7) The absorbance of the solution (tube 2) at 530 nm was measured with a spectrophotometer. Color development and fading were monitored as a function of time. The absorbance at 352 nm of the solution from step 2 was also measured to determine the concentration of the ozone solution being tested.

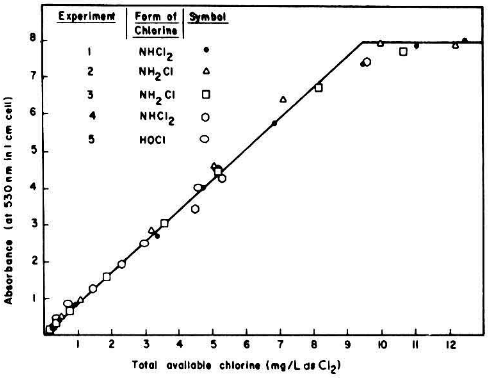


Figure 1. Beer's law plot for the modified FACTS procedure.

Results and Discussion

The results obtained with the modified FACTS procedure for total available chlorine (Figure 1) indicate that the color reaction obeys Beer's law over an experimentally determined range of 0.2–10 mg/L (as Cl_2) and is reproducible on a day-to-day basis. The upper limit of the concentration range is determined by the solubility of syringaldazine in 2-propanol and the solubility of the colored product in the test solution. A dilution step would be necessary for higher concentrations.

The data collected over a period of several days were analyzed by least-squares linear regression to obtain the following equation that best represents the linear portion of the curve (correlation coefficient, 0.995):

$$A = 0.835[X] - 0.005 \qquad (2)$$

where A is the absorbance and [X] is the concentration of total available chlorine in mg/L as Cl_2. The data at the lower end of the concentration range, 0.20–0.98, were analyzed by least-squares linear regression to give the following equation (correlation coefficient, 0.987):

$$A = 0.908[X] - 0.0124 \qquad (3)$$

Color development and fading were studied as a function of total available chlorine and time. A plot of the data for the synthetic waters is shown in Figure 2. In all cases maximum color development took less than 1 min. Fading was appreciable only at relatively high available chlorine concentrations (i.e., greater than 6 mg/L). However, even at the higher chlorine concentrations fading did not appear to be a problem if reasonable care was taken in the analysis.

In order to check the accuracy of the modified FACTS procedure, we also analyzed each test sample for total available chlorine by amperometric titration. A comparison of the results given by the two methods is tabulated in Table II.

The variance between the two sets of data was calculated by the equation:

$$V = \frac{\sum_{i=1}^{n} d_i^2}{n}$$

where n = the number of determinations and d = the difference between the amperometric value and the modified FACTS result (mg/L). The variance was 0.413 yielding a standard deviation of 0.643 mg/L as Cl_2.

Color development and fading are shown in Figure 3 for the organically polluted samples. The curves shown in this figure are for selected cases where fading was most severe. Fading is not a problem during the time span needed to make an analysis.

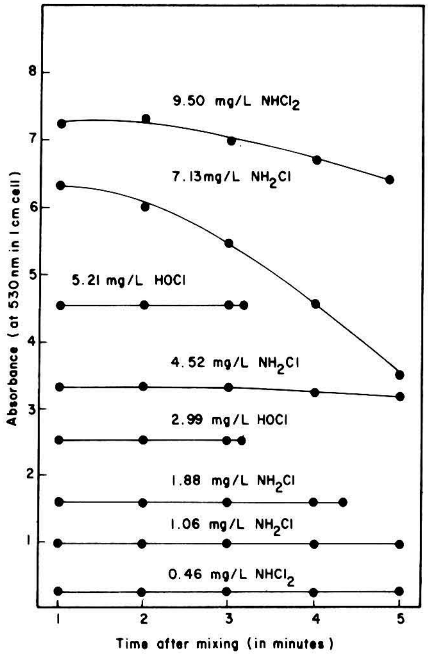


Figure 2. Color development and fading for the modified FACTS procedure using synthetic waters. Concentrations are mg/L Cl_2.

Table II. Amperometric Titration and the Modified FACTS Procedure Using Organically Polluted Waters

chlorine added, mg/L	total chlorine (amperometric titration), mg/L	total chlorine (modified FACTS procedure), mg/L
sample A, day 1		
10	7.09	5.72
20	4.47	5.27
27	1.77	2.12
sample A, day 2		
15	1.20	1.03
20	5.04	5.16
25	9.74	10.30
34	19.50	19.33
sample B		
10	7.67	6.70
15	10.36	10.59
20	8.29	9.16
25	3.77	3.84

Previously the FACTS procedure has been shown to be the most specific colorimetric test for determining free available chlorine in the presence of common interferences (NH_2Cl, $NHCl_2$, Mn(IV), Fe(III)) (*1, 3*). Therefore, if the presently developed test procedure for total available chlorine is combined with the very specific test for free available chlorine, a much more accurate colorimetric determination of available chlorine is possible. This procedure could be adapted to field test comparators which would allow determination of free and total available chlorine.

The results obtained with the modified FACTS procedure for ozone are shown in Figure 4. As can be seen, agreement

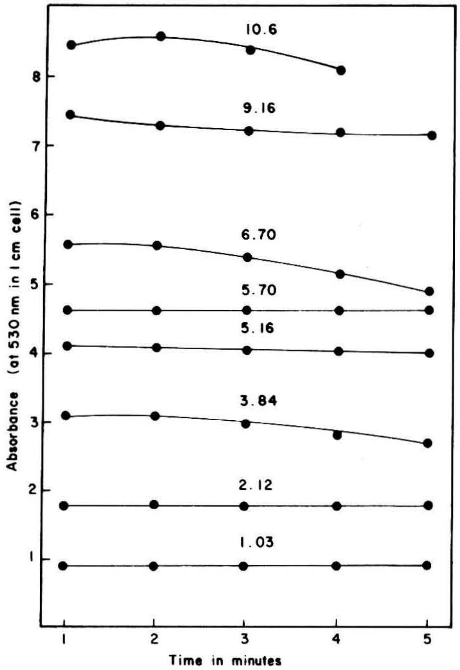


Figure 3. Color development and fading for the modified FACTS procedure for determining total available chlorine in organically polluted water. Concentrations are mg/L Cl_2.

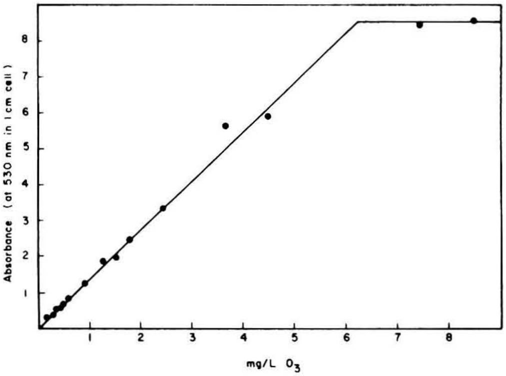


Figure 4. Beer's law plot for the determination of ozone using the modified FACTS procedure.

with Beer's law was excellent and allowed determination of ozone concentrations from 0.17 to 4.5 mg/L as O_3 (actual concentrations were determined by the referee method). Higher ozone concentrations could be determined by dilution of samples; however, ozone concentrations greater than this are rarely encountered in water treatment.

All of the data collected were analyzed by least-squares linear regression to obtain the following equation which best represents the linear portion of the curve (correlation coefficient, 0.995):

$$A = 1.49[O_3] - 0.068 \qquad (4)$$

$[O_3]$ = the concentration of ozone in mg/L O_3. The data at the lower end of the concentration range, O_3 concentrations of 0.17–.92 mg/L, were analyzed by least-squares linear regression to give the following equation (correlation coefficient, 0.990):

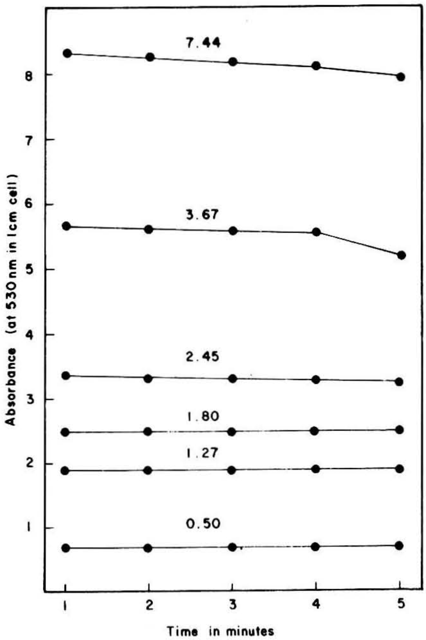


Figure 5. Color development and fading for ozone determination with the modified FACTS procedure. Concentrations are mg/L O_3.

$$A = 1.30[O_3] + 0.063 \qquad (5)$$

Figure 5 shows the color development and fading for the ozone solutions tested as a function of concentration. The color development reached a maximum within the time needed for the analysis, and fading was not severe for the samples tested.

Thus, by using the syringaldazine indicator for ozone determinations, it would be possible to develop a colorimetric comparator which would allow for the determination of ozone in the field.

Conclusions

Chlorine. The FACTS procedure was modified to determine total available chlorine in aqueous solutions. This method was shown to be simple, accurate, and precise for analysis of standardized samples of total available chlorine. It was used to analyze organically polluted water and was found to give acceptable results as determined by comparison to amperometric titration of the same samples. However, the amount of FACTS buffer may have to be increased for samples of high alkalinity (>500 mg/L as $CaCO_3$).

The modified FACTS procedure for total available chlorine obeys Beer's law through the range of 0.2–10 mg/L (as Cl_2).

The maximum color was found to develop within 1 min and for most samples was stable over a period of 5 min. In some cases, higher concentrations of total available chlorine did show fading near the end of 5 min.

Ozone. The FACTS procedure was also modified to determine residual ozone in aqueous solutions. This method was shown to be simple, accurate, and precise for determining ozone concentrations in laboratory-produced waters. The modified FACTS procedure obeys Beer's law through the range 0.2–4.5 mg/L O_3.

As with the procedure for total available chlorine, color development was complete within 1 min and fading over most of the applicable concentration range did not appear to be a problem as long as reasonable care was exercised in the analysis.

Literature Cited

(1) Guter, K. J.; Cooper, W. J.; Sorber, C. A. *J. Am. Water Works Assoc.* **1974,** *66,* 38.
(2) Sorber, C. A.; Cooper, W. J.; Meier, E. P. In "Disinfection Water and Wastewaters"; Johnson, J. D., Ed.; Ann Arbor Science Publishers: Ann Arbor, MI, 1975; Chapter 5.
(3) Cooper, W. J.; Sorber, C. A.; Meier, E. P. *J. Am. Water Works Assoc.* **1975,** *67,* 34.
(4) McCarthy, J. J.; Smith, C. H. *J. Am. Water Works Assoc.* **1974,** *66,* 718.
(5) Manley, T. C.; Niegowski, S. J. "Encyclopedia of Chemical Technology", 2nd ed.; Wiley: New York, 1967; Vol. 14, pp 410–32.
(6) "Standard Methods for the Examination of Water and Wastewater", 14th ed.; American Public Health Association: New York, 1975; p 309.
(7) Schechter, H. *Water Res.* **1973,** *7,* 729.
(8) Hodgeson, A.; Baumgardner, R. E.; Martin, B. E.; Rehme, K. A. *Anal. Chem.* **1971,** *43,* 1123.
(9) Kopczynski, S. L.; Bulfalini, J. J. *Anal. Chem.* **1971,** *43,* 1126.
(10) Byers, D. H.; Saltzman, B. *Adv. Chem. Ser.* **1959,** *No. 21,* 93.
(11) Boyd, W. A.; Willis, C.; Cyr, R. *Anal. Chem.* **1970,** *42,* 670.
(12) Pitts, J. N., Jr.; McAfee, J. M.; Long, W. D.; Winer, A. M. *Environ. Sci. Technol.* **1976,** *10,* 787.
(13) Alder, M. G.; Hill, G. R. *J. Am. Chem. Soc.* **1950,** *72,* 1884.
(14) Marks, H. C.; Joiner, R. R. *Water Sewage Works* **1948,** *95,* 175.
(15) Marks, H. C.; Williams, D. B.; Glasgow, G. W. *J. Am. Water Works Assoc.* **1951** *43,* 201.
(16) Johnson, J. D. "Field Test for Free Chlorine and the Kinetics of Bromine Residuals," Progress Report to USAMRDC, Contract No. DA-49-193-MD-2442, Sept. 1970, p. 7.

Received for review February 27, 1979. Accepted July 7, 1980. Work supported by Grant No. DAMD 17-77-G-9436 of the Department of the Army. Presented at the Division of Environmental Chemistry, the American Chemical Society, Anaheim, CA, March 1978.

Supplementary Material Available: *Raw data for Figures 1 and 4 (1 page) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper or microfiche (105 × 148 mm, 24× reduction, negatives) may be obtained from Business Operations, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Full bibliographic citation (journal, title of article, author) and prepayment, check or money order for \$5.50 for photocopy (\$7.00 foreign) or \$3.00 for microfiche (\$4.00 foreign), are required.*

A Submicron Aerosol Mode in Flue Gas from a Pulverized Coal Utility Boiler

G. R. Markowski,* D. S. Ensor,† and R. G. Hooper‡
Meteorology Research, Inc., P. O. Box 637, Altadena, California 91001

R. C. Carr
Electric Power Research Institute, 3412 Hillview Avenue, Palo Alto, California 94303

■ A submicron aerosol with a mass median diameter near 0.16 μm and a narrow number and volume distribution is present at both the inlet and the outlet of a high-efficiency electrostatic precipitator following a pulverized coal utility boiler. The aerosol is distinct from the much larger fly ash distribution and appears to result from a vaporization–condensation process in the boiler.

Measuring emissions from coal combustion, especially emissions produced by electric power generating plants, is an important step in determining and limiting their environmental effects. Among these emissions, fine particles, smaller than 3 μm in diameter, are particularly significant. They reside in the atmosphere for several days, and, because of their efficiency in scattering light, they reduce atmospheric visibility and may affect climate (*1*). The potential effects of fine particles on health are also of interest because of their retention in the respiratory system and their reported enriched concentrations of toxic elements (*2*). The most common flue gas cleaning equipment used on utility boilers—electrostatic precipitators (ESPs) and scrubbers—is least efficient in the 0.1–1.0-μm particle diameter range (*3, 4*).

A condensation submicron aerosol is predicted to be a general feature of pulverized coal combustion (*5*); however, quantitative size data from a field site supporting this prediction have not, to our knowledge, been reported. Earlier data have been inconclusive largely because of a lack of precision in available sampling and data reduction techniques and the difficulties in sampling under field conditions. Observations by Schultz et al. (*6*) and by Ragaini and Ondov (*7*) suggest a distinct submicron mode. The data from Schmidt et al. (*8*) give similar results to those which we report here when size selectivity of our instruments is considered.

Experimental Section

We measured particle size distributions simultaneously at the inlet and the outlet of a high-efficiency ESP on a modern 520-MW boiler firing pulverized subbituminous western coal. The coal heating value and ash content were ~11 400 Btu/lb and 11%, respectively. The cold-side electrostatic precipitator was designed for an overall efficiency of 99.7% by weight and the high resistivity fly ash, $\sim 10^{13}$ Ω cm. The design specific collection area was 2.89 m^2 per actual m^3/min of flue gas at 123 °C.

We used source cascade impactors to measure, in situ, size distributions above 0.3 μm in diameter (*9, 10*). The size-segregated fractions were collected on greased stainless steel foils. The particles passing the last stage were collected on a filter. Three inlet and two outlet sets of impactor samples were analyzed by neutron activation analysis (NAA) for elemental composition. These samples were collected on Kapton disks attached to the collection foils with Apiezon L grease.

Size distributions below 1.0 μm were measured with two factory calibrated Model 3030 electrical aerosol analyzers (EAAs) (*11, 12*). The flue gas was diluted to reduce aerosol concentration to within EAA limits, and the charge on the particles was neutralized with radioactive sources (*13*). Because the EAA measures aerosol distributions cumulatively, the smaller size channels were dominated by fluctuations in

---

† Currently affiliated with the Research Triangle Institute, P.O. Box 12194, Research Triangle Park, NC 27709.

‡ Currently affiliated with the Electric Power Research Institute.

0013-936X/80/0914-1400\$01.00/0

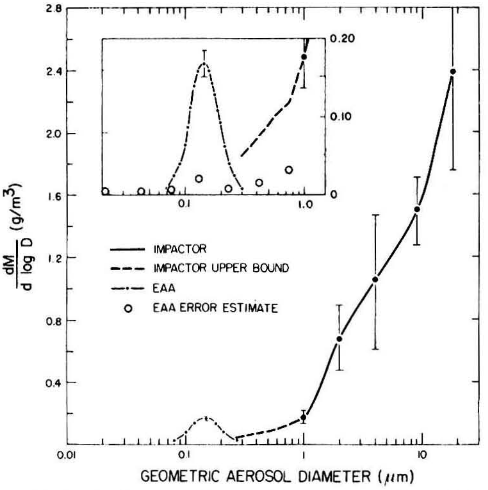


Figure 1. Typical differential mass distributions at precipitator inlet. Electrical aerosol analyzer data are averages of two sampling periods. Cascade impactor data are the averages of four runs. The dashed line is the upper bound indicated by cascade impactor data. The insert shows the submicron data with the vertical scale expanded by a factor of 5. Error bars on cascade impactor data indicate the standard deviation of individual values. The error bar on the submicron peak indicates the variation in peak height. The particle density is 2.6 g/cm^3.

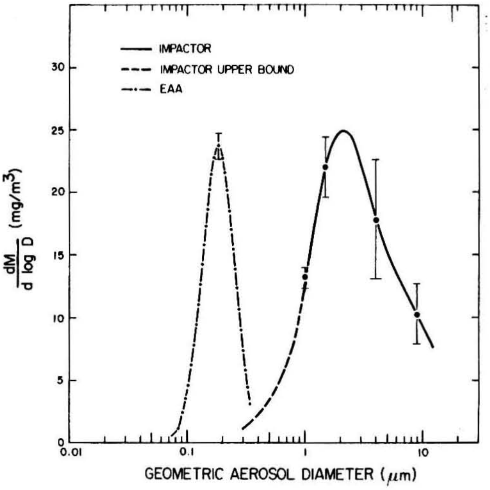


Figure 2. Typical differential mass distribution at precipitator outlet. The data were obtained simultaneously with those in Figure 1. Electrical aerosol analyzer data are the averages of two sampling periods. Cascade impactor data are the averages of four runs. The dashed line is the upper bound indicated by cascade impactor data. Error bars on cascade impactor data indicate one standard deviation of individual values. The error bar on the submicron peak indicates the variation in peak height. The fly ash density is 2.6 g/cm^3.

the total aerosol concentration. To minimize noise, we calculated the averages and standard deviations of EAA output in the last five or six size channels for three to seven analyzer cycles for representative periods of time at both the ESP inlet and outlet. The raw EAA output is electrical current. Typical inlet currents (multiplied by the dilution, average of 3 cycles) and individual standard deviations in picoamps for channels 4–10 were as follows: 7.9, 29; 30, 16; 159, 23; 277, 22; 87, 6; 16, 1.9; 3.6, 0.5. Although the EAA classifies aerosol into 10 size channels between 0.001 and 1.0 μm, a monodisperse aerosol will generate a response in several channels (*11, 12*). We used two inversion techniques which include this cross sensitivity. The first technique assumes that the measured distribution is log normal or is the sum of two log-normal distributions and adjusts its distribution to give a best fit to the EAA output. The program was developed at the University of Minnesota Particle Laboratory and is commercially available (*14*). The second technique does not assume a functional form and constructs a synthetic distribution from 10 aerosol sizes equally logrithmically spaced from 0.056 to 0.75 μm. The concentration in each size is adjusted to give a best fit to the measured currents. The cross sensitivities were taken from Figure 6 and Table 1 in ref *11*. Both techniques produced similar results.

To check the EAA and impactor results, the smallest two or three size fractions and filters from four inlet and four outlet impactor runs were examined with a scanning electron microscope (SEM).

Results

We detected a sharp peak in the submicron aerosol mass and number distribution in the flue gas that was emitted directly from the boiler. Figure 1 is a representative mass distribution vs. size at the ESP inlet. The submicron peak, clearly separate from the larger fly ash, contains ~1.5% of the total mass. Figure 2 is a representative ESP outlet mass distribution. The submicron mode contains ~20% of the total mass. The penetration of the submicron mode through the ESP is ~10%, which is ~30 times the overall penetration. The high submicron penetration may have been caused by the large backcorona current in the ESP. Submicron penetrations we have measured at other ESPs, all collecting lower resistivity ash, were typically more than an order of magnitude less. The truncation of the larger fly ash mode in Figure 2 is caused by the increasing ESP collection efficiency with increasing particle diameter (*15*). Log-normal fits to the submicron mode by the Minnesota routine had geometric standard deviations from 1.18 to 1.48 and geometric median number and volume diameters from 0.101 to 0.138, and 0.144 to 0.168 μm, respectively. Log-normal fits are shown in Figures 1 and 2. Cascade impactor concentrations in Figures 1 and 2 below 1.0 μm are shown as upper bounds since SEM examination of the collection foils indicated considerable transfer of particles from the preceding stage.

SEM examination of the cascade impactor filters showed a cake of solid spherical particles, mostly between 0.07 and 0.15 μm, with little blowoff. Resolution ranged between 0.03 and 0.07 μm. In situ agglomeration could not be measured; however, if uniform concentration within the boiler is assumed, we calculate coagulation by Brownian motion to be small. Submicron concentrations calculated from the EAA data and impactor filters agreed satisfactorily, typically within a factor of 1.5.

We ratioed elemental concentrations (μg/g of sample) of the submicron mode collected on the impactor filter to the impactor samples 2–8 and 1–3 μm in diameter for the three inlet and two outlet impactor runs analyzed by NAA. The size ranges above were chosen because the concentrations were most reproduceable between adjacent impactor stages and the inlet and outlet samples of the same particle size. The variation in the elemental concentration results for particles of the similar size was large for some elements so that we consider the chemical data to be semiquantitative. The variability appeared to result mainly from the small sample amounts analyzed. The average concentrations in the submicron mode were at least 2.5 times higher than in the larger fly ash for As, Sb, Cr, Rb, V, and Ni. These enrichments were statistically significant ($p \leq 0.1$, one-tailed Student's t test). Similar enrichments were noted for Zn, Cd, and Se, but the data were poor. Fe and Ti had little differences in concentrations. Al and Hf showed statistically significant depletions; their concentrations in the submicron mode were ca. 0.4 and 0.6, respectively, of the fly ash mode. Mg and Ta depletions were between 0.6 and 1.0 and were not statistically significant. Mn had a depletion of 0.4, but only the submicron data from the outlet filters were good. Submicron enrichments with respect to particles larger than 8 μm or smaller than 1 μm are expected to be larger or smaller, respectively, than those presented here. See Davidson et al. (*16*), for example. Bulk elemental inlet and outlet concentrations are reported by Ensor et al. (*15*).

Discussion

The distinctness of the submicron mode and its differences in chemical composition suggest that it is formed by a different mechanism than the much larger fly ash aerosol. Its sharp distribution, small diameter, and high concentration are evidence that this submicron aerosol results from condensation of ash components that vaporize during combustion. Other mechanisms, such as bubble bursting, are less likely to produce such a small, narrow mode of the observed concentration (*17*). The enrichments in volatile elements, As, Sb, Rb, Cd, Zn, and Se, and the depletion in refractory elements, Al, Hf, Mn, Mg, and Ta, are consistent with a vaporization–condensation mechanism.

Qualitatively, our data agree well with predictions by Flagan and Friedlander (*5*). The material in the submicron mode may also collect on the surface of the larger fly ash particles. Linton et al. (*18*) reported measurement of layers of volatile elements on fly ash. Davidson et al. (*16*) reported that the volatile element enrichment could be explained by a surface deposition model. Flagan and Friedlander discuss formation mechanisms in greater detail.

EAA data we have gathered at five other coal-fired plants, including a high- and low-sulfur coal and one stoker-fired unit, indicate qualitatively similar submicron distributions (*19, 20*). We believe it likely that the submicron mode is a general feature of coal combusion in utility boilers.

Literature Cited

(1) Friedlander, S. K., "Fundamentals of Aerosol Behavior"; Wiley: New York, 1977.

(2) Natusch, D. F. S.; Wallace, J. R.; Evans, C. A. *Science* **1974,** *183,* 202.

(3) McCain, J. D.; Gooch, J. P.; Smith, W. B., *J. Air Pollut. Control Assoc.* **1975,** *25,* 117.

(4) Ensor, D. S.; Jackson, B. S.; Calvert, S.; Lake, C.; Walton, D. V.; Nilan, R. E.; Campbell, K. S.; Cahill, T. A.; Flocchini, R. G. Washington, D.C., 1975, EPA Report No. 600/12-75-074.

(5) Flagan, R. C.; Friedlander, S. K. In "Recent Developments in Aerosol Science"; Shaw, David, Ed.; Wiley-Interscience: New York, 1978; p 25.

(6) Schultz, E. J.; Engdahl, R. B.; Frankenburg, T. T. *J. Atmos. Environ.* **1975,** *9,* 111.

(7) Ragaini, R. C.; Ondov, J. M.; "Trace Contaminants from Coal-Fired Power Plants", presented at the International Conference on Environmental Sensing and Assessment, Las Vegas, NV, Lawrence Livermore Laboratory UCRL No. 76794, 1975.

(8) Schmidt, E. W.; Gieseke, J. A.; Allen, J. M. *J. Atmos. Environ.* **1976,** *10,* 1065.

(9) Pilat, M. J.; Ensor, D. S.; Bosch, J. C. *J. Atmos. Environ.* **1970,** *4,* 671.

(10) Markowski, G. R.; Ensor, D. S. "A Procedure for Computing Particle Size Dependent Efficiency for Control Devices from Cascade Impactor Data", presented at the 70th Annual Meeting of the Air Pollution Control Association, Toronto, Canada, Paper 77-35.5, 1977.

(11) Liu, B. Y. H.; Pui, D. Y. H. *J. Aerosol Sci.* **1975,** *6,* 249.

(12) Liu, B. Y. H.; Pui, D. Y. H.; Kapadia, A. In "Aerosol Measurement"; pp 384–399, Lundgren, D. A., Harris, F. S., Jr., Marlow, W. H., Lippmann, M., Clark, W. E., Durham, M. D., Eds.; University Presses of Florida: Gainesville, FL, 1979.

(13) Ensor, D. S.; Hooper, R. G. In "Proceedings of Seminar on In-Stack Particle Sizing for Particulate Control Devices Evaluation"; van Osdell, D., Ed.; Environmental Protection Agency: Washington, D.C., 1977; EPA-600/2-77-060, p 314.

(14) Thermosystems, Inc., 500 Cardigan Rd., St. Paul, MN 55112.

(15) Ensor, D. S.; Cowen, S.; Hooper, R.; Markowski, G.; Scheck, R.; Farrell, J. D.; Burnham, J., "Evaluation of the George Neal No. 3 Electrostatic Precipitator," EPRI Final Report Contract RP 780-1, 1979.

(16) Davidson, R. L.; Natushch, F. S.; Wallace, J. R., *Environ. Sci. Technol. 8,* **1974,** 1107.

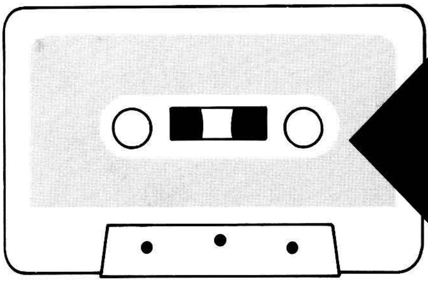
(17) Tomaides, M.; Whitby, K. T. in "Fine Particles"; Lui, B. Y. H., Ed.; Academic Press: San Francisco, 1976; p 235.

(18) Linton, R. W.; Williams, P. W.; Evans, C. A.; Natusch, D. F. S., *Science* **1976,** *191,* 852.

(19) Ensor, D. S.; Hooper, R.; Scheck, R. W., "Determination of the Fractional Efficency, Opacity Characteristics, and Engineering and Economic Aspects of a Fabric Filter Operating on a Utility Boiler", EPRI Final Report, Contract RP 534-1, 1976.

(20) Ensor, D. S.; Markowski, G.; Legg, R.; Cowen, S.; Murphy, M.; Shendrikar, A. D.; Pearson, R.; Scheck, R., "Evaluation of Electrostatic Precipitator Performance at San Juan Unit No. 1", EPRI Contract RP-780. Ensor, D. S.; Cowen, S.; Shendrikar, A. D.; Markowski, G.; Woffinden, G.; Pearson, R.; Scheck, R. "Kramer Station Fabric Filter Evaluation", EPRI Contract RP-1130-1. Markowski, G. R.; Ensor, D. S.; Shendrikar, A. D.; Cowen, S.; Woffinden, G.; Pearson, R.; Scheck, R. "Mt. Storm Unit No. 1 Electrostatic Precipitator Evaluation", EPRI Contract RP-1259-1, final reports in preparation.

Received for review April 10, 1980. Accepted July 21, 1980. This study, Contract RP-780, is part of a larger effort funded by the Electric Power Research Institute to develop a quantative data base of fine particle removal performance of commercially available state-of-the-art gas cleaning equipment.



Explore alternative sources of energy

At the touch of a button you can get instant access to accurate, in-depth information on energy.

Listen to the alternatives on these cassette tape recordings.

☐ **SOLAR ENERGY**

A look at Photovoltaic Conversion, J.A. McMillan, Argonne National Laboratory; Solar-Thermal Energy Conversion, D.E. Soule, Western Illinois University; Thermal Energy Storage, A.I. Michaels, Argonne National Laboratory

☐ **FUELS FOR THE NEXT FIFTY YEARS**

A panel discussion on Direct Utilization of Coal, G.R. Hill, Electric Power Research Institute; Gaseous Fuels From Coal & Petroleum, L.G. Massey, Consolidated Natural Gas Company; Liquid Fuels From Coal, E. Gorin, Conoco Coal Development Corporation; Role of Liquid Fuels From Petroleum & Oil Shale During the Next Fifty Years, R.J. Cameron, Cameron Engineers; Natural Gas & LNG, T.J. Joyce, Consultant to Industrial & Research Organizations; Hydrogen, Methanol, & Other Nonconventional Fuels, D.P. Gregory, Institute of Gas Technology; Fuels From Plant & Waste Materials, I. Wender, Bureau of Mines

☐ **ROLE OF TECHNOLOGY IN THE ENERGY CRISIS**

Information on Enhanced Recovery Technology For Domestic Crude Oil, H.H. Hasiba, Gulf Research & Development Company; Process Applications of Nuclear Heat, R.N. Quade, General Atomic Company; Engineering Perspective of a Hydrogen Economy, L.W. Russum, Amoco Oil Company; Oil Shale Development & Its Environmental Considerations, R.T. Stone, U.S. Department of the Interior, Geological Survey

☐ **UNUSUAL FUELS PRODUCTION**

A rundown on Natural Gas & Nonfossil Renewable Carbon, D.L. Klass, Institute of Gas Technology; Methanol or Ammonia Production From Solid Waste, R.G. Sheehan, Seattle City Light; Production of Ethanol & Vegetable Protein By Grain Fermentation, W.A. Scheller, University of Nebraska; Use of Methanol as an Auto Fuel, P.E. Cassady, Northwest, Inc.; Test Results of Gasohol in Autos, W.A. Scheller, University of Nebraska

☐ **COAL—NATURE'S BLACK DIAMOND**

A report on Synthetic Fuels Based on Coal, R.T. Eddinger, COGAS Development Company; Genesis of a Formed-Coke Process, Raymond F. Moran, FMC Corporation; Clean Fuels for Power Generation From High-Sulfur Coals, John F. Jones, FMC Corporation; COGAS Process for Pipeline Gas, L. Seglin, Bechtel Associates Professional Corporation

☐ **ENERGY FROM RENEWABLE RESOURCES**

An examination of How Much Energy Do We Really Need, C.M. Mottley, Energy Research & Development Administration; Renewable Organic Resources, D.A. Tillman, Materials Associates; Energy From Waste Materials, M.D. Schlesinger, Wallingford Group; Energy Recovery From Municipal Wastes, J.R. Greco, National Solid Wastes Management Association; Thermal Analysis of Forest Fuels, F.S. Shafizadeh, University of Montana

These selected cassette tapes come with printed copies of slides which illustrate the important points for you. No projector is needed.

Each recorded title is $19.95 or, three titles for $54.00. California residents—add 6% state use tax.

American Chemical Society

To order, check the titles you want and send this ad with your payment to **American Chemical Society**, Department 308, 1155 Sixteenth Street, N.W., Washington, D.C. 20036, or call toll free 800-424-6747.

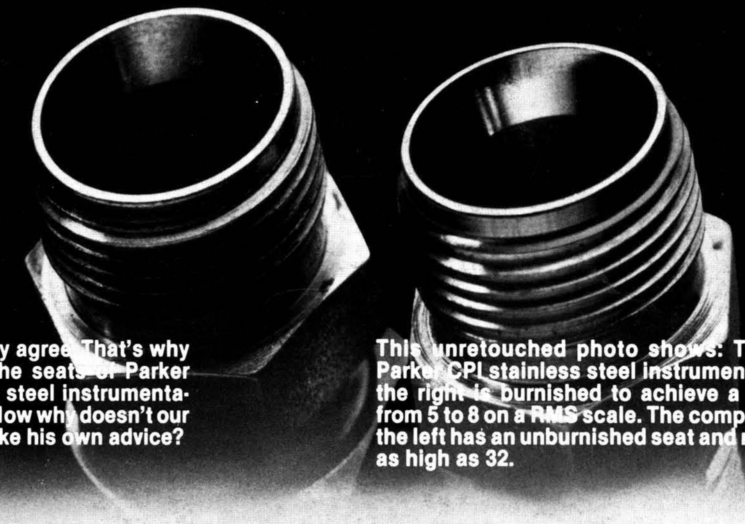
(Allow 4 to 6 Weeks For Delivery)

Name ____________________
Title ____________________
Company ____________________
Street ____________________
City ____________ State ____________ Zip ________

Payment Enclosed For $ ________
Bill Me ____ Bill Company ____ P.O. # ____________

Parker CPI Critique: Series III on Fitting Seat Finish

"The smoother the surface, the better the seal," says a competitor.



And we totally agree. That's why we burnish the seats of Parker CPI stainless steel instrumentation fittings. Now why doesn't our competitor take his own advice?

This unretouched photo shows: The seat of the Parker CPI stainless steel instrumentation fitting on the right is burnished to achieve a smoothness of from 5 to 8 on a RMS scale. The competitive fitting on the left has an unburnished seat and may have a RMS as high as 32.

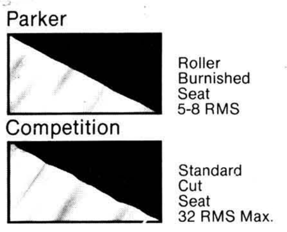
Industry tests have shown that a 50% improvement in the surface finish of a seat can result in an 800% improvement in the sealing of a fitting. Parker CPI (and to our knowledge only Parker CPI) burnishes the seats of its stainless steel fittings for two reasons: 1) To smooth out the microscopically pitted surface, and, 2) to harden that surface substantially. Here's what happens:

Flattening the Peaks and Valleys

The smoothness of a surface is defined by its RMS (root mean square) value. The lower the number, the smoother the surface. Glass surfaces usually have a smoothness of from 2 to 5 RMS. Parker CPI burnished stainless steel seats range from 5 to 8 RMS. Unburnished stainless steel seats in competitive fittings have gone as high as 32 RMS.

When you have a stainless steel fitting that does not have a burnished seat you have potential sealing problems. The unburnished seat has microscopic peaks and valleys that can cause leaks. In remaking a stainless steel fitting with an unburnished seat, you are still attempting to seal against the same uneven surface and still have the potential for leaks.

Seat Finish



Burnishing defined*

Smoothing surfaces through frictional contact between the work and some hard pieces of material such as hardened steel rollers.

*Definitions of metallurgical terms by the ASM Committee of metallurgical terms.

American Society of Metals/ September 1977

Hardness also makes a better sealing surface.

When Parker CPI burnishes the seat of a stainless steel instrumentation fitting, it is hardened beyond the hardness of the ferrule it seals against. The Rockwell Hardness Measurement Scale shows that burnished seats are 20% harder than the stainless steel ferrule. This makes the seat practically impervious to the scuffs and scars that can occur when a fitting is remade often. You get a tight seal *every* time.

Burnishing is value-added.

There is of course, extra time and expense required in burnishing seats. But the resultant quality finish and reliability are well worth the operation. That's why Parker CPI burnishes the seats of its stainless steel and monel fittings.

If you would like more information on this and other steps that are taken to ensure top quality CPI fittings, we suggest you contact, our Chief Engineer, Fred Zikas, at the Parker Hannifin Corporation, Instrumentation Connectors Division, 9400 South Memorial Parkway, Huntsville, Alabama, 35802.

Parker

CIRCLE 23 ON READER SERVICE CARD