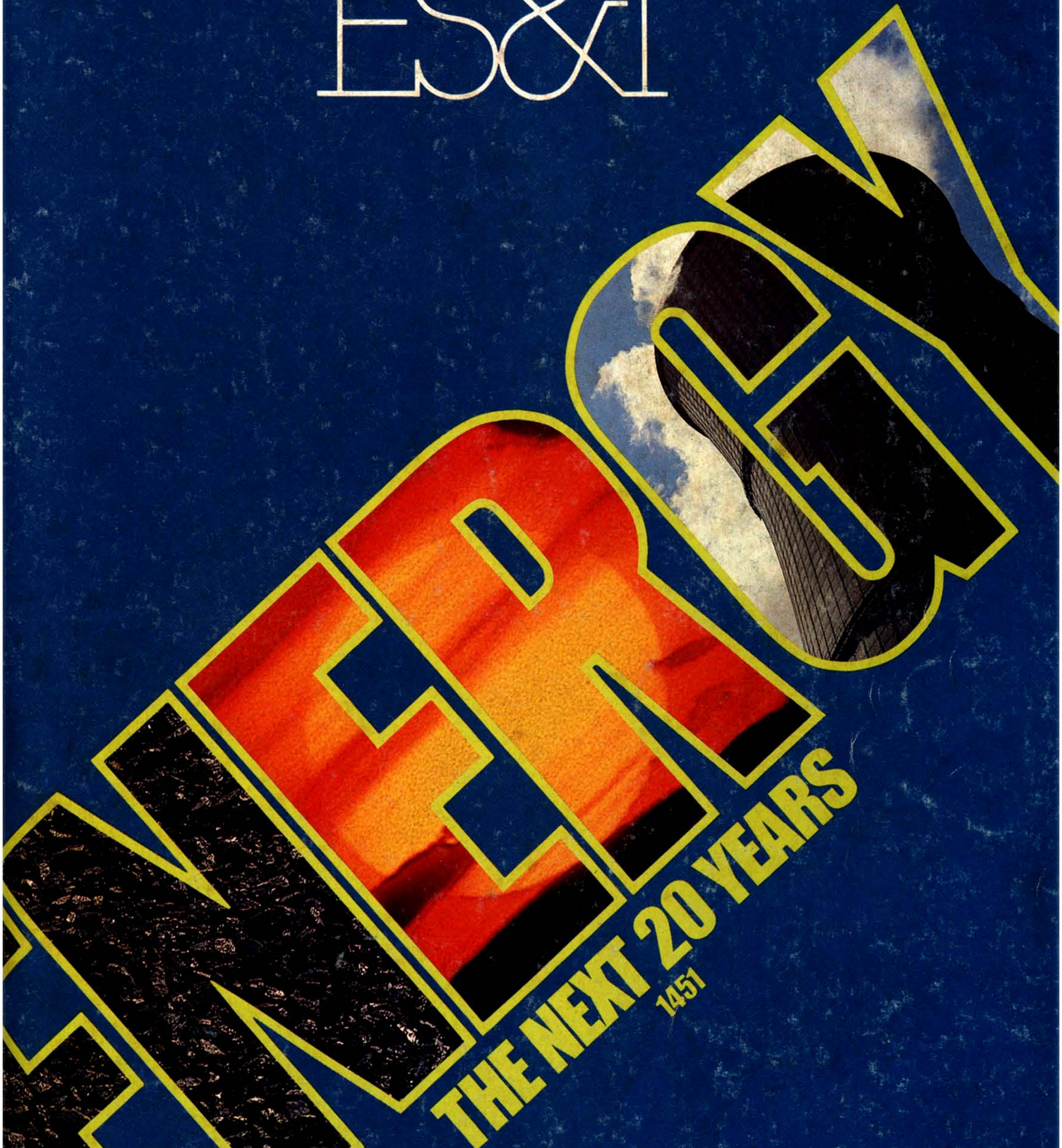
DECEMBER 1979
ENVIRONMENTAL SCIENCE & TECHNOLOGY

ES&T



THE NEXT 20 YEARS
1451

"NEITHER TOXIC GAS NOR MOLTEN LEAD CAN STAY THE ECOLYZER FROM ITS APPOINTED TASK."

Recently this ECOLYZER 6000 HIPSTER® took a searing bath in molten lead. The outside really took a beating. But when tested later, the vital sensor inside still monitored perfectly. Even after some lead was drawn into the sample port!

Chances are you'll never abuse your ECOLYZER like this. But it's good to know these life savers are tough enough to protect in the most hostile environments you can imagine. From pocket-size dosimeters to 16-point sequencer systems, ECOLYZ is reknowned for accuracy, superior protection and long-term reliability. We're the experts in toxic, combustible a oxygen gas monitoring systems. For more information our entire line, or specific products, call or write us direct.

Energetics Science
Division of Becton Dickinson and Company
85 Executive Boulevard
Elmsford, New York 10523
(914) 592-3010
Telex 137361

ECOLYZER

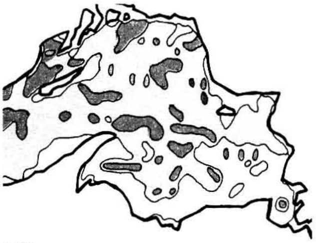
THE EXPERTS IN CO, H_2S, NO, NO_2
O_2 & COMBUSTIBLES.

CIRCLE 1 ON READER SERVICE CARD

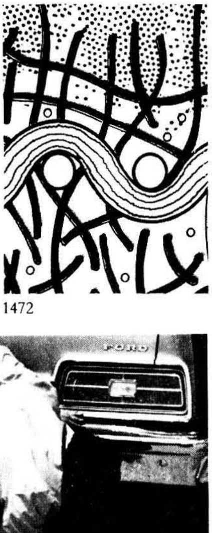
ESTHAG 13(12) 1439-1566 (1979)
ISSN 0013-936 X

ES&T CONTENTS

Volume 13, Number 12, December 1979



1462



1472

1476

OUTLOOKS

1451
Energy. Ford Foundation Report comments that energy—expensive today—is likely to be more expensive tomorrow.

1454
WPCF Houston meeting. Science and engineering are needed for the job of improving water quality.

1456
Nuclear plant waste. Industry spokesmen comment on approaches including burial at geologic sites.

REGULATORY ALERT

1459
Hazardous waste disposal. ERT's Michael Deland, Esq., labels it the environmental problem of the 1980's.

PAT REPORT

1460
Utility savings. Apollo Technologies, Inc. has ways to save on oil consumption in electric utility industry boilers.

FEATURES

1462
Toxic substances in the Great Lakes. Joseph J. Delfino, University of Wisconsin-Madison

1469
Analysis of organic water pollutants. Lawrence H. Keith, Radian Corp., Austin, Tex.

1472
Needled felts for fabric filters. Lutz Bergmann, Filter Media Consulting, LaGrange, Ga.

1476
Inspection and maintenance program for automotive emissions. John C. Elston, Bureau of Air Pollution Control, Trenton, N.J.

RESEARCH

1479
Fish and *Daphnia* toxicity as surrogates for aquatic vascular plants and algae. Eugene E. Kenaga* and Robert J. Moolenaar

Toxicity data from thousands of chemicals were reviewed to determine which aquatic organisms were most sensitive to chemical contaminants.

1481
Kinetics of reaction of cyanide and reduced sulfur species in aqueous solution. Richard G. Luthy* and Samuel G. Bruce, Jr.

Experimental rate kinetic data are presented for thiocyanate production from the interactions between cyanide and polysulfide and between cyanide and thiosulfate.

1488
Seasonal variations in the removal rate of material injected into the lower stratosphere. Robert W. Holloway

Possible explanations for the seasonal variations in tropospheric ^{91}Y and ^{144}Ce concentrations are discussed.

Environmental Science & Technology

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

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

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 addresses with ZIP code accompanied by a recent mailing label. Allow six weeks for change to become effective.

MICROFILM OR MICROFICHE. For information, write to: Microform Program, ACS, 1155 16th St., N.W., Washington, D.C. 20036, or call (202)872-4554.

Credits: 1449, Curtis Studios (Los Angeles, CA); 1454, *ES&T*'s Julian Josephson

Cover: Design by Alan Kahan; photos courtesy of LENSMAN: Robert Rathe (coal at Norfolk, VA), Ron Larson (sunset at Carlsbad, NM), Michael Crosby (Rancho Seco, CA nuclear plant)

1491

An evaluation of column chromatography and flameless atomic absorption spectrophotometry for arsenic speciation as applied to aquatic systems. Dennis G. Iverson, Marc A. Anderson*, Thomas R. Holm, and Robert R. Stanforth

Quantitative characteristics and modifications of reported methods for arsenic speciation are presented.

1494

Differences in particle size distributions of major organic pollutants in ambient aerosols in urban, rural, and seashore areas. L. Van Vaeck*, G. Broddin, and K. Van Cauwenberghe

Analysis by GC-MS showed TSP distribution shifts toward larger particles at the rural station as compared to the two other stations.

1503

Multielement analysis of municipal sewage sludge ashes. Absorption of elements by cabbage grown in sludge ash-soil mixture. A. Keith Furr, Thomas F. Parkinson, Timothy Wachs, Carl A. Bache, Walter H. Gutenmann, Patricia C. Wszolek, Irene S. Pakkala, and Donald J. Lisk*

Results are given for an analytical survey of 42 elements and polychlorinated biphenyls conducted on municipal sludge ashes from 10 American cities.

1506

Estimating rate constants for the uptake and clearance of chemicals by fish. W. Brock Neely

A method is proposed for estimating the rate constants for chemical uptake and clearance by fish based on the physiology of the fish and the properties of the chemicals.

1511

Prediction of removal of vapors from air by adsorption on activated carbon. Eric B. Sansone*, Yadu B. Tewari, and Leonard A. Jonas

Carbon adsorption capacities and rate constants are predicted using current adsorption theory and data obtained from characterization with a reference adsorbate.

1513

Atmospheric fallout in the vicinity of a base metal smelter at Flin Flon, Manitoba, Canada. William G. Franzin*, Gordon A. McFarlane, and Andrew Lutz

The composition and quantity of atmospheric fallout are reported, together with a comparison of two methods of collecting atmospheric deposition data.

NOTES

1522

Particulate matter. Its association with microorganisms and trace metals in an estuarine salt marsh microlayer. Leonard W. Lion, Ronald W. Harvey, Lily Y. Young, and James O. Leckie*

Water samples collected from the air-water interface in a salt marsh were found to contain elevated levels of particulates, plate count bacteria, and lead.

1526

Association of hydrophobic organic compounds with dissolved organic matter in aquatic systems. John P. Hassett* and Marc A. Anderson

Results indicate that cholesterol and TCB may be bound and held in aqueous samples by dissolved organic matter.

1530

Chemical heterogeneity of aerosol samples as revealed by atomic absorption and X-ray photoelectron spectroscopy. Brigitte Barbaray, Jean-Pierre Contour, Gérard Mouvier*, René Barde, Gérard Maffiolo, and Bernard Millancourt

By comparison of XPS and AA results, three types of heterogeneity have been noted in samples of atmospheric particles.

1532

Cyanoarenes in soot: Synthesis and mutagenicity of cyanoacenaphthylenes. S. Krishnan, Debra A. Kaden, William G. Thilly, and Ronald A. Hites*

The synthesis of two cyanoacenaphthylene isomers verified their presence in soots generated by the combustion of aromatic hydrocarbon fuels doped with pyridine.

1534

An estimate of the NO_x removal rate in an urban atmosphere. Tai Yup Chang*, Joseph M. Norbeck, and Bernard Weinstock

This analysis estimates the average residence time for NO_x in the LA Basin (all year) and St. Louis (summer) to be less than 2 days.

1537

Effects of organic and inorganic binding on the volatilization of trace elements during coal pyrolysis. Bill T. G. Ting and Stanley E. Manahan*

Results suggest that chemical forms of elements are important in determining their mobilization during coal conversion processes.

* To whom correspondence should be addressed.

This issue contains no papers for which there is supplementary material in microform.

DEPARTMENTS

ANNUAL INDEX

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

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

MANUSCRIPT REVIEWING
Manager: Katherine I. Biggs
Editorial Assistant: Rosalind M. Bish

MANUSCRIPT EDITING
Associate Editor: Deborah A. Wilson
Copy Editor: Kathleen Chaconas

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

Advisory Board: Robert J. Charlson, Charles Coutant, Rudolf B. Husar, Roger A. Minear, Francois M. M. Morel, Frank P. Sebastian, R. Rhodes Trussell, Charles S. Tuesday, William E. Wilson, Jr.

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*
Bacil Guiley, *Head, Magazine and Production Department*
Seldon W. Terrant, *Head, Research and Development Department*
Marion Gurfein, *Circulation Development*

ADVERTISING MANAGEMENT
Centcom, Ltd.
For officers and advertisers, see page 1550

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

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

CLEAN AIR ACT AMENDMENTS OF 1977:

We can lead you through.

Monitoring, Modeling, PSD Review, BACT Review — are these the things that are confusing you? If so, we'll guide you in getting the pre-construction permit, and in meeting all the complicated requirements — and then we'll stand by you with proof that you've met them.

We're in a unique position to help you. We not only took part in writing the quality assurance guidelines, we do quality assurance for monitoring throughout the U.S. for EPA. We manufacture and install air monitoring systems large or small. We understand the special problems industry is facing.

We have available all of the approved EPA models, along with the skill and expertise to use them. If you need special models, we can develop them.

If your requirements include special studies such as environmental assessment, emission inventories, special testing, development of emission factors, guidance on control technology — the whole sphere of environmental activities — we're prepared to help you.

We even offer a training course to help you understand the Clean Air Act and its amendments.

For full information contact
R. Yelin, Environmental Monitoring & Services Center, Environmental & Energy Systems Division, Rockwell International, 2421 West Hillcrest Drive, Newbury Park, CA 91320, or phone (805) 498-6771.

Rockwell International

...where science gets down to business

CIRCLE 5 ON READER SERVICE CARD

Manuscript processing time revisited

With added pages this year, we were able to cut through our backlog of accepted manuscripts so that processing lag-time at the production stage has been minimal, a goal we have been striving for over the past two years. Processing from receipt to acceptance is a different story. For some years, we have received, from the Advisory Board, authors, and reviewers, the suggestion that we could save much time by telephoning prospective reviewers *before* sending them manuscripts to review. It was their contention that we would thus be assured that reviewers were willing and able to perform the task and would send comments within the designated time (two week plus mailing time). Not so. We tried it and we didn't like it.

There were some advantages to the telephoning system, as noted by Dr. Christman in his October editorial. However, improvement in processing time was not one of them. It took *more* time in the initial handling because of the many calls to get willing, available reviewers. Our data showed that the average time per manuscript to get a positive response from two reviewers was 23 minutes (range 2 75). And we made just as many telephone calls to tardy reviewers as we had in the past. No time was saved in that part of the process. Authors whose manuscripts were delayed during this experiment (many were also reviewers) were generally understanding and patient. This year we owe particular thanks to our authors for their courteous and prompt response to requests for revision, even after lengthy delays in initial handling of their manuscripts.

In the period November 1, 1978 through October 31, 1979, we received 341 new manuscripts for consideration in the Current Research Section. During the same period, 503 reviewers assisted us - many of them more than once. Academe accounted for 236; government, 125; and industry, 142.

We thank all our reviewers for their support of the peer review process. It is an essential component of a quality research publication. To quote the late Howard Gerhart from his December 1975 editorial in *Industrial & Engineering Chemistry, Product R/D Quarterly*: "You are unseen and, to the authors, anonymous persons who exercise talents to write professional judgments in support of the peer review process. The results come back in many forms, degrees, and emotions. Depending upon circumstances, we observe various descriptive classifications of attitude and emphasis. But there are the many scholars who, knowing the subject matter, pass mature judgment in a fair manner and recite the concurrence along with the bias in a brief itself worthy of publication. The replies from two or three can never be a statistic. Neither can the editor be an adequate impartial judge. Yet the system works. Authors need a medium; librarians need expanding archives, and subscribers need to be informed."

Katherine I. Biggs

ES&T
LETTERS

Educational opportunities

Dear Sir: Because of the increasing demand for professional personnel educated in the various fields of environmental health, the Harvard School of Public Health has announced expanded opportunities for graduate education, both at the Masters and doctoral levels, in Industrial Hygiene and Occupational Health, Environmental and Respiratory Physiology, Air Pollution Control, Occupational and Environmental Radiation Protection, Radiation Biology, Toxicology, Medical Radiological Physics, and Environmental Health Management. Traineeships and fellowships are available for the financial support of students in most of these programs. The deadline for submission of applications for the Fall 1980 class is February 1, 1980. Interested persons should contact:

Dade W. Moeller
Harvard School of Public Health
665 Huntington Ave.
Boston, MA 02115

Hazardous waste disposal

Dear Sir: Please allow me to correct several apparent errors of inference that appeared in the recent article of the Valley of the Drums in Louisville, Kentucky (*ES&T*, August 1979 p 913). Almost two years prior to federal involvement, the technical staff of the Division of Hazardous Material and Waste Management and it's Director sent a strongly worded request for legal action to the Department's legal staff. As all know that have followed the developments in this matter, nothing happened. Several employees were "sacrificed" for being associated with the problem but the blame for the failure to act rested much higher.

Observing the situation from the inside, it is apparent also that mismanagement of situations like the Valley of the Drums will continue so long as the capacity to assimilate highly technical data and reach technically oriented decisions is lacking at the higher levels of regulatory agencies.

I wish to point out that the initial response was that the "Valley" had the same degree of potential hazard as Love Canal; technical evaluations were to the contrary. The incinerator proposal was less a well thought out "solution" than an attempt to get the agency to be an advocate for an incinerator which was rejected by three other Kentucky communities, one where the zoning was already correct.

The bottom line, an environmentally sound cleanup and disposal plus cessation of the illegal operation, took a back seat to playing to the press. When the "Valley" was officially escalated to the status level of a Love Canal, seeking cooperation from industry was much like trying to get someone to sign up to be a guinea pig in a cancer study.

The more salient point, however, is frequently lost in the fog created by the emotional issues, that is, that hazardous waste is not all the same, i.e., it is not all so dangerous that mere contact brings risk of death or serious injury. This glaring deficiency is adequately documented in numerous comments to the proposed federal regulations (*F.R.*, Dec. 18, 1978). Not all hazardous waste should be directed to Alabama's or North Carolina's secure facilities, but neither should they be left to cook in the summer heat south of Louisville.

Daniel R. Dolan
Chief, Hazardous Material Section
Division of Hazardous Material & Waste Management
Kentucky Department for Natural Resources and Environmental Protection
Frankfort, KY 40601

Editorial, SI units

Dear Sir: I read with heavy heart the effect of the heavy hand of bureaucracy in the ACS decision to switch to the SI units recommended by the NBS.

Incidentally, although I have taught chemistry for many years, and have been a member of the ACS for many years, a Guggenhein Fellow, and a past Gordon Conference Chairman, I don't remember anyone asking my opinion on this matter. Come to think of it, I don't remember asking the ACS to solve this invented dilemma for me. However, I am sure it does not matter either way; the die is cast.

The objective of publishing research is to communicate findings to your fellow workers, be their fields IR, Raman, X-ray, NMR, Clinical Chemistry, etc., and this is best done by communicating in the language and units to which they are accustomed.

In general, we understand units 1 to 10 best and 1 to 100 next best. Any change from that requires a little mental juggling. I have yet to meet anyone baffled by the units used.

Have our "leaders" in the ACS and NBS lost contact with the civilized world or is it vice versa.

Are we really going to switch to mols/m^3 (presumably × 10^{-3} to get it to a useful range)?

Are we really going to Kelvin, which virtually no one uses in the lab or industry, except to calculate a few theoretical constants?

I note, with alarm, that °Celsius is "acceptable" (for a while), a term hitherto reserved for the weather forecast. The term °Centigrade seems to have gotten lost. Angstroms are a thing of the past, although all X-ray spectrographers use nothing else.

How do we express concentration if we don't know the molecular wt, presumably % wt/wt or % volume/wt are not allowed. No doubt uniformity of units is tidy, especially for the nonexpert. Why not extend this completely and define all sources as hydrogen lamps, all detectors as photomultipliers, and all monochromators as gratings?

The beauty of the English language is the many subtleties available in communication. Adoption of the SI units will close many doors, open none, and appears to have little to recommend them except they are tidier and appeal to the bureaucratic mind (who probably never uses them anyway).

I realize that this letter is only a token gesture of resistance to ease my conscience before our "leaders" legislate each of us separately into a common suit of unisex clothes on a uniform flat piece of soil, each pointing towards Washington and all of us stretched or compressed to 5′10″ (sorry 1.778 m) and 160 lbs (oops 725.76 kg). But at least it made me feel better.

First down and 9.148 m to go.

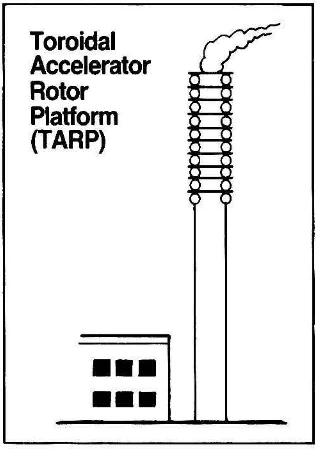
Good-bye Cruel, Cruel World.

J. W. Robinson
Professor of Chemistry
Louisiana State University
Baton Rouge, LA 70803

Wind Energy

Dear Sir: We wish to express our sincere thanks to *ES&T* for presenting the TARP WECS to its readers, ("Currents" *ES&T*, August 1979, p 905). However, I would like to clarify two important points.

First, the Toroidal Accelerator Rotor Platform (TARP) is not simply another variation on the windmill. Rather, the TARP represents a unique design in that its structure specifically serves a multifunctional, hence important, resource-conserving and economizing role as part of the energy system. TARP is thus highly suited for economical, environmentally sound, and practical widespread application including interface with tall emission stacks for energizing electrostatic precipitators.



Second, the TARP rotors should be illustrated at 90 degrees or greater (rather than less as shown) from the free-stream stagnation point on the TARP. This is significant in that it features free-yaw rotor stability which is supported by recent wind-tunnel tests at Rensselaer Polytechnic Institute.

Alfred L. Weisbrich
Eneco
Windsor, Conn. 06095

CHALLENGING OPPORTUNITIES WITH THE TENNESSEE VALLEY AUTHORITY

ENVIRONMENTAL SCIENTIST - AIR QUALITY STUDIES SD-4

To provide the theoretical basis and coordination for work done by the Air Quality Branch in atmospheric dispersion technology. You will direct the evaluation of existing and proposed air quality legislation and standards as they apply to the operation and design of TVA power plants. You should have a broad general knowledge of fluid dynamics, advanced math, atmospheric processes, air quality regulations and computer modeling. You should have a PhD or equivalent in atmospheric science, meteorology, environmental engineering or closely related field and at least 3 years experience, or a Master's Degree with at least 5 years related experience.

ENVIRONMENTAL SCIENTIST SD-3

Develop, evaluates, and applies atmospheric dispersion technology for analyses of the regulatory compliance of TVA projects and programs. You will apply and adapt existing dispersion models in compliance analysis studies and in assessment of the effects of existing and proposed governmental air quality regulations on TVA facilities. Familiarity with air quality regulations and a working knowledge of advanced mathematics, physical science, and computer modeling relating to atmospheric processes are required. You should have a PhD or equivalent in meteorology, atmospheric science, environmental engineering, or closely related discipline or a M.S. degree and a minimum of two years' applicable experience.

METEOROLOGISTS - AIR QUALITY STUDIES

To plan monitoring systems for power plants and provide emergency support for operational nuclear plants. You will prepare air quality assessments and revise data for site reviews, safety reports, environmental impact statements and licensing documents. You should have a PhD or equivalent in meteorology or an MS in meteorology and 2 years of related experience. A knowledge of computer simulation will be helpful.

All positions offer an excellent salary, complete benefits, and the potential for professional advancement. If unable to interview at this time, please send your resume to:

TVA
TENNESSEE VALLEY AUTHORITY
Employment Branch (ET 0437)
Room 240 MIB
Knoxville, TN 37902

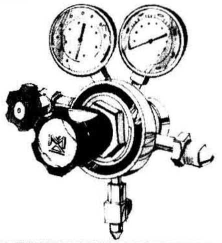
TVA may consider for appointments only U.S. citizens and others eligible for payments under section 602, Pub. L. 94-363, and section 750 Pub. L. 94-419.

An Equal Opportunity Employer

CIRCLE 9 ON READER SERVICE CARD

A Special Regulator For GC

The Matheson 3104 regulator is a high purity, two-stage regulator with a stainless steel diaphragm. Two-stage design provides even regulation regardless of cylinder pressure changes. Stainless steel diaphragm minimizes inboard leakage of air or water from the atmosphere, and does not outgas impurities into carrier or fuel gas systems. Five minute helium leak rate is $< 2 \times 10^{-9}$ ccs. Excellent for applications involving trace components. Circle Reader Service No. 31



High Purity Carrier Gases

Matheson makes carrier gases available in a variety of purity classifications – choose the specifications that most nearly meet your requirements. Routine analyses can be performed using Helium, High Purity, 99.995%. For more critical applications, you may choose Ultra High Purity 99.999% and Matheson Purity 99.9999%. For other applications, Argon, Hydrogen, and Nitrogen are all available in a variety of purities. Circle Reader Service No. 32

Calibration Standards

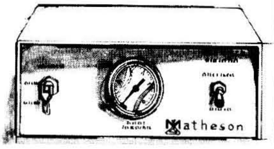
When the level (TLV) of a toxic vapor is to be monitored the instrument must be accurate – for the physical well-being of those who may be exposed.

The **only** way to do this is to calibrate the instrument with an analyzed standard. Matheson pioneered such standards, accuracy traceable to NBS, if available, or to Matheson Primary standards. Calibration standards are readily available for: benzene, vinyl chloride, acrylonitrile, carbon monoxide. . . virtually any vapor forming material. Circle Reader Service No. 33

Gas Miser

A device which allows one or more GCs to be set on standby during non-working hours. The flow of carrier gas is reduced with the flick of a switch without upsetting the equilibrium conditions of your instrument. Then normal operating conditions are resumed the same way.

Gas Miser, for the GC laboratory. Saves expensive time and carrier gas. Pays for itself in less than a year. Circle Reader Service No. 34



Zero Gases

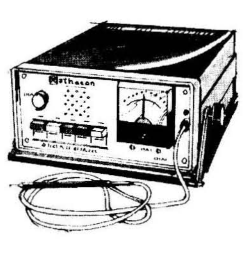
For the carrier gas, fuel gas, and oxidizer gas—all required for flame ionization and flame photometric gas chromatography-Matheson offers Ar, He, H_2, N_2, 40% H_2/60% N_2, and 40% H_2/60% He Zero Gases each having a total hydrocarbon content of less than 0.5 ppm (as CH_4). Air, Zero Gas is available with hydrocarbon content < 2.0 ppm. Circle Reader Service No. 35

Gas Leak Detector

Simple to operate. Detects helium and other gases with great sensitivity. Enables you to check your entire GC system without the mess usually associated with leak detection solutions.

The smallest imaginable leak in your GC system can invalidate your results completely – especially if you're working with trace concentrations.

We recommend that one be handy in every instrument lab. Circle Reader Service No. 36



How to Succeed at Gas Chromatography

Gases -- carrier gases, calibration gases, or fuel gases are key to good GC techniques. Matheson has equipment to help you improve this gas system and you should use it.

The wrong regulator or porous tubing can permit diffusion into the gas stream and influence results.

But some equipment will help in other ways like saving money or zeroing in on a defective connection.

Further, todays detectors are so sensitive that a welding grade of helium is counter productive.

To find out how you might improve the efficiency of your GC system, ask for our free wall chart describing methods that can be used with common and uncommon detectors in use today. Contact us for your copy.

Matheson®
Lyndhurst, NJ 07071

East Rutherford, NJ 07073
Morrow, Georgia 30260
Bridgeport, NJ 08014
Gloucester, Massachusetts 01930
Joliet, Illinois 60434
Dayton, Ohio 45424
LaPorte, Texas 77571
Cucamonga, California 91730

Newark, California 94560
Dorsey, Maryland 21227
Gonzales, Louisiana 70737
Whitby, Ontario, Canada L1N 5R9
Edmonton, Alberta, Canada T5B 4K6
B 2431 Oevel, Belgium
6056 Heusenstamm, West Germany

ES&T CURRENTS

INTERNATIONAL

Sweden will sharply limit the use of cadmium and cadmium compounds, beginning next July. Citing the steadily rising levels of cadmium which have been observed in human tissues, and the dangers of lung and kidney damage which may result from exposure, the Swedish government has moved to ban the use of cadmium in electroplating, as a stabilizer, and as a coloring agent. The country is also working to reduce the level of cadmium impurities in phosphorus fertilizer.

WASHINGTON

The EPA estimates a total cost of $360 billion for federal pollution control programs for the period 1977 to 1986. $142 billion of the total represents private-sector capital investment. A sharp rise in private industry's share of the costs of pollution control is forseen for the 1980's. EPA's estimates are based on the measures necessary for compliance with current environmental legislation, using existing control technology; technological innovations could cut the price, while enactment of proposed legislation creating a hazardous waste cleanup fund could greatly increase the price.

The Tennessee Valley Authority has authorized the spending of $5 million for the initial design of a coal gasification demonstration plant. Construction of the plant, which depends upon continued funding by Congress, is expected to be completed by 1989. When operating at full capacity, the plant will convert 20 000 tons of coal to gas each day. Total cost of the project is estimated at $1-2 billion. The site of the plant, probably somewhere in northern Alabama, will be decided on early next year.

EPA's Costle

The nation is behind schedule in its plan to clean up polluted waters, according to EPA Administrator Douglas M. Costle. Drawn out court challenges to EPA regulations, as well as EPA approval of overly sophisticated and expensive treatment plant designs have contributed to the delay. A General Accounting Office study echoed this last point: Advanced wastewater treatment facilities, expensive to build and operate, have been approved in several areas where they are not needed to meet water quality standards. The EPA has established a review and planning program in an attempt to correct this problem.

Further restrictions on the use of asbestos are being considered by the EPA and by the Consumer Product Safety Commission. The new regulations could affect the manufacture of household appliances, automobile brake linings, and building materials. The EPA is also considering a limitation on the total annual production and importation of asbestos. Current regulations prohibit using sprayed asbestos materials in buildings and set limits on workplace exposure.

A bill that would provide $152 million over the next 11 years for a study of acid rain is before the Senate. Acid rain results when pollutants such as oxides of sulfur and nitrogen react in the atmosphere with water to form strong acids. Supporters of the bill (S.1754) have emphasized that the problem is a national one: Acid rain often occurs far from sources of pollution, a result, in part, from use of tall smokestacks built to disperse pollutants and so satisfy local air quality standards. Acid rain is known to have caused direct damage to plant foliage, rendered lakes incapable of supporting fish life, and leached toxic heavy metals from the soil into the water table. State programs would receive $15 million to develop plans for dealing with acid rain.

The Occupational Safety and Health Administration has cited American Cyanamid Company for working conditions that threaten the fertility of female workers. OSHA ordered American Cyanamid to correct the hazardous conditions in its lead pigment section and pay a $10 000 fine. The move apparently represents a new interpretation by OSHA of its authority to protect workers against occupational illness and injury.

STATES

Nuclear waste dump sites in Nevada and Washington will remain closed, by order of the states' governors, until a national policy for waste disposal is established. South Carolina, where the only other dump site in the country is located, has refused to accept any wastes normally sent to other dumps, and further has banned dumping of any liquid wastes. Hospitals, medical research facilities, and some nuclear power plants are facing serious disposal problems. The Nuclear Regulatory Commission and DOE are asking the states in which the wastes are produced to establish their own temporary storage sites. National laboratories involved in nuclear research—including Brookhaven, Oak Ridge, and Los Alamos—may also be used for temporary storage.

New York is seeking $30 million directly from Congress for cleaning up PCB pollution in the Hudson River. The state had wanted to use a portion of its share of Clean Waters Act funds for the project. The EPA, however, would not allow that money to be used for purposes other than sewage treatment.

Geothermal power is making a come-back in Boise, Idaho. The city began using water piped from nearby hot springs for space heating in the 1890's, but shifted to gas and electricity in the 1930's. With the help of an expected $4.9 million from DOE over the next 3 years, Boise will revitalize and expand the existing system, and construct a second system which will supply heat to buildings in the business district. The result will be a saving of 350 000 barrels of oil per year.

Southern California has been chosen by the National Commission on Air Quality as the subject of the first in a series of regional studies aimed at evaluating alternative approaches to achieving air quality. The study will benefit both the NCAQ, which is preparing recommendations to Congress on the nation's overall air quality program, and Southern California. According to Los Angeles Mayor Tom Bradley—who is also a member of NCAQ—the study will help the L.A. area to learn "how increased refinery capacity to accomodate deregulation of heavy crude oil in Kern County will affect air quality and related public health issues."

L.A. Mayor Bradley

Michigan has reached a $15 million settlement with Hooker Chemical Co. Hooker will spend the money to clean up a chemical waste dump responsible for the contamination of water supplies in Montague, MI. The settlement also grants the state control over future use of the site and establishes an independent monitoring system to watch for any further leaks.

VIEWPOINT

An Energy Mobilization Board (EMB) would be an "energy dictatorship," says Colorado Senator Gary Hart. Under legislation passed by the Senate, the EMB could override state and local laws and could exempt projects, once underway, from the force of any new laws or regulations. Sen. Hart sees this as "an unprecedented usurpation of power reserved for state and local governments" and "an abdication of the responsibility of Congress and the President" for getting important energy projects started. In early November, the House passed its own version granting the EMB authority to waive federal, but not state and local, law; a compromise must now be worked out.

MONITORING

Imagine being able to detect all elements from beryllium to uranium. Spark source mass spectrometry (SSMS) may make this possible with 50-mg samples, and with a sensitivity consistent with proposed EPA multimedia environmental goals. This technique must be capable of detecting such a range of elements without prior knowledge of source species, in order to be a primary elemental analysis technique for Level 1 environmental assessments (*ES&T,* May 1978, p 513). Developed by EPA's Industrial Environmental Research Lab (Research Triangle Park, NC), the philosophy allows comparison of all sources because sampling/analysis is uniform.

TECHNOLOGY

Aluminum and other metals can be recovered from coal combustion wastes, according to Oak Ridge National Laboratory. ORNL's "Calsinter" process would sinter fly ash to 1200 °C with limestone and gypsum. A sulfuric acid leach would then remove about 98% of aluminum content, and over 90% of other metals. More attractive processes may be coming, too.

Solar-based electricity competing head-on with coal? Possibly, with a line-focus heliostat system, says SRI International (Menlo Park, CA). The main key is sunlight heating salt, thus generating steam, in a long receiver on which a heliostat bank is focused. Its main uses would be in the West and Southwest.

The problem of sewer connection moratoria could be alleviated by a total recycling toilet system which reprocesses its own "black" wastewater. Such a system, the Cycle-Let developed by Thetford Corp. (Ann Arbor, MI), is now in commercial-scale use for 12 buildings at the 13-acre Village Centre (Great Falls, VA). Thetford's David Calhoun says that the "black" water is processed virtually to the quality of rainwater. The key is a closed nitration/oxidation/ultrafiltration approach, with active carbon and ozone disinfection for final "polishing". Microprocessor control/monitoring provides environmentally "fail-safe" operation.

Ozone disinfection with high-purity oxygen-activated sludge is also a key to innovative installations at Thurston County, WA. This approach was brought about by The Massart Co., in a joint venture with Peter Kiewit & Sons. Other new techniques involve a 2.5 million-gal underground basin to equalize stormwater flow to about 25% of peak volume, allowing for a smaller treatment plant. Methane from waste sludge will supply heat to the digesters, as well as the administrative/maintenance offices. All mathematical processes, including payroll, are handled by computer.

A pollution-free bus using no petroleum products—it uses a 3000-lb flywheel—is under development at General Electric (GE, Erie, PA), with Depts. of Energy (DOE) and Transportation (DOT) support. The flywheel, fabricated from a stack of steel discs, would spin at 10 000 rpm, and could power a 28 000-lb bus with a full payload of passengers for 3.5 mi in stop-and-go city driving. The flywheel could be re-energized at a curbside charging station in 90 seconds. Energy is taken off the flywheel by a special motor-alternator developed by GE. Storage in low-pressure helium reduces windage losses.

Processing litho plate with water

A nonpolluting printing chemistry would involve aqueous processing. This is now made possible with "Hydrolith", a lithographic printing plate developed by 3M (St. Paul, MN). The plate would perform with the same materials, such as negatives, inks, and the like, as for any presensitized offset plate. However, after processing in water, to remove sensitized material, a special fluid with a "gum" is sparingly spread over the plate to desensitize the image. This gum can be washed off with water, and leaves no excess to flush. Any kind of water—even seawater—is usable, and 3M says that the plates will perform very well on press. No chemical developers are used for processing.

A method of filtering even fine particulates out of power house flue gases will earn General Motors (GM) an "Innovative Technology Order" from the EPA. The trick is a "side stream separator" which could allow GM to burn coal instead of scarce oil at its own powerhouses, to comply with Clean Air laws. Large particulates are caught inside conventional dust collectors. The remaining fines are captured in small filter bags into which they are sucked through "side stream" exhaust ducts. GM says that particulate control is thus improved by up to 50%, at less cost, and it is willing to make this technology available to other industrial firms.

Knock out bugs with "bugs"—use a bacterial pesticide, such as *Bacillus thuringiensis,* which can kill moths that damage stored grain. The germ will also protect certain crops and trees. It affects only certain insects; and not, apparently, "beneficials". About 0.75 lb of formulation will take care of 100 bu of grain, says the U.S. Dept. of Agriculture.

INDUSTRY

"Plenty of energy in the wind, but it's not much good unless the federal government does more to spur its development." So said Art Jackson of Hamilton Standard (Windsor Locks, CT) to a House committee. Among other things, he called for tax incentives, and noted that his own organization invested heavily in wind energy.

Safety and reliability for U.S. fossil and nuclear power plants—for this purpose, the Nondestructive Evaluation Center (NDE)—the first research facility of its kind in the U.S.,—is being set up at Charlotte, NC. It will be operated by J. A. Jones Applied Research Co. (Charlotte) for the Electric Power Research Institute. Programs will emphasize fast technology transfer, training, proper inspection, and work with universities to provide a pool of trained people. The idea is to come up with reliable nondestructive testing and inspection techniques.

In meeting regulation costs, fully 77% is incurred through compliance with EPA's, according to a recent study of 48 leading U.S. industrial firms. This is one reason why Richard Lesher, president of the Chamber of Commerce of the U.S., called for finding out if environmental costs can be reduced without sacrifice of environmental goals. One significant cost reducer he named was the "bubble concept", rather than, say, stack-by-stack controls. That concept emphasizes pollution control by an entire plant, rather than for each stack. Its use, Lesher said, could have a beneficial effect on costs, and, equally important, could speed up compliance.

The "superfund" for hazardous waste disposal site cleanup may be unfair, according to the National Association of Manufacturers (NAM). NAM Vice President, Resources and Technology, John Castellani suggested that any legislation for "hazwaste" areas be part of RCRA. He proposed that EPA first try to recover cleanup costs from those whose willful or negligent acts caused disposal site trouble. Castellani said that Congress . . . should review cleanup laws every 2 years, and appropriate maybe $20–50 million/y, at first, unless greater needs are indicated. He also made recommendations concerning EPA's role concerning public health threats, and recovery for damages/injury.

ARCO President Bradshaw

The U.S. is "beginning to feel its way toward a solution" to the energy problem. This is the cautious hope of Atlantic-Richfield Co. President Thornton Bradshaw who said that the most important energy initiative is petroleum product conservation, development of new U.S. resources, and keeping an oil import ceiling of 8.5 million bbl/d. He also said that President Carter's proposal for $88 billion over 10 years to generate 2.5 million bbl/d of synfuels "is wildly unrealistic".

AMBIO A JOURNAL OF THE HUMAN ENVIRONMENT RESEARCH AND MANAGEMENT

Now distributed for the Royal Swedish Academy of Sciences by Pergamon Press.

Launched in 1972 prior to the United Nations Conference on Human Environment, AMBIO is already recognized by many as the leading interdisciplinary periodical in the environmental sciences.

Now, with the aim of broadening an already international coverage and readership, AMBIO will be published and distributed through a joint arrangement between the Royal Swedish Academy of Sciences and Pergamon Press.

Regular issues contain general articles on current environmental problems and challenges and reports on original research in the field. Special issues give a more comprehensive treatment of some topical subjects.

". . . The most authoritative journal of its kind on international environmental problems."
GILBERT F WHITE, *President, Scientific Committee on Problems of the Environment, The International Council of Scientific Unions*

". . . AMBIO is the best magazine of its kind."
IGNACY SACHS, *Centre Nationale de Recherche sur L'Environnement*

FREE SPECIMEN COPY AVAILABLE ON REQUEST

Published 6 issues p.a.

Annual subscription (1980) **US$60.00** Two-year rate (1980/81) **US$114.00** Individual rate **US$25.00**

Prices include postage and insurance and are subject to change without notice.

Pergamon Press
Headington Hill Hall, Oxford OX3 0BW
Fairview Park, Elmsford, New York 10523

CIRCLE 12 ON READER SERVICE CARD

Pesticide and Xenobiotic Metabolism in Aquatic Organisms

ACS Symposium Series No. 99

M.A.Q. Khan, *Editor*
University of Illinois

John J. Lech, *Editor*
Medical College of Wisconsin

Julius J. Menn, *Editor*
Stauffer Chemical Company

A symposium sponsored by the Division of Pesticide Chemistry of the American Chemical Society.

Timely and broad in scope, this international symposium contains current state of the art papers on the metabolism and disposition of pesticides and other xenobiotic chemicals in aquatic organisms. Twenty-four chapters are divided into two sections: the first dealing with in vivo metabolism of xenobiotics and the second describing biotransformation and elimination processes in aquatic species.

CONTENTS

Organophosphorus Insecticides Metabolism • Polychlorinated Biphenyls • Cyclodiene Insecticides Metabolism • Aromatic Hydrocarbons • Phthalate Esters Metabolism • Thiocarbamate Herbicide Molinate Metabolism • Biotransformation of Chemicals • Pentachlorophenol • Disposition and Biotransformation of Organochlorine Insecticides • Insect Growth Regulators • Brominated Aromatic Hydrocarbons • Terrestrial-Aquatic Model Ecosystem • Modeling Aquatic Ecosystems • Investigation of Xenobiotic Metabolism in Intact Aquatic Animals • Pharmacokinetics in the Dogfish Shark • Disposition of Toxic Substances in Mussels • Cytochrome P-450 • Microsomal Mixed-Function Oxidation • Hepatic Microsomal Enzymes • Petroleum Hydrocarbons • In Vivo and In Vitro Studies of Mixed-Function Oxidase • Algae and Aquatic Microorganisms • Dietary Casein Levels and Aflatoxin B_1 Metabolism • Carbon Tetrachloride or Monochlorobenzene

436 pages (1979) Clothbound $33.50
LC 79-4598 ISBN 0-8412-0489-6

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

THE SUPER GAS-TIGHT SPIROMETER SYRINGE.

Here's a two liter gas-tight syringe that's accurate to ± 1%, well below the government-required 1.5% for calibration of spirometers used to sample airborne contaminants.

Constructed with a gas tight acrylic cylinder, sealed by a rubber o-ring, the syringe will collect and deliver two liters of air to ± 20 ml. For leak-proof spirometer attachment, the syringe is equipped with a tapered tracheal tip. A Luer lock Adapter is available for special connections. For other large volume requirements, 0.5, 1.0, and 1.5 liter syringes are available. Let us ship yours today. Call toll-free, 800-648-5950 for the dealer nearest you, or write for a free catalog to Hamilton Co., P.O. Box 10030, Reno, Nevada 89510.

HAMILTON

CIRCLE 11 ON READER SERVICE CARD

ENERGY

The Next Twenty Years

In a recent book with the above title (the third book in a series of Ford Foundation ventures reporting to the nation on energy topics), a group of 19 experts, about half of them economists, point out seven realities concerning energy and offer nine recommendations for an energy policy. The book is the result of an 18-month study that was sponsored by the Ford Foundation, administered by Resources for the Future, and chaired by Hans H. Landsberg, director of the Center for Energy Policy at Resources for the Future.

First off, this group notes that the use of energy resources has been and will continue to be constrained by political or environmental factors. But the world is not "running out" of energy. The foreword states that, in the words of former Ford Foundation President McGeorge Bundy, "The single most important element in the continuing crisis of energy policy may be the continuing failure in our national understanding of it." He continued, "The central message of the present report is that energy—expensive today—is likely to be more expensive tomorrow and that society as a whole will gain from a resolute effort to make the price that the user pays for energy, and for saving energy, reflect its true value. And I myself think that the message will prove right and timely in 1979."

Themes

Several themes thread their way through the 15-chapter book. A pervasive one is that to think of energy as a "crisis" will likely lead to both unhelpful public attitudes and to mistaken policies. Rather, Landsberg notes in his commentary that was prepared for a press briefing, that energy is a problem that society as a whole and government at all levels, have to learn to manage and to cope with. To be sure, energy issues are apt to trigger crises—and we have already passed through some of them; but managing energy is best perceived as a continuous process of adjustment, requiring an interplay of all the tools our society possesses for facilitating adjustment.


Hans H. Landsberg
chaired the study group

According to the chairman, chief among those tools—and this is the second theme—is the market with its pricing system which sends signals to consumers and producers to enable them to make rational choices as to kinds and timing of expenditures. Rapid decontrol of oil and gas prices and dismantling of the entire oil-control apparatus are, therefore, at the top of the group's recommendations, accompanied by careful analyses of their impact on inflation and income distribution.

In the light of strong attempts to make the windfall-profits tax on oil a near-permanent feature of energy policy and the slow decontrol timetable for natural gas, there is good reason to worry that decontrol now underway may not be as firmly in place as one would wish.

A third theme is the central role of imported oil. Again in his commentary, Landsberg notes that the reduction of oil imports is of the highest

The seven realities for understanding issues critical to managing the energy problems in the next two decades:

- The world is not running out of energy.
- Middle-East oil holds great risks, but is so valuable that the world will remain dependent on it for a long time.
- Higher energy costs cannot be avoided, but can be contained by letting prices rise to reflect them.
- Environmental effects of energy use are serious and hard to manage.
- Conservation is an essential "source" of energy in large quantities.
- Serious shocks and surprises are certain to occur.
- Sound R&D policy is essential, but there is no simple "technical fix".

priority, and is welcome around the globe. To promote it, the study group favors such indirect means as higher prices, conservation measures, and possibly import fees over physical or financial ceilings, or quotas on imports. Its conviction is that either of the latter "direct" methods would further ensnare us in new bureaucratic mazes and entrench government in a role that is better left to the market, however far it is from functioning as an "ideal" model.

A fourth theme is the international character of energy and energy problems. The group says that we cannot stop the world and get off. The international oil market provides a major link through its effect on every country's economic well-being. Additionally, several environmental impacts transcend national and even continental boundaries. Every action the U.S. takes in the energy field should be evaluated in terms of its effect, not only at home but abroad. The different objective situations as well as perceptions that exist in other countries must be taken into account in our decisions, according to the commentary; the book devotes an entire chapter to foreign trends, perceptions, and policies.

The need for and scope of international considerations is pervasive. Oil is traded throughout the world, and even small fluctuations in output in a single country cause reverberations in every importing nation. For example, economically producible uranium reserves are concentrated in a small number of countries, and just as oil importers watch the Middle East, Venezuela, and Mexico, so uranium importers watch the U.S., Canada, Australia, and southern Africa for signs of future feast or famine. Similarly, Landsberg continues, the future direction of Soviet oil and gas output can tighten or loosen the supply/demand balance worldwide.

Conservation

The study group strongly supports conservation as a generally inexpensive and potentially large "source" of energy, even though the diversity and diffusion of decision-makers in the conservation area present substantial obstacles to achieving the potential.

A barrel saved is truly a barrel produced (for other purposes). Yet, the group states, "There is nothing inherently good about these energy conserving activities, just as there is nothing inherently good about pumping oil from the ground. Energy conservation, like oil production, is an economic activity that can be pushed so far that is ceases being cheap and easy and becomes costly and inconvenient—but it may still be preferable on economic grounds to the alternatives."

The energy sources

The report deals extensively with coal, nuclear, and solar energy. The first two are the ones we need to rely on more heavily for the next 10–20 years; solar appears to have great promise for the tail-end of our period and beyond. Though the group shares the vulnerability and political risks associated with oil imports, it by no means discounts oil and gas.

These two fuels will still provide the bulk of most industrialized countries' energy, though a shrinking share, by the end of the century; but oil and gas from several hitherto barely tapped, economically marginal sources may come to fill the gap, and the group makes a strong plea for an intensive investigation into the nature, likely cost, and possible timetable of emergence of such hydrocarbon sources.

The group's strong endorsement of solar energy is rooted in its judgment that an energy future based increasingly on the twin support of coal and nuclear means relying on two flawed options and is not an attractive outlook. Concern regarding coal ranges from health impact to possible climate modifications from carbon dioxide accumulation in the earth's atmosphere; concern regarding nuclear energy ranges from ever present risks of safety and health to diversion of fission products for weapons manufacture. The group does not conclude, however, that we must abandon either coal or nuclear, but urges policies to render both of them more acceptable.

Specific recommendations for air-pollution policy:

- De-emphasize rigid deadlines and standards.
- Make continuous progress over time towards cleaner air, giving priority to areas where the value of cleaner air is greater for health, economic, or aesthetic reasons.
- Research on scientific facts underlying pollution should seek to define general relationships among pollution, human health and other values protected by cleaning the air, not to find "no-damage levels".
- Provide cost-effective incentives for progress towards cleaner air, such as emission charges and marketable-discharge permits.

Coal, air, health

The principal obstacle to the growth of coal use lies in the disinclination of potential users. In the group's judgment, current air pollution control policy is the principal reason for this attitude.

In the matter of air pollution, the study group states that "... society must deal with two related but distinct problems; basic judgments must be made about what level of costs and risks should be incurred in one area of life in order to reduce costs and risks elsewhere; and social processes and institutions must be established for implementing and continually modifying these judgments in the light of new information and changing circumstances. Failure either to make the required social judgments or to provide mechanisms for implementing and modifying them effectively can result in environmental management programs that are ineffective and too costly."

In the matter of risks to health, the group's critical attitude toward past philosophy and policy is best expressed in this quotation: "Both energy and environmental values would benefit by adoption of alternative policy approaches that would leave to government what it should be doing—setting the basic objectives or providing the proper incentives—while leaving to the private sector the job of figuring out the details."

The study group noted in one of its recommendations that nuclear power should not be excluded as an energy option either in the U.S. or abroad, either in the short or long run. There is still enough of a likelihood that we will need breeders that we should continue to have a broad and substantial research development and demonstration program. The group also cautioned that the final word would be with the electric utilities that must make the investment decision.

On solar, the report cites, "Our own position is that solar energy should and will become an increasingly important part of the energy picture within the next 20 years, even though it is now impossible to quantify its likely impact. . . . We are basically optimistic about the contribution that solar energy can actually make to energy supply within our 20 year period."

With specific reference to air pollution, the report states that current concepts and programs "make the conflicts between energy and environmental values more severe, disruptive, and costly than they need to be—and threaten to damage both energy and the environment in the long run." Some moves recently made by EPA seem to be going in a fruitful direction, the group believes, i.e., toward market-like mechanisms.

While noting that the environmental effects of energy use will remain "serious and hard to manage", the authors say they are "cautiously optimistic" about the environmental effects of future energy production: ". . . given careful and flexible management, energy can be produced and consumed in the U.S. at levels we think likely over the next 20 years, without undue harm to human health, natural systems or aesthetic values in general."

Earlier reports

McGeorge Bundy, in the report's foreword, noted that the central message delivered by the authors of the first study, *A Time to Choose,* was that this country could and should get along with less energy than historic patterns of growth suggested. That message was right and timely in 1974. The central message of the group that did the second study, *Nuclear Power Issues and Choices,* was that over the next generation we could and should handle nuclear power in ways that would reduce the dangers of nuclear proliferation, without giving up light-water reactors for the present and other nuclear options for the future. That message was right and timely in 1976–1977. SSM

The book:
Energy: The Next Twenty Years
Ballinger Publishing Company
Cambridge, Mass.
$9.95, paper; $25, hard cover

Its nine recommendations for energy policy:

- Decontrol oil- and gas-producer prices.
- Make utility prices to consumers better reflect real costs.
- Use science and technology to generate and define basic options, while relying primarily on the private sector to develop and deploy technology.
- Adopt a different approach to air-pollution control.
- Prepare for disruption in world oil markets.
- Continue efforts to reduce the problems associated with nuclear power.
- Work to improve the acceptability of coal.
- Vigorously pursue conservation as an economical energy source.
- Remove impediments to use of solar energy.

Its 15 chapters:

- Overview,
- The Future Demand for Energy,
- Energy Conservation: Opportunities and Obstacles,
- Economic Management of the Energy Problem,
- Regulating Crude Oil Prices: Gainers and Losers,
- Oil Imports,
- Energy in an International Setting,
- Global Energy Resources,
- Trends and Policies Abroad,
- Coal: an Abundant Resource—with Problems,
- Coal Production: Potential and Constraints,
- Coal: Climate and Health Hazards,
- Managing Air Pollution,
- Alternatives to Fossil Fuels,
- Nuclear Power,
- Solar Energy,
- Improving the Process,
- Jurisdiction, Regulation, and Decision Making,
- The Role of Science and Technology.

Its 19 authors:

Hans H. Landsberg is a senior fellow and former director of the Center for Energy Policy Research at Resources for the Future.

Kenneth J. Arrow is professor of economics at Stanford University and is a recipient of the Nobel Memorial Prize in Economic Science (1972).

Francis M. Bator is professor of political economy at the John F. Kennedy School of Government, Harvard University.

Kenneth W. Dam holds the Harold J. and Marion F. Green Professorship and is director of the Law and Economics Program, University of Chicago Law School.

Robert W. Fri is president of the Energy Transition Corporation, a company which assists industry in managing the marketing, technological, financial, and governmental aspects of new energy developments.

Edward R. Fried is U.S. executive director of the World Bank.

Richard L. Garwin is adjunct professor of physics at Columbia University and professor of public policy at Harvard University.

S. William Gouse is vice president and chief scientist at the Mitre Corporation.

William W. Hogan is professor of political economy and director of the Energy and Environmental Policy Center at the John F. Kennedy School of Government, Harvard University.

Harry Perry is energy consultant to the Center for Energy Policy Research at Resources for the Future.

George W. Rathjens is professor of political science at the Massachusetts Institute of Technology.

Larry E. Ruff is an energy economist at Brookhaven National Laboratory.

John C. Sawhill is deputy secretary of the U.S. Department of Energy.

Thomas C. Schelling is the Lucius N. Littauer professor of political economy at the John F. Kennedy School of Government, Harvard University.

Robert Stobaugh is professor of business administration and director of the energy project at the Harvard University Graduate School of Business Administration.

Theodore B. Taylor is an energy consultant who served on the President's recent Commission on the Accident at Three Mile Island.

Grant P. Thompson is presently senior associate at The Conservation Foundation.

James L. Whittenberger is a physiologist with special interest in environmental health.

M. Gordon Wolman is chairman and professor of geography in the Department of Geography and Environmental Engineering at Johns Hopkins University.

While regulations, injunctions, and penalties will act as stimuli, it is hard science and engineering that will do

The job of improving water quality

Reputedly, "they do things big in Texas." The growth of Houston's population—presently 80 000/y—is an example of how that adage is borne out. Welcoming the 52nd Annual Conference of the Water Pollution Control Federation (WPCF) to that fast-growing city, Mayor Jim McConn reaffirmed a commitment to provide good quality water and proper wastewater treatment (wwt) for its rapidly burgeoning population. Mayor McConn noted his city's $500-million investment in wwt over the last five years, and said that the forthcoming 69th Street Plant will serve 500 000 people "within the next few years". The WPCF conference hosted about 10 000 people, featured 325 exhibitions representing a diversified technical program, and was the largest U.S. exhibit of its kind.

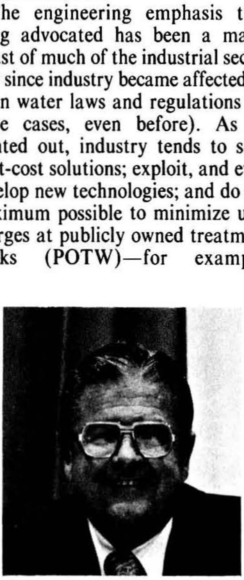
So Houston may be on the way to meeting municipal wwt goals. But not all municipalities in EPA Region 6, in which Houston is located, seem to be doing as well. Indeed, Adlene Harrison, Region 6 administrator, said that while progress is certainly being made, about 75% of the municipal wwt plants in her region do not meet provisions of their National Pollutant Discharge Elimination System (NPDES) permits. Their noncompliance ranges "from trivial, administrative infractions to serious violation", she complained. She also predicted, as did this year's WPCF President Martin Lang, that water quality goals of 1985 will not be met.

"Tailor to real needs"

Still, there has been considerable progress toward cleaner water, numerous specific instances of which were listed by EPA Administrator Douglas Costle, who addressed the Federation luncheon. However, one can speak happily of water improvement triumphs or complain of delays in meeting goals, but what is the principal means by which water quality improvements will be achieved? These improvements will be attained "by engineering and scientific efforts, much more than by injunctions, fines, or other legal penalties", as Lang reminded the conference.

The engineering approach he called for was "a reasoned move toward cost-effective treatment austerely tailored to the real needs of receiving waters." This approach, he forecast, "would save billions of dollars over the useful life of treatment facilities." For example, Lang pointed out that some local conditions could indeed warrant expensive, perhaps capital- and energy-intensive advanced wastewater treatment (AWT). In other cases, however, degrees of sewage treatment somewhat less than secondary may present no undue threat to receiving waters. Nevertheless, Lang did commend the new focus on toxics removal as a demonstration that "priorities can indeed shift to bear on those areas where human health is concerned, and to get maximum return for an environmental dollar."

The engineering emphasis that Lang advocated has been a major thrust of much of the industrial sector ever since industry became affected by clean water laws and regulations (in some cases, even before). As he pointed out, industry tends to seek least-cost solutions; exploit, and even develop new technologies; and do the maximum possible to minimize user charges at publicly owned treatment works (POTW)—for example, through constant improvement of pretreatment techniques.



Houston Mayor McConn
"$500 million for wwt"

Incidentally, Lang said that he had forecast this industrial initiative as far back as 1973; and, at the time, recommended against the industrial capital cost recovery (ICR) program. He believed that whoever assumed that industry would invariably go straight to POTW, rather than to pretreatment or to setting up its own wwt systems, was mistaken. He also noted that tax laws passed since 1972 make it increasingly profitable for industries to pretreat their wastes, and that in 1977, EPA's own consultant confirmed the assessment of how industry would perform, and recommended termination of ICR.

Carbon and sludge

A salient example of industrial initiative is DuPont's PACT^{SM} (powdered activated carbon treatment) process to remove organics, including any priority pollutants, from wastewater. The key phrase here is "priority pollutants". The process is operated at DuPont's Chambers Works (Deepwater, N.J.), and must handle more than 50 priority pollutants in its wastewater, which can amount to 23–50 mgd and have a pH averaging 2.0.

The Chambers Works process essentially calls for neutralization with a lime slurry and settling at the primary treatment stage. Much of the metal contaminants is taken out at this stage. For secondary/tertiary treatment, the PACT powdered activated carbon-activated sludge process comes on line, and is used with effluent from the primary clarifier. In this step, returned PACT sludge from secondary clarifiers is added to biological aeration tanks, along with make-up carbon. After aeration, effluent is treated with polyelectrolytes to coagulate fines, before going to the secondary clarifier tank. Treated secondary clarifier effluent is discharged.

Excess PACT sludge goes to a thickening/storage tank, and from there, to filter presses where it is dewatered to 45% solids. The solid cake is heated in a multiple-hearth furnace so that biomass is destroyed and powdered carbon is regenerated. This regenerated carbon—with make-up carbon added as required—is acid-washed, to prevent ash buildup, and recycled to the biological aerators. About 32% of the carbon was regenerated during 1978, the first full year of operation.

David Hutton and Stanley Temple of the Chambers Works say that overall organic pollutant removal with PACT averages 82% when measured as dissolved organic carbon. Indeed, for some individual priority organics, removal can exeed even 99.9%. Some metals are also removed quite well, although most of those are taken out during primary treatment. While the larger part of their results were obtained in a bench-scale simulator, Hutton and Temple believe that the PACT process, as scaled up, represents "best available", and generally works better than activated sludge without carbon—with certain compounds, such as some phenolics and nitrobenzenes, markedly better.

Organics recovery

Activated carbon might also be a significant vehicle for recovery/recycling of certain organics. Such recovery becomes more economically "interesting", now that "virgin" chemicals' prices have increased commensurately with the cost of petroleum, from which many of these chemicals are derived. However, recovery of the granular activated carbon (GAC) through thermal approaches generally destroys the compounds one wants to recover, as well as a goodly portion of the GAC. In addition, recovery techniques, such as distillation and extraction, have heretofore found limited application, according to R. Fox and his colleagues at Hydroscience, Inc. (Knoxville, Tenn.).

Fox set forth three principal methods by which organics desorption/recovery and GAC regeneration could be enhanced:

- pH shift for weak acids and bases,
- solvent elution for a wide variety, of organics, and
- steam for volatile organics.

He said that more than 100 cycles of adsorption-desorption have been achieved with actual wastes. In addition, water-miscible solvents that cannot be used for liquid-liquid extraction of wastes from water can often be used to regenerate the carbon.

One pilot test, which apparently convinced Hydroscience's client to "go full-scale" by the end of this year, involved wastewater mostly from brominated organics manufacture. Discharge is to a POTW, so pretreatment is in order. Wastewater contains mainly ethylene dichloride (EDC), with traces of other materials.

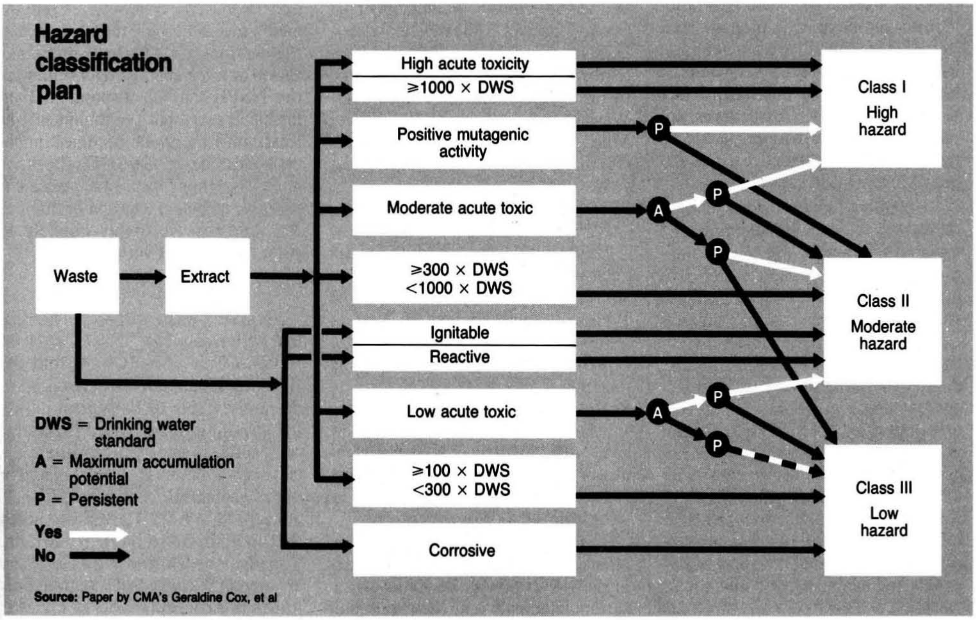
Tests over four months used Witco Chemical's Witcarb 950 grade GAC. Ultimately, they showed EDC removal exceeding 99.9%, with a typical EDC loading of 0.35 lb/lb of GAC. Final brominated organic concentration in effluent, with one exception, ranged 2-11 μg/L.

The capital cost for the full-scale system for 50 gpm, containing about 1700 lb/d of EDC, is estimated at $150 000. Operating costs are pegged at 12¢/lb of EDC removed; 0.3¢/gal of waste treated; and 4.4¢/lb of carbon regenerated over 100 cycles. Maintenance and depreciation are put at 15% of capital.

Solar digesters

These days, energy conservation is a major consideration in wwt; indeed, a municipal project could be granted "innovative and alternative" (I&A) status, because of proposed energy-saving features. For instance, the first wwt project in EPA Region I to be declared I&A is one in Hillsborough, N.H., and is to have a capacity of about 475 000 gpd, according to Edward Rushbrook, Jr. of Anderson-Nichols & Company, Inc. (Concord, N.H.). In the facilities, primary sedimentation will be followed by rotating biological contactors, secondary clarification, disinfection, and then discharge. Sludge handling will be anaerobic—with methane generation—and sludge dewatered on a belt filter will be landfilled.

What is "I&A" is that, for openers, the digesters will be heated by solar energy. Then, methane from anaerobic digestion will help to generate electric


Hazard classification plan

Source: Paper by CMA's Geraldine Cox, et al power to supplement the public utility's power supply. The wwt plant's generator will feature heat recovery. Moreover, a heat pump will extract heat from the plant effluent, as well as from the secondary anaerobic digester.

Maximum construction cost estimates (Fall 1978 dollars) are slightly more than $2.05 million. Annual operation/maintenance costs are $52 395, but a credit of $5560 should be applied to that figure for methane plus reclaimed heat. The plant study and cost estimates were prepared by Anderson-Nichols with assistance from Douglas Wilke, architect-engineer of Glen Head, N.Y.

RCRA costs

Engineering capabilities will be increasingly called upon to meet certain provisions of the Resource Conservation and Recovery Act of 1976 (RCRA). This law has a bearing on wwt, in that it would require NPDES-permitted facilities to meet hazardous waste ("hazwaste") disposal criteria, if they handle such wastes. The Chemical Manufacturers Association (CMA, Washington, D.C.) estimates a chemical industry retrofit cost, for this purpose, of $2.1 billion, just for surface impoundment facilities, to comply with RCRA. The American Petroleum Institute speaks of a $34-billion capital, and $3.4-billion/y operating cost to meet RCRA, especially if drilling muds and brines remain designated by EPA as hazwaste.

CMA's Geraldine Cox and other industry representatives proposed that hazwastes be classified as to *degree* of hazard. These degrees would comprise high, medium, and low hazard (see chart). In this way, Cox believes, applicable RCRA provisions "could be met with the most effective use of disposal capacity and capital."

Regulations that chemical and other industries face may have provided much of the impetus for the development of equipment and systems to improve water quality. The same holds true for regulations to which municipalities are, and will be subject. But, to repeat what WPCF President Lang pointed out, the laws and their accompanying regulations, and threats and impositions of civil and criminal penalties, though they may indeed act as a stimulus, do not bring about water quality improvement. Meeting water cleanup goals cost-effectively, whether by 1985 or later, will be accomplished, finally, through the know-how of scientists and engineers, and much hard work. JJ

Nuclear power plant waste management

Industry spokesmen say that the technology is there. Here are several approaches, most of which involve long-term burial at stable geologic sites

Nuclear power plant wastes: what is to be done with them? If this often-asked question isn't answered fairly quickly, it is possible that the controversy over nuclear power as an energy option could become academic. Indeed, a lack of recognized means of protecting man and his environment from these wastes might lead, essentially, to the foreclosure of the use of nuclear power.

It is hardly surprising, then, that solving the nuclear-waste problem is a high-priority item for the federal government and the nuclear-power industry. Thus, this effort is the subject of meetings and workshops devoted solely to that topic. One example of such a gathering of experts was the Workshop on the Management of Spent Fuel and Radioactive Wastes, held in Washington, D.C., in September. The workshop was sponsored by the Atomic Industrial Forum (AIF, Washington). In the wake of the Three Mile Island episode, perhaps such meetings become particularly cogent.

"Levels" of waste

Before one discusses what to do with nuclear wastes, perhaps it is helpful to address what the waste comprises. As Walton Rodger, partner of Nuclear Safety Associates (Bethesda, Md.), explained to a recent Washington meeting of the National Society of Professional Engineers (NSPE, Washington), one speaks of "high-level" and "low-level" wastes. Examples of high-level wastes might consist of those containing isotopes such as strontium-90 (^{90}Sr), cesium-137 (^{137}Cs), iodine-129 (^{129}I), and certain others. The low-level waste comprises principally, slowly decaying transuranic elements and their daughter elements. For definitions of high-level, and low-level waste, see the *Code of Federal Regulations,* 10 CFR 40, Appendix F.

At the NSPE meeting, Rodger pointed out that if spent nuclear fuel is reprocessed—which he believes will happen—the reprocessing waste stream will contain high-level material. If, however, spent nuclear fuel is not reprocessed—and such reprocessing is indefinitely deferred by U.S. policy at present—then it becomes high-level waste, since it contains all of the radio-isotopes that would have ended up in the high-level waste had the fuel been reprocessed to recover uranium and plutonium.

Rodger also defined "containment" and "isolation" concisely. "Containment" means keeping the waste within the confines of its place of immobilization or interment. Rodger reminded the NSPE that *no* disposal method unable to accomplish containment—at least, until the waste becomes innocuous—can be employed. On the other hand, "isolation" means the placement of waste in such a location or manner that humans are highly unlikely to come into contact with it.

"Problem with a solution"

"Nuclear waste disposal is a problem with a solution," Neal Carter, of Battelle/Columbus (Ohio), told the AIF workshop. He believes that a presently viable technological option for disposing of contained high-level radioactive wastes from civilian nuclear power plants is to isolate them in mined geological repositories (*ES&T,* June 1978, p 632). Carter also noted that in addition to the U.S., Britain, Canada, Sweden, and West Germany are among the nations whose programs utilize this concept.

In the U.S., at least, the first such repository will not be ready until after 1990. Carter observed that the reason for such a long time lag is partly political and partly technical, though some other experts say that there is actually no technical basis for not proceeding. For instance, after the waste is properly contained, it must be determined that the geologic formation of, and material in the respository will be stable, seismically and otherwise, for very long periods of time. It should also be ascertained that the wastes cannot migrate from their resting place into the rock, soil, air, surface, or ground water. However, one expert told *ES&T* that migration itself is not bad, as long as the waste materials do not reach the biosphere.

Will the geologic host media receiving the wastes be salt, shale, basalt, granite, tuff, or some or all of these? It is the job of the National Waste Terminal Storage (NWTS) program of the U.S. Department of Energy (DOE)—a program on which Battelle and other contractor organizations are working—to select the proper sites and media, be they in salt beds or domes, deep mines in rocks, or whatever.

The NWTS program is also to formulate a time schedule for devising and validating disposal methods for use in several geologic host rock media. Validation will require rigorous *in situ* testing/demonstration. Some such testing would be done with electric heaters, for example, in salt beds or domes in Louisiana, or in deep iron mines in Sweden, perhaps to create thermal conditions similar to those that wastes may bring about. Repository tests with actual encapsulated waste fuel assemblies could be slated for Nevada (granite, an igneous rock), and the State of Washington (basalt, also an igneous rock).

Starts and stops

To reprocess or not to reprocess? Shifts in policy, rapid starts, stops, reviews, and re-reviews of items pursued through the 1960's and early 1970's have left unclear which way to go to manage civilian nuclear power plant waste. Denny Condotta, manager, Reprocessing and Field Services, Exxon Nuclear Co., Inc., told the AIF meeting, "We are still awaiting clear definition of a governmental policy and plan for action."

These starts and stops, Condotta noted, have led to public perception that the nuclear industry has no solution to the waste problem, despite the fact that the *federal authorities* have the responsibility to lead this effort. This federal responsibility extends to both defense and commercial high-level nuclear wastes. Condotta noted that technology to support a waste management program is available, but what is needed is a strong *implementation* program. More specifically, Condotta called for:

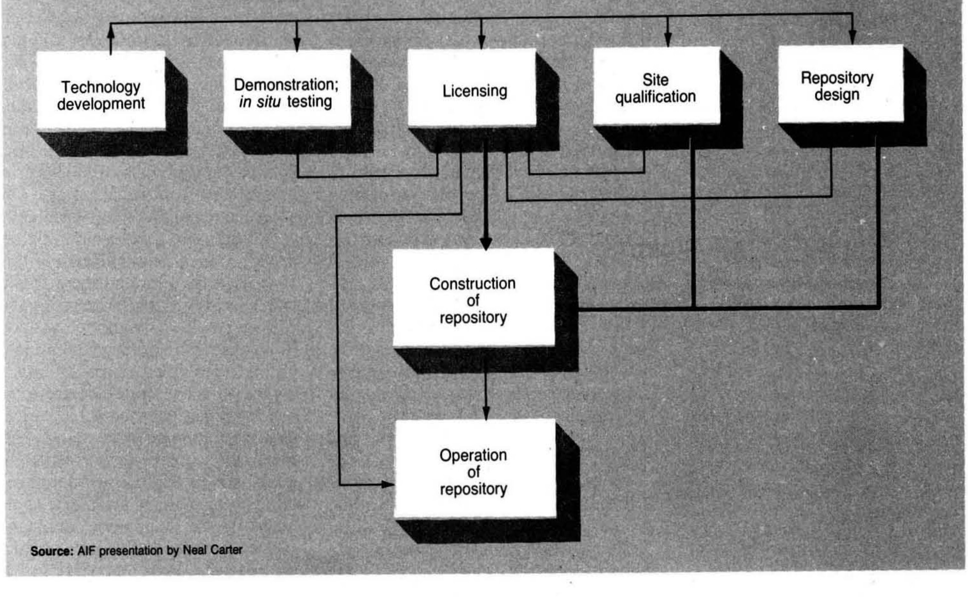
- government assertion of a clear leadership role,
- establishment of a specific program plan, and of a strong project organization,
- criteria that establish roles for government and industry; that is, the "government-industry interface",
- procedures to resolve local issues, and
- continuation of supporting research/development, especially to devise one or two viable backup techniques, should those be needed.

Sweden's approach

KBS stands for Kärnbränslesäkerhet which, in Swedish, means "nuclear fuel safety". Representing the KBS program, Lars Nilsson explained to the AIF workshop that for the present, waste isolation without reprocessing seems to be preferred in Sweden, although a plan for storing high-level waste that takes reprocessing into account has been approved. Either way, the wastes would be stored in Sweden's very stable Precambrian shield rock; indeed, no other host media were studied there.

The spent fuel or vitrified high-level waste would be buried 500-m deep in the stable rock whose ground-water conductivity is very low. Burial holes would be drilled from a system of tunnels in the rocks. The contained high-level waste capsules, in titanium-lead canisters, would be placed

Repository construction/operation steps



Source: AIF presentation by Neal Carter in the holes—one per hole—and each would be backfilled with a quartz sand-bentonite mixture. By comparison, spent-fuel capsules in copper canisters would be placed in similar holes backfilled with pure, highly compressed bentonite, Nilsson said.

Steps would be taken to keep storage temperatures low. For example, fission products would never exceed 9% of the blocks containing waste glass. Waste or spent fuel would be in controlled storage for 40 years before final disposal. Also, the heat in the repository would be limited to the energy equivalent of 5 W/m^2 at the time of the material's placement.

The concept of burying spent-fuel bundles, high-level wastes, or both, deep in igneous rock is also part of the Canadian plan. Canada hopes to have a site chosen by late 1982, with startup of operation in the early 1990's, T. Rummery, of Atomic Energy of Canada Ltd., told the AIF workshop.

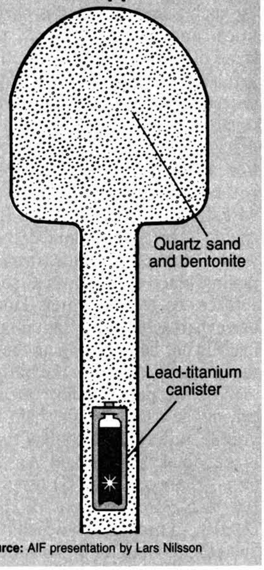
With respect to vitrification of waste, Argonne National Laboratory is looking into two approaches. One involves encasing fission products in glass beads which are then embedded in lead. The other entails incorporating the waste into the structure of chemically stable glass; Battelle and others are involved in this effort. Of special concern, here, are waste transuranics, such as neptunium and plutonium. Stability of the containments will be studied exhaustively. The aim is to deposit the "glassified" wastes at the proper geologic sites.

Byproduct utilization?

Perhaps, an alternative approach is to separate and purify the ^{90}Sr. This is being done with stored high-level wastes from the deactivated defense production reactors at Hanford, Wash., Harold Fullam of Battelle/Northwest told the 178th national meeting of the American Chemical Society (ACS). The ^{90}Sr is converted to strontium fluoride ($^{90}SrF_2$), which can then be used to power remote systems, such as navigation aids, signal beacons, and weather stations. In fact, to a limited extent, such ^{90}Sr-powered devices fueled with $^{90}SrTiO_3$ (strontium titanate), were used during the 1960's and were known as Small Nuclear Auxiliary Power, or SNAP devices.

However, ^{90}Sr is high-level and toxic; therefore, it would require rigorous safety precautions during all phases of its separation, purification, and use. But, according to Fullam, such shielding meeting licensing requirements can be made available. He said that the 29-year half-life of ^{90}Sr would give a device using it as a heat source (maximum, 800 °C) a useful, unattended life of at least 10 years. Such a device would be especially useful at remote polar locations where batteries, fossil fuel, or solar power may be impractical or unavailable.

High-level waste storage: a Swedish approach



Source: AIF presentation by Lars Nilsson

Data presented by David Woodbridge of Hittman Associates, Inc. (Columbia, Md.) at the ACS meeting suggested that, if properly handled and shielded, ^{137}Cs—a pure gamma-ray emitter—could be used to disinfect and detoxify wastewater. He said that these rays and their secondary effects can inactivate pathogens, and chemically break down organics, including those formed by chlorination of water and wastewater. Woodbridge also pointed out that if ^{90}Sr and ^{137}Cs can be removed from nuclear waste and used, the remaining waste's radiation would decay to that of naturally occurring Canadian pitchblende within 50–150 years after the spent fuel is taken away from the reactor.

Nevertheless, whether a once-through or reprocessing fuel cycle is ultimately decided upon, or even if high-level waste materials are to be separated, purified, and put to various uses, certainty as to waste-management policy and procedure has to be established by the federal government. Otherwise, those who are betting on nuclear power as a major petroleum-replacing energy option could be in for considerable disappointment. JJ

Hazardous waste disposal

Michael R. Deland
ERT, Concord, MA

"Among the many pressing environmental problems currently facing EPA and the nation, I consider hazardous waste to be the most serious." There is much to substantiate this recent statement by U.S. Environmental Protection Agency Administrator Douglas Costle.

The volume of hazardous waste generated annually in the U.S. is enormous. According to EPA estimates, it exceeds 77.1 billion pounds, of which "only 10% is disposed in an environmentally safe manner." The remaining 90% is disposed of haphazardly, such as in an illegal 23-acre site in Kentucky, "The Valley of the Drums", where thousands of barrels of hazardous wastes have been stacked. Many barrels have burst, spilling their contents on the ground, thereby polluting local surface waters.

The health problems associated with hazardous waste were first dramatized by the Love Canal tragedy which unfolded 16 months ago. Since then, many other problems of similar magnitude have come to light, with untold more "ticking time bombs" remaining throughout the country. This aspect of the problem is magnified by the fact that one-half of the American population relies on groundwater for its drinking water supply.

The projected cleanup costs are staggering. EPA estimates that to control hazardous waste, which poses a "danger to public health and the environment", will cost between \$13.1-22.1 billion. The estimated costs to ensure that hazardous wastes are safely disposed of in the future are even larger; the American Petroleum Institute projects a \$34 billion capital cost and \$3.4 billion annual operating cost for industry to meet the standards.

Statutory scheme

In the fall of 1976, Congress enacted the Resource Conservation and Recovery Act (RCRA), which was intended to establish a comprehensive program for the management of solid waste. The heart of the law is "Subtitle C, Hazardous Waste Management", which requires "cradle to grave" tracking of hazardous wastes from the time of generation, through storage and transportation, to their ultimate disposal. Most of the other federal environmental statutes are either directly or peripherally involved, further complicating the regulatory scheme. In the three years since the passage of RCRA, it has become evident that "the problem is far larger than the Act anticipated." (Report of the Committee on Interstate and Foreign Commerce, House of Representatives, September 1979.)

Regulatory delay

RCRA requires EPA to promulgate a series of regulations, many within 18 months of enactment. When it became evident that EPA would miss these deadlines, suits were filed resulting in a court order requiring EPA to file quarterly reports on the status of the regulations and setting a deadline of December 31, 1979 for EPA to promulgate final regulations. In its effort to meet this deadline, EPA published proposed rules in December 1978 covering classification of hazardous wastes and standards for generators, transporters, and disposal facility operators.

In its latest quarterly report to the courts (October 12, 1979), EPA stated that the Agency would miss the deadline and that the key regulations would not be issued until April 1980 or later. Costle noted that EPA had received over 1200 sets of comments, "which, when placed together, constitute a stack of text over seven feet high." EPA must respond in detail to each comment, including difficult issues such as the criteria for defining a waste as hazardous and strictness of facility design standards adequate to protect health and the environment. Many of the key regulations will have to be changed so significantly that EPA must "repropose" them, thereby providing opportunity for still more public comment.

Environmentalists have characterized EPA delay as "inexcusable" and estimate it will add another two years to the implementation of a program to address "the most significant environmental problems currently facing us". The Environmental Defense Fund has filed a request with the court for a hearing on EPA's failure to meet the deadline.

Interim actions

While regulatory controls remain mired in technical debate, EPA has enlisted the enthusiastic cooperation of the Justice Department to use RCRA's emergency powers to initiate court action to stop illegal dumping and order cleanup in those cases where "an imminent and substantial endangerment to health or the environment" can be shown. The Justice Department has established a new hazardous waste section, headed by a long-time public interest advocate.

"Everyone wants these wastes managed, but not in their backyard and our entire nation is someone's backyard," is how Costle summarizes the heart of the problem. Actions during the next several months by EPA, industry, environmental groups, Congress, and the courts, will shape the manner in which hazardous waste, the environmental problem of the 1980's, is managed, and we all hope, controlled.

0013-936X/79/0913-1459$01.00/0 © 1979 American Chemical Society

ES&T

PAT REPORT

PRACTICAL, AVAILABLE TECHNOLOGY

First step, always the hardest

Apollo Technologies, Inc. has a way to save up to 2% of the oil consumed in many electric-utility boilers; lower the exit-gas temperature 40° or more and protect the metal parts of the boiler by neutralizing the condensed acid as it forms

In the national effort to reduce our dependence upon foreign oil, an important component of our strategy has been a program of energy conservation. To the general public, conservation has come to mean reduction of energy use by the consumer. However, fuel savings through the use of more efficient operational and production methods is a concern of the major energy producers, the electrical utility industry.

The recent OPEC price increases make it more important than ever to use whatever methods are available to save energy, especially where the cost of this energy-savings technology is only a small fraction of the savings that can be gained.

One way to achieve such savings is to operate the boiler at lower exit-gas temperatures. Controlled studies have shown that a 40 °F reduction in exit-gas temperature will allow a 1% efficiency gain.

Lowering exit-gas temperatures

The effect of lowering the exit-gas temperature on utility boilers in order to gain greater fuel efficiency is well accepted. The energy yield of any heat process is described as its Carnot efficiency:

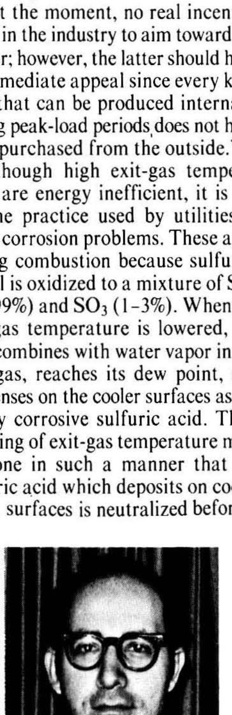
$$\frac{T_2 - T_1}{T_2} = E$$

where T_2 is the flame temperature and T_1 is the exit-gas temperature.

Wallace Chinitz, professor of mechanical engineering at The Cooper Union (N.Y. City), says, "Thermodynamic calculations indicate that improvements in plant heat rates of up to 3% are possible in some power plants. Most coal-burning plants, in particular, would show dramatic improvement in their operating efficiencies by shutting down or reducing the flow through their steam coils. The resulting improvement could be used to reduce fuel input requirements and/or to increase the power output from the plant.

"At the moment, no real incentive exists in the industry to aim toward the former; however, the latter should have an immediate appeal since every kilowatt that can be produced internally during peak-load periods does not have to be purchased from the outside."

Although high exit-gas temperatures are energy inefficient, it is the routine practice used by utilities to avoid corrosion problems. These arise during combustion because sulfur in the oil is oxidized to a mixture of SO_2 (97–99%) and SO_3 (1–3%). When the exit-gas temperature is lowered, the SO_3 combines with water vapor in the flue gas, reaches its dew point, and condenses on the cooler surfaces as the highly corrosive sulfuric acid. Thus, lowering of exit-gas temperature must be done in such a manner that the sulfuric acid which deposits on cooler metal surfaces is neutralized before it can attack the metal.



Professor Chinitz
"could be used to reduce fuel input"

How exit-gas temperatures are lowered depends upon the individual utility. In some facilities, temperatures can be reduced quickly and simply by removing or bypassing the steam coils which preheat incoming air. These coils are fed by steam from the power turbines. By shutting off these coils and conserving this steam, greater performance is gained by the turbine.

In other cases where steam coils do not exist, the same effect can be gained by increasing the surface area of the air heater. In many instances, heat-transfer surfaces in the form of baskets have been removed. Replacement of these baskets increases heat transfer surface area and allows this heat-transfer unit to operate at maximum efficiency. The combination of steam-coil removal and increasing surface area in the air heater has an additive effect on reducing exit-gas temperature.

Flue gas neutralization

Flue-gas neutralization to reduce flue-gas acidity is not new. Apollo Technologies (Whippany, N.J.) has successfully used this system as a cold-end, corrosion-control technique in more than 40 utilities over the past 10 years. In essence, this powder-formulation system containing basic oxides and ammonia releasing agents is injected before the air heater and coats the entire cold end of the boiler.

Sulfuric acid may be partially neutralized in the gas phase but the bulk condenses on metal surfaces pretreated with the basic oxide.

Neutralization occurs immediately. Powder does not build up because the flue gas exerts an errosive effect on the deposits. Thus, both the unreacted oxide and its reaction product with SO_3, a neutral sulfate salt, are swept into particle-collecting devices. If the boiler system does not have such a device, the dense particles collect at the bottom of the smoke stack. About 20% loss of oxide or neutral salt through the stack does occur. In total weight this is far less than the amount of SO_3 which would have occurred without flue-gas-neutralization treatment.

Economics of flue-gas neutralization

Although flue-gas neutralization has been widely used, the chief motivation for adopting it in the past has not been energy savings. Rather, special problems of acid-smut emissions or corrosion and blockage of air heaters served as justifications. Now, with the 50% rise in OPEC oil prices in 1979 alone and with the planned decontrol of domestic oil, a number of utilities can now consider this technology purely for economic reasons.

D. B. McMillan, manager of production at the South Carolina Electric and Gas Co., says, "A significant reduction in fuel-oil consumption was achieved when we were able to reduce the steam coil usage at the Williams Station, Columbia, S.C. With the lower exit-gas temperature allowable by chemical treatment with Apollo Coaltrol M, fuel savings were in excess of \$200 000/yr, after deducting the chemical and any capital cost." He continued, "These savings were based on a fuel-consumption rate of 833 bbl/hr at a current fuel cost of \$19.18/bbl. Since the injection system has been in place since 1976, the original capital cost of \$80 000 was absorbed in the first year's savings."

Figure 1 documents the price history of OPEC oil since 1971. Figure 2 illustrates the changes in flue-gas neutralization economics that have occurred as a result of these price rises. Whereas lower priced high-sulfur oil required the utility to use this system for more than half its operating time in order to justify it economically, the more expensive oils burned today break even at 1/3-1/6 on-line time.

FIGURE 1

Price history — OPEC oil 1970–July 1979

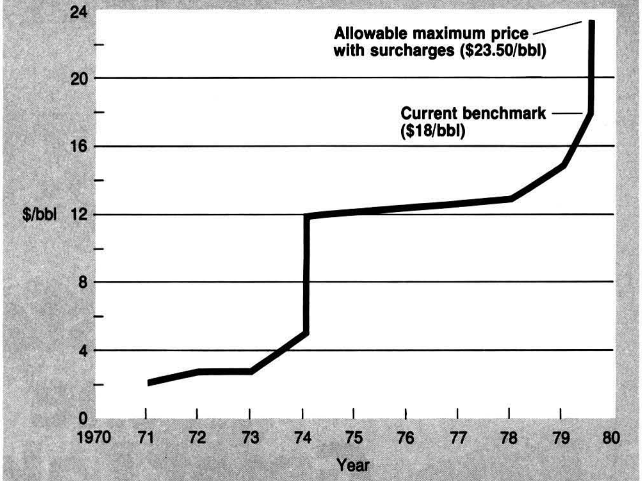
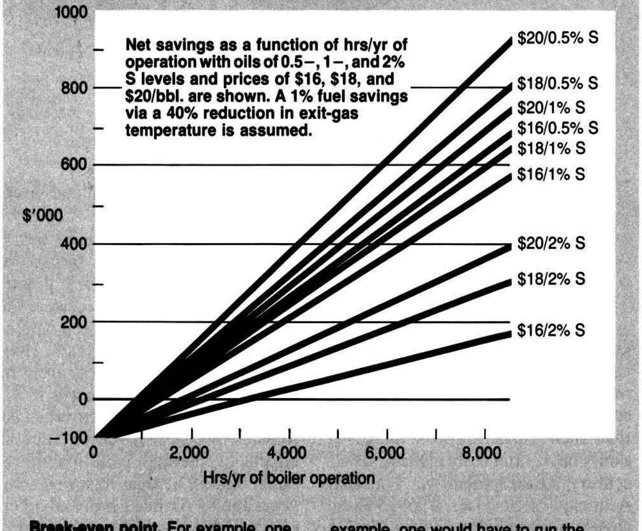


FIGURE 2

Net savings at reduced exit-gas temperature with flue-gas neutralization for a 500-MW boiler



Break-even point. For example, one would have to run the 500-MW boiler 3000 hrs/yr on 2% S oil at \$16/bbl before any savings would accrue. Another example, one would have to run the 500-MW boiler 2000 hrs/yr on 2% S, \$18/bbl oil before savings would accrue, etc.

Incentives

The question may well be asked, why, if the technology has such favorable features, has it not been used in every instance where applicable? One can only speculate, but it is known that, as with similar technologies, the capital and operating costs must be justified to the individual Public Utility Commissions. As a consequence, the recovery of costs can by no means be guaranteed. However, the savings that are achieved result in an automatic adjustment of the fuel rates, thereby leaving the utility with no economic benefits to show for its conservation efforts.

Douglas Bauer, senior vice president of the Edison Electric Institute, the organization representing investor-owned utilities, has commented: "By and large, most utilities would welcome the opportunity to pursue additional energy-conservation measures. The documented savings, after deduction of capital and other costs, should be divided in an equitable manner between themselves and the consumer. I guess the bottom line for adopting a measure of this type is: Will the consumer benefit? I believe he will."

Toxic substances in the Great Lakes

Here is an overview of the origin, distribution, and fate of some heavy metals and organics, and some suggestions as to what may be done about them

Joseph J. Delfino
Laboratory of Hygiene
University of Wisconsin-Madison
Madison, Wisconsin 53706

Concern over the presence of chemicals in the Great Lakes has increased in recent years. Alfred Beeton reviewed historical trends of many common anions and cations, and found that their concentrations increased slowly but continuously in the past half century (*Eutrophication,* National Academy of Sciences, 1969). These changes were accompanied by changes in the biota, particularly the algae, as populations evolved from so-called clean-water species to those indicating eutrophic symptoms. Beeton hypothesized that man's activities were influencing the limnology of the Great Lakes, resulting in decreased water quality. These conditions were noted particularly in Lakes Erie and Ontario and in the southern basin and Green Bay in Lake Michigan.

An international conference, held in Madison, Wis., in 1967, focused on eutrophication and spurred greater research interest. Numerous additional conferences have been held on this topic in the past 12 years. However, environmental issues rarely remain simple, and in the early 1970's the eutrophication problem was confounded by concern over the potential effects of thermal pollution in the Great Lakes, a topic reviewed some years ago by Arthur Levin and others (*ES&T,* March 1972, p 224). For instance, as demands for electric power increased, especially in the Midwest, many power plants were constructed on Great Lakes shorelines.

Citizens and regulatory agencies, already alarmed by the specter of eutrophication-influenced water quality changes, attempted to restrict the discharge of power-plant cooling water into the lakes. By 1972, these two issues had created sufficient attention that an interstate enforcement conference on Lake Michigan pollution was convened. Also in 1972, the Great Lakes Water Quality Agreement between the United States and Canada was first signed. It established water-quality objectives and timetables, and espoused a nondegradation philosophy.

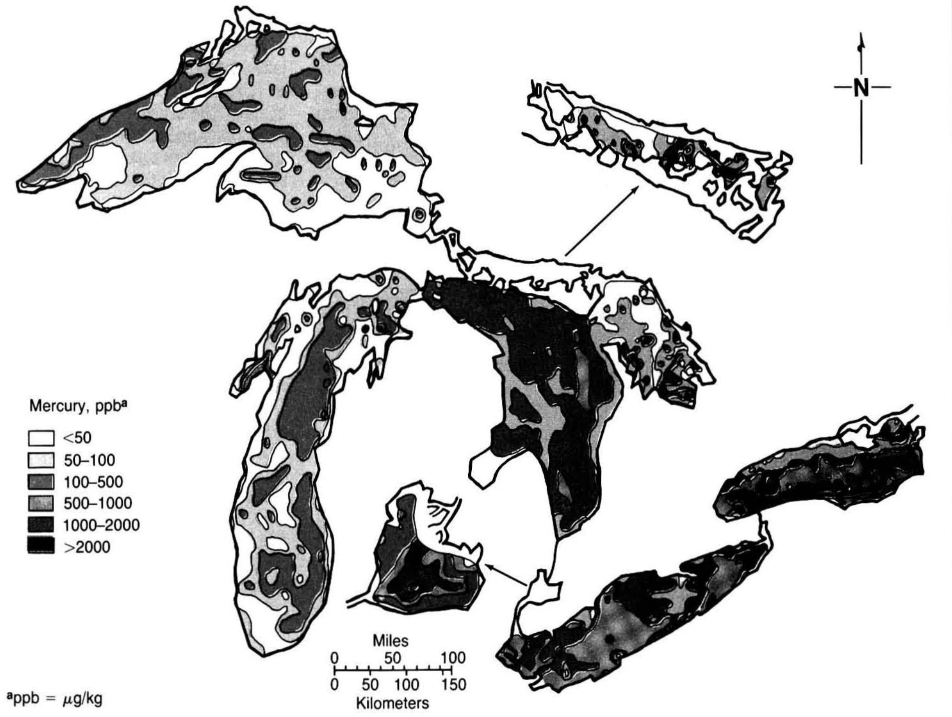
While these environmental issues in the early 1970's originally emphasized phosphorus loading and thermal pollution in the Great Lakes, the toxic-chemical problem was also developing. Although the first serious alert concerning toxic chemicals, particularly pesticides, had been sounded by Rachel Carson in *The Silent Spring* in 1962, it was not until the late 1960's and early 1970's that the combination of increased environmental awareness and laboratory analytical capability led to the discovery of pesticides throughout the Great Lakes Basin. The chemical stability of many pesticides, coupled with their capacity to bioaccumulate, resulted in high concentrations of compounds such as DDT and dieldrin in fish. Fish that exceeded U.S. Food and Drug Administration (FDA) tolerance levels for pesticides could not be sold commercially.

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/79/0913-1462$01.00/0

FIGURE 1

Mercury concentrations in surface sediments of the Great Lakes



During the time that extensive effort was mounted to document DDT levels in Great Lakes fish, chemists noted that additional compounds were also present. In fact, some of these other substances created significant problems in the analysis of DDT. It was soon recognized that these troublesome compounds were polychlorinated biphenyls (PCB's), and that they were also present at levels as high as 25 μg/g. These historical levels have been documented by scientists from the U.S. Fish and Wildlife Service (FWS), the U.S. Environmental Protection Agency (EPA), and particularly by Gilman Veith at EPA's Duluth, Minn., laboratory. Thus, what was first a problem involving nondegradable pesticides, such as DDT, soon blossomed into a major issue of contamination by all types of toxic chemical substances.

To be sure, there is still concern about the input of phosphorus and thermal discharges into the Great Lakes. But, according to the Pollution from Land Use Activity Reference Group (PLUARG) of the International Joint Commission (IJC), toxic chemicals have now become the predominant water-quality issue in the Great Lakes Basin. This concern is also shared at the national level by the President's Council on Environmental Quality.

What are toxic substances?

Webster's *Seventh New Collegiate Dictionary* defines toxic as something "of, relating to or caused by a poison or toxin", where a poison is "a substance that through its chemical action usually kills, injures, or impairs an organism." The Congress of the United States defined toxic substances in October 1976, when it enacted the Toxic Substances Control Act (Public Law 94-469). That law defines toxic substances as those chemical substances "whose manufacture, processing, distribution in commerce, use, or disposal may present an unreasonable risk of injury to health or the environment." More specific definitions of a toxic substance and a hazardous polluting substance were included in the Great Lakes Water Quality Agreement of 1978, signed by the U.S. and Canada on Nov. 22, 1978.

Numerous industrial chemicals, such as PCB's, have been entering the environment for many years and, like DDT, have accumulated in living organisms including Great Lakes fish and in the people that consume them. PCB's have been identified essentially everywhere in the world, despite the fact that they were produced for uses that should not have resulted in such widespread distribution. These uses included capacitors, transformers, and hydraulic fluids. Their careless use and disposal have led to ubiquitous contamination of the environment.

Details about certain toxic chemicals, including lists of the so-called "priority pollutants", were published recently by Larry Keith and William Telliard (*ES&T*, April 1979, p 416). These should be consulted for additional information.

Distribution in water

The extent of toxic-substances distribution in the water, sediments, and fish of the Great Lakes Basin is only now beginning to be understood. For example, a comprehensive inventory of information on the distribution of organic and trace-metal contaminants in the basins of all of the Great Lakes, except Lake Ontario, has been prepared for a committee of the IJC's Water Quality Board by Dennis Konasewich and his co-workers. This inventory will serve as a basis for an assessment that will determine those contaminants that may present a hazard to human health and the environment. Data were obtained from municipal, state, provincial and federal agencies in the U.S. and Canada, as well as from reports and papers published by university researchers, government scientists and consulting firms. Among those groups that have performed considerable work and compiled extensive data on the Great Lakes are the Canada Centre for Inland Waters, the Ontario Ministry of the Environment, various EPA laboratories, the National Oceanic and Atmospheric Administration, and the natural resources departments of the Great Lakes states.

Chemicals in Lake Michigan

The most complete interpretive compilation of historical data for chemicals in Lake Michigan was published by Marguerite Torrey in 1976. No similarly thorough treatise for the other Great Lakes has been prepared.

At one time, organochlorine pesticides were widely used in the Lake Michigan Basin and were applied to forest and agricultural lands, and to noncrop lands. Pesticides were also used in industry and for household-pest control. According to a 1972 EPA report, the extensive use of DDT and dieldrin in Wisconsin led to the transport of these chemicals to Lake Michigan via tributaries, land runoff, and wastewater-treatment plants. Atmospheric precipitation was also implicated because of the wind-borne transport of these pesticides following aerial spraying.

The concentrations of pesticides in the waters of the Great Lakes is relatively low, due partly to their low aqueous solubility. As reported by Torrey, typical concentrations were generally below 1 $\mu g/L$, and often near 1 ng/L. In addition to DDT and dieldrin, numerous other compounds were detected by gas chromatography, including PCB's, lindane, heptachlor, heptachlor epoxide, endrin, aldrin, and methoxychlor. Much of the early DDT and dieldrin data from Lake Michigan and other waters, prior to the late 1960's, are now considered only approximate because of the likely interference of PCB's in the analysis of these pesticides.

Torrey demonstrated that the concentrations of the main toxic inorganic materials (Hg, Pb, As) are quite low in Lake Michigan. There, inorganic substances do not appear to pose significant problems, except for As in the Green Bay area (currently being studied by Marc Anderson and associates at the University of Wisconsin-Madison), and Pb in the southern basin.

Distribution in sediments

Great Lakes sediments are the ultimate sink for many, but not all, of the toxic contaminants that enter the lakes. Some of the contaminants, such as mercury, can be converted to more biologically active forms. Also, compounds such as PCB's are taken up by bottom organisms that either live or feed in the sediments, and which are subsequently eaten by larger carnivores. This results in an eventual increase in the concentration of this contaminant in carnivorous fish. Thus, despite the fact that the sediments are many meters below the water's surface, they do not always act as the ultimate sink for toxic substances.

A toxic substance means "a substance which can cause death, disease, behavioral abnormalities, cancer, genetic mutations, physiological or reproductive malfunctions or physical deformities in any organism or its offspring, or which can become poisonous after concentration in the food chain or in combination with other substances." A hazardous polluting substance is defined to mean "any element or compound which, if discharged in any quantity into or upon receiving waters or adjoining shorelines, would present an imminent and substantial danger to public health or welfare. For this purpose, public health or welfare encompasses all factors affecting the health and welfare of man including but not limited to human health, and the conservation and protection of flora and fauna, public and private property, shoreline and beaches."

Source: Great Lakes Water Quality Agreement of 1978, International Joint Commission

The presence of many contaminants in the Great Lakes sediments was summarized in the 1978 PLUARG Final Report to the IJC. Of particular concern were Hg, Pb, and PCB's. A contour map prepared by PLUARG, showing the approximate distribution of mercury (Hg) in Great Lakes sediments, is reproduced as Figure 1.

The highest Hg concentrations generally appear in Lakes Erie, Ontario, and St. Clair. Previous industrial discharges, apparently current atmospheric deposition into the Great Lakes, and runoff from the land surface appear to be sources of Hg.

Prior to 1970, major inputs into the lakes' system were discharges from the St. Clair and Detroit Rivers. On the basis of the sediment patterns, Lake St. Clair appears to be a continuing source of Hg to Lake Erie, despite the elimination of the chloralkali-plant source.

The transport of Hg-enriched sediments from Lake St. Clair, through the Detroit River, and into western Lake Erie, continues to be a problem. The resuspension of Hg-contaminated sediments from western Lake Erie, and subsequent in-lake transport, has carried Hg along the southern shoreline and led to its ultimate deposition in the eastern basin. The western basin of Lake Erie is an active area of sediment resuspension because of wind-induced wave action.

In Lake Ontario, Hg appears to be carried by the Niagara River, with eventual dispersal throughout the eastern basin. The sharp decrease in point-source inputs of Hg to the lakes should result in a gradual decrease in Hg content of the surface sediments, according to PLUARG.

The concentrations of most organic contaminants in Great Lakes sediments have not been well mapped. PCB contours, however, were compiled by PLUARG for Lakes Huron, Erie, and Ontario. These indicate a general occurrence of PCB's in the sediments, with higher loadings in the western and southern areas of Lake Erie and in the south central area of Lake Ontario. The PLUARG Report estimated that nonpoint sources, including atmospheric inputs, account for the major reflux of PCB's to the lakes.

Distribution in fish

Data for PCB's in Great Lakes fish were compiled in the PLUARG Report with additional data provided by the State of Wisconsin. These appear in Table 1. The most significant PCB contamination occurs in Lake Michigan, according to data now available.

One interesting aspect of PCB, DDT, and dieldrin contamination of fish in Lake Michigan is the slightly decreasing trend in concentrations that has developed over the past five to eight years. Data from the FWS and EPA indicate such a trend, but further analysis and monitoring will be required in the future to verify the trend. The PCB concentrations in fish can vary from one season to another, as well as during spawning periods. Thus, fish monitoring programs must be conducted in a consistent manner to avoid bias in the interpretation of the data.

One reason that PCB's continue to appear in relatively high concentrations in Lake Michigan fish is that the chemical is easily bioaccumulated; that is, passed through the food chain as smaller organisms are consumed by larger ones, ultimately reaching the primary carnivores in the lake (salmonids) which are highly prized sport fishery species. This process is illustrated in Figure 2.

Mercury concentrations in Great Lakes fish are not too much of a concern, except for those caught in Lake Erie. Concentrations from fish in that lake indicate that the FDA consumption guideline of 1.0 μg/g is still being exceeded, although trends of decreasing concentrations have been noted. The PLUARG Report noted that lead (Pb) concentrations are nowhere close to the recommended consumption-advisory limit of 10 μg/g in any of the Great Lakes.

Effects of toxic substances

One effect on citizens in the Great Lakes Basin, particularly those who consume relatively large amounts of locally caught fish, is contamination from certain species by chemicals, especially PCB's. Most of the species that have sport fishery importance, particularly the salmonids, consistently exceed the proposed FDA tolerance guideline of 2 μg/g in Lake Michigan. However, sportsmen are not prevented from consuming their catch, and many of these people are unwilling to abandon their sport (which involves considerable financial investment), particularly since toxicological studies have not conclusively linked the dietary intake of low levels of PCB's with human health problems.

Despite the lack of firm human health evidence, there is ample documentation that the intake of PCB's near the FDA guideline significantly affects rhesus monkeys. James Allen and co-workers at the University of Wisconsin-Madison have shown that infants born to monkeys that were fed 2.5–5.0 μg/g of PCB's developed facial acne and edema, swelling of the eyelids, loss of facial hair including eyelashes, and hyperpigmentation of the skin. Half of the PCB-exposed infant monkeys died within eight months following birth, assumedly from PCB intoxication. Surviving infant monkeys proved to be hyperactive in locomotor tests, and to be slow in learning how to

Toxic substances: classes and sources

According to the Great Lakes Basin Commission, the general classes of toxic substances that are presently of concern in the Great Lakes Basin are:

- halogenated organic compounds (PCB's, PBB's, chlorophenols),
- radioactive substances,
- pesticides,
- heavy metals and toxic nonmetals (Hg, Pb, As), and
- petroleum products.

There are many sources for the toxic substances that enter the Great Lakes. The Great Lakes Basin Commission and others have itemized these as:

- point sources (municipal- and industrial-effluent discharges),
- nonpoint sources (land application of toxic materials followed by runoff; the atmosphere),
- urban runoff (Pb from automobile exhausts; grease and oil; metals; household pesticides),
- toxic and hazardous waste disposal sites or "phantom" disposal activities (legal or illegal waste disposal that results in the pollution of the Great Lakes; transportation accidents),
- the atmosphere (*ES&T*, November 1979, p 1337) (can be considered a nonpoint source but represents a major point of entry of PCB's, Pb and other toxic substances to the lakes),
- agricultural runoff (nonpoint source but emanates from specific useage of chemicals in agriculture).

TABLE 1

PCB concentrations in Great Lakes fish.

Lake	Sampling period	Mean PCB concentrations[a] μg/g	Range μg/g
Superior	1968–1975	0.61	<0.1–3.7
Michigan	1972–1974	10.2	2.1–18.9
	1974–1978	NC[b]	1.2–37[c]
Huron	1968–1976	0.82	<0.1–7.0
Erie	1968–1976	0.88	<0.1–9.3
Ontario	1972–1977	2.37	<0.1–21.1

[a] The FDA tolerance level is 2 μg/g

[b] Not calculated

[c] Based on the analysis of 35 fish consisting of chubs, lake trout and coho salmon. Data from the State of Wisconsin Department of Natural Resources

Source: PLUARG, 1978

The PLUARG Report

The 1978 PLUARG Report summed up the toxic substances control problem very well and the following points are excerpted from that document. In order to control toxic substances and reduce their inputs to the Great Lakes:

- Toxic substances must be controlled at their source.
- Closer cooperation between the U.S. and Canada in implementing toxic substances control legislation must occur.
- Proper management control, and the means of ultimate disposal of toxic substances presently in use, must be developed.
- Identification and monitoring of historic and existing solid waste disposal sites (where there is an exisiting or potential discharge of toxic substances) must be done, and control programs at those sites must be executed as needed.
- Joint U.S.-Canadian expansion of efforts to assess the cumulative and synergistic effects of increasing loads of toxic contaminants on environmental health must be given high priority.
- The rapid translation of these assessments into revised water-quality objectives must be made; moreover, for certain toxic substances, a zero loading to the Great Lakes must be a requirement.

solve various types of discrimination problems, when compared to control animals.

The linkage of rhesus monkey health effects to potential human health problems is still not firm. However, the animal studies suggest that humans should limit their consumption of PCB-contaminated fish taken from the Great Lakes, especially Lake Michigan, until epidemiological research determines the extent, if any, of low-level dietary intake effects of PCB's on humans.

The most serious effect of toxic substances in the Great Lakes seems to be the diminished value of the Great Lakes as a natural resource, particularly in the production of fish that are suitable for human consumption. Commercial fishing has already been impaired. Sportsmen now enjoy their pastime with the caveat that their catch is tainted, and that their fish intake should be limited to no more than one meal per week. Pregnant or nursing women have been advised to eliminate the PCB-contaminated fish entirely from their diets.

Problems in the Lake Michigan basin

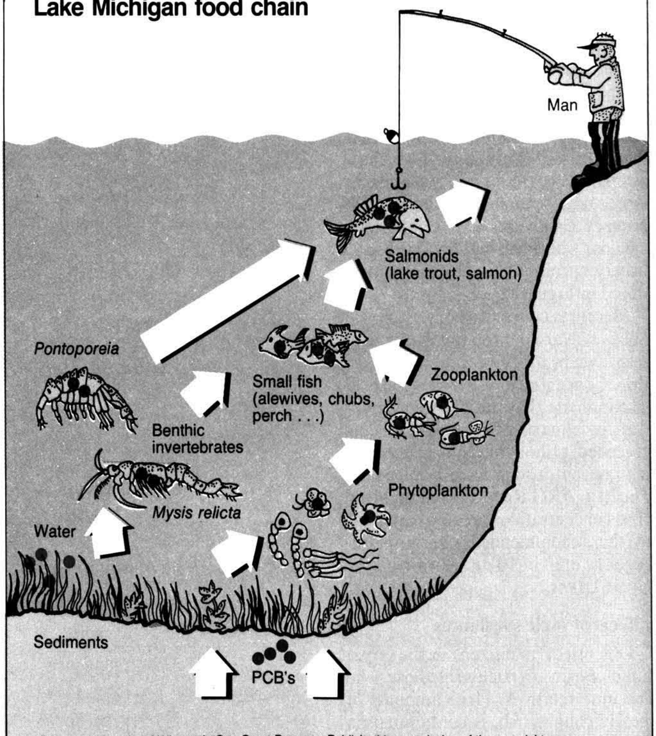
In recent years, numerous toxic and potentially hazardous organic compounds have been identified in the Wisconsin waters of the Lake Michigan basin. The findings in Wisconsin are representative of experiences in the other Great Lakes states, and will be discussed further here to provide an overview of some current problems.

Perhaps the best studied of the toxic organic compounds are the PCB's. A National Conference held in Chicago, Ill., in 1975 (*ES&T*, February 1976, p 122) addressed this industrial contaminant in detail. The unusual stability of the PCB's in the environment, and their capability to bioaccumulate, have contributed to the fishery problems mentioned above.

Contamination of Lake Michigan waters by PCB's has been a matter of concern since the late 1960's when the Wisconsin Department of Natural Resources (DNR) found that PCB's in fish collected from the lake exceeded the FDA guidelines (which were set at 5 μg/g at that time). PCB sources were found to be industrial and municipal effluents; but also, perhaps more significantly, the atmosphere was implicated as a possible major contributor of PCB's to the lake. Indeed, as the point-source contributions of PCB's are eventually closed off, nonpoint sources, such as the atmosphere, will take on a more important role.

Nevertheless, according to Stanton Kleinert of the Wisconsin DNR, the PCB problem in Wisconsin is chiefly a fishery problem, in terms of natural-resources management. Public water supplies in the state, for example, do not contain detectable amounts of PCB's, while nearshore waters of Lake Michigan and its tributaries contain only small concentrations of the contaminant.

FIGURE 2
How PCB's are passed through the Lake Michigan food chain



Source: University of Wisconsin Sea Grant Program. Published by permission of the copyright owner.

PCB's in the Sheboygan River

In March 1978, very high concentrations of PCB's were reported in fish collected in the Sheboygan River, a Lake Michigan tributary in northeastern Wisconsin. The fish, originally collected in late 1977, showed PCB concentrations ranging from 26 to almost 1000 μg/g. Recall that the FDA guideline is 5 μg/g; lowering it to 2 μg/g is proposed.

Because of these very high concentrations, an intensive sampling program was begun. The results verified the earlier findings that the PCB concentrations in the Sheboygan River fish were significantly elevated above the values normally found in the Lake Michigan basin.

These findings indicated the probable existence of a previously unidentified source of PCB's. Investigative work by the Wisconsin DNR quickly identified a metal-casting plant as the PCB source. The plant had been disposing PCB-contaminated wastes behind its building and along a dike adjacent to the Sheboygan River. High water, runoff, and erosion deposited the PCB's in the river sediments, and through food-chain accumulation, contaminated numerous fish species.

The PCB-contaminated shoreline material has now been isolated and placed in sealed drums, and awaits final disposal. The sediments, however, are still loaded with PCB's and continue to contaminate fish. They also are washed out into Lake Michigan through normal stream sediment transport processes. The question of dredging the sediments has not been resolved, since dredging might mobilize the PCB's, and lead to more contamination of the nearshore Lake Michigan area. Also, an adequate dredge spoil disposal site would have to be developed, and such sites can be placed only on land or in contained shoreline areas. The disposal of contaminated dredge spoils in Lake Michigan waters is unlawful, posing the dilemma that both action and inaction will result in continued PCB pollution problems. This case is an example of the type of toxic substance control problem that is likely to arise again in the future.

The company involved in the Sheboygan River case has changed ownership since the period when PCB's were used in the hydraulic systems of the casting machinery. PCB's are no longer in use, but their careless disposal in the past haunts the present owners, as well as the environment near the casting plant. A similar case is now the object of considerable research and regulatory interest in the Waukegan, Ill., harbor area.

Wastewater: the Lower Fox River

Probably the most industrialized drainage basin entering into Lake Michigan is the Lower Fox River, a tributary to the waters of Green Bay in northeastern Wisconsin. Leading from Lake Winnebago to Green Bay, it receives wastewaters from many pulp and paper mills, and other industrial and municipal wastewater treatment facilities.

A study initiated in 1976 sought to identify the sources of PCB's and other chlorinated organic compounds in the river. Many organic and chlorinated organic compounds were identified in the wastewaters, river water, sediment, and fish collected throughout the watershed. Included in these results were 20 of the "priority pollutants" that were discussed by Keith and Telliard (*ES&T*, April 1979, p 416).

Representative data from this study appear in Table 2. They indicate that the Lower Fox River system receives considerable loadings of chemicals from a variety of sources. The heavy use of chlorine as a bleaching agent in pulp-mill operations, the recycling of paper products contaminated with PCB's, and chlorination of municipal treatment plant effluents are sources of many of the chlorinated organic compounds.

The environmental significance and ultimate fate of these materials are not fully known at present, except of course, for PCB's which are found in high concentrations in fish taken from the Lower Fox River. Research sponsored by state and federal organizations, including the University of Wisconsin Sea Grant Program, is underway and will help to resolve many of the current uncertainties.

TABLE 2

Selected organic compounds identified in the Lower Fox River watershed in Wisconsin[a]

	Concentration ranges		
Compound	**Wastewaters (µg/L)**	**Sediments (µg/g)**	**Fish (µg/g)**
Anisole,			
Tetrachloro-	0.04–0.08	—[b]	—
Pentachloro-	0.05–0.38	—	0.005–0.06
Benzothiazole	10–30	—	—
Hydroxy-	10–30	—	—
Methylthio-	10–40	—	—
Dehydroabietic acid	100–8500	2.7	—
Dieldrin[c]	—	—	0.008–0.022
Guaiacol,			
Trichloro-	10–60	—	—
Tetrachloro-	10–50	—	—
Hexachlorocyclohexane[c]	0.04	—	—
Phenol(s),			
Dichloro-[c]	15–40	—	—
Trichloro-[c]	5–100	—	—
Tetrachloro-	2–20	—	—
Pentachloro-[c]	0.1–40	0.22–0.28	—
Polychlorinated biphenyls (PCB's)[c] (Aroclors 1242, 1248 and 1254)	0.1–56	0.05–61	0.5–90
Polycyclic aromatic Hydrocarbons (PAH's)[c]	0.5–10	—	—

[a] Source: Wisconsin Department of Natural Resources, 1978

[b] Not determined or not detected

[c] Compound on EPA priority pollutant list

PCB's in lake trout

A recently completed study has added substantially to knowledge of how PCB's are taken up by salmonid species, particularly lake trout in Lake Michigan. This research was performed by David Weininger, under the direction of David Armstrong, at the University of Wisconsin-Madison. In his Ph.D. thesis, Weininger developed a bioenergetic model to account for the accumulation of PCB's by Lake Michigan lake trout. With some modification, the model might apply to related species in other lakes that have similar feeding habits and metabolic processes.

The primary source of PCB's accumulated in the lake trout is adult alewives. Furthermore, for an average adult lake trout, the PCB concentration is more related to its age than its size, signifying that accumulation is more a function of time or exposure than of diet alone.

Of major importance in Weininger's work is the prediction that greater than 50% of the PCB's in adult lake trout have cycled through Lake Michigan sediments. This emphasizes food-chain processes, since benthic invertebrates are eaten by adult alewives which, in turn, are consumed by adult lake trout.

To reduce future concentrations in lake trout, the PCB content of the alewives must be reduced. Weininger speculated that if the alewife population could be reduced, then lake trout might switch to smelt as a primary food source. Smelt have much lower PCB concentrations; thus, lake trout PCB levels should decrease rapidly. This might result in lake trout eventually meeting the FDA tolerance limit in the future.

Weininger's hypothesis is intriguing, and fish resource managers have now been challenged to take innovative steps to reduce the PCB content of prized Lake Michigan stocked species (salmonids). The alternative is to abandon salmonid stocking for many years until PCB's in the sediments are buried beyond those levels at which they would be available to invertebrate organisms.

Control of contamination

Resource-management strategies in the Great Lakes Basin must contend with the toxic-substances issue. This involves human and environmental health, thereby elevating itself to a position of prominence above some of the earlier Great Lakes problems, such as eutrophication and thermal pollution. The task will not be easy because it requires resource managers to adopt nontraditional concepts. However, progress can and must be made.

A toxic substances control plan has been developed by the Great Lakes Basin Commission. It draws on numerous sources for its background information including publications and policies of the IJC, PLUARG and EPA. Some of the important cornerstones of the Basin Commission's plan are the many existing environmental statutes, including the following (*ES&T*, February 1978, p 154):

- Toxic Substances Control Act,
- Federal Insecticide, Fungicide and Rodenticide Act,
- Federal Water Pollution Control Act Amendments,
- Resource Conservation and Recovery Act,
- Clean Air Act,
- Hazardous Materials Transportation Act,
- Ports and Waterways Safety Act,
- Safe Drinking Water Act,
- Atomic Energy Act,
- Marine Protection, Research and Sanctuaries Act, and
- Food, Drug and Cosmetic Act.

Despite the laws that have been enacted to control pollution, serious contamination incidents still occur in the Great Lakes Basin. These problems indicate the need for continued concern and cooperation on the part of those who produce, use, and discharge toxic substances. Regulatory surveillance and enforcement must continue, and will remain a major stimulus in controling the release of toxic substances in the basin.

In addition to surveillance, increased emphasis must also be placed on research. During the course of the analysis of environmental samples, numerous unknown compounds still appear as recorder traces on gas chromatographs. Resources must be made available to government and university scientists so that the number of these "unknowns" can be reduced. Expanded research efforts should result in a decrease in the number of incidents that were at one time sarcastically referred to as "pollutants of the month".

It is known that many toxic substances are transported to the Great Lakes Basin from other areas of the U.S. and Canada. This emphasizes the need for environmental-protection personnel to learn more about atmospheric chemical transport and reaction phenomena. Atmospheric chemistry is now receiving attention in a number of Great Lakes area universities. A symposium on atmospheric chemistry at the ACS meeting in September (*ES&T*, November 1979, p 1337) highlighted much of the current research in this area.

Why controls would be difficult

- A number of toxic substances are already present in the Great Lakes.
- Some toxic pollutants in the Great Lakes are derived from sources well removed from the basin and are carried hundreds of kilometers by atmospheric processes, illustrating the need for national and international planning.
- The national goal of zero discharge of toxic substances into natural waters must be vigorously pursued, particularly in the Great Lakes where residence times can be long.
- Methods must be sought for the attenuation or removal of those toxic substances already present in the Great Lakes Basin.
- Existing laws must be enforced to reduce and ultimately eliminate the discharge of toxic substances to the aquatic environment.

The Great Lakes states and the EPA should ultimately agree on a common list of priority pollutants that will receive primary emphasis for monitoring, research, and eventually control in the basin. The Great Lakes Basin Commission has stated that federal and state cooperation is critical in solving toxic-substances problems. And, importantly, research is also needed to determine the human health implications and environmental significance of the toxic substances that have been found distributed throughout the area.

Another item involves the analytical detection of lower and lower concentrations of chemicals which were not previously anticipated in the Great Lakes Basin. Should government regulate these substances "just because they are there", or should they await appropriate toxicity testing to determine their potential environmental and human health impacts? It is an important question that may require the wisdom of Solomon to answer to everyone's satisfaction.

In summary, it should be clear that there are toxic-substances problems in the Great Lakes Basin, and that steps are now being taken to resolve them. This process will take considerable time and money, but for the more than 15% of the U.S. population that lives in the Great Lakes area, these investments will provide long-term dividends in terms of improved water quality and enhanced utilization of the Great Lakes as a natural resource.

Note: This article is a condensed version of a report that was originally prepared for a course on water-quality issues entitled, "Decisions for Lake Michigan", funded by the U.S. Office of Education as part of the Interstate Water Quality Training Program, and coordinated by the Purdue University Calumet Campus and the Lake Michigan Federation.

Additional Reading

Great Lakes Basin Commission, Toxic Substances in the Great Lakes Basin; and Toxic Substances Control Plan for the Great Lakes Basin, Draft Reports, Ann Arbor, Mich. (1978).

Konasewich, D., Traversy, W., Zar, H., Status Report on Organic and Heavy Metal Contaminants in the Lakes Erie, Michigan, Huron and Superior Basins, International Joint Commission, Water Quality Board Report, Appendix E, Windsor, Ont., Canada (1978).

Pollution from Land Use Activity Reference Group (PLUARG), Environmental Management Strategy for the Great Lakes System, Final Report to the International Joint Commission, Windsor, Ont., Canada, July, 1978. (Note: The noncopyrighted reports of the IJC including those of PLUARG and the Water Quality Board can be obtained, at no cost as the supply lasts, from the Great Lakes Regional Office, International Joint Commission, 100 Quellett Ave., Windsor, Ont., Canada N9A 6T3.

Torrey, M.S., Environmental Status of the Lake Michigan Region, Vol. 3, Chemistry of Lake Michigan, Argonne National Laboratory Report No. ANL/ES-40, May, 1976.

Wisconsin Department of Natural Resources, Investigation of Chlorinated and Nonchlorinated Compounds in the Lower Fox River Watershed, EPA-905/3-78-004, September, 1978.

Joseph J. Delfino is an associate professor of Civil & Environmental Engineering and head of The Environmental Sciences Section at the Laboratory of Hygiene, University of Wisconsin-Madison.

Coordinated by JJ

Analysis of organic water pollutants

A list of consensus voluntary reference compounds (CVRC's) serves as a basis for establishing references against which variations or improvements in analytical methodology can be compared

Lawrence H. Keith
Radian Corporation
Austin, Texas 78766

Only recently has it become possible to identify and analyze a large variety of specific organic (nonpesticide) environmental pollutants which exist at trace levels in the presence of thousands of other organic compounds. Advances both in techniques of separation (high-resolution gas and liquid chromatography) and in methods of identification (computerized mass spectrometry and, to a lesser extent, selective detectors and Fourier transform infrared spectrophotometry) have been key factors in this achievement.

The result has been a dramatic increase in the number of papers dealing with the identification and analysis of organic compounds in the environment in general. Most of the attention, however, has been focused on organics in water. An important and complex facet of this subject is the preparation of samples before instrumental analysis. Research involving sample preparation is often fragmentary by nature. Although many papers deal with the same aspect of sample preparation, they cannot be directly correlated because of differences in the samples, sample handling, and/or model compounds used.

TABLE 1
Panel members of the Council on Environmental Pollutants

NAME	REPRESENTING
Lawrence Keith (chairman)	American Chemical Society
Ryoshi Ishiwatari	Chemical Society of Japan
Krister Lindström	Swedish Chemical Society
Harry Hertz	U.S. National Bureau of Standards
James Lichtenberg	American Society for Testing Materials and U.S. Environmental Protection Agency
Steven Heller	U.S. Environmental Protection Agency's "Water DROP" (Distribution Register of Organic Pollutants in Water)
Edo Pellizzari	U.S. Environmental Protection Agency's "Master Scheme"

TABLE 2
Consensus voluntary reference compounds by chemical class

I. ALCOHOLS
1. Ethanol
2. 2-Chloroethanol
3. Cyclohexanol
4. 2-Chlorocyclohexanol
5. α-Terpineol
6. Cholesterol
7. Benzyl alcohol
8. 3-Chlorobenzyl alcohol
9. 2-Ethylhexanol
10. Glucose
11. Glycerol

II. ALDEHYDES
1. Acetaldehyde
2. Benzaldehyde
3. 3-Chlorobenzaldehyde
4. Crotonaldehyde
5. Vanillin
6. Chloral
7. Furfural

This became apparent when the first major symposium involving the identification and analysis of organic pollutants in water was held during the 1975 Chemical Congress of the North American Continent. At that meeting it was suggested that a council be organized to establish a consensus voluntary system that could be used easily as a basis for establishing references against which variations or improvements in analytical methodology could be compared.

The guidelines for choosing the reference compounds were:

- to provide a wide selection of functional groups,
- to represent, where possible, a range of pertinent physical properties such as volatility and polarity,
- to choose compounds readily available in pure form at modest expense,
- to avoid, where possible, multiple functional groups,
- to choose, where possible, known water pollutants, and
- to select, when possible, halogenated derivatives of several parent compounds.

In addition, extra weight was given to the selection of those compounds that have deuterated or carbon isotope isomers available, and to those compounds on the U.S. Environmental Protection Agency's list of Priority Pollutants.

The American Chemical Society's Division of Environmental Chemistry supported this concept. Subsequently, a Division steering committee was established to direct a Council on Environmental Pollutants (CEP). The first objective was to formulate a list of voluntary reference compounds that could be widely used to compare improvements in new or modified techniques with existing methodology. This objective was met by convening an international panel of environmental chemists who chose by consensus a list of model reference compounds.

The recent Pacific Conference in Honolulu, sponsored by the American Chemical Society and the Chemical Society of Japan, was selected as the forum for that panel discussion. (The representatives who comprised that panel are noted in Table 1). Panel members, as well as interested members of the audience, nominated

III. ALIPHATICS

1. Pentane
2. *n*-Hexadecane
3. Cyclopentadiene
4. Hexachlorocyclopentadiene*
5. Cyclohexane
6. Chlorocyclohexane
7. α-Pinene
8. Chloroform*
9. Bromoform*
10. Tetrachloroethylene*
11. 1,2-Dibromoethane
12. Heptachlor (1,4,5,6,7,8,8-heptachloro-3a,4,7,7a-Tetrahydro-4,7-methanoindene)

IV. AMINES

1. Diethylamine
2. Aniline
3. 2-Chloroaniline
4. Piperidene
5. Quinoline
6. 4-Chloroquinoline
7. Benzidine*
8. 3,3′-Dichlorobenzidene*
9. Indole
10. 5-Chloroindole
11. Atrazine [2-chloro-4-(ethylamino)-6-(Isopropylamino)-*s*-triazine]
12. 3-Chloropyridine

V. BENZENOIDS

1. Benzene*
2. Chlorobenzene*
3. Hexachlorobenzene*
4. Bromopentafluorobenzene
5. Biphenyl
6. 4,4′-Dichlorobiphenyl
7. Decachlorobiphenyl
8. Decabromobiphenyl
9. Indan
10. 4-Isopropyltoluene
11. 2,2-Diphenylpropane
12. *p,p*′-DDE (1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethylene
13. 1,2,4-Trichlorobenzene*

VI. CARBOXYLIC ACIDS

1. Acetic acid
2. Dichloroacetic acid
3. Benzoic acid
4. 4-Chlorobenzoic acid
5. Phthalic acid
6. 4-Chlorophthalic acid
7. Stearic acid
8. Trimesic acid
9. Succinic acid
10. Phenylalanine
11. 4-Chlorophenylalanine
12. Dehydroabietic acid

VII. ESTERS

1. Ethyl acetate
2. 2-Chloroethyl acetate
3. bis(2-Ethylhexyl) phthalate*
4. Phenyl benzoate
5. 4-Chlorophenyl benzoate
6. Methyl stearate
7. Methyl methacrylate
8. Methyl abietate
9. Glyceryl tripalmitate

VIII. ETHERS

1. Diethyl ether
2. bis(2-Chloroethyl) ether*
3. Diphenyl ether
4. Anisole
5. Pentachloroanisole
6. Dibenzofuran
7. 1,4-Dioxane
8. Tetrahydrofuran

IX. KETONES

1. Acetone
2. 1,1,3,3-Tetrachloroacetone
3. Acetophenone
4. 4-Chloroacetophenone
5. Cyclohexanone
6. 2-Chlorocyclohexanone
7. Anthraquinone
8. 2-Chloroanthraquinone
9. Methyl isobutyl ketone
10. 9-Fluorenone
11. Fenchone
12. Isophorone*

X. NITROGEN COMPOUNDS

1. Urea
2. 1,2-Diphenylhydrazine*
3. *N*-Nitrosodi-*n*-propylamine*
4. *N*-Nitrosodiphenylamine*
5. Caprolactam
6. Nitrobenzene
7. 1,4-Nitrochlorobenzene
8. Acrylamide
9. Nitromethane
10. Acrylonitrile*
11. Azobenzene
12. Caffeine
13. Carbazole
14. Uracil
15. 5-Chlorouracil
16. Uridine
17. 5-Chlorouridine
18. *N*-methylcarbamate

XI. ORGANOMETALLICS

1. Tetraethyl lead
2. Dimethyl mercury
3. Tetrabutyl tin
4. Ferrocene

XII. PHENOLS

1. Phenol*
2. Pentachlorophenol*
3. 4-Phenylphenol
4. 4-Nitrophenol*
5. Guaiacol
6. Catechol
7. Tetrachlorocatechol
8. Bisphenol A
9. Tetrabromobisphenol A
10. 1-Napthol
11. 4-chloro-1-napthol
12. 2,6-Di-*tert*-butyl-4-methylphenol
13. 2,4-Dichlorophenol*

XIII. PHOSPHORUS COMPOUNDS

1. Tri-*n*-butyl phosphate
2. Triphenyl phosphate
3. Triethyl phosphine
4. Triphenyl phosphite
5. Diethyl phosphoric acid
6. Malathion (diethyl mercaptosuccinate, *s*-ester of *o,o*-dimethylphosphorodithioate)
7. tris(2-Chloroethyl) phosphate
8. Leptophos [o-4-bromo-2,5-dichlorophenyl) *o*-methyl phenylphosphonothionate]

XIV. POLYNUCLEAR AROMATICS

1. Naphthalene*
2. 2-Chloronaphthalene
3. Acenaphthylene*
4. Anthracene*
5. Pyrene*
6. Benzo[a]anthracene*
7. Benzo[a]pyrene*
8. Perylene
9. Coronene
10. Fluoranthene*

XV. SULFONIC ACIDS

1. Benzenesulfonic acid
2. Methanesulfonic acid
3. 1-Naphthalenesulfonic acid
4. 2,6-Naphthalenedisulfonic acid

XVI. SULFUR COMPOUNDS (OTHER THAN SULFONIC ACIDS)

1. Carbon disulfide
2. Dimethyl disulfide
3. Diphenyl disulfide
4. *tert*-Butyl mercaptan
5. Dimethyl sulfone
6. 2-Acetylthiophene
7. Thiophenol
8. Ethylisothiocyanate
9. Dimethyl sulfoxide
10. Benzothiophene
11. 1,4-Propanesulfone
12. α-Endosulfan* (6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepin-3-oxide)

* Compounds on the U.S. Environmental Protection Agency Priority Pollutant list.

chemicals as consensus voluntary reference compounds (CVRC's). This list is presented in Table 2 and has been approved by the Executive Committee of the ACS Division of Environmental Chemistry and has been endorsed by the ACS Joint Board/Council Committee on Environmental Improvement.

Known water pollutants were the prime candidates for reference compounds; the choice, however, was not restricted to water pollutants, for it was more important to obtain a wide variety of representative compounds. For example, relatively few water pollutants containing nitrogen and sulfur have been identified. Perhaps this is because they are not as abundant as organic pollutants that do not contain these heteroatoms. But a major contributing factor could also be that present methodology is inadequate to concentrate, fractionate, isolate and/or detect them even if they are present.

Of course, no representative list of model compounds will be completely adequate. On the basis of our present knowledge and technology, however, the CEP list of CVRC's should be adequate to handle at least 90% of projected current needs.

As this list is used, we hope that constructive criticism will be forwarded to CEP so that appropriate additions and/or modifications can be made. Presently, this can best be achieved by channeling comments through Dr. Keith and the ACS Division of Environmental Chemistry.

Pending the successful acceptance of this first venture by the world scientific community, other objectives of CEP will be pursued. These may include, but are not limited to, similar lists of CVRC's for developing methodology related to air pollution and sediment/soil pollution (e.g., from uncontrolled chemical landfills).

Dr. Lawrence H. Keith is manager of the Analytical Chemical Division at Radian Corporation in Austin, Texas. He is also chairman of the ACS Division of Environmental Chemistry and, prior to joining Radian, worked for EPA at the Athens, Georgia Environmental Research Laboratory.

Needled felts for fabric filters

Widely used in Europe, needled felts enjoy 85% of the market share of all fabrics used in dry filtration and are finding increasing use in the U.S. due to ever stringent federal regulations to control particulate matter

Lutz Bergmann
Filter Media Consulting
LaGrange, GA 32041

Air pollution control in the U.S. is being progressively enforced by the Environmental Protection Agency (EPA) and has created a fast-growing market for fabric filters. In general, particulate emissions are estimated to constitute 13% of total air pollution, coming from four different areas:

- air pollution control (as in public utilities),
- dust collection (in cement plants, hot asphalt mixing),
- product recovery (carbon black, primary smelting), and
- powdered-material handling (spray drier, mining, food industry).

The most versatile gas-stream cleaning systems involve the use of fabric filters (baghouses). The fabric-filter system selected depends on several variables such as:

- type of fumes,
- cleaning system (pulse jet, shaker, reverse air, combinations),
- temperature of effluent,
- inlet concentration of particles,
- pressure drop limits,
- filter efficiency required,
- chemistry of gas stream,
- nature of particles (size, surface area, shape), and
- space requirements and access to filter unit needed.

In general, fabric-filter units are giant vacuum cleaners with basically one additional element. Both have in common the housing, the fan, and the "bag" doing the filtering. Fabric filters, however, also have a cleaning mechanism to ensure continuous operation. The fabric, often called the "bag", is the heart of every filter, capturing solid particles while allowing air or gas to pass through.

There are two basic, but important, differences:

Collection:	Inside	Outside
Collector:	Reverse Air, Shaker	Cage type (pulse jet)
Fabric Type:	Woven	Needled

This article is devoted to "outside" collection units utilizing needled fabrics; however, the type of collector determines the kind of fabric being used.

Incoming air or gas enters the collectors; all solid particles are trapped at the fabric's surface, forming a cake but still permitting air to pass through. In such filter installations, it is essential to maintain a continuous process, thus avoiding a complete blinding or plugging of the filter media. For that purpose each filter bag is cleaned by methods shown in Figure 1.

A certain amount of dust remains within the fabric; this is called a primary dust layer. It is important, however, in designing needled felts, to maintain the highest possible air handling capacity, while at the same time capturing the fine dust. A balance has to be found in these different parameters and always towards the maximum goal of the "ideal" filter media which provides the highest attainable efficiency with the greatest possible air flow at the lowest possible pressure drop across the fabric.

0013-936X/79/0913-1472$01.00/0

Fabric filters are the most efficient type of filtration equipment. The performance of any fabric filter depends on the type of fabric chosen for a certain application. The filter media therefore must perform at least three basic functions. They must:

1. separate and collect particulate matter,
2. provide for cake-dust removal or cleaning operation, and
3. have good durability-resistance to chemical, thermal and physical breakdown.

Needled felts are three-dimensional filter media. The active element is the single filter and not the yarn as in woven fabrics. To improve dimensional stability, most needled fabrics have a scrim sandwiched in the center of the felt between mechanically interlocked fiber layers. Felts made of highly shrinkable fibers—as increasingly used in Europe—permit elimination of the scrim support, and thus are more economical.

A unique feature of needled felts is fiber which is the distribution random in three dimensions (Figure 2). Fiber orientation is partly horizontal, partly vertical and at many angles. Size, shape, and physical properties of the pores are of major importance for the task of the filter function. The filter has to separate the submicron fine particles efficiently and also permit the passage of a large volume of air or gas. Thus, formation of the pores should be fairly uniform so that filtering pressure is distributed uniformly.

The main objectives in designing the most useful needled felt for fabric filters are concentrated in three basic areas:

1. highest obtainable efficiency,
2. lowest possible differential pressure, and
3. sufficient life cycle for economy.

The fibrous structure and porous surface of needled fabrics permit efficient collection of even submicron fine dust, adhesive fumes, mechanically abrasive particles, hygroscopic chemicals, or even oily substances provided the surface of the felt is properly treated, the right fiber is selected, the cleaning frequency is adjusted, and all of this is based on experienced A/C ratio relationship.

Surface modification

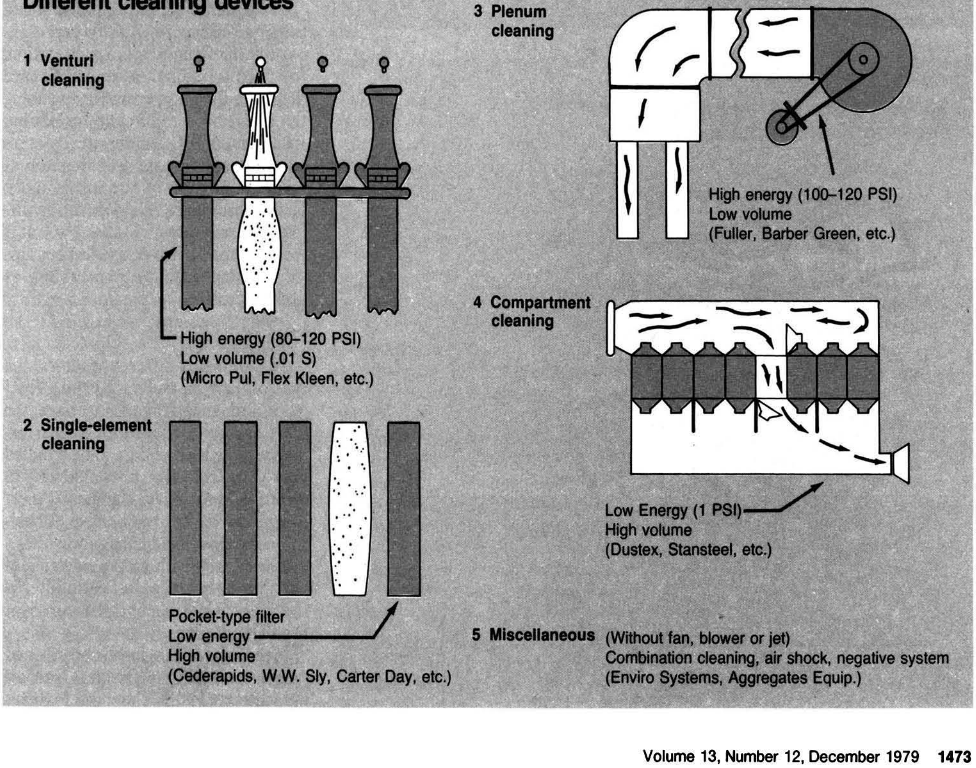
Capacity, cleanability, and efficiency are greatly influenced by the fabric surface. Therefore, surface modifications have been shown to have an especially marked influence on the performance of filter fabrics—notably filter felts. Through controlled heat treatment, fabric surface alteration can be achieved to prevent serious penetration of particles into the inner structure of the felt. Instead, the dust is encouraged to form a protective primary layer on the outer surface.

As a result, permeability at equilibrium can be maintained at a high level, and, therefore, provide better overall filter capacity. Often, the improved surface encourages formation of a more porous dust layer. The advantages of such treated felts are better cleaning and simpler dust removal. It is then immaterial whether the cleaning is carried out by reverse air, shaking, oscillating, or high-pressure air.

Laboratory observations of deposits on felted-filter media indicate that an initial "depth" filtration period is followed by cake formation in constant velocity filtration. These observations suggest that classical liquid-solid filtration theory may be applicable to gas-solid systems; microscopic examination of these deposits confirm that cake filtration is the principal mode of separation.

FIGURE 1

Different cleaning devices



1 Venturi cleaning

High energy (80–120 PSI)
Low volume (.01 S)
(Micro Pul, Flex Kleen, etc.)

2 Single-element cleaning

Pocket-type filter
Low energy
High volume
(Cederapids, W.W. Sly, Carter Day, etc.)

3 Plenum cleaning

High energy (100–120 PSI)
Low volume
(Fuller, Barber Green, etc.)

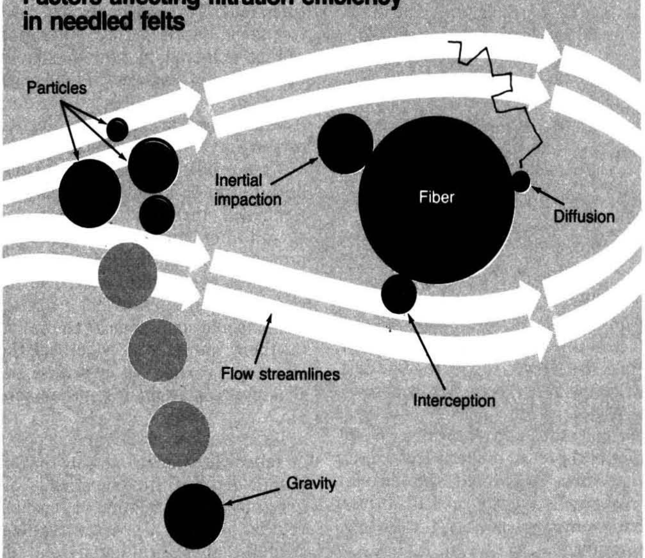
4 Compartment cleaning

Low Energy (1 PSI)
High volume
(Dustex, Stansteel, etc.)

5 Miscellaneous (Without fan, blower or jet)
Combination cleaning, air shock, negative system
(Enviro Systems, Aggregates Equip.)

FIGURE 2

Factors affecting filtration efficiency in needled felts

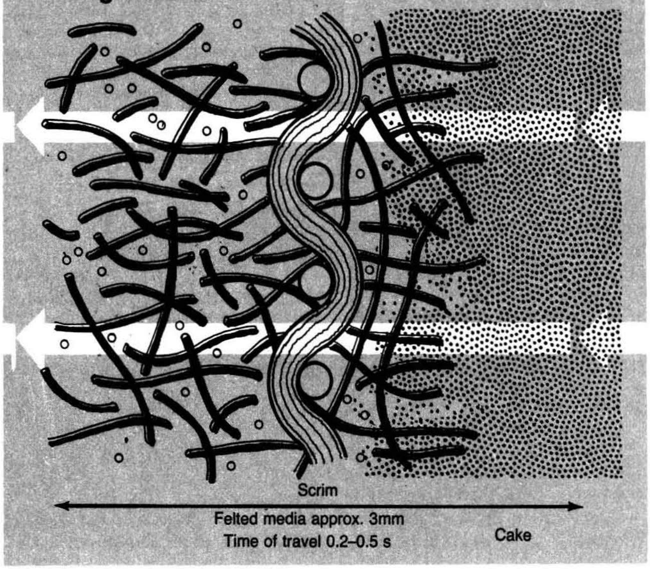


Efficiency due to:

Increase in:	Gravity	Inertial sieving	Direct impaction	Interception	Diffusion
Face velocity	Increased	No effect	Increased	No effect	Decreased
Particle size	Increased	Increased	Increased	Increased	Decreased
Particle density	Increased	No effect	Increased	No effect	Decreased
Fiber diameter	No effect	Decreased	Decreased	Decreased	Decreased
Decrease in fiber diameter	No effect	Increased	Increased	Increased	Increased significantly

FIGURE 3

Section through felted-filter media showing distribution of dust



These observations are tremendously important. We must try to design the felt so that cake forms on the outside of the fabric rather than traveling into the center, thus making it more difficult to remove. This fact is still not fully recognized in our industry and, more importantly, not fully understood by original equipment manufacturers, as well as end-users.

The multifiber-layer design concept, as shown in Figure 3, is a successful step toward that direction. This concept incorporates different layers of fibers of different fineness all needled into a filter felt. The theoretical thesis behind this concept demands the ability to capture particles on the surface or not at all. Very fine dust shall travel, if not trapped at the surface, all the way through the felt, rather than halfway, and then settle.

Air permeability

Air permeability, as commonly reported in cfm (cubic feet per square foot of cloth measured at $\frac{1}{2}$-in.-W.G.), for the new fabric represents a close approximation of the starting air-transfer qualities of the filtration fabric. Generally, rapid changes occur in air flow early in filter use. The air flow rate is largely dependent upon the fabric structure and the filtrate characteristics, reaching a new and steady state known as "service permeability".

Thus, while the initial fabric structure and air permeability represent only part of the fabric specification, they are fundamental and influence the entire filtration operation including the type and rate of cake formation. Air permeability, under steady-state working conditions, will remain at roughly 20–50% of the initial clean cloth throughout, at an operating differential pressure of 3–6 in. W.G. It is the target in fabric design to keep this value of equilibrium permeability as high as possible.

Efficiency

In looking at different factors, the type of fiber, its dullness, crimp, fineness, and generic heritage have the most dramatic effect on field performance. The kind of dust to be handled may vary from fine to coarse, dry to moist, light to heavy, chemically inert to aggressive, soft to abrasive; it basically has less effect on the fabric filter's performance. With proper selection of the right fabric type, a fabric filter is the most versatile control equipment for effluent gases.

Needled fabrics have contributed substantially to an excellent performance reputation. The main features

Guidelines for filter rates in ft/min

Application / Cleaning system	Fine dusts <1 μm and fumes, aluminum	Dye stuffs, chemical industry, foundries, power plants, dryers	Asphalt, cement, lime	Wood industry, food industry	Plastic powders
Conventional bag filters with mechanical cleaning (shaking, vibration) discontinuous with or without reverse flow (woven fabric)	1–2	2–3.5	2.5–5	4–7	6–8
Bag filter with pulse jet cleaning in rows or low-pressure pulsating reverse flow (needled felt)	2.5–5	3–7	5–10	8–13	12–17
Bag filter with high-volume pulse jet cleaning 0.5–3 atm, each bag separately (needled felt)	5–10	6–13	10–20	16–26	23–30

Source: Dietrich, Conference in 1978

of needled felts can be summarized as:

- highest obtainable efficiency on fine, submicron particles,
- greatest air handling capacity at high A/C ratios,
- excellent cleanability due to surface treatments,
- superb stability and durability,
- permanently antistatic and special fiber mix, and
- suitable for virtually every type application.

Experience

A summary of experience in Europe as well as in the U.S. shows that needled fabrics currently used have dimensional stability under temperature conditions of ±0.5%, are available with treated surfaces, have a tear strength of 180 lb/in., have an air permeability of 30 cfm at ½ in. W.G., and a calibrated pore size depending on the dust. Emission rates may be below 20 mg/m^3 (0.1 gr/ft^3) with filter-bag life in some industries up to several years.

From an extensive study, completed just a few weeks ago, we can derive the usage of needled felts in the U.S. for dry filtration. For 1978, the total yardage was listed as 4.84 million sq yds. The largest segment, approximately 3.3 million sq yds, was made out of polyester; 1.31 million sq yds, Nomex®; 0.18 million sq yds, homopolymeracrylic; and 0.05 million sq yds, other fibers.

Future potential

For a number of reasons, needled fabrics are more widely accepted elsewhere, notably Europe. Baghouse design differs from the average U.S. installation. Some industries have almost completely converted to needled fabrics, like cement plants in France, Germany, and Scandinavia. Needled fabrics in these countries are no longer limited to cage-type collectors; they are successfully applied to reverse air and shaker baghouses, which are furnished in the U.S., predominantly with woven fabrics.

Excellent field performance for more than 15 years has motivated manufacturers to develop unique constructions, and they have found ways to employ available fibers in new techniques in manufacturing. Keen competition has resulted in major accomplishments in the filtration industry. It is felt that in the U.S. the potential for needled felts is very promising, probably focusing in the following areas:

- lightweight (8–10 oz/sq yd) scrimless polyester felts,
- extra-thin polyester felts for filter bags, replacing current woven fabrics,
- scrimless Nomex® felts (10–12 oz/sq yd)
- antistatic-conductive felts with stainless-steel fibers,
- special surface-modified felts for critical applications with high cleanability potential,
- 100% stainless-steel fiber felts for brand new applications,
- needled felts for metal fumes as replacement for woven constructions currently used,
- felts with water-repellent surface treatments,
- numerous felt constructions with high volume potential for wet filtration, not covered in this paper, and
- 100% needled glass felt.

Depending on the willingness of the needled-felt manufacturer, the equipment engineer, and an open-minded end-user, years of substantial growth lay right ahead of us. I predict an enormous demand for sophisticated filter felts created by ever stringent government regulations to control particulates in an efficient, economical, and reliable manner. I can't think of any other "best available control technique". It is, therefore, essential that the responsible individuals promote fabric development toward needled felts to be accepted as widely as in Europe.

Acknowledgment

The context of this feature article was presented at the INDA conference (Association of the Nonwoven Fabrics Industry, headquartered in New York City) in March 1979, New Orleans, La.

Additional reading

Lutz Bergmann, "Status Report of Fabric Filtration in Europe", APCA Conference—Buffalo, N. Y., October 1975.

W. Budrow, "Durability of Textile Filter Media", *APCA Journal,* May 1978.

Hans Dietrich, "The Profit from Sophisticated Filter Felts", APCA Conference—Niagara Falls, N. Y., October 1978.

Filtration and Separation, November/December 1978.

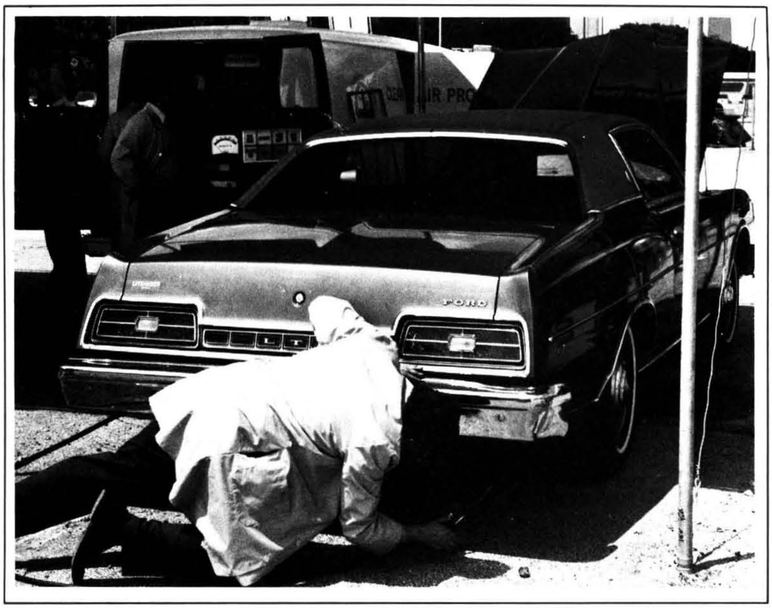
R. F. Hall, "Needled Felts in Dust Filtration", Webron Products Ltd., Rossendale Lancs. BB4 7JL, England.

Lutz Bergmann, "Filter Media and Fabric Filtration", a Market Study completed in January 1979.

Lutz Bergmann *is a consultant for Filter Media Consulting. He has been involved in R&D for high temperature fiber and fabric applications involving Nomex®, glass, and metal fibers. Previously Mr. Bergmann was product manager—filtration for Milliken & Co., LaGrange, Ga. He has also held positions as vice president for A. Kayser and T.J. Heimbach in Germany and has more than 25 years experience in fabric filtration.*

Improving air quality

New Jersey is making progress with its inspection and maintenance (I/M) program for automotive emissions



John C. Elston
Bureau of Air Pollution Control
Trenton, N.J. 08625

In New Jersey, emissions inspections are carried out by state inspection stations, and are operated by the Department of Motor Vehicles, originally established to provide safety inspections. In 1972, the inspection lanes were equipped with 125 Sun infrared HC/CO emissions analyzers. At the time this was a pioneering role, both for the state and Sun, in the application of a measurement technique well known in the laboratory to a high-volume testing situation with relatively low-cost series production-type equipment.

In fact, those inspection lanes have now made over 28 000 000 emissions tests which have resulted in about 4 200 000 vehicle repairs or adjustments to reduce exhaust emissions levels below state in-use standards.

With more than five years experience in mandatory emissions testing, New Jersey is advanced in relation to other areas, and since the passage of the Clean Air Act, which made compliance by 1982 (or 1987 at the latest) mandatory for the cited metropolitan areas, has maintained its efforts to stay in the forefront of I/M programs.

During 1978-9, in response to a state initiative and specification, Sun developed and installed prototype equipment which has now completed over 5000 emissions tests and has been extensively evaluated in both laboratory and test lanes. Replacement of original equipment will be completed in 1980.

The IR technique

Although the infrared principle is still used, Sun has extended both measurement and control technologies greatly, indeed beyond the original expectations of the state. Each unit includes a microprocessor enabling such features as:

- automatic correction for span and zero drift,
- a calibration gas economizer,
- automatic test commencement and conclusion,
- exhaust air-dilution detection and compensation,
- poor fuel-efficiency indication,
- self-diagnosis in the event of breakdown,
- built-in vehicle emissions standards, and
- an interface with printing and magnetic recording devices.

In addition, the vital "Pass or Fail" decision is a function of the tester, not the operator, thus contributing to the consistency and integrity of the system and preserving the good public acceptance already achieved.

To nationally extend New Jersey's success in improving air quality requires more than agreements between the federal government and the auto industry. It must involve all levels of government—federal, state, and municipal, together with auto manufac-

0013-936X/79/0913-1476$01.00/0 © 1979 American Chemical Society

turers, dealers, and repairers, as well as us, the motoring public who create air pollution as we drive our vehicles.

A mandatory program

The New Jersey mandatory test and repair program has had a favorable impact. There has been a 40% reduction in average ambient CO, equivalent to an average rate of 8% per annum. It is much more difficult to quantify the HC improvement since almost equal contributions are made by mobile and stationary sources, and large quantities of the pollutant come from other areas.

From the viewpoint of the federal government, it is necessary to establish clear guidelines for a national air monitoring network. The federal Environmental Protection Agency (EPA) has indicated that during this same period the rate of CO reduction in areas without an I/M program is about 5%. New Jersey's advantage is attributed to the inspection and maintenance program.

Although the information generated by the air quality monitoring stations in New Jersey is accurate, it is difficult (often impossible) to relate this data to that of other states due to nonuniformity in location of air quality monitoring sites. This is not the only area requiring clarification on a national basis, but it is a critical one since it serves as the benchmark for the measurement of overall attainment and progress in air quality improvement.

One other consideration of critical importance is the role of the auto industry. Already faced with the threefold task of manufacturing products that meet emissions standards, fuel economy (CAFE) specifications, and provide acceptable performance, it should recognize a further obligation—informing customers of the changed nature of the vehicle in today's society compared with 10 years ago.

Because of much more stringent specifications for emissions control and changes in vehicle design to accomplish this, there is a need for a new public consciousness of the requirement to maintain vehicles properly and thus to maintain low emissions levels.

Role of industry, public

The auto industry should play a leading role in making the public aware of the impact of their own actions on ambient air quality levels. With respect to the industry's service and repair branches, the majority of repair organizations do an orderly and effective job, even if certain exceptional unscrupulous elements need to be monitored and controlled. One area which has made good progress in New Jersey is the vocational education and training of auto service and repair technicians. It is required that institutions offering courses in automotive service and repair keep pace with developments in vehicle emissions controls. This favorable trend should be projected nationally.

Public acceptance in New Jersey has been good; the majority of residents appreciate the need for annual inspection and willingly perform needed repairs to vehicles with safety defects and excessive emissions. The rising costs of vehicles, gasoline, and repairs has stimulated an awareness of the need for properly functioning fuel-efficient automobiles. This awareness is national and should be an advantage to those groups, nationwide, charged with consumer education as part of I/M implementation.

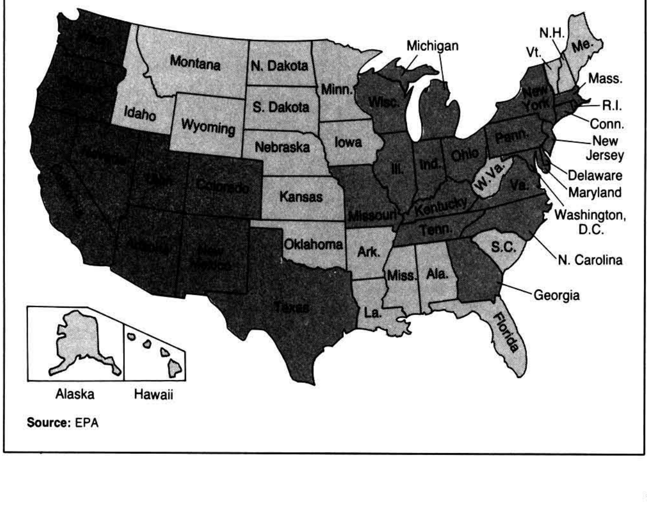
Stimulating public awareness is an ongoing task and needs national coordination to achieve consumer support for, and cooperation with, I/M programs in all the cited areas. Strong efforts are being made to combine fuel savings with reductions in emissions.

One factor in public acceptance is cost. In New Jersey, the average repair cost has been around $28 per rejected vehicle. The annual fee, which includes safety inspection, is $2.50. It should be noted, however, that the New Jersey safety program has been in operation since 1938, so that land and facility costs have been fully amortized over a long period. If the state were to start anew, the fee would obviously be much greater and would have to reflect current real-estate values and construction costs.

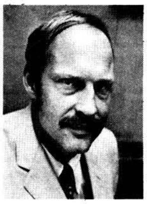
Improving air quality, both nationally and in specific areas or jurisdictions, is a complex and demanding task. It needs a systems approach to consider all aspects of the problem and determine effective solutions. A key concept in this respect is that inspection without maintenance/repair is like a ship without a rudder—not effective in reaching any destination.

The motto, "Let's Protect Our Earth", which is part of the logo adopted by the New Jersey Department of Environmental Protection, states a national and indeed supranational goal worthy of our closest consideration and attention.

29 states need I/M programs to meet air quality standards



Source: EPA



Since 1972, **John C. Elston** *has been closely associated with auto emission inspection in New Jersey, first during the voluntary phase from 1972–1974, and later with the mandatory inspection/maintenance (I/M) program for all licensed gasoline-powered vehicles under 6000 lbs.*

In 1979, he was given a year's leave of absence to assist the National Center for Vehicle Emissions Control and Safety at Colorado State University, formed to propagate vehicle inspection concepts nationally.

Radioactive Waste in Geologic Storage

ACS Symposium Series No. 100

Sherman Fried, *Editor*
Argonne National Laboratory

Based on a symposium sponsored by the Division of Nuclear Chemistry and Technology of the American Chemical Society.

Overall interest in the safe disposal of radioactive waste has deepened and the government as well as private concerns have initiated programs to understand the processes by which radionuclides migrate from a geologic repository into the environment.

The material persented in this volume outlines the conceptual, chemical, and geological facets of the current radioactive waste isolation program, covering the most recent disposal concepts and proposals as well as significant experimental results.

CONTENTS

Department of Energy Isolation of Radioactive Waste • WIPP: A Bedded Salt Repository • Radioactive Waste Management • Radioactive Waste Disposal • Leaching of Radioactive Waste Glass • Single-Pass Leaching • Leach Rates • Ceramic Forms for Nuclear Waste • Radionuclide Migration • Nuclide Migration in Fractured or Porous Rock • Kinetic Effects in Migration • Sorption Behavior on Clay Minerals • Actinide Sorption • Biogeochemistry of Actinides • Radionuclide Sorption Studies • Clays for Waste Isolation • Ion-Exchange Equilibria

344 pages (1979) Clothbound $29.50
LC 79-9754 ISBN 0-8412-0498-5

- - - - - - - - - -

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

Please send ________ copies of *SS 100 Radioactive Waste in Geologic Storage* (ACI 0498-5) at $29.50 per copy.

☐ Check enclosed for $________. ☐ Bill me.
Postpaid in U.S. and Canada plus 75¢ elsewhere.
California residents please add 6% state use tax.

Name

Address

City State Zip

N-Nitrosamines

ACS Symposium Series No. 101

Jean-Pierre Anselme, *Editor*
University of Massachusetts

A symposium presented at the Eighth Northeast Regional Meeting of the American Chemical Society.

Fear of human exposure to known carcinogens and mutagens in the workplace, in the environment, and in consumer products (foods, cosmetics, pharmaceuticals, and pesticides) has triggered a dynamic interest in *N*-nitrosamine chemistry.

Eleven chapters by prominent investigators in the field consolidate the latest findings in this critically important area, focusing on the possible mechanisms of biological action, and on the detection and environmental impact of these compounds.

CONTENTS

Organic Chemistry of *N*-Nitrosamines • Chemistry of *N*-Nitrosamides and Related *N*-Nitrosamino Acids • Stereochemical Effects on *N*-Nitrosamine Chemistry • Chemistry of α-Substituted *N*-Nitrosamines • Oxidative Activation of *N*-Nitrosamines • α-Amino Nitrite Esters • *N*-Nitrosamine Fragmentation and Transformation • Tobacco Specific *N*-Nitrosamines • Quantitative Aspects of Exposure and Mechanism in *N*-Nitrosamine Carcinogenesis • *N*-Nitrosamines As Environmental Carcinogens • *N*-Nitrosamines in Consumer Products and in the Workplace

204 pages (1979) Clothbound $22.50
LC 79-12461 ISBN 0-8412-0503-5

- - - - - - - - - -

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

Please send ________ copies of *SS 101 N-Nitrosamines* (ACI 0503-5) at $22.50 per copy.

☐ Check enclosed for $________. ☐ Bill me.
Postpaid in U.S. and Canada plus 75¢ elsewhere.
California residents please add 6% state use tax.

Name

Address

City State Zip

Federal R&D and Scientific Innovation

ACS Symposium Series No. 105

Leonard A. Ault, *Editor*
NASA

W. Novis Smith, *Editor*
Air Products and Chemicals, Inc.

Based on a symposium sponsored by the Division of Industrial and Engineering Chemistry of the American Chemical Society.

Authors from government and non-government organizations who are directly involved in the ongoing challenge of commercialization address the complex problems that arise from the unique nature of federally funded R&D: these include ownership of patent rights, lack of incentives, and questions as to the extent of government involvement.

Although the book's central focus is on the role of federally funded R&D in generating commercialization, it also examines the larger context of rationalizing the infrastructure of innovation.

CONTENTS

Political Nature of Civilian R&D Management • Can You Innovate in Uncle Sam's Embrace? • Federal Policy Concerns Regarding Commercialization • Productivity • Cooperative Agreements • Industrial Energy Conservation Technology • NASA Technology Utilization Program • Patents and Technology Transfer • Commercialization of Technology Through the Federal Laboratory Consortium for Technology Transfer • Assessment of Federal R&D • Federal R&D as an Internal Push for Commercialization of Technology • A New Starch-Based Polymer

170 pages (1979) Clothbound $23.50
LC 79-13114 ISBN 0-8412-0507-8

- - - - - - - - - -

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

Please send ________ copies of *SS 105 Federal R&D and Scientific Innovation* (ACI 0507-8) at $23.50 per copy.

☐ Check enclosed for $________. ☐ Bill me.
Postpaid in U.S. and Canada plus 75¢ elsewhere.
California residents please add 6% state use tax.

Name

Address

City State Zip

ES&T
RESEARCH

Fish and *Daphnia* Toxicity as Surrogates for Aquatic Vascular Plants and Algae

Eugene E. Kenaga* and Robert J. Moolenaar

Health and Environmental Sciences, The Dow Chemical Company, Midland, Mich. 48640

■ The relative degree of acute toxicity of thousands of chemicals of heterogeneous structures was compared for fishes, daphnids, aquatic vascular plants, and algae. Aquatic animals were more sensitive indicators of toxic effects than were plants or algae. Compounds that were toxic at under 1 ppm for daphnids, fishes, aquatic vascular plants, and algae represented 2.4, 1.3, 0.12, and 0.02%, respectively, of the total tested for each of these four groups of organisms. Of the 27 781 chemicals tested on aquatic plants and 49 082 tested on the alga *Chlorella*, all but 3 compounds were either not toxic to these organisms under 1 mg/L, or were toxic to fish and *Daphnia* at 1 ppm or less.

During the manufacture, distribution, use, and disposal of chemicals, the potential exists for some of them to reach the water environment. The water environment, in contrast to the air environment, has a relatively small volume, is generally not rapidly mixed, and is more unreactive toward chemicals. The potential impact of chemicals on aquatic organisms is therefore usually greater than their potential impact on terrestrial organisms exposed to contact with air. Consequently, laboratory ecotoxicity testing programs have stressed studies on aquatic organisms rather than terrestrial organisms.

The choice of organisms that are indicative of toxicity to aquatic species must be very selective. The number of organisms living in the aquatic environment is very large (20 000 species of fish alone), so the selection of appropriate indicator organisms is critical. Kenaga (*1*) correlated acute toxicity data for eight organisms commonly used for evaluation of environmental hazards, and concluded that both *Daphnia* and fish were appropriate indicators for the toxicity of chemicals to aquatic animals. This is consistent with proposed guidelines for the registration of pesticides in the United States (*2*).

Plants are also important in the ecology of the aquatic environment. Biologists generally regard aquatic plants as less sensitive than aquatic animals to chemical toxicants, but documentation for a wide spectrum of chemicals is lacking.

For a number of years screening tests against a variety of aquatic organisms have been carried out at The Dow Chemical Company. Included was a daphnid, four species of fish, an alga, and five species of vascular plants. Tests performed on these organisms were the basis for the comparison of the relative acute toxicities of chemicals to aquatic plants and animals reported in this paper. It was felt that this large data base of chemicals was very useful for initial hazard evaluation even though not meeting the strict standards of present day LC_{50} studies.

Test Methods

The chemicals tested were obtained sequentially from many sources inside and outside The Dow Chemical Company over a period of more than 20 years, and routinely screened at Dow for many different types of biological activity. The chemicals tested include those originally prepared for screening or for use as insecticides, fungicides, nematocides, fumigants, terrestrial herbicides, aquatic herbicides, coccidiostats, plasticizers, drugs, algacides, microbiocides, deflocculation, chelation nitrogen stabilizers, catalysts, solvents, ion exchange materials, resins, cleaners, latexes, coatings, pigments, lubricants, preservatives, flotation agents, emulsifiers, organic and inorganic chemical intermediates, inhibitors, stabilizers, antifreezes, hydraulic fluids, plastic monomers, plastic surfactants, adhesives, flame retardants, highway products, metals, and other inorganic and organic chemicals. The Dow Chemical Company screening list of over 100 000 compounds can roughly be divided chemically as 0.86% inorganic, 52.0% with benzene rings, 35.7% with heterocyclic rings, 8.2% with carbocyclic rings (excluding benzene), 5.3% containing P, 63.0% containing N, 6.2% containing Br, and 27.2% containing Cl compounds. Most, but not all, of the compounds included in the smaller lists were tested on the same organisms as those in the longer list of compounds.

Chemicals were formulated for testing as ball-milled powders or acetone–water suspensions. Dilutions of the chemical were made in chlorinated Lake Huron water, which has a pH of 7.6 and total alkalinity of 85 mg/L. The water was aerated for several days before being used as static test water for fish and *Daphnia*. Concentrations were not replaced during the test. Untreated and solvent controls on the organisms rarely showed mortality and if in excess of 10% were discounted. Normally compounds showing 100% activity at the initial concentration were reduced in concentration by one-half until less than 100% activity was shown. Tests were conducted at 65–70 °F and were not replicated.

The following species of fish were tested as alternates for each other in about equal frequency in the screening tests: emerald shiner, *Notropis atherinoides;* fathead minnow, *Pimephales promelas;* goldfish, *Carrasius auratus;* and carp, *Cyprinus carpio.* Two fish were placed in a plastic box containing 500 mL of water usually exposed to an initial concentration of 2 mg/L. Mortality counts were taken after 24-h exposure.

About 50 *Daphnia magna* were used for each test as mixed adults and nymphs using the same test conditions as those used for fish.

The following five species of aquatic submersed and floating vascular plants were tested: Carolina fanwort, *Cabomba caroliniana;* waterweed, *Anacharis* (*Elodea*) spp.; moneywort, *Lysimachia nummularia;* coontail, *Ceratophyllum* spp.; and *Salvinia rotundifolia.* Plants were usually tested in 500 mL of water in concentrations of 10 or 100 ppm for 24 h, and held in untreated water for approximately 3 weeks before final mortality readings were taken.

0013-936X/79/0913-1479$01.00/0

Table I. Comparative Toxicity of Chemicals Screened on *Daphnia*, Fish, Aquatic Plants, and Algae

concn tested, ppm	compounds giving 100% control of organism							
	Daphnia		fishes		aquatic plants		*Chlorella*	
	no.	%[a]	no.	%[a]	no.	%[a]	no.	%[a]
1–1.99	992	2.9	1 529	4.3	196	0.71	263	0.54
0.1–0.99	823	2.4	473	1.3	33	0.12	12	0.02
0.01–0.09	203	0.6	51	0.14	0	0	3	0.006
total no. of compds tested	33 909		35 305		27 781		49 082	

[a] Percent of total compounds tested giving 100% mortality (control) as defined in the text.

The alga was tested in an aqueous nutrient solution (Hoagland's) beginning at 10 mg/L. Vapor losses were reduced by use of a Saran film over the opening of the glass container. Mortality was determined visually by change in color (death) or by use of colorimetry to measure chlorophyll density comparative to the control after 1-week exposure to the test compound.

Tabulation of Data. Using the lowest concentration giving 100% mortality as the comparative index of biological activity, data from each of the four groups of organisms (fish, daphnids, aquatic vascular plants, and *Chlorella*) were divided into three toxicity classes as follows: (1) 0.01–0.09 mg/L, (2) 0.1–0.99 mg/L, (3) 1.0–1.99 mg/L. All compounds in toxicity classes 1 and 2 also appear in class 3.

Results and Discussion

The number of chemicals tested against the four groups of organisms listed in Table I varied from 27 781 to 49 032, and thus represented a much larger number and more varied sample of chemical structures than is ordinarily available for comparison. At concentrations below 2 mg/L, a greater percentage of chemicals showed toxicity toward fish or daphnids than toward aquatic plants or alga, confirming the generally held view that aquatic animals are more sensitive to chemical toxicants than aquatic plants. None of the 22 781 compounds tested were toxic to aquatic plants below 0.1 mg/L. *Chlorella* was generally less sensitive than aquatic vascular plants despite the fact that exposures were for 7 days compared to 1 day for the other organisms. There were only 3 chemicals out of 49 082 tested on *Chlorella* that were toxic at concentrations below 0.1 mg/L.

Recent studies of organic contaminants in water have shown their concentrations rarely exceed 1 mg/L. Sheldon and Hites (*3*) identified 100 chemical contaminants in Delaware River water, but reported none at concentrations higher than 15 μg/L. In a study by the EPA (*4*) of priority pollutants in wastewater effluents, concentrations reported were generally below 10 μg/L, with a few in the 10 to 100 μg/L range. In view of these observations, it seemed appropriate to examine further the relative toxicities of chemicals to aquatic plants and animals for those compounds that are toxic to plants below 1 mg/L.

Thirty-three chemicals (or 0.12% of the total tested) were lethal to aquatic plants below 1 mg/L, as shown in Table I. Two of these compounds were not tested for toxicity to fish or daphnids. Of the remaining 31 compounds, 22% were toxic (compounds killing 100% of the organisms) to daphnids, 62% to fish, and 68% to fish or daphnids at concentrations below 1 mg/L. At <2 mg/L (usually 1 to 1.25 mg/L in actual tests), 77% of the 31 compounds were toxic to daphnids, 90% to fish, and 100% to fish or daphnids.

Twelve chemicals (or 0.02% of the total tested) were lethal to the alga *Chlorella* below 1 mg/L, as shown in Table I. One of these compounds, an antibiotic, was not tested for toxicity to fish or daphnids. Of the remaining 11 compounds, 45% were toxic to daphnids, 45% to fish, and 55% to fish or daphnids at concentrations below 1 mg/L. Of the same 11 compounds, all but one were tested on daphnids and fish and all were toxic at 1 mg/L or less. The 11 compounds consisted of 9 metallic derivatives (5 organoarsenicals, 3 organotins, and 1 silver compound), 1 dithiocarbamate, and one bromoketone derivative (see Table II).

Table II. Comparison of Chemicals Toxic to Algae with Toxicity of the Same Chemicals to Fish and Daphnids

compound	lowest mg/L causing 100% mortality		
	algae[a]	fish	*Daphnia*
silver salt	0.01		1.0
organotin	0.01	0.1[b]	1.0
organotin	0.5	0.05[b]	0.2
organotin	0.5	0.1[b]	0.2
bromoketone derivative	0.1	1.0[b]	1.0
dithiocarbamate derivative	0.5	1.0[b]	0.2
organoarsenical	0.5	0.2[b]	0.2
organoarsenical	0.5	0.1[b]	0.2
organoarsenical	0.5	1.0[c]	1.0
organoarsenical	0.5	1.0[c]	1.0
organoarsenical	0.5	1.0[c]	

[a] *Chlorella*. [b] Fathead minnow. [c] Lake emerald shiner.

Within the limits of reliability of acute toxicity testing ($\pm$1 order of magnitude) shown by Kenaga (*1*), the two animal organisms made safe surrogates for all of the aquatic plants and algae studied.

Conclusions

A review of toxicity data for a large number of chemicals to four species of fish, one species of *Daphnia*, five species of vascular aquatic plants, and one species of algae has shown that animals are generally more sensitive indicators of acute toxicity than plants. Out of 49 082 compounds tested against the alga *Chlorella*, only 12 (0.02%) showed 100% mortality below 1 mg/L. The corresponding numbers for aquatic vascular plants were 33 out of 27 781 or 0.12%. Of the chemicals showing toxicity to plants or algae below 1 mg/L, all tested were indicated by toxicity to fish or daphnids at 1 mg/L or less. Based on these observations, water quality limitations based on toxicity data for fish and daphnids should be sufficiently restrictive to protect algae and aquatic vascular plants.

Literature Cited

(1) Kenaga, E. E., *Environ. Sci. Technol.*, **12**, 1322–9 (1978).
(2) U.S. Environmental Protection Agency, *Fed. Regist.*, 43(132), 29696–741 (July 10, 1978).
(3) Sheldon, L. S., Hites, R. A., *Environ. Sci. Technol.*, **12**, 1188 (1978).
(4) *C&E News*, 41 (Sept 25, 1978).

Received for review February 21, 1979. Accepted August 14, 1979. This paper is Dow Chemical Co. Publication No. B-600-035-79.

Kinetics of Reaction of Cyanide and Reduced Sulfur Species in Aqueous Solution

Richard G. Luthy* and Samuel G. Bruce, Jr.

Department of Civil Engineering, Carnegie-Mellon University, Pittsburgh, Pa. 15213

■ Interactions of cyanide and reduced sulfur species in aqueous solution can produce thiocyanate. Kinetics of the reactions of cyanide and polysulfide and cyanide and thiocyanate were investigated. Initial rate kinetic data for the reaction of cyanide and polysulfide showed the reaction is mixed order and that the order decreases from 1.9 to 1.3 as pH increases from 8.2 to 12; this was largely accounted for by a decrease in reaction order with respect to cyanide as pH increases above the pK_a for hydrogen cyanide. Catalysis and inhibition studies showed that high concentrations of ammonia were inhibitory and that coal char fines were catalytic. The rate of reaction of cyanide and polysulfide is approximately three or more orders of magnitude faster than reaction of cyanide and thiosulfate depending on pH value. A neutral or slightly alkaline solution containing the order 10^{-3} M or more total sulfide may form polysulfide on exposure to oxygen, and in the presence of cyanide there should be reaction to yield thiocyanate.

Cyanide, sulfide, and thiocyanate are environmentally significant pollutants in industrial wastewaters from coke manufacturing and iron making, and from coal gasification and liquefaction. These species plus complexes of cyanide and thiocyanate comprise an important group of constituents with regard to treatment and reuse of wastewaters from these industries. Effluent limitation guidelines have been specified for cyanide and sulfide in coal coking, iron making, and related industries (*1*). Cyanide and thiocyanate can enter into corrosion and deposition reactions with steel process lines and equipment, and therefore have important implications for development of wastewater reuse strategies. The purpose of this paper is to present some aspects of aqueous chemistry of cyanide and sulfur in order to better understand how cyanide may react with sulfide oxidation products to form thiocyanate.

Formation of Cyanogen Compounds

Wastewater Characteristics. The occurrence of cyanide, sulfide, and thiocyanate in coal coking effluents results from pyrolysis of coal at high temperature. Coke is manufactured in by-product recovery ovens where coal is heated without air at temperatures ranging from 1500 to 2000 °F. Coal volatiles are collected in a gas main and cooled, which results in the condensation of tars and flushing liquor. The tar and liquor are separated, and a portion of the liquor is recirculated to flush the gas main. The process produces water that originates from moisture in the coal; the excess liquor is called weak ammonia liquor and may be processed for by-product recovery of ammonia, phenol, and light oils comprised predominately of benzene, toluene, and xylene. Table I (*2–10*) shows general characteristics of coke plant weak ammonia liquor, and the characteristics of this liquor after processing for ammonia recovery by steam distillation with addition of lime.

At present there are no large commercial scale coal gasification plants or coal liquefaction facilities in this country. However, increased emphasis on augmenting natural gas and petroleum supplies via coal conversion has stimulated a number of research projects, some of which have advanced to substantial pilot plant testing programs. Coal gasification entails the reaction of coal, steam, and air for low BTU gas or oxygen for medium and high BTU gas, to convert coal carbon to gaseous constituents. Present process research activity is focused on evaluation of improved efficiencies by use of pressure, bed fluidization, and catalysts (*11*). Coal liquefaction entails the reaction of coal and hydrogen under temperature and pressure to produce liquid hydrocarbons from coal. Coal gasification and coal liquefaction produce foul condensates, which contain many of the same constituents as found in coke plant weak ammonia liquor. The amount of organic contaminants in coal gasification raw product gas quench condensates is dependent on operating variables and coal type. Reactors with the highest volatilization temperatures produce the cleanest product gas and condensates relatively free of organic contamination. Other factors that affect effluent quality are: gas residence time, coal heatup rate, and gas–solid mixing (*12*). Table I compares effluent composition for two hydrocarbon-bearing coal gasification condensates and a coal liquefaction effluent with coal-coking wastewaters. This comparison shows that cyanide, sulfide, and thiocyanate are common to coal coking and coal conversion effluents.

Source of Cyanide and Thiocyanate. At present little specific information is available to explain mechanisms for formation of cyanide or thiocyanate during coal coking or coal conversion. Various authors (*13, 14*) believe that under conditions existing during coal carbonization and gasification that ammonia released from coal may be converted to cyanide. Ammonia is formed as a result of release of amino or substituted amino type side chains from the coal structure. Nitrogen that remains in the coal after release of amino compounds is thought to be much more refractory than amino type nitrogen. Hydrogenation conditions during gasification result in more ammonia formation than during carbonization, probably as a result of reaction of ammonia with C, CH_4, C_2H_2, and/or CO (*13*). Thus, cyanide production is the result of secondary reactions. Its production is enhanced by high temperatures, as it has not been observed in low-temperature (~400 °F) treatment of coal whether by extraction or distillation. It may be derived to a minor extent by pyrolysis of nitrogenous products obtained as a result of coal decomposition, such as from pyridine.

Less is known about the formation of thiocyanate during coal coking and coal gasification. It is not known if thiocyanate may form as a result of gas-phase reactions (*1, 13*). Ammonia and carbon disulfide will react under pressure to produce thiocyanate (*15*). However, this may not be applicable to coal coking or gasification, because carbon disulfide is a minor component of product gas.

As explained in this paper, it is known that cyanide can react with oxidized products of sulfide to produce thiocyanate in the aqueous phase. The extent to which these reactions may occur in the gas phase is unknown. These reactions presuppose the existence of an oxidizing agent and presumably, if there were no oxidizing agent, then the reactions cannot proceed to yield thiocyanate. Hence, at present it is not possible to predict the extent to which gas-phase cyanide may be converted to thiocyanate. Careful gas-phase sampling programs are required in order to answer this question.

Regardless if thiocyanate can be formed in significant quantities as a result of gas-phase reactions, there is no question that thiocyanate is found in coal gasification raw product gas quench condensates, coke plant ammonia liquors, and in coke oven gas distribution line condensates and deposits (*1, 16*). A review of possible aqueous phase reaction pathways for production of thiocyanate in coke plant am-

0013-936X/79/0913-1481$01.00/0 © 1979 American Chemical Society

Table I. Characteristics of Coal Coking and Coal Conversion Effluents

parameter	coke plant weak ammonia liquor[a]	coke plant ammonia still effluent[b]	Synthane process by-product water[c]	Hygas process wastewater[d]	H-coal liquefaction foul water[e]
COD	2500–10000	3400–5700	15000–43000	3000–5100	88000 (26500)
phenolics	400–3000	620–1150	1700–6600	560–900	6800
NH_3-N	1800–6500	22–100	7200–11000	2600–4600	17000
NO_3^--N		<0.2		1–5	<1
organic-N		21–27		4–10	50
P	<1	0.9		0.5–1.8	
CN^-	10–100	1.6–6	0.1–0.6	0.1–0.7	
SCN^-	100–1500	230–590	22–200	17–45	
S^{2-}	200–600	8		60–220	29000
SO_4^{2-}		325–350		60–180	
alkalinity (as $CaCO_3$)	3800–4300[f]	525–920	10000–20000	9800–15000	
conductivity ($\mu\Omega^{-1}$/cm)		3500–6000		30000	
pH	7.5–9.1	9.3–9.8	8.5–9.3	7.8–8.0	9.5

[a] Data sources: ref *2–5*. [b] Reference *6*. Free and fixed leg stripping with addition of lime. [c] Reference *8*. [d] Reference *9*. Hygas wastewater was comprised of equal volumes of cyclone and quench effluents. [e] Reference *10*. Stripped foul water with sulfide removed had an average COD of 26 500 mg/L. [f] Calculated from data of Jablin and Chanko (*7*).

monia liquors and in coal gasification plant quench waters was presented by Luthy et al. (*17*). That paper reviewed possible reactions of cyanide with sulfur, and discussed these reactions in light of studies on the oxygenation of sulfide in aqueous solution. A conclusion from that work was that the dominant reaction pathways for formation of thiocyanate with sulfide oxidation products entail reaction of cyanide with polysulfide (S_x^{2-}) or thiosulfate ($S_2O_3^{2-}$). The following discussion interprets those findings in view of sulfur oxidation chemistry and kinetics.

Sulfur–Cyanide Interactions

Recent kinetic studies on the oxygenation of sulfide in aqueous solution have revealed the complex nature of these reactions. The stoichiometry of sulfide–oxygen reactions depends on pH, concentration of reactants, and the existence of inhibitory or catalytic substances. In the pH range of 6.5 to 8.0, Chen and Morris (*18*) found that at high sulfide concentration there was maximum polysulfide formation. Thiosulfate was the principal product in laboratory solutions at pH greater than 8.5, regardless of the sulfide to oxygen ratio; some sulfite (SO_3^{2-}) may form and may be slowly oxidized to sulfate, or sulfite may react with sulfur of polysulfide to form thiosulfate. Eventually all sulfur and its oxyanions will be oxidized to sulfate in the present of oxygen. The work of Chen and Morris showed that polysulfides can form by reaction of monosulfide and oxygen at neutral pH when the S_{tot}^{2-}/O_2 ratio was 3.75. At pH values greater than 8.2, polysulfide formation was neither very rapid nor very extensive. O'Brien and Birkner (*19*) did not observe formation of polysulfide at pH values of 4, 7.55, and 10 when the initial S_{tot}^{2-}/O_2 ratio was less than 1.2. They reported thiosulfate and sulfite to be important reaction intermediates. Thus, the relative abundance of polysulfide and thiosulfate appears to depend largely upon the initial conditions, which tend to favor the formation of one intermediate over another.

The second dissociation constant for sulfite, $HSO_3^- \rightarrow H^+ + SO_3^{2-}$, has a pK_2 of 7.2. The equilibrium shown in Equation 1 shifts to favor thiosulfate rather than sulfite and sulfur at increasing pH values:

$$HSO_3^- + S \rightarrow S_2O_3^{2-} + H^+ \qquad (1)$$

Hence, elemental sulfur is thermodynamically unstable at high pH in the presence of sulfite. The lack of polysulfide as an oxidation product of sulfide at pH greater than 8.5 may result from its consumption to form thiosulfate.

Polysulfide ions, S_x^{2-}, form through sequential combinations of neutral sulfur atoms with sulfide. Schwarzenback and Fisher (*20*) have found that the polysulfuration index, x, can be 2 to 5, and that tetra- and pentapolysulfide dominate in aqueous polysulfide solutions. The second dissociation constants for H_2S_4 and H_2S_5 are $10^{-6.3}$ and $10^{-5.7}$, respectively (*20*). Thus, at pH values greater than 6.3, S_4^{2-} and S_5^{2-} are the principal forms of the polysulfide ion.

As a result of these studies, it is concluded that possible reactions of cyanide with sulfide oxidation species may proceed according to the reactions summarized in Figure 1. This figure incorporates the sulfide oxygenation pathway proposed by Chen and Morris (*18*) and cyanide chemical reactions with sulfur compounds reviewed in Luthy et al. (*17*), and the equilibrium represented by Equation 1. Data presented in Table I show that coke plant weak ammonia liquors and coal conversion quench waters typically have total sulfide concentrations ranging from 5×10^{-3} to more than 10^{-2} M. Upon contact with oxygen, this condition should promote a relatively high S_{tot}^{2-}/O_2 ratio, which may favor the formation of polysulfide at near neutral or slightly alkaline conditions.

The reaction of cyanide with polysulfide shown in Figure 1 may be described as:

$$S_xS^{2-} + CN^- \rightarrow S_{x-1}S^{2-} + SCN^- \qquad (2)$$

In this reaction, one polysulfide sulfur atom, poly-S^0, is reduced from oxidation state 0 to 1−, while the cyanide carbon atom is oxidized from oxidation state 2+ to 3+.

Cyanide is also reactive with thiosulfate. This reaction may be described as:

$$S_2O_3^{2-} + CN^- \rightarrow SO_3^{2-} + SCN^- \qquad (3)$$

One thiosulfate sulfur atom undergoes oxidation from oxidation state 2+ to 4+, while the other thiosulfate sulfur atom is reduced from the 2+ to the 1− oxidation state.

Thus, there are two predominate pathways for the reaction of cyanide with sulfide oxidation products to yield thiocyanate. The Experimental portion of this study presents results of investigations of the kinetics of these reactions. Previous studies have shown that cyanide was not reactive with monosulfide species (HS^-) at pH 10 (*17*).

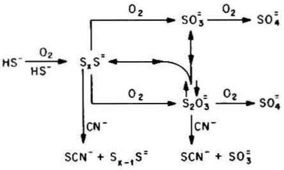


Figure 1. Possible reactions of cyanide with reduced sulfur species in aqueous solution to yield thiocyanate

Experimental

Reagents. All stock solutions were prepared using certified analytical salts, acids, and bases. Each solution was prepared in laboratory distilled water and stored under refrigeration. Laboratory distilled water was made devoid of oxygen by purging with nitrogen, and reaction solutions were maintained under nitrogen gas blankets.

Buffer solutions were prepared at pH 8.2, 10, and 12 at 0.1 M strength. The pH 12 buffer was prepared with 10.6 g/L Na_2CO_3; the pH 10 buffer with 4.2 g/L $NaHCO_3$ and 5.3 g/L Na_2CO_3; the pH 8.2 buffer with 8.4 g/L $NaHCO_3$. Hydrochloric acid (6 N) was used for adjusting the pH to the appropriate value.

A 10 g/L stock cyanide solution (CN^-) was prepared by diluting 25.1 g of KCN and approximately 2 g of NaOH pellets to 1 L. This solution was standardized regularly through the course of the experimentation.

A strong solution of polysulfide was prepared by placing 10 to 20 g of sodium tetrapolysulfide (Ventron-Alfa Products) in 1 L of buffer solution. A portion of the polysulfide solution was analyzed immediately following preparation to determine the concentration. The solution was then diluted with buffer as required for the experiment. It was found that polysulfide salt was unstable when exposed to air and moisture, and that the polysulfide solution would gradually degrade over several days even when refrigerated in a closed container. For these reasons, polysulfide solutions were prepared fresh daily and standardized immediately before use.

Standard thiosulfate solutions were prepared by dissolving $Na_2S_2O_3$ in pH buffer solution.

Analytical Procedures. Cyanide concentrations were measured as total cyanide after distillation with magnesium chloride reagent. The pyridine–barbituric acid colorimetric procedure was used to measure cyanide in the distillate. Stock cyanide solution was standardized by the silver nitrate titrimetric method (*21*).

Polysulfide was measured by a procedure adopted from Krachner (22). In this procedure polysulfide is reacted with excess cyanide under anaerobic conditions in boiling boric acid to form one molecule of thiocyanate for each polysulfide sulfur atom at oxidation state zero, poly-S^0. Fifty milliliters of 200 g/L boric acid solution was placed in a 125-mL beaker, covered with a watch glass, and brought to a strong boil to expel oxygen. While the solution was still hot, there was then added a measured amount of polysulfide containing not more than 200 mg of poly-S^0 followed immediately by 2 mL of 10% cyanide. The solution was brought to a second boil and the reaction went to completion in about 5 min due to the rapid rate at elevated temperature and the presence of excess cyanide. Boiling was continued for another 10 min to volatilize excess cyanide. The procedure must be performed in a laboratory hood to assure no contact with highly toxic hydrogen cyanide gas evolved. The sample was cooled and analyzed for thiocyanate.

The thiocyanate analytical method used in the kinetic studies with polysulfide is based on a copper–pyridine method developed by Kruse and Mellon (*23*) and Danchik and Boltz (*24*). This method has been discussed by Luthy et al. (*17*); details of the procedure are provided by Luthy (*25*). Thiocyanate is reacted with cupric copper and pyridine to form dithiocyanatopyridine:

$$2SCN^- + Cu^{2+} \rightarrow Cu(SCN)_2$$

$$Cu(SCN)_2 + 2C_5H_5N \rightarrow Cu(C_5H_5N)_2(SCN)_2 \qquad (4)$$

This forms a light green precipitate that is extracted with chloroform. The reaction is stoichiometric and the resulting color of the chloroform adheres to Beer's law to permit spectrophotometric determination at 407 nm against a chloroform blank. The first step in this procedure is addition of 1:1 HNO_3 to lower the sample pH to 3.0 to 3.5. This results in precipitation of polysulfide in the sample as a cloudy white precipitate. The sample is coarse filtered after pH adjustment, and then filtered through a 0.45-μm membrane filter to remove sulfur prior to addition of reagents.

The thiocyanate analytical procedure has proved successful on a variety of wastewaters; the method was checked for interferences from the reactants and oxidation products encountered in this study. No problems were identified except with solutions containing on the order of 0.2 M thiosulfate. This solution resulted in a cloudy sulfur precipitate in the chloroform that could not be removed easily by filtration. In this case thiocyanate was measured instead by the ferric nitrate procedure (*21*).

Thiosulfate solutions were standardized by titrating against KI and standard diiodate.

Approach. The reaction order was determined with respect to each constituent in the cyanide–polysulfide reaction at pH 8.2, 10, and 12. These values were chosen somewhat arbitrarily; however, it should be noted that pH values of 10 and 12 are above the pK_a for hydrogen cyanide, $pK_a = 9.2$, and a pH value of 12 is that recommended for sample preservation for analysis of cyanide and thiocyanate (*21*). A pH value of 8.2 was selected because it is representative of the pH of some coal conversion gas quench waters; this pH is above pK_2 for tetrapolysulfide and below pK_a for hydrogen cyanide.

The determination of the order and reaction rate for the cyanide–polysulfide reaction was performed by the van't Hoff (differential) method. This procedure is based on the following assumption of a general kinetic equation:

$$\frac{dSCN^-}{dt} = R_i = k_{a+b}[CN_{tot}]_0{}^a\,[\text{poly-}S^0]_0{}^b \qquad (5)$$

where R_i = initial reaction rate, M/(L·min); k_{a+b} = specific rate constant; $[CN_{tot}]$ = molar concentration of $HCN + CN^-$; $[\text{poly-}S^0]$ = molar concentration of polysulfide sulfur (the molar ratio of poly-S^0 to total sulfur in tetrapolysulfide (Na_2S_4) is 3 to 4, but because Na_2S_4 decomposes, polysulfide solutions must be standardized regularly prior to use); a = reaction order with respect to $[CN_{tot}]$; b = reaction order with respect to $[\text{poly-}S^0]$. This expression written in logarithmic form becomes:

$$\log R_i = \log k_{a+b} + a \log\,[CN_{tot}]_0 + b \log\,[\text{poly-}S^0]_0 \quad (6)$$

The equation shows the sum of linear terms for each component of the reaction. The value of a can be determined from initial rate tests in which the concentration of poly-S^0 is held constant and different concentrations of cyanide are used. Thus, Equation 6 can be written as:

$$R_i = k_a[CN_{tot}]_0{}^a \qquad (7)$$

where k_a is the rate constant with the same initial poly-S^0 concentration and varying cyanide levels. Similarly, the value of b can be obtained by conducting tests in which the concentration of cyanide is kept at the same level with different initial poly-S^0 concentrations:

$$R_i = k_b[\text{poly-S}^0]_0{}^b \quad (8)$$

where k_b is the rate constant with the same initial cyanide concentration and different initial poly-S^0 concentrations.

The order of reaction obtained by the differential method entails the determination of slopes of initial production rates. The change in concentration of reactants is small in the initial stages of the reaction; therefore, Equations 7 and 8 will not change materially even if the reactant held at the same initial concentration is not in excess. In logarithmic form, Equation 7 becomes:

$$\log R_i = \log k_a + a \log [\text{CN}_{\text{tot}}]_0 \quad (9)$$

Thus, by plotting measured values of R_i logarithmically against $[\text{CN}_{\text{tot}}]_0$, linear plots should be obtained with slope equal to a. Likewise, the logarithmic form of Equation 8 is:

$$\log R_i = \log k_b + b \log [\text{poly-S}^0]_0 \quad (10)$$

A logarithmic plot of variation of initial rate with different poly-S^0 levels should yield a straight line with a slope b.

The overall specific rate constant, k_{a+b}, in Equation 5 can be found either by substituting experimental data for R_i, $[\text{CN}_{\text{tot}}]$, and $[\text{poly-S}^0]$, and using values of a and b as established from the logarithmic plots, or by statistical regression of all experimental rate data at each value of pH. In this study experimental data were reduced by multiple regression techniques.

Six different sets of experimental kinetic studies were performed to determine the rate and order of the reaction with respect to each reactant at three pH values. The experimental techniques employed concentrations of cyanide and polysulfide to yield in a short interval an easily determined amount of thiocyanate. Each individual rate experiment was repeated three times. Data points presented later in Figures 2, 3, and 4 represent average production rates.

The polysulfide solution was standardized and diluted with the proper buffer to 138 mg/L as poly-S^0 (4.3×10^{-3} M poly-S^0). Two hundred milliliters of this solution was placed in a 250-mL Erlenmeyer flask. Cyanide was added at concentrations ranging from 26 to 780 mg/L (1×10^{-3} to 3×10^{-2} M) by pipeting stock solution into the flask. This operation ensured an accurate measure of initiation time and prevented volatilization of cyanide, since only small amounts of stock cyanide were required and no pH adjustment had to be made to the stock solution prior to the experiment. The reaction was allowed to proceed for 5 min; during this period the flasks were swirled several times to assure a uniform mixture. The reaction was stopped by adding several milliliters of 1:1 HNO_3 to lower sample pH to a value between 3.0 and 3.5. This caused the polysulfide solution to change from a characteristic golden brown color to a milky yellow and then to a white precipitate. The precipitate was removed by coarse filtering and then by filtering through a 0.45-μm membrane filter to yield a clear sample that was analyzed for thiocyanate.

A special series of tests was performed at a pH of 8.2 to check for cyanide losses by volatilization. These tests consisted of adding cyanide to samples containing no polysulfide, waiting for 5 min, and then analyzing for cyanide. This test showed that there was no loss of hydrogen cyanide over the time interval employed here. Another set of tests was performed to ensure that the reaction was indeed stopped by acidification and filtration. Replicate kinetic test samples were acidified and filtered and allowed to stand from several minutes up to 4 h prior to analyzing for thiocyanate. Analysis showed that there was no increase in thiocyanate over this period.

Catalysis and Inhibition. Additional kinetic studies were performed at a pH of 8.2 to evaluate potential catalytic and inhibitory effects of inorganic and organic species. Compounds selected for this work were chosen by their prevalence in coal coking and coal conversion wastewaters and by reported effects on sulfur oxidation kinetics. Chen and Morris (26) studied the effects of addition of various metal ions and organic compounds on sulfide oxidation. Other studies in this area have been performed by Krebs (27), Bulfer et al. (28), and Cline and Richards (29). As a result of these studies, the following compounds were selected for study of the effect of small additions on cyanide–polysulfide reaction kinetics: B, Ba^{2+}, Ca^{2+}, Cu^{2+}, Mg^{2+}, Mn^{2+}, Ni^{2+}, $NH_4{}^+$, Zn^{2+}, phenol, ferricyanide, and coal char fines. Coal char fines were obtained from Hygas coal gasification pilot plant Run 72.

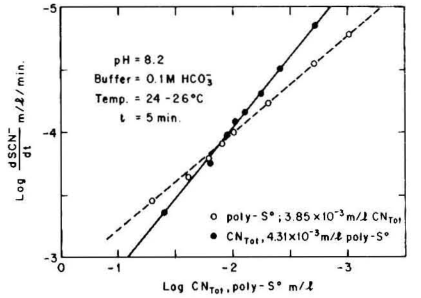


Figure 2. Initial rate kinetic data for the polysulfide–cyanide reaction at pH 8.2

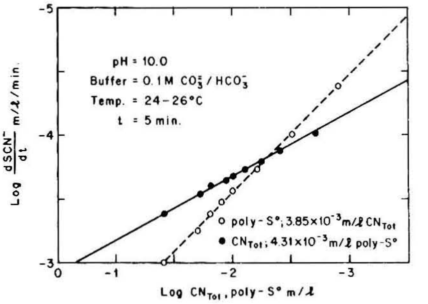


Figure 3. Initial rate kinetic data for the polysulfide–cyanide reaction at pH 10

It is recognized that cyanide can form a variety of complex compounds with species such as copper, nickel, and zinc. This introduces another factor that may have significant effects on cyanide–polysulfide kinetics. It was not the intent of this study to separate these possible effects. The studies presented here are perhaps purely abstract in nature, since little is understood about interactions leading to catalysis or inhibition. The final results are at least indicative as to the importance that these substances may have on thiocyanate production.

Results

Cyanide–Polysulfide Reaction. Experimental results for estimation of initial reaction rates and order of reaction for formation of thiocyanate from reaction of cyanide and polysulfide are presented in Figures 2, 3, and 4 for pH values 8.2, 10, and 12, respectively. These data conform to the straight line relationships given by Equations 9 and 10. The order of the reaction with respect to each constituent and the rate constant for the reaction was determined according to Equation 6 by multiple linear regression of all experimental data taken collectively at each pH value. Empirically determined kinetic coefficients for the cyanide–polysulfide reaction system are summarized in Table II, including estimates of t

Table II. Kinetic Coefficients for the Cyanide–Polysulfide Reaction System

pH values	rate expression[a]
8.2	$\log R_i = 0.15 + 1.04 \log [\mathrm{CN^-}] + 0.85 \log [\text{poly-S}^0]$ (0.80) (16.9) (18.9) $R^2 = 0.97$
10.0	$\log R_i = -0.57 + 0.51 \log [\mathrm{CN^-}] + 0.87 \log [\text{poly-S}^0]$ (−5.14) (15.3) (29.0) $R^2 = 0.98$
12.0	$\log R_i = -0.86 + 0.49 \log [\mathrm{CN^-}] + 0.78 \log [\text{poly-S}^0]$ (−7.11) (13.4) (24.0) $R^2 = 0.98$

[a] Temperature, 24–26 °C; 0.1 M carbonate buffers; units are consistent with reaction rate expressed as M/(L·min). Values of *t* statistics are given in parentheses.

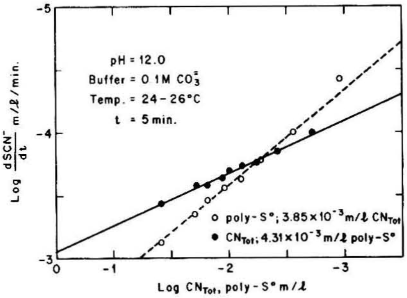


Figure 4. Initial rate kinetic data for the polysulfide–cyanide reaction at pH 12

statistics and regression coefficients. It is seen that the reaction order and rate change with pH value. Reaction order increases with decreasing pH; at a pH of 8.2 the reaction is close to second order.

The catalysis and inhibition studies with the cyanide–polysulfide reaction system were performed in the same manner as for the initial rate studies with the only difference being the addition of a new agent. The results of this work are presented in Table III as R/R_0, where R_0 is the initial rate of reaction without the agent, and R is the rate of reaction with the agent present at the specified concentration. These studies were performed at a pH of 8.2 and further study is required to determine if pH may have a large effect on catalysis and inhibition.

Because of the noticeable effect of ammonia and coal char fines, additional tests were performed with a range of concentration of ammonia as inhibitor and with a range of concentration of coal char fines as a catalysis agent. Figure 5 is a plot of percent decrease of thiocyanate production vs. ammonia concentration, and Figure 6 is a plot of percent increase in production of thiocyanate vs. concentration of char fines.

Cyanide–Thiosulfate Reaction. An extensive analysis of the kinetics of reaction of cyanide and thiosulfate was not performed due to data presented on this reaction by Bartlett and Davis (*30*). These authors measured the rate of reaction between sodium cyanide and sodium thiosulfate in water and found that the reaction proceeded irreversibly, and that the cyanide ion is a stronger thiophile than the sulfite ion. The reaction at 25 °C with an ionic strength of 0.9 M was second order with a rate constant of 2.3 × 10^{-3} L/(M·min). The pH value was not specified in their work. It may be presumed that the reaction mixture was alkaline, as the authors reported results with cyanide ion rather than HCN. The value of the reported rate constant was confirmed in this study within a factor of two by conducting initial rate studies with equimolar solutions of cyanide and thiosulfate at a pH of 12 in 0.1 M carbonate buffer. Here cyanide and thiosulfate were reacted at 0.19 M concentration for 20 min. In these tests the production of thiocyanate was measured by the ferric nitrate procedure after lowering pH and filtering precipitated sulfur.

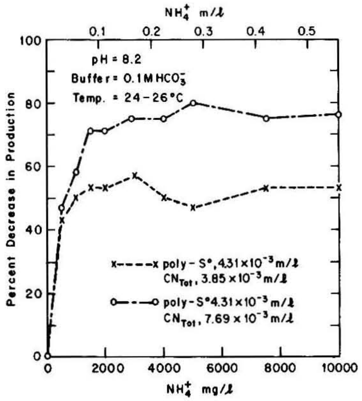


Figure 5. Inhibitory effect of ammonium on thiocyanate production via the polysulfide–cyanide reaction pathway

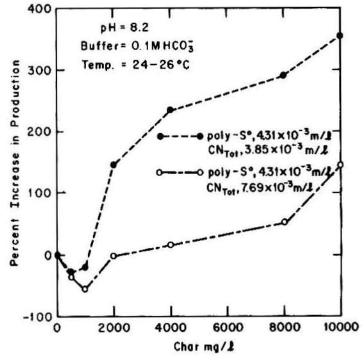


Figure 6. Catalytic effect of coal char fines on thiocyanate production via the polysulfide–cyanide reaction pathway

Discussion

In a previous paper (*17*) initial observations on the formation of thiocyanate from the cyanide–polysulfide aqueous reaction were investigated. Those studies were preliminary batch test reactions and provided only general information about the reaction rate. The present study was performed in order to better understand the complexities of this system and to increase knowledge about interactions between sulfur and cyanide chemical systems. The data presented here involved initial rate kinetic studies on the cyanide–polysulfide reaction pathway and also entailed observations on a small group of possible catalytic and inhibitory agents.

The initial rate kinetic data for the cyanide–polysulfide reaction showed the reaction was mixed order and that both reaction order and reaction rate change with pH. The overall order decreased from 1.89 to 1.27 as pH increased from 8.2 to 12.0. There is a pronounced decrease in the reaction order with respect to cyanide as pH is increased above the pK_a for hydrogen cyanide. The rate constant for cyanide is observed to decrease from 1.04 to 0.51 over the pH range from 8.2 to 10. The specific rate constant for the cyanide–polysulfide reaction

Table III. Inhibitory and Catalytic Effects of Various Components on the Cyanide–Polysulfide Reaction System[a]

substance	salt used	concn, M/L	R/R_0	notes
boron (B)	H_3BO_3	9.25×10^{-4}	1.06	
		9.25×10^{-3}	0.83	
calcium (Ca^{2+})	$CaCl_2$	2.5×10^{-4}	1.03	
		2.5×10^{-3}	0.99	
magnesium (Mg^{2+})	$MgCl_2 \cdot 6H_2O$	4.11×10^{-4}	1.12	white cloudiness
		4.11×10^{-3}	0.99	
ferricyanide ($Fe(CN)_6^{3-}$)	$K_3Fe(CN)_6$	4.72×10^{-5}	0.99	a strong color imparted
		4.72×10^{-4}	0.50	
barium (Ba^{2+})	$BaCl_2 \cdot 2H_2O$	7.28×10^{-7}	1.03	
		7.28×10^{-5}	1.03	
manganese (Mn^{2+})	$MnSO_4 \cdot H_2O$	1.82×10^{-6}	1.03	
		1.82×10^{-4}	1.02	
zinc (Zn^{2+})	$ZnSO_4 \cdot 7H_2O$	1.53×10^{-6}	1.29	a white precipitate formed
		1.53×10^{-4}	1.06	
nickel (Ni^{2+})	$NiCl_2 \cdot 6H_2O$	1.70×10^{-6}	1.19	dark color developed
		1.70×10^{-4}	0.86	
copper (Cu^{2+})	$CuSO_4 \cdot 5H_2O$	1.57×10^{-6}	1.12	initial yellow color then returning to normal
		1.57×10^{-4}	0.99	
phenol	C_6H_5OH	1.06×10^{-2}	0.99	
		5.31×10^{-2}	0.92	
ammonia (NH_4^+)	NH_4Cl	5.54×10^{-2}	0.70	
		2.77×10^{-2}	0.63	
char	gasification	1000 mg/L	0.79	
	coal char fines	10000 mg/L	1.89	

[a] pH 8.2, 0.1 M HCO_3^- buffer. $[CN_{tot}] = 3.85 \times 10^{-3}$ M. $[Poly\text{-}S^0] = 4.31 \times 10^{-3}$ M.

decreased from 1.41 to 0.14 over the pH range 8.2 to 12. These findings show that cyanide–polysulfide reaction is rapid, and that the reaction rate increases with pH for equimolar concentrations of reactants less than approximately 5×10^{-3} M.

Screening studies on the cyanide–thiocyanate reaction generally confirmed the second-order specific rate constant presented by Bartlett and Davis (*30*). The significance of the rates of reaction of cyanide with polysulfide and with thiosulfate is shown in Figure 7, which compares predicted initial rates of reaction of cyanide with polysulfide at pH 8.2, 10, and 12.0 with predicted rates of reaction of cyanide with thiosulfate. These data show that the reaction rate with polysulfide at a pH of 8.2 is approximately three orders of magnitude faster than that with thiosulfate. Note also that the rate of reaction of cyanide with polysulfide is sensitive to pH at low concentration levels of reactants.

These findings indicate that the cyanide–polysulfide reaction pathway can dominate over the cyanide–thiosulfate reaction pathway to form thiocyanate. However, in a system initially containing cyanide and sulfide, the thiocyanate production kinetics must be viewed in light of sulfide oxygenation pathways. In a system containing on the order of 10^{-3} M or more sulfide in a slightly alkaline solution, the sulfide oxygenation pathway as discussed in Figure 1 should prevail. In this case polysulfide may exist as a sulfide oxidation product, and results of this study show that as polysulfide is produced it can react rapidly to form thiocyanate. If thiosulfate were the predominate sulfide oxidation product, the production of thiocyanate from cyanide would be greatly reduced.

Inhibition and catalysis studies demonstrated the effect of various compounds on the cyanide–polysulfide reaction. Of the metal ions studied, Ca^{2+}, Mg^{2+}, Ni^{2+}, and Zn^{2+} had the greatest catalytic effect at their lower concentration; when larger concentrations were employed, metal ions inhibited the reaction rate slightly. Though these compounds had an effect on the reaction rate, their effect was relatively small at the concentrations employed here. Metals such as zinc, nickel, and copper can form complexes with cyanide and it would be expected that extensive complexation would reduce the reactivity of cyanide with polysulfide. The metal ion concentrations used in the catalytic inhibitory tests were on the order of a factor of 20 or less than the total analytical concentration of cyanide. This may explain the relatively small effect on reaction rate. Screening studies showed that complexed cyanides may not be reactive with polysulfide, as no reaction was observed between polysulfide and ferricyanide. This finding is consistent with Bartlett and Davis's (*30*) observation that ferricyanide or ferrocyanide ions do not attack elemental (S_8) sulfur at a measurable rate.

The cyanide–polysulfide reaction was inhibited by approximately 50 to 80% at a pH of 8.2 in the presence of more than 2000 mg/L ammonia-nitrogen. Small concentrations of coal char fines also had an inhibitory effect, but at concentrations greater than several thousand milligrams/liter, coal char fines had a pronounced catalytic effect. This effect appears to be more pronounced for lower cyanide concentrations. Phenol was the only soluble organic constituent investigated, and it showed little effect on the reaction of cyanide and polysulfide.

Though not evaluated here, the reaction of cyanide with thiosulfate is expected to show a pH dependency. Equation 1 shows that, as pH is decreased, thiosulfate equilibrium shifts to favor sulfite and sulfur (*18, 31*). In the presence of HS^- this could result in the formation of polysulfide.

Conclusions

Procedures and data have been presented for the study of aqueous phase formation of thiocyanate resulting from interactions between cyanide and polysulfide, and cyanide and thiosulfate. Experimental data were used to describe the production of thiocyanate from polysulfide; it was found that both reaction order and rate change with pH and that the rate increases as pH is varied from 8.2 to 12 for reactant concentrations less than approximately 5×10^{-3} M/L. The rate of

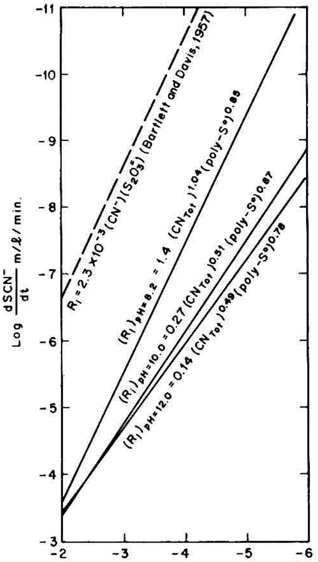


Figure 7. Comparison of production rates for formation of thiocyanate from reaction of equimolar concentrations of cyanide and polysulfide, and cyanide and thiosulfate

production of thiocyanate from polysulfide is shown to be at least three orders of magnitude faster, depending on pH, than the rate of formation of thiocyanate from thiosulfate. The importance of the cyanide–polysulfide pathway depends upon the presence of polysulfide in the reaction mixture, which in turn is dependent upon the production of polysulfide from the oxidation of monosulfide.

These experiments have implications for describing quality changes that may result when processing wastewaters containing sulfide and cyanide in the pH range of 6.5 to 8.0. Upon exposure to oxygen, sulfide may be oxidized to polysulfide if the $[S_{tot}^{2-}]/[O_2]$ ratio is high. This would cause reaction of cyanide to form thiocyanate. Thus, cyanide would be converted from a highly toxic and volatile compound to a relatively nontoxic, strongly ionic species. If it is desired to process wastewaters for reuse, thiocyanate can present problems due to its tendency to enter into corrosion and deposition reactions with steel process units.

Acknowledgment

Dennis Mialki and James C. Cook assisted with the experimental studies.

Nomenclature

a = reaction order with respect to CN_{tot}

b = reaction order with respect to poly-S^0

$[CN_{tot}]$ = molar concentration of $HCN + CN^-$

k_{a+b} = specific rate constant

k_a = initial rate constant with same initial poly-S^0 concentration

k_b = initial rate constant with same initial CN_{tot} concentration

[poly-S^0] = molar concentration of polysulfide sulfur

R_i = initial reaction rate, M/(L·min)

$[S_{tot}^{2-}]$ = molar concentration of $H_2S + HS^- + S^{2-}$

Literature Cited

(1) Luthy, R. G., Massey, M. J., Dunlap, R. W., Proceedings of the 32nd Purdue Industrial Waste Conference, Purdue University, Lafayette, Ind., 1977.
(2) Rubin, E. S., McMichael, F. C., *Environ. Sci. Technol.*, **9**, 112 (1975).
(3) Wong-Chong, G. M., Caruso, S. C., Patarlis, T. G., paper presented at the 84th National Meeting of the AIChE, Atlanta, Ga., Feb 1978.
(4) Kostenbader, P. E., Flecksteiner, J. W., *J. Water Pollut. Control Fed.*, **41**(2), Part 1, 199 (1969).
(5) EPA, "Development Document for Effluent Limitation Guidelines and Performance Standards for the Steel Making Segment of the Iron and Steel Manufacturing Point Source Category", EPA-44011-74-024a, Washington, D.C., 1974.
(6) Luthy, R. G., Jones, L. D., "Biological Treatment of Coke Plant Wastewater", Center for Energy and Environmental Studies, Carnegie-Mellon University, May 1979.
(7) Jablin, R., Chanko, G. P., paper presented at AIChE Advances in Water Pollution Control Meeting, New York, 1972.
(8) Johnson, G. E., Neufeld, R. D., Drummond, C. J., Strakey, J. P., Haynes, W. P., Mack, J. D., Valiknac, T. G., Pittsburgh Energy Research Center Report, DOE/PERC/RI-77/13, Nov 1977.
(9) Luthy, R. G., Tallon, J. T., "Biological Treatment of Hygas Coal Gasification Wastewater", DOE NTIS FE-2496-43, 1978.
(10) Reap, E. J., Davis, G. M., Duffy, M. J., Koon, J. H., paper presented at the 32nd Purdue Industrial Waste Conference, Purdue University, Lafayette, Ind., 1977.
(11) Mills, G. A., *Chemtech.*, 418 (July, 1977).
(12) Massey, M. J., Luthy, R. G., Pochan, M. J., "C-MU Technical Contributions to the DOE Environmental Assessment Program", DOE FE-2496-39, 1978.
(13) Hill, W. H., in "Chemistry of Coal Utilization", Vol. 2, Chapter 27, Lowry, H. H., Ed., Wiley, New York, 1945.
(14) Nakles, D. V., Ph.D. Thesis, Carnegie-Mellon University, 1977.
(15) Williams, H. E., "Cyanogen Compounds", 2nd ed., Edward Arnold and Co., London, 1948, Chapter XI.
(16) Massey, M. J., McMichael, F. C., Dunlap, R. W., *Chem. Eng.*, 109 (Aug 30, 1976).
(17) Luthy, R. G., Bruce, S. G., Jr., Walters, R. W., Nakles, D. V., *J. Water Pollut. Control Fed.*, **51** (9), 2267 (1979).
(18) Chen, K. Y., Morris, J. C., *Environ. Sci. Technol.*, **6**, 529 (1972).
(19) O'Brien, D. J., Birkner, F. B., *Environ. Sci. Technol.*, **11**, 1114 (1977).
(20) Schwarzenbach, G., Fisher, A., *Helv. Chim. Acta*, **169**, 1365 (1960).
(21) American Public Health Association, "Standard Methods for the Examination of Water and Wastewater", 14th ed., APHA, Washington, D.C., 1975.
(22) Krachner, J. K., "Analytical Chemistry of Sulfur and Its Compounds", Wiley-Interscience, New York, 1970, p 349.
(23) Kruse, J. M., Mellon, M. G., *Sewage Ind. Wastes*, **23**, 1402 (1951).
(24) Danchik, J. M., Boltz, D. F., *Anal. Chem.*, **40**, 2215 (1968).
(25) Luthy, R. G., "Manual of Methods: Preservation Analysis of Coal Gasification Wastewaters", ERDA, NTIS FE-2496-8, 1977.
(26) Chen, K. Y., Morris, J. C., *J. San. Eng. Div., Am. Soc. Civ. Eng.*, **98** (SA1), 215 (1972).
(27) Krebs, H. A., *Biochim. Z.*, **204**, 343 (1929).
(28) Bulfur, G., Boyle, A. J., Baldinger, L. H., *J. Am. Pharm. Soc.*, **25**, 1104 (1936).
(29) Cline, J. D., Richards, F. A., *Environ. Sci. Technol.*, **3**, 838 (1969).
(30) Bartlett, P. D., Davis, R. E., *J. Am. Chem. Soc.*, **80**, 2513 (1958).
(31) Latimer, W. M., Hildebrand, J. H., "Reference Book of Inorganic Chemistry", 3rd ed., MacMillan Co., New York, 1951, Chapter XII.

Received for review December 15, 1978. Accepted August 15, 1979. This work was sponsored by the Department of Energy in conjunction with Carnegie-Mellon University's efforts to assist, help coordinate, and provide evaluative services in DOE's coal gasification environmental assessment program.

Seasonal Variations in the Removal Rate of Material Injected into the Lower Stratosphere

Robert W. Holloway[1]

Department of Chemistry, University of Arkansas at Pine Bluff, Pine Bluff, Ark. 71601

■ The 3-megaton Chinese thermonuclear explosion of June 27, 1973, injected substantial amounts of fission products into the stratosphere of the northern hemisphere. The concentrations of radioactive ^{91}Y (58-day half-life) and ^{144}Ce (285-day half-life) were measured radiochemically in rainwater collected at Fayetteville, Ark., for 1 year after the explosion. The decay-corrected deposit for these nuclides during July through October of 1973 was approximately 1% of the deposit during March through June of the following year. Although seasonal variations in tropospheric fission product concentrations are well known, a seasonal difference of this magnitude was not expected. Possible explanations for this large seasonal variation in fallout deposits are discussed. The ^{91}Y data in this work are the first long-term measurements of that isotope in the atmosphere.

The fact that there are large seasonal variations in the concentrations of fission products in the troposphere was first observed by Stewart et al. (*1*). They found that the ^{90}Sr concentration in rainwater in the United Kingdom showed a marked seasonal variation, with peaks in the late spring and troughs in the late fall. The many years of fallout study since 1957 have consistently shown this effect and it is now generally accepted that it is caused by a maximum rate of transfer to the troposphere during the spring. Seasonal variations also occur in cosmic ray produced isotope concentrations.

In view of the significance of this interesting feature of atmospheric circulation, it is surprising that there is very little published information relative to quantitative comparisons of the seasonal transfer rates. The lack of information about the seasonal effects may be causing significant errors in various stratospheric transport calculations. Bauer et al. (*2*) noted recently that seasonal variations are not included in most one-dimensional models and may have resulted in an overestimate by such models of the calculated ozone reduction following the massive Soviet atmospheric nuclear tests of 1961 and 1962.

A few authors have mentioned the seasonal variations of stratospheric transport in a quantitative or semiquantitative sense. For example, Krey and Krajewski (*3*) concluded that the debris injected into the lower stratosphere in June, 1967, by a 3-megaton Chinese explosion did not begin to leave the stratosphere until November of that year. More recently, Bauer et al. (*2*) concluded that material injected into the stratosphere in summer does not leave until the following winter. A somewhat different viewpoint was offered by Danielson and Mohnen (*4*), whose calculation assumes that the transfer is continuous throughout the year. They suggest that the rate during the late spring is three times the rate of the late fall for ^{90}Sr transport.

If the transfer of material from the stratosphere to the troposphere is in fact negligible during the summer, it is a feature of atmospheric circulation that has been unknown until recently. If it is not negligible, then it seems worthwhile to determine as accurately as possible the relative transport rates on a seasonal basis. The conclusions of Krey and Krajewski (*3*) and Bauer et al. (*2*) were based on stratospheric inventories of fission products. The estimate of Danielson and Mohnen (*4*) was derived from ^{90}Sr mixing ratios. The results presented here are from ground level fallout deposits and provide an independent method of estimating the seasonal variation of the removal rate of material residing in the lower stratosphere.

The conditions required to compare the seasonal transfer rates using fallout deposits are rather special. One can imagine an ideal experiment in which an aerosol tracer is injected into the stratosphere at the beginning of summer. If the tracer was not previously present in the troposphere, the surface deposit of the tracer during the summer would give an estimate of the transfer rate of the tracer during that season. This assumes that the tropospheric residence time of the tracer is on the order of 1 month or less. While there is substantial disagreement in the published estimates of the tropospheric residence time of natural aerosols, most estimates range between 4 days and slightly greater than 1 month. See, for example, Gavini et al. (*5*), Moore et al. (*6*), and Nevissi et al. (*7*).

An injection into the stratosphere in the fall, winter, or spring would not be useful in estimating the summer transport of material from the stratosphere. This is because the troposphere would acquire an inventory of the tracer before the beginning of summer, thus giving a summer deposit that would include material transported across the tropopause previous to the summer months.

For the same reason, the commonly measured fission products such as ^{90}Sr and ^{137}Cs are not useful for such an experiment because a significant tropospheric inventory is almost always present for these nuclides. This residual burden, although rapidly decreasing in the summer, would interfere with the identification of the ^{90}Sr or ^{137}Cs that may enter the troposphere from above during the summer.

One reason that ^{90}Sr and ^{137}Cs are almost always present in the atmosphere is that their half-lives are 29 and 30 years, respectively. In recent years, the Chinese nuclear tests have been frequent enough to maintain detectable amounts of these nuclides in the atmosphere continuously. Fission products with shorter half-lives, such as 58-day ^{91}Y, are not always present in the atmosphere, and the problem of an initial inventory of the tracer is greatly reduced.

From the discussion above, it is obvious that the tracer in the ideal experiment must be injected into the stratosphere only, since an initial tropospheric inventory of the tracer is to be avoided. This restriction prevents the use of the lower yield nuclear explosions, since much or all of their debris is injected into the troposphere. Atmospheric nuclear explosions of the 2- or 3-megaton range inject most of their debris into the stratosphere and may be useful for the estimation of seasonal transfer rates.

The Chinese thermonuclear explosion of June 27, 1973, provided conditions very close to that of the ideal experiment discussed above. It was a 3-megaton test that occurred after the time normally associated with the spring peak of tropospheric fission product concentrations. In this work 58-day ^{91}Y and 285-day ^{144}Ce were measured in rain following the test. The conditions were such that the ^{91}Y deposit could be identified unambiguously with the test for a period of 1 year following the explosion.

Experimental

Rain samples were collected on the roof of the Chemistry

---

[1] Present address, Environmental Transport Division, Savannah River Laboratory, Aiken, S.C. 29801.

0013-936X/79/0913-1488$01.00/0

Table I. Equivalent Deposit of ^{91}Y and ^{144}Ce at Fayetteville, Ark., from the Chinese Test of June 27, 1973

month	no. of rains	rainfall, mm	equiv deposit,[a] pCi/m² ^{91}Y	equiv deposit,[a] pCi/m² ^{144}Ce
1973				
July	5	48	8.6×10	3.3×10
Aug	2	21	9.4×10	1.5×10
Sept	4	187	7.4×10^2	1.1×10^2
Oct	6	152	7.0×10^2	6.7×10
Nov	4	247	2.6×10^3	2.2×10^2
Dec	5	144	2.3×10^3	2.8×10^2
1974				
Jan	3	26	8.0×10^2	8.1×10
Feb	5	67	7.1×10^3	9.9×10^2
March	4	102	1.1×10^4	1.5×10^3
April	5	162	3.3×10^4	6.7×10^3
May	5	175	4.2×10^4	4.5×10^3
June	4	158	6.0×10^4	8.5×10^3

[a] The equivalent deposit is the actual deposit that has been decay corrected to the day of the explosion.

Building at the University of Arkansas. A 20-L portion of each rain was taken for analysis. Stable yttrium and cerium carriers were added, and the samples were analyzed for radioactive ^{91}Y and ^{144}Ce by the method previously described (*8*). The ^{91}Y sample was lost for one of the rains in September, 1973. An estimated ^{91}Y activity was used for that rain based on the measured ^{144}Ce activity and the expected ^{91}Y/^{144}Ce activity ratio.

The most significant source of error for these data is expected to be the uncertainty arising from counting statistics. This leads to an uncertainty of 10% or less for the calculated monthly deposits.

Results and Discussion

The Chinese test of June 27, 1973, was only the second multi-megaton Chinese test to occur in the summer, although it was the 15th Chinese atmospheric nuclear test. The explosion occurred at Lop Nor, China (40°N, 90°E), and the rain samples were collected at Fayetteville, Ark. (36°N, 94°W). The explosion occurred at a time when the stratospheric and tropospheric inventories of fission products were very low. The most recent previous test was on March 18, 1972, and had resulted in large amounts of tropospheric fallout but little addition to the stratospheric inventory (*9*).

Although no effort was made to detect ^{91}Y in rain just prior to the June 27th explosion, there is good reason to believe that it was not present in either the stratosphere or the troposphere. A nuclide with a similar half-life, ^{89}Sr (50 days), had disappeared from the atmosphere in March, 1973 (*10*). The extremely light ^{91}Y fallout in the 2 months after the explosion is an indication that the isotope was most likely absent from the atmosphere before the test.

After the June 27, 1973, explosion, ^{91}Y and ^{144}Ce were measured in rainfall along with several other nuclides of interest. For the next 12 months, ^{91}Y could be definitely identified as having originated in this single test, and thus is a valuable tracer with which to study the transfer of material from the stratosphere to the troposphere.

The results are given in the figures and in Table I. In order to make the desired seasonal comparison, the data in Table I are expressed in terms of "equivalent deposit". The equivalent deposit is the actual deposit decay corrected back to the date of the explosion. This calculation was done for each rain.

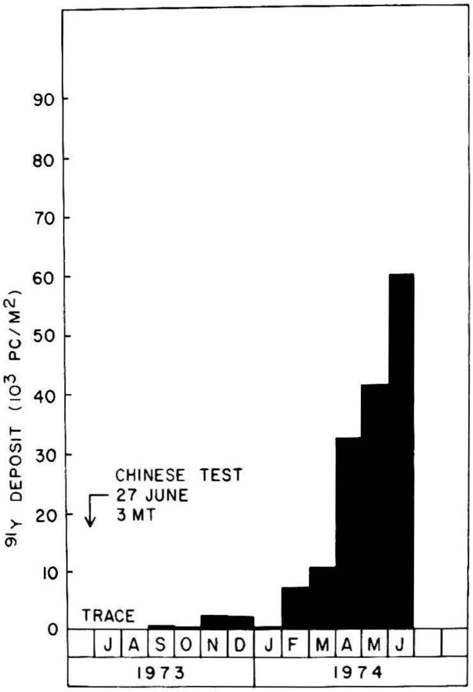


Figure 1. The equivalent deposit of ^{91}Y collected at Fayetteville, Ark., after the Chinese test of June 27, 1973

As can be seen from Figure 1, very little of the ^{91}Y was deposited during the months of July through October. A possible explanation for this is that the debris stabilized at an extremely high altitude. The recent paper by Bauer et al. (*2*) provides useful information with which to decide this question. Their Figure 2 shows that at 11 weeks after the 1973 explosion, almost all of the stratospheric inventory of ^{95}Zr (65-day half-life), was located between 15 and 21 km with the maximum activity at approximately 19 km. The debris was clearly above the mean tropopause, a fact which partially explains the light summer deposit. A more significant inference is that the light deposit may be related to the absence of an effective transfer mechanism during the summer and fall. The small deposit in the summer and fall is even more striking in view of the fact that some of the deposit could have reached the troposphere without being transported with stratospheric air. At least a portion of the July–October deposit may have been injected into the troposphere directly on the day of the explosion. In addition, some of the deposit during this period could have been the result of sedimentation of large particles (above 1-μm radius) from the stratosphere. The deposit during this period could have a very significant sedimentation component without requiring that a very high percentage of the stratospheric burden be attached to particles in the sedimentation range.

It is interesting to compare the ^{91}Y deposit during the July through October period with the deposit in the spring of 1974. The July through October deposit is 1.1% of the deposit during the equal time interval of March through June, 1974. There was another Chinese test on June 17, 1974, but because there was no rain in June after the explosion, the deposit shown for June, 1974, is entirely from the test of the previous year. ^{91}Y fallout did not cease in July of 1974 but with the arrival of fresh debris it was no longer possible to identify the deposit with a single explosion.

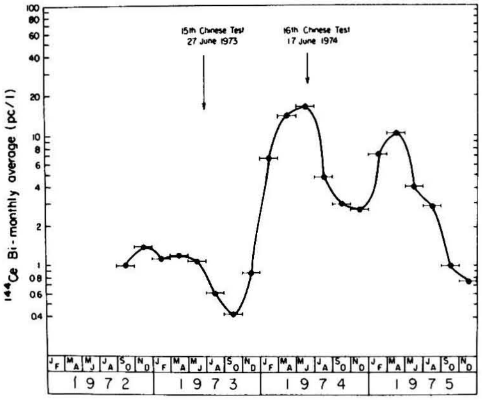


Figure 2. The ^{144}Ce bimonthly average concentration in rainfall at Fayetteville, Ark., from September, 1972, to December, 1975. The bimonthly averages are obtained from actual concentrations that are not decay corrected for the 285-day half-life of ^{144}Ce

For the very special conditions of the June, 1973, test, the ^{91}Y deposit shown in Figure 1 may be a reasonably accurate estimate of the amount of material transported across the tropopause in the various seasons. If the deposit shown in Figure 1 is a good estimate of the seasonal variation in the transfer rate of debris from the stratosphere, then it appears that the transfer rate is almost zero during the summer and fall. This interpretation is consistent with the reports of Bauer et al. (*2*) and Krey and Krajewski (*3*), who found no significant decrease in stratospheric fission product inventories for several months after summer injections. It should be noted that there are alternative explanations for the slight ^{91}Y summer and fall deposits reported in this work. During the summer, much of the rain in Arkansas occurs in northward moving tropical air masses, which might have low concentrations of radioactive aerosols from the stratosphere. Thus, the results observed here may not be typical of the summer deposit for the northern hemisphere. However, the deposit remains relatively light even in the months of October through December when the rain is mostly associated with cold fronts from the northwest.

The seasonal movement of the mean position of the tropopause discontinuity may also influence the deposition of stratospheric aerosols. Significant intrusions of stratospheric aerosols are believed to occur in the vicinity of the discontinuity. Since its mean position is displaced northward in the summer, ^{91}Y deposits obtained from more northerly locations might show somewhat greater summer and fall deposits.

Although ^{144}Ce was detectable in the atmosphere before the 1973 explosion, the results for ^{144}Ce are almost identical with that of ^{91}Y. The decay-corrected deposit of ^{144}Ce during July through October of 1973 was only 1% of the deposit during March through June of 1974. This compares with 1.1% for ^{91}Y. Apparently the small amount of ^{144}Ce in the atmosphere prior to the explosion was not enough to cause the seasonal deposits to be significantly different from the ^{91}Y deposit. The longer half-life of ^{144}Ce explains the presence of this nuclide before the 1973 test, even though ^{91}Y was almost certainly absent from the atmosphere.

The negligible effect of fresh debris from the stratosphere upon summer and fall tropospheric concentrations can be seen in Figure 2. The bimonthly ^{144}Ce concentration in rain continued to decrease in the summer of 1973 according to the usual seasonal trend. The surprising point is that the explosion of 1973 greatly increased the ^{144}Ce inventory in the stratosphere without having an appreciable effect on the tropospheric concentrations sampled in this study.

The ^{144}Ce concentrations shown in Figure 2 are not very sensitive to variations in monthly rainfall totals, while the deposits of ^{144}Ce and ^{91}Y are directly related to the rainfall amounts. In the comparison of the seasonal variations of the ^{91}Y and ^{144}Ce deposits, the difference in rainfall totals for each season was neglected. If a correction is applied for the rainfall difference, the deposit ratio for the two 4-month periods becomes 60:1, rather than 100:1. This assumes that the deposit in a particular season is proportional to rainfall.

Conclusions

The data presented here show a remarkably low level of ^{91}Y and ^{144}Ce fallout during the summer and fall of 1973 compared to the heavy fallout observed in the spring of the following year. Since the lower stratosphere contained a substantial inventory of fission products in the summer and fall of 1973, the small deposit during the warm months is unexpected. A possible explanation is that the transfer rate of material from the stratosphere is negligible during the summer and fall. This interpretation is consistent with the observations of other investigators who noted that for summer injections, there is no significant decrease in stratospheric inventories during the summer and fall.

An alternative explanation is that the data presented here are not typical of the average tropospheric deposits during the July through October period and therefore fail to reveal the full extent of transfer of stratospheric aerosols during the summer and fall.

Future studies of stratospheric summer injections may provide the information necessary to decide between these two alternatives and to fully define the seasonal variations in the removal of aerosols from the stratosphere.

Literature Cited

(1) Stewart, N. G., Osmond, R. G., Crooks, R. N., Fisher, E. M., *U.K. At. Energy Res. Establ.*, **Publ. No. AERE HP/R 2354** (1957).

(2) Bauer, E., Oliver, R. C., Wasylkiwskyj, W., *J. Geophys. Res.*, **83**, 4019–25 (1978).

(3) Krey, P. W., Krajewski, B., *J. Geophys. Res.*, **75**, 2901–8 (1970).

(4) Danielson, E. F., Mohnen, V. A., *J. Geophys. Res.*, **82**, 5867–77 (1977).

(5) Gavini, M. B., Beck, J. N., Kuroda, P. K., *J. Geophys. Res.*, **79**, 4447–52 (1974).

(6) Moore, H. E., Poet, S. E., Martell, E. A., *J. Geophys. Res.*, **78**, 7065–74 (1973).

(7) Nevissi, A., Beck, J. N., Kuroda, P. K., *Health Phys.*, **27**, 181–8 (1974).

(8) Holloway, R. W., Sumerlin, N. G., Beck, J. N., Kuroda, P. K., *J. Geophys. Res.*, **79**, 4453–9 (1974).

(9) Daniel, P. Y., Ph.D. Thesis, Department of Chemistry, University of Arkansas, Fayetteville, 1974.

(10) Sumerlin, N. G., Progress Report, U.S. Energy Research and Development Administration, Contract No. At-(40-1)-2529, 1975, Appendix IX.

Received for review April 26, 1979. Accepted August 17, 1979. This study was supported in part by a grant from the former Atomic Energy Commission.

An Evaluation of Column Chromatography and Flameless Atomic Absorption Spectrophotometry for Arsenic Speciation as Applied to Aquatic Systems

Dennis G. Iverson, Marc A. Anderson*, Thomas R. Holm, and Robert R. Stanforth
Water Chemistry Program, 660 North Park Street, University of Wisconsin, Madison, Wis. 53706

■ Flameless atomic absorption (FAA) and chromatographic methods for routine analysis and speciation of environmental arsenic are presented. Matrix modification with $Ni(NO_3)_2$ was used with FAA to measure As concentrations in river water and sediment samples. Detection limits were 2 μg of As/L and FAA response for As concentration was independent of As species. Inorganic As [As(V) and As(III)], monomethylarsonic acid (MMAA), and dimethylarsinic acid (DMAA) were separated on cation exchange columns and detected by FAA. These methods were applied to samples collected from the Menominee River, Wis., where As contamination has resulted in As levels ranging from 1 to 1000 μg/L in river water, from 10 to 7000 mg/L in sediment pore water, and from 4 to 30 mg/g in sediment solids. Field data are presented to illustrate the application of the procedures. Sampling methods and preparation are included.

Knowledge concerning the chemical speciation of elements is important to the understanding of elemental transport, attenuation, and biochemical processes in aquatic systems. For arsenic, the species of special interest include arsenate [As(V)], arsenite [As(III)], monomethylarsonic acid (MMAA), dimethylarsinic acid (DMAA), and volatile arsines. Chemical reactivities and physical properties of environmental As are largely dependent on speciation. For example, the formation rate of trimethylarsine by fungi in sewage (*1*), by bacteria in cultures (*2*), and by microorganisms in soils (*3*) is a function of the As species. Adsorption properties of As in soils also vary among chemical species (*4*). Several workers using soil extraction procedures (*5*) found differences in soil binding mechanisms among As species (*6, 7*). Similar phenomena affect solid-pore water equilibria within sediments and transport across the sediment–water interface. It is evident that studies of As species and transformations among species are essential to understanding the As cycle. Such studies require techniques capable of speciating and measuring As levels in various types of environmental samples.

Several methods for speciating As have been reported. Examples include various chromatographic techniques: electrophoresis and ion-exchange chromatography (*8*), paper chromatography (*9*), and high-pressure liquid chromatography (*10*). The most extensively reported method is volatile hydride generation with $NaBH_4$ followed by various separation and detection systems. These systems include gas chromatography–microwave emission spectroscopy (*11, 12*), gas chromatography with flame ionization and electron-capture detectors (*13*), boiling point separation–spectral emission (*14*), flameless atomic absorption (*15*), and flame atomic absorption (*16*). The above methods have been applied to a variety of samples: commercial pesticides (*11*), coal and fly ash (*12*), soil and geological samples (*15, 16*), plant tissue (*9*), bovine liver (*12*), and natural water samples (*17*). Each method provides advantages and disadvantages that must be considered with regard to the scope of the study and the available laboratory facilities.

The work in this laboratory requires analytical procedures that can be performed on various types of samples with a minimum of sample preparation, and speciation methods that can be performed independently of available instrumentation. The FAA method of Ediger (*18*) and chromatography described by Yamamoto (*17*) require little sample preparation, no instrumental modifications, and make economic use of time spent in analysis. In this report, quantitative characteristics of these methods and modifications made in this laboratory are presented. In addition, the application of these procedures to samples obtained from the Menominee River, Wis., is illustrated. Although inorganic As was speciated as a part of this study, the methods used are presented elsewhere (*19–21*) and are not included in this report.

Experimental

Apparatus. All labware and containers were washed in KOH solution and stored in dilute HCl. Glass chromatography columns (35 cm × 1 cm i.d.) were fitted with Teflon stopcocks and 100-mL reservoirs. A Perkin-Elmer 603 atomic absorption spectrophotometer and the Model 2100 heated graphite atomizer fitted with a pyrolyzed graphite tube were used with a deuterium arc background corrector. The line source was an arsenic electrodeless discharge lamp at 193.7 nm. Instrument settings were as specified in the manufacturer's operation procedures. Temperature programming consisted of drying at 105 °C for 30 s (including a 10-s temperature ramp), charring at 1000 °C for 25 s (including a 10-s temperature ramp), and atomizing at 2600 °C for 7 s. Maximum absorption was read for 5 s during atomization. A normal argon purge at 40 cm^3/min was used and sample injections were typically 10 μL using an Eppendorf pipet or a Perkin-Elmer AS-1 Auto Sampling System. To measure low As concentrations, 50-μL injections were used and argon flow was interrupted during atomization. A Finnigan 6110 GC–MS–DS was used to identify organic arsenicals in selected samples.

Chemicals and Materials. Stock solutions for arsenic compounds were made with sodium arsenate, sodium arsenite (Analyzed Reagent, J. T. Baker Chemical Co.), monomethylarsonic acid (assay 99.9%, Ansul Company), and dimethylarsinic acid (assay 99.8%, Ansul Company). All stock solutions contained 1 mg/mL arsenic and were used to prepare standards for analysis each day. Chromatographic methods (described later) indicated that no further purification of the arsenic compounds was necessary. Other chemicals were reagent or analytical reagent grade and were used without further purification. Distilled–deionized water was used for all analytical work as well as cleaning of glassware. The cation exchange resin (AG 50W-X8, 100–200 mesh) was washed and reconditioned before each use with 1 M NH_4OH and 1 M HCl followed by a rinse in 4% HCl. New resin was exposed to each As species (50 μg of As/25 mL of resin) in order to assure quantitative recovery during chromatography.

Sampling. Environmental samples were obtained from the lower Menominee River near Marinette, Wis., where the Ansul Company had produced MMAA and DMAA as agricultural herbicides. Ansul disposed of the waste materials on the banks of the river, which led to the contamination of the river sediments and water. Water samples were collected at each site 20 cm below the water surface and 50 cm above the sediments. Deep water samples were collected using a Lucite Van Dorn sampler, and all samples were stored in acid-cleaned polyethylene containers. Half of each sample was filtered (0.4-μm Nuclepore) on site and the remaining portion was acidified to pH 1 with HNO_3 in order to prevent bacterial decomposi-

0013-936X/79/0913-1491$01.00/0

tion of MMAA and DMAA. Sediment cores were taken with a piston corer and immediately extruded in 7- and 11-cm sections. Extrusion involved placing a plastic bag over the top of the coring barrel and pushing a measured segment into the bag. Although the procedure was done in air, exposure of the mud was minimized by sliding the filled bag off the core while twisting the bag and simultaneously placing another bag over the barrel. Once an entire core was extruded (less than 5 min), each bag was subsampled, placed into polyethylene tubes, capped, and centrifuged immediately at 12 000 rpm. Significant oxidation of the sediments was avoided by completely filling the tubes displacing all the air space and limiting centrifugation time to 15 min. Subsamples of pore water were filtered (0.45-μm Millipore) while other subsamples were measured for Eh with an Orion combination Pt electrode. Solids were immediately frozen. Holdren (*22*) found that sediment cores could be extruded in this manner without significant changes in Eh. It was further demonstrated in this laboratory that whole sediments were not rapidly oxidized during aeration. However, separated pore waters were susceptible to rapid oxidation and were measured rapidly for Eh.

Procedures. Samples were brought back to the laboratory and stored at 4 °C until analysis. River water and pore water samples required no preparation for analysis other than dilution for FAA analysis or concentration for chromatography. Because the optimum amount of As for column chromatography was about 1 μg, heavily contaminated samples (e.g., pore waters) were diluted and less contaminated samples (e.g., river waters) were concentrated by evaporation. Arsenic volatility during evaporation was eliminated by adjusting the pH of the sample to 10 before evaporation. This ensured that all As species were in the ionic state. Arsenic associated with sediment solids was extracted using a modification of the extraction method for soil phosphorus (*5*). A series of 1 M solutions of NH_4Cl, NH_4OH, acid ammonium oxalate (*23*), and HCl was applied to dried sediment solids and equilibrated for 24 h at room temperature in a slow inversion mixer. The fractions are operationally defined as water-soluble As, Fe and Al–As, occluded As, and Ca–As, respectively.

Total As concentrations in river water, pore water, and sediment extracts (*5*) were measured by FAA with matrix modification using $Ni(NO_3)_2$ (*18*). Each standard, sample, and blank was prepared to contain 0.1% $Ni(NO_3)_2$ and 1% HNO_3 before FAA analysis, and triplicate measurements were made on each. Linear standard curves were calculated with a least-squares linear regression calculator program (*24*), which yielded 90% confidence limits for calculated As concentrations.

Inorganic As, MMAA, and DMAA in river water, pore water, and sediment extracts were separated on AG 50W-X8 cation exchange columns by a modification of the procedure reported by Yamamoto (*17*). Columns (25 cm to 30 cm long × 1 cm i.d.) were conditioned with 50 mL of 1 M NH_4OH, 70 mL of 1 M HCl, and 30 mL of 0.5 M HCl such that the column pH was less than 1.5 before sample introduction. Samples (at pH <2) were introduced such that 1–5 μg of As was placed on each column (not more than 2 mL). Samples were eluted with 30 mL of 0.2 M trichloroacetic acid and then with 70 mL of 1 M NH_4OAc, while effluents were collected in 5-mL fractions and saved for FAA analysis (described above). Replicate FAA measurements on each vial were made and standard deviations were calculated for the relative concentrations in each vial. Speciation was calculated from those measurements in each group of vials that composed one chromatographic peak. Chromatographic effluents from selected environmental samples were reduced with $NaBH_4$ and injected into a Finnigan gas chromatograph/mass spectrometer (*11*).

When the columns were eluted with gravity flow, approximately 30 min for each sample was required for separation when eight columns were operated simultaneously. Column conditioning took several hours under these conditions, but did not require constant attention. Separation and conditioning times were reduced to 10 and 5 min, respectively, when the columns were operated under 2–5 psig. Pressure was applied using a tank of purified nitrogen fitted with a regulator and connected to several columns by a tygon-tubing manifold.

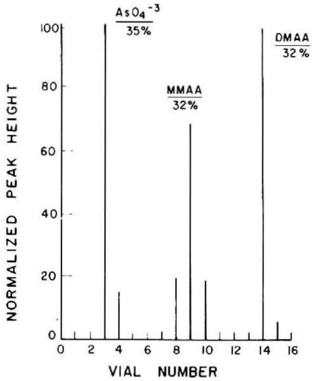


Figure 1. Chromatogram of 1 mL of mixed standard containing 500 ppb of As, each, as AsO_4^{3-}, MMAA, and DMAA. Each vial contained 4 mL of effluent

Results and Discussion

FAA Analysis. The FAA procedures described yielded linear absorbance response with up to 3 ng of As in the furnace and a furnace detection limit of 0.1 ng of As. Routine procedures with 10-μL injections and normal Ar flow resulted in a linear working range of 10–300 μg of As/L, while optimum conditions using dilute standards (2–20 μg of As/L) lowered the detection limit to 2 μg of As/L. Detection limits were defined as a signal-to-noise ratio of 2, where noise was calculated from the standard deviation of replicate sample measurements and the standard deviation of the residuals (s_y) in the standard curve (*23*). Procedural blanks were included in all standardizations and were indeterminable from distilled-deionized water blanks with 10-μL injections. With 50-μL injections, absorbances of the two blanks were within 2 standard deviations of furnace and deionized water blanks which were indeterminable at either injection size. Although standards were normally made with deionized water, standards made in uncontaminated river water and standard addition methods yielded identical results indicating that interferences were not detectable. In addition, 90% confidence limits were used to define procedural detection limits. Confidence intervals were typically 3–10% of measured concentrations for samples at or above 10 μg/L in As and up to 30% for samples below 6 μg of As/L.

The precision and sensitivity of this procedure are due to the addition of $Ni(NO_3)_2$, which is thought to form nonvolatile nickel arsenides at charring temperatures between 310 and 1200 °C (*18, 25–27*). The higher charring temperatures remove organic interferences that may be found in natural and polluted waters. In addition, $Ni(NO_3)_2$ normalizes FAA response among various As species. Without matrix modification, Brinkman (*28*) found that FAA response to inorganic As, MMAA, and DMAA differed significantly in standards with identical As concentrations. Tests in this laboratory showed that linear standard curves for sodium arsenate and DMAA did not differ significantly based on the comparison of calculated line parameters with 90% confidence limits. Additional

Table I. Selected Data for As Concentration and Speciation in River Waters and Sediments (90% Confidence Limits Included)

sample,[a] type and site no.	total As concn, µg/L	As species, %		
		inorganic	MMAA	DMAA
river water				
69A	1200 ± 200	10 ± 1	81 ± 2	9 ± 0.4
70A	170 ± 5	4 ± 0.2	88 ± 2	8 ± 1
55C	43 ± 5	30 ± 0.6	54 ± 2	17 ± 0.5
pore water				
69A	mg/L			
40 cm	6880 ± 240	10 ± 0.5	90 ± 2	0
72 cm	5850 ± 450	6 ± 0.2	93 ± 2	1 ± 0.1
sediment solids				
69A, NH_4Cl	3.3 ± 0.3	0	96.8 ± 0.4	3.2 ± 0.011
NH_4OH	1.2 ± 0.2	0	100	0
oxalate	28.6 ± 1.8	3.6 ± 0.01	96.4 ± 0.01	0
HCl	0.24 ± 0.03	2.8 ± 0.01	97.2 ± 0.1	0
total	33.3 ± 1.84			

[a] Site numbers refer to map of sampling area published elsewhere (*31*).

evidence for FAA response normalization is offered in the discussion of chromatographic methods.

Chromatography Procedures. Modifications made on the chromatography methods of Yamamoto (*17*) resulted in complete separation of inorganic As, MMAA, and DMAA with theoretical recovery within a 2% relative error (see Figure 1). Zero base-line values were maintained by using ammonium salts for eluting and conditioning solutions. Eluting solutions were less concentrated than solutions used previously (*17*), allowing the ion-exchange resin to retain Na^+, K^+, Mg^{2+}, or Ca^{2+} ions that interfere with FAA detection. Separation of inorganic As and MMAA was improved considerably by initializing column pH to 1.5 rather than 4 as suggested by Yamamoto (*17*), allowing the use of shorter columns. Their separation was not significantly affected by column pressurization up to 10 psig. Furthermore, separation of MMAA and DMAA was not affected by eliminating the third eluting step used by Yamamoto (*17*). As previously explained, the inorganic As was further speciated by colorimetry. Chromatography of evaporated standard in deionized and river water resulted in theoretical recovery with a maximum of 6% relative error. There was no significant effect on speciation during evaporation up to 100-fold concentration.

Solid Extraction Procedures. The precision of the solid extraction procedure was as good as or better than FAA precision. Replicate extractions on identical sets of sediment samples spiked with MMAA and DMAA had 6% relative error (90% confidence limits) for both sets. The relative uncertainty of individual fractions varied from 3% for concentrated extracts to 100% for very dilute extractions. It was found, however, that extraction was not complete, and that efficiencies of recovery for As(V), As(III), MMAA, and DMAA were 58, 48, 70, and 68%, respectively (each with a relative uncertainty of ±4%).

Field Applications. Total As concentrations and As speciation in selected field samples are listed in Table I along with 90% confidence limits. With one exception, the confidence limits reveal relative uncertainties between 3 and 11% for total As in solution and up to 6% relative error for total solid-phase As. Confidence limits for the environmental data were similar to those obtained with laboratory standards. This indicated that precision was not lost because of environmental interferences.

The accuracy of these methods, in addition to being supported in laboratory samples, has been supported by comparisons with standard addition methods on environmental samples. It should be pointed out that speciation data in appropriate samples corresponded well with the known speciation of the waste material (*29*). A mass balance performed in this laboratory using the above methods has corresponded well with a similar independent study contracted by Ansul (*30*). It has been found that field results using the methods described confirm their environmental reliability.

Although sediment solid extracts could be accurately speciated, such data were not considered to be an accurate representation of the actual solid-phase As speciation in sediments. The difference in extraction efficiency among As species reported above suggests the need for further study in extraction procedures and reinterpretation of reported data concerning soil and sediment solid-phase As species.

Summary

The methods presented (along with other analytical procedures not discussed) have proven to be useful for routine analyses of environmental samples and in studies currently underway in this laboratory. The precision of the methods permits reliable observations of speciation and concentration changes for As in natural and laboratory conditions—that is, significant variations found in such conditions can be reliably attributed to the processes being studied. The methods are convenient, since many samples may be processed simultaneously and instrumental time is efficiently used. Statistical interpretation of speciation data can easily be made from a single chromatogram because detector variance is evaluated from replicate analyses of column effluent. Minimal sample preparation easily allows replicate determinations of As concentration. Modifications made in this laboratory, along with proper precautions, have reduced analytical interferences to nondetectable levels. Detection limits are sufficient for any As-contaminated system and may be easily lowered by preconcentration methods in order to study uncontaminated systems.

These procedures can be performed in any laboratory equipped with an atomic absorption spectrophotometer with minimal investment for new hardware such as flow systems or reactor vessels. Such methods, therefore, are accessible not only to research laboratories, but also for nonresearch applications where elemental speciation is required for meaningful environmental interpretation. Such requirements are becoming more apparent with growing knowledge of elemental cycling and biochemical processes for other elements in addition to As such as Sb, Se, and Te. Therefore, such methods should be available to all environmental laboratories regardless of the scope of the analysis.

Literature Cited

(1) Cox, D. D., Alexander, M., *Bull. Environ. Contam. Toxicol.*, **9,** 84–8 (1973).
(2) McBride, B. C., Wolfe, R. S., *Biochemistry,* **10,** 4312–7 (1971).
(3) Woolson, E. A., *Weed Sci.*, **25,** 412–6 (1977).
(4) Wauchope, R. D., *J. Environ. Qual.*, **4,** 355–8 (1975).
(5) Jackson, M., "Soil Chemical Analysis—Advanced Course", 5th Printing, Department of Soil Science, University of Wisconsin, 1969, p 499.
(6) Woolson, E. A., Kearney, P. C., *Environ. Sci. Technol.*, **7,** 47–50 (1973).
(7) Jacobs, L. W., Syers, J. K., Keeney, D. R., *Soil Sci. Soc. Am. Proc.*, **34,** 750–4 (1970).
(8) Overby, L., Boechier, S., Frederickson, R., *J. Assoc. Off. Agric. Chem.*, **48,** 17–22 (1965).
(9) Sachs, R. M., Michael, J. L., Anastasia, F. B., Wells, W. A., *Weed Sci.*, **19,** 412–6 (1971).
(10) Brinckman, F. E., Blair, W. R., Jewett, K. L., Iverson, W. P., *J. Chromatogr. Sci.*, **15,** 493–503 (1977).
(11) Talmi, Y., Bostick, D. T., *Anal. Chem.*, **47,** 2145–50 (1975).
(12) Talmi, Y., Norvell, V. E., *Anal. Chem.*, **47,** 1510–6 (1975).
(13) Andreae, M. O., *Anal. Chem.*, **49,** 820–33 (1977).
(14) Braman, R., Johnson, D., Foreback, C., Ammons, J., Bricker, J., *Anal. Chem.*, **49,** 621–5 (1977).
(15) Thompson, A. J., Thoresby, P. A., *Analyst*, **102,** 9–16 (1977).
(16) Terashima, S., *Anal. Chim. Acta*, **86,** 43–51 (1976).
(17) Yamamoto, M., *Soil Sci. Soc. Am. Proc.*, **39,** 859–61 (1975).
(18) Ediger, R., *At. Absorpt. Newsl.*, **14,** 127–139 (1975).
(19) Johnson, D. L., Pilson, M. E. Q., *Anal. Chim. Acta*, **58,** 289–99 (1972).
(20) Murphy, J., Riley, J. P., *Anal. Chim. Acta*, **27,** 31–6 (1962).
(21) Stauffer, R. E., U.S. Geological Survey, Menlo Park, Calif., unpublished results, 1977.
(22) Holdren, G. C., University of Wisconsin, Madison, Department of Water Chemistry, personal communication, 1977.
(23) Saunders, W., *N. Z. J. Agric. Res.*, **8,** 30–57 (1965).
(24) Blaedel, W. J., Iverson, D. G., *Anal. Chem.*, **48,** 2027–8 (1976).
(25) Walsh, P. R., Fasching, J. L., Duce, R. A., *Anal. Chem.*, **48,** 1012–4 (1976).
(26) Walsh, P. R., Fasching, J. L., Duce, R. A., *Anal. Chem.*, **48,** 1014–6 (1976).
(27) Denyszyn, R. B., Grohse, P. M., Wagoner, D. E., *Anal. Chem.*, **50,** 1094–6 (1978).
(28) Brinkman, R. E., U.S. National Bureau of Standards, personal communication, 1978.
(29) Moore, L., Ansul Company, Weslaco, Tex., personal communication, 1977.
(30) Nicholas, J., Ansul Company, Marinette, Wis., personal communication, 1979.
(31) Holm, T. R., Anderson, M. A., Iverson, D. G., Stanforth, R. R., *ACS Symp. Ser.*, **No. 93,** 711–36 (1979).

Received for review October 23, 1978. Accepted August 20, 1979. This work has been supported in part by a Grant (No. R-804-881-010) from the U.S. Environmental Protection Agency and by a Grant (No. DACW23-77-C-0046) from the U.S. Army Corps of Engineers.

Differences in Particle Size Distributions of Major Organic Pollutants in Ambient Aerosols in Urban, Rural, and Seashore Areas

L. Van Vaeck*, G. Broddin, and K. Van Cauwenberghe

Department of Chemistry, University of Antwerp (U.I.A.), B-2610-Wilrijk, Belgium

■ Airborne particulate matter was collected in suburban, rural, and seashore sites, using a Hi-Vol cascade impactor. Detailed chemical analysis was performed by GC–MS in the multiple ion monitoring mode. The size distributions for total suspended particulates (TSP) as well as for the individual organic pollutants are compared. Maximum TSP concentrations are found for the submicron particles in the suburb. In contrast, more important contributions from larger particles are observed in the background samples. The size distribution of the individual pollutants in the rural samples shows a depletion of the fraction between 0.5 and 1 μm, compensated by an increase of the one between 1 and 1.5 μm. These size distribution shifts are the result of a particle growth process occurring with aging of the aerosol. In view of the dust retention characteristics of the human respiratory tract, a more important fraction of the rural aerosol will be deposited into the lungs, though absolute concentrations will be lower.

The evaluation of the impact on human health of the organic compounds present in ambient aerosols requires that measurements of the pollutant concentrations be supplemented with data on the particle size distribution of these compounds. Indeed, the sedimentation of particles in the respiratory tract from inhaled air strongly depends on the particle size (*1, 2*).

The purpose of the present study is to assess the differences in particle size distribution for organic compounds between urban samples and these obtained at locations with considerably less pollution. In a previous paper, we described results for a typical suburban residential area (*3*). New sampling stations were set up in a rural region covered with forest as well as near the seashore. No important industrial activity was situated in the vicinity of each of these stations. In addition to yielding data of direct toxicological interest, i.e., the concentrations on respirable particles, these stations will also give information on the existence and nature of the aging processes that the aerosol undergoes during transport through the atmosphere.

In the different fractions of a size-fractionated aerosol sample, about 60 organic compounds belonging to the classes of the aliphatic, polycyclic aromatic hydrocarbons (PAHs), N-containing analogues, and carboxylic acids are determined by gas chromatography–mass spectrometry (GC–MS). This method provides reliable, sensitive, and in its most developed form (preprogrammed multiple ion detection) relatively fast analyses (*4*). Yet, an important fraction of the aerosol extractables in organic solvents consists of less volatile or more polar compounds that cannot be subjected to GC–MS analysis.

The cascade impactor is not an ideal device for the separation of particles according to their aerodynamic diameter, since the range of the particle diameters collected on each stage is not exactly defined (cut-off at 50% efficiency). The performance of the slotted impactor used in this study was evaluated by Willeke (*5*).

0013-936X/79/0913-1494$01.00/0

Table I. Equivalent Aerodynamic Cut-Off Diameters at 50% Collection Efficiency for the Sierra Hi-Vol Impactor at 40 scfm

stage	cut-off diameters, μm	stage	cut-off diameters, μm
1	7.2	4	1.5–1.0
2	7.2–3.0	5	1.0–0.5
3	3.0–1.5	6	0.5

Previously, the possibility of losses by volatilization from collected particles during sampling was established for some organic compounds (*6–9*). Cautreels and Van Cauwenberghe (*10*) reported quantitative data on the distribution of some pollutants between the gas phase and particulate matter for Hi-Vol filtration.

Experimental

Sampling. Sampling was performed with a Hi-Vol cascade impactor of Sierra Instruments Inc. (series 230), equipped with five stages and a back-up filter, mounted in a standard EPA shelter. The approximate equivalent aerodynamic cut-off diameters at 50% collection efficiency for a flow-rate of 40 scfm are given in Table I. The total air flow is led without splitting through a rotameter (ROTA, RNH G4 10 000, Germany) equipped with a photorelay system. Sampling is interrupted automatically when filter clogging or motor inefficiency reduces pumping speed by 5% for at least 4 min. The sampled air is released about 2 m away from the sampling unit.

Particulate matter is collected on glass fiber filters (Whatmann, GF/A), preextracted with methanol and benzene.

The location of the sampling stations and the prevailing wind direction during sampling are indicated in Figure 1. Other important sampling data are summarized in Table II.

To collect the suburban samples, the impactor was mounted on the roof of a university building, located in the residential area of Wilrijk, near Antwerp. There was no obstruction to free air circulation. Emission sources in the vicinity include a municipal incineration plant at 1 km and several industrial plants in the port region of Antwerp. Typically, 10 000 m^3 was sampled for about 1 week, resulting in the collection of about 100 mg of particulate matter on each stage. The back-up filter was changed every 3 days (loading up to 200 mg).

The rural samples were obtained at the meteorological station in Botrange at an altitude of 690 m above sea level. Air circulation in the southwest direction may have been hindered by the forest. A road (medium traffic density) was 20 m away. Important industrial activity is found at 40 km (Aachen).

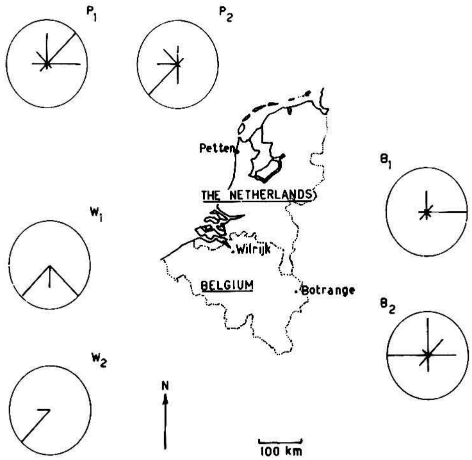


Figure 1. Sampling stations and main wind directions during the periods of sampling

Sampling of 30 000 m^3 of air was performed in about 1 month, during which the same filters remained on each stage. The back-up filter was changed every week.

The seashore samples were taken at the Energy Research Center in Petten (North-Netherlands). The sampling unit was placed on a dune hill, 100 m away from the sea. There were no important obstructions to the air stream. Sampling periods and frequency of filter changes were as for the Botrange samples. During the second sampling period, the dominant wind direction was from the seaside and the collected aerosol will be representative of marine influences.

Chemical Analysis. The filters were weighed up to 0.1 mg after equilibration and extracted in a Soxhlet apparatus during 8 h with benzene ("zur Rückstandsanalyse", Merck) and methanol (p.a., Merck) consecutively. After the solvent was evaporated under reduced pressure at low temperature, the residue of the combined extracts was redissolved in redistilled diethyl ether (p.a., Merck). The inorganic substances, previously extracted with methanol, were removed by washing with water. The water layer was discarded. The acidic compounds were methylated by addition of an excess of diazomethane in ether. A solution of two internal standards (methyl octadecanoate-d_3, isotopic purity 99%, and pyrene-d_9, isotopic purity 98%) in benzene was added just before GC–MS analysis. The extract was finally concentrated to about 1 mL, of which 1 to 3 μL was injected into the GC–MS.

Analyses were carried out on a Finnigan 3100 GC–MS quadrupole type instrument, coupled to a Finnigan 6100 D

Table II. Volumetric and Gravimetric Data

sample code	sampling period	vol, m^3	TSP concn, μg m^{-3}	TSP MMED	TSP σ_g
suburban samples					
W$_1$	March 8–15, 1977	11 362	72.1	1.4	5.4
W$_2$	July 21–28, 1977	11 556	44.4	1.3	6.2
W$_3$	Dec 22–30, 1976	11 242	104.1	1.0	4.4
rural samples					
B$_1$	May 9–June 12, 1977	32 641	34.3	0.7	5.5
B$_2$	June 12–July 9, 1977	38 979	43.8	1.2	3.5
seashore samples					
P$_1$	July 29–Aug 22, 1977	29 751	41.1	1.4	10.0
P$_2$	Aug 22–Sept 16, 1977	33 450	34.3	2.9	6.3

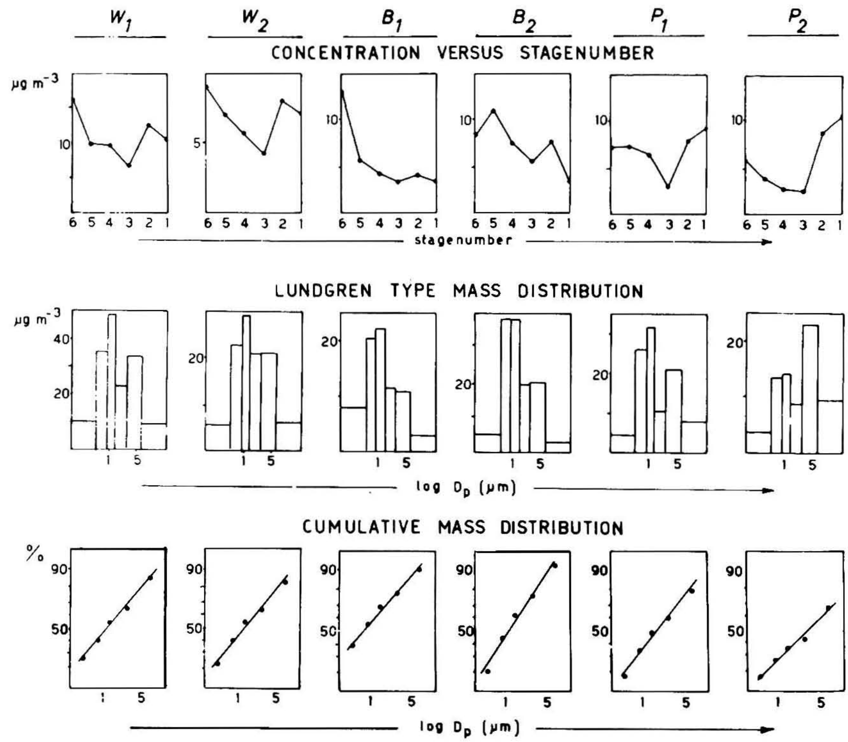


Figure 2. Summary of the TSP distributions: concentration vs. stage number, Lundgren type mass plots, and cumulative mass distributions

data system. The GC column of 3 m length was packed with 3% Dexsil 300 GC on Gas-Chrom Q. The mixture was eluted using temperature programming from 130 to 285 °C at 4 °C min^{-1}. The elution took about 45 min. For reasons of sensitivity and accuracy, the samples were run in multiple ion detection mode (MID). The selective ions focused were *m/e* 87 for the acids, *m/e* 99 for the aliphatic hydrocarbons, and the molecular ions for the PAH and N-containing aromatic hydrocarbons.

After modification of the data system, the set of alternatively focused ions can be changed very quickly at moments chosen by the operator during the actual elution (*4*). In this way, all 60 compounds can be monitored during the same GC run.

Determinations are based on calibration curves, reconstructed daily from three standards and going through the origin. The precision of the method is about 5–10%, and the detection limit reaches 10 pg (absolute amount injected, 11).

Results and Discussion

The major goal of this study was to evaluate if significant differences in particle size distributions of organic pollutants could be found between urban and rural sampling locations in a highly industrialized and populated country.

Several suburban samples taken before during a 1-year study showed only little variation in particle size distributions of individual pollutants (*4*). The dilution of the aerosol in the rural and seashore region requires sampling periods of about 1 month instead of 1 week for the suburb. Therefore, in each background station only two samples could be taken successively during the summer, and a problem of statistical foundation of the interpretation of the results remains.

A point of interest is the collection efficiency of the sampling unit. Quantitative recovery of the particles (especially >5 µm) can be affected by the geometry of the instrument and shelter or the ratio of wind velocity to sampling rate as pointed out by Fuchs (*12*). However, discrimination of large particles seems to be less important in turbulent air, encountered in ambient sampling (*13*). Furthermore, most organic pollutants in ambient air samples are found in the lower particle size range (<3 µm) and can be assumed to be less influenced by such effects. We checked the consistency of the impactor results with samples taken by Hi-Vol filtration according to Dams and Heindryckx (*14*). In most cases, the individual pollutant concentrations for the impactor samples agreed within 20% with the Hi-Vol filtration results (*9*).

It is necessary to discuss the particle size distributions in three different ways:

1. Concentration vs. Stage Number. This is the most straightforward way in which distributions are directly derived from the analysis. All particles with aerodynamic diameters within the range of a given stage are considered collectively, and the characteristic distribution patterns depend on the cut-off diameters of the stages.

2. Cumulative Mass Distribution. Here the fraction of a pollutant present on particles below a given diameter is calculated. The mean mass equivalent diameter (MMED) and the geometric standard deviation (σ_g) define the median and the width of the distribution. The determination of the respirable (<3 µm, *15*) and the submicron fraction provides an excellent means to summarize quantitatively a large amount of particle size distribution data.

3. Lundgren Type Mass Distribution. By differentiation of the cumulative mass distribution, a nearly Gaussian-shaped profile is obtained (*16*). The limited number of fractions col-

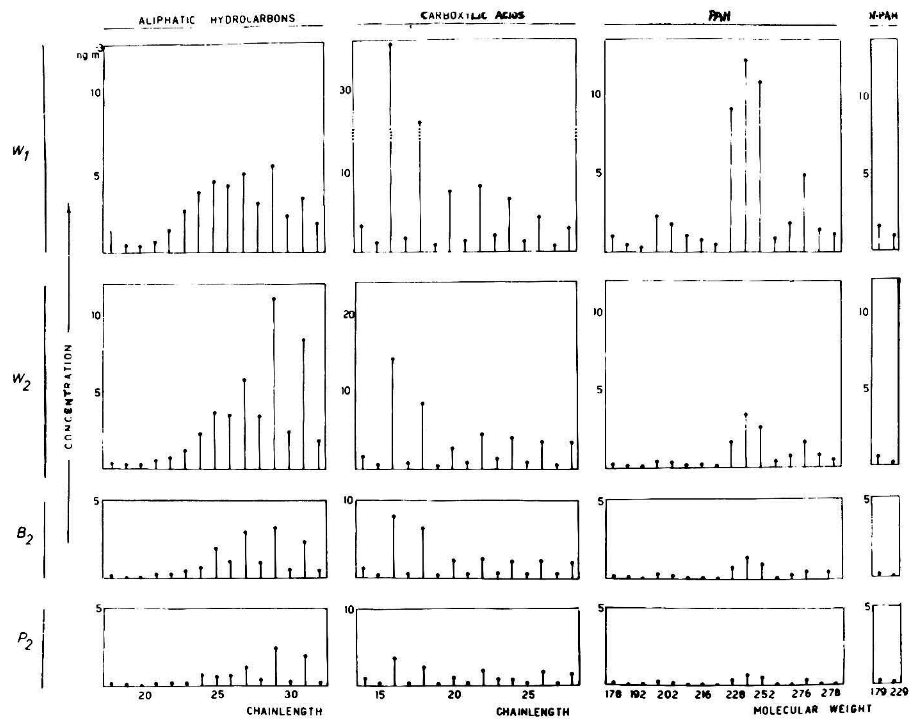


Figure 3. Total concentration vs. molecular weight or chain length for the aliphatic hydrocarbons, carboxylic acids, polycyclic aromatic hydrocarbons, and N-containing aromatics (see also Table III for the molecular weights of the PAHs)

lected by a Hi-Vol impactor and the assumptions made for the upper and the lower limits of the collected particle size range (conversion of data involves cut-off diameters of each stage) reduce the sensitivity of this method for the detection of particle size distribution shifts.

In the discussion we will treat consecutively: (A) the distribution of the total suspended particulates (TSP); (B) the relative composition of the aerosol with respect to the 60 organic pollutants; (C) the particle size distributions for the individual pollutants including concentration vs. stage number, cumulative, and Lundgren type distributions.

(A) Distribution of the Total Suspended Particulates (TSP). As seen from Table II, during summer the TSP concentration reaches similar values in the background stations as in the suburb, but is lower than in the suburb during other seasons. The apparent agreement between different sampling stations can be partially due to the long sampling periods that will filter out short-term variations.

In contrast, TSP is found to be distributed differently in the three stations. For all suburban samples, a maximum is found in the submicron range and TSP concentrations decrease continuously from stages 6 to 3. This is illustrated in Figure 2.

In the rural region, the distribution tends to flatten. At the seashore, particles of greater size contribute most by weight to the total TSP concentration. Since the apparatus was placed on a dune hill, the collection of fine sand raised by wind may have been important.

The Lundgren type mass plots give the concentration for an infinitely small interval of particle diameters. Figure 2 also illustrates the particle size distribution shifts between the suburban and other samples. In the suburb, the maximum is reached between 1 and 1.5 μm. For the rural region, the distribution broadens with a less localized maximum between 0.5 and 1.5 μm. At the seashore, a maximum concentration is found between 3 and 7 μm. However, the value for fraction 1 (>7 μm) directly depends on the assumed upper cut-off diameter of the sampler (*16*).

Compared to the suburban aerosol, the rural samples show a depletion of the particle size range below 0.5 μm and an enhancement of the contribution from somewhat larger particles (1–1.5 μm). Since dust retention in the human respiratory tract drops near the upper end of the particle size range (>3 μm) as well as below 0.5 μm, a more important fraction of the rural aerosol is deposited than of the suburban particles. Near the sea, the depletion of the submicron range is compensated by the contribution from particles of 3 μm or larger, and therefore the risk for sedimentation is greatly reduced.

(B) Relative Composition of the Aerosol and Total Pollutant Concentrations. The total concentrations for each class of pollutants are plotted vs. molecular weight in Figure 3.

The aliphatic hydrocarbons follow a characteristic alternating pattern with lower concentration levels for the even homologues than for the uneven ones with similar chain length. All samples show a maximum of the distribution at *n*-nonacosane.

During summer, the concentration difference between homologues with even and uneven chain length is enhanced in the suburb with respect to the other seasons and this tendency becomes even more important at the background stations.

Volatilization from collected material during sampling can be expected for the more volatile organic compounds such as the aliphatic hydrocarbons, the low molecular weight PAH, and carboxylic acids (*10*).

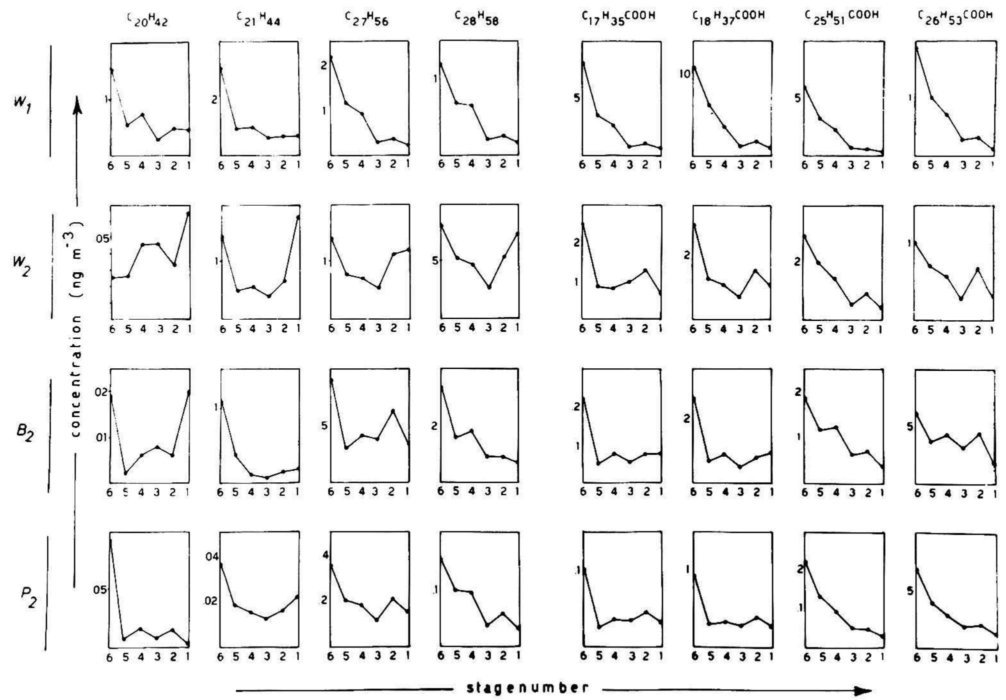


Figure 4. Summary of the particle size distributions for the aliphatic hydrocarbons and carboxylic acids

The alternation of the aliphatic hydrocarbons is explained tentatively by assuming selective volatilization of the even n-alkanes compared to the uneven ones, as discussed in an earlier paper (9). However, it seems that desorption of the even aliphatic hydrocarbons could occur not only from collected material during sampling but also during transport of the aerosol in the atmosphere ("aerodynamic elution", 7). Furthermore, during the formation process of the aerosol, the uneven homologues could also adsorb preferentially to the particles from the gas phase.

As seen in Figure 3, the concentration of the aliphatic hydrocarbons, summed over all stages, showed variations within a factor 2 in the suburb, but these pollutants were up to 5 times more diluted at the background stations.

The carboxylic acids with an even number of carbon atoms are found in higher concentrations than those with uneven chain length, but this alternation is probably related to their sources rather than to preferential losses or condensation. Major components in this class are palmitic and stearic acid. The distribution of the higher even acids reaches a maximum for docosanoic acid. During summer, the distribution becomes more flat with higher levels for the high molecular weight acids (C_{20}–C_{28}) compared to the lower homologues. The excess of palmitic and stearic acid decreases drastically at the coastal station.

Surprisingly, the total concentrations of the carboxylic acids with even carbon number agree within a relatively narrow range for all samples (factor of 2 or less).

The relative abundance of the different PAHs is remarkably constant in all samples. However, the concentrations of the individual analogues (see Figure 3) vary significantly in different locations. Suburban PAH concentrations for the summer increase 5-fold during spring and autumn, and even 25-fold during the winter. In nonurban environments, a five- to tenfold further dilution is observed.

(C) Size Distributions of the Individual Pollutants. In previous experiments, the particle size distributions of organic pollutants in the suburb were revealed to be characteristic, with only minor seasonal variations. Deviations could be related to the origin and history of the aerosol, e.g., the enrichment of submicron particles in PAH by combustion processes for domestic heating during the winter.

In the comparison between suburban and background samples, a major interest lies in the effect of increasing distance between the sampling station and the emission sources. The aerosol can undergo not only simple dilution, conserving its original composition, but the longer residence time in the atmosphere will also allow an aging process including several physical and chemical transformations (coagulation, chemical reactions). However, from the particle size distribution of a given pollutant the nature of such transformation cannot be defined. Since most organic pollutants are adsorbed on the smallest particles by condensation, a depletion in the submicron fraction can be due both to particle growth and to gas–particle reactions.

1. Concentration vs. Stage Number. In Figure 4 some typical particle size distributions are given for aliphatic hydrocarbons and carboxylic acids in the different samples.

With the exception of the summer sample, the distributions of the n-alkanes in all suburban samples are quite similar: decreasing concentrations on larger particles and increasing ratio of the concentration in fraction 6 (<0.5 μm) to that in 1 (>7 μm) with chain length. In the summer sample, however, the lower homologues (C_{18}–C_{21}) are about equally distributed over all fractions, while the higher homologues (C_{22} and higher) follow the usual patterns, but with higher concentrations for fractions 1 and 2 (>3 μm).

In the rural and coast summer samples, the same tendency is observed: the lower homologues (up to C_{22}) reach a nearly constant level in fractions 1 to 5 (>0.5 μm) and twice or higher concentrations for fraction 6. The distribution shapes of the higher homologues are again comparable to those of the suburban nonsummer samples.

Since volatilization artifacts are related to the sampled volume, the observed differences can be explained by these effects. For the lower homologues, more important losses could be expected for stages 1–5 than for the back-up filter, the latter being renewed more frequently.

For the carboxylic acids, the distribution patterns are found to be highly reproducible in all samples: there are no significant seasonal variations in the suburb and no important differences between this station and the background ones. The small range of total concentrations and the identical distributions seem to indicate that the major source of these compounds in ambient aerosols is not combustion processes and that other mechanisms, probably involving natural sources, are important.

The PAH distributions are less conforming but can be classified according to a number of typical profiles. The main differences between the various types are the relative abundances of the submicron fraction compared to the others. These distributions are illustrated in Figure 5. In Table III, the PAHs and their corresponding distribution types are listed.

The suburban winter sample shows a conversion of the distributions to types with a more dominant submicron fraction. During the summer, the reverse tendency is observed: most PAHs follow distributions with a smaller contribution in the submicron range. Only the high molecular weight PAHs yield significant concentrations in the submicron fraction.

In the background stations, a similar behavior is observed: PAH concentration maxima in the aged aerosol at the background areas shift from the submicron particles to the micron range.

It was also observed in the suburban samples that the more volatile PAHs followed preferentially a distribution type with less important contributions in the submicron range: volatilization losses could deplete preferentially these fractions. Since stage 5 collects the particles with the smallest aerodynamic diameter (the back-up filter being renewed frequently), the minimum of the distribution on that stage could be partially due to volatilization. Nevertheless, it is not obvious that the particle density and shape, the two quantities that correlate geometric diameters, are the same throughout the whole size range, and a tentative explanation for a blow-off artifact, based on the active surface of a fraction, could be erroneous.

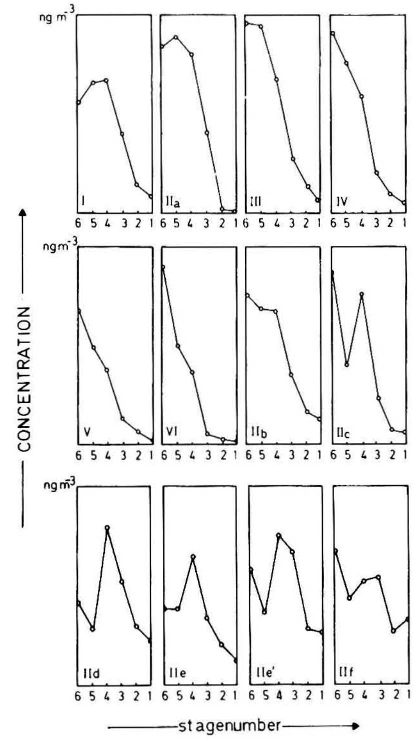


Figure 5. Typical size distributions for the PAHs

2. *Cumulative Mass Distribution.* In the suburb, most organic pollutants are predominantly found on particles with aerodynamic diameters less than 3 μm, i.e., the respirable fraction. Although this gives important information about the health hazards involved, it is not a sensitive parameter for the characterization of particle size distribution shifts. Other in-

Table III. Distribution Types of the PAHs

	mol wt	W_1	W_2	W_3	B_1	B_2	P_1	P_2
phenanthrene + anthracene	178			II_f	$\mathrm{II}_{b,c}$	$\mathrm{II}_{e'}$	II_d	II_c
methylphenanthrene	192	II_c	$\mathrm{II}_{b,c}$	VI	II_c	$\mathrm{II}_{d,e'}$	$\mathrm{II}_{c,d}$	II_c
methylanthracene	192	II_c	II_f	VI	II_c	II_c	II_d	II_c
fluoranthene	202	II_b	II_c	IV	II_c	$\mathrm{II}_{d,e'}$	II_d	II_d
pyrene	202	II_b	II_c	IV	II_c	$\mathrm{II}_{d,e'}$	II_d	II_d
benzo[*a*]fluorene	216	I	$\mathrm{II}_{e'}$	IV	II_c	II_d	$\mathrm{II}_{e'}$	II_c
benzo[*c*]fluorene	216	I	$\mathrm{II}_{c,e'}$	IV	II_c	II_d	II_c	II_c
methylpyrene	216	I	II_f	II_b	$\mathrm{II}_{b,c}$	II_c	II_c	VII
benzo[*a*]anthracene + chrysene	228	II_a	II_b	VI	II_a	$\mathrm{II}_{c,d}$	II_e	II_c
benzo[*b* + *k*]fluoranthenes	252	III	V	VI	II_a	II_c	I	II_c
benzo[*a* + *e*]pyrenes	252	II_a	II_a	VI	II_a	$\mathrm{II}_{c,d}$	I	II_c
perylene	252	I	II_a	II_c	II_a	II_c		II_c
o-phenylenepyrene	276		IV	II_c	II_a	II_a		
benzo[*ghi*]perylene	276	VI		VI	II_a			$\mathrm{II}_{b,c}$
dibenzanthracenes	278	V	IV	VI	II_a			VI
picene	278	V	IV, V	VI	III	V		V

Table IV. Cumulative Mass Distribution Data

	W_1						W_2					
	fraction (%) below μm						fraction (%) below μm					
	3	1.5	1	0.5	MMED	σ_g	3	1.5	1	0.5	MMED	σ_g
aliphatic hydrocarbons												
n-heneicosane	83	70	61	50	0.6	5.6	56	46	38	27	1.9	
n-docosane	85	74	66	55	0.5	5.8	40	31	25	18	5.8	
n-tricosane	89	80	68	51	0.6	3.5	48	37	32	22	3.5	
n-tetracosane	91	84	73	54	0.5	2.8	56	46	40	31	1.9	
n-pentacosane	90	83	71	53	0.6	3.0	68	57	48	31	1.1	1.3
n-octacosane	88	80	65	44	0.7	2.9	66	54	42	24	1.3	9.2
n-nonacosane	87	79	66	48	0.6	3.4	55	39	30	17	2.4	5.0
n-triacontane	84	74	59	38	0.8	3.7	59	47	38	22	1.7	
n-hentriacontane	87	78	65	46	0.7	3.6	53	34	24	14	2.7	4.1
n-dotriacontane	79	69	53	31	1.0	4.6	60	42	31	16	2.0	
carboxylic acids												
palmitic acid	93	87	76	46	0.5	2.4	59	48	42	32	1.7	5.0
heptadecanoic acid	91	84	74	55	0.5	2.8	75	60	50	34	1.0	5.1
stearic acid	91	83	73	47	0.5	3.0	75	60	51	35	1.0	5.4
nonadecanoic acid	95	87	76	47	0.5	2.4	86	75	65	42	0.6	4.2
eicosanoic acid	95	89	80	50	0.5	2.5	78	64	54	37	0.9	5.1
tetracosanoic acid	93	88	76	48	0.5	2.5	79	67	56	34	0.8	4.9
pentacosanoic acid	94	88	76	47	0.5	2.5	87	77	64	37	0.7	3.4
hexacosanoic acid	92	84	72	46	0.5	2.9	78	66	53	31	0.9	4.7
heptacosanoic acid	92	85	74	44	0.6	2.6	86	75	63	38	0.7	3.8
octacosanoic acid	90	80	68	40	0.6	3.1	72	54	44	25	1.2	4.5
PAHs												
phenanthrene + anthracene	80	64	47	24	1.1	3.6	78	58	45	24	1.2	3.4
fluoranthene	90	78	60	29	0.8	2.5	87	68	53	28	0.9	2.9
benzo[*a*]anthracene + chrysene	95	86	67	31	0.7	1.9	92	78	54	30	0.8	2.2
benzo[*b* + *k*]-fluoranthenes	96	86	70	42	0.7	2.1	94	79	61	35	0.7	2.6
benzo[*a* + *e*]pyrenes	96	85	68	41	0.7	2.0	92	78	64	31	0.8	2.4
o-phenylenepyrene							86	74	60	34	0.8	3.4
dibenzanthracenes	88	76	59	28	0.8	2.8	60	46	34	18	1.9	5.0

teresting features are the MMED and σ_g because these yield information about the formation process of the aerosol. If a pollutant adsorbs to the particles during emission, the MMED of that compound remains below the MMED of the TSP distribution (*17*).

In Table IV we listed for some selected pollutants in each class the fractions below 3, 1.5, and 0.5 μm and the graphically derived MMED and σ_g. The following conclusions can be drawn:

- The respirable fraction in the suburban samples contains about 85–90% of the aliphatic hydrocarbons, 80–95% of the carboxylic acids, and 90–95% of most PAHs. During the year, these values are reasonably constant except for the summer sample where the percentage lowers significantly to 50–70% for the aliphatic hydrocarbons, 60–85% for the carboxylic acids, and 75–90% for the PAHs. In winter, the PAHs are more abundant in the respirable fraction.
- In the rural and coast samples, 70–85% of the aliphatic hydrocarbons and acids and 80–90% of the PAHs are found on respirable particles. These values are within the range observed for the suburban samples and even exceed the summer suburban values.
- The comparison of the corresponding size fractions in the suburban and background samples shows a slight depletion for all fractions in the background areas, but, in particular, the fraction between 0.5 and 1 μm is affected. The decreased contribution of this stage is compensated to some extent by an increase in the next stage (1–1.5 μm), indicating particle growth processes.
- The comparison of the suburban summer sample with those taken during other seasons shows that for most pollutants a smaller fraction is found on respirable particles. There is no clear depletion/enrichment of a few stages, but all stages collecting particles below 3 μm contribute partly to the reduction of the respirable fraction. This could be due to volatilization artifacts during sampling at more elevated temperatures, but, in contrast, the background samples show evidence for a depletion/enrichment on some stages, although the particles are collected from an even larger air volume.
- The MMEDs of most pollutants are below 1 μm in the suburb. During the summer, increased MMEDs are observed for the aliphatic hydrocarbons. This can be related to elution both during transport and during collection, as well as to condensation onto more aged and full-grown particles.
- The geometric standard deviation (σ_g) remains remarkably constant for the PAH and the MMEDs vary only slightly and regularly. This indicates a common generating process and only minor variations in the particle size distribution during transport for the PAHs.
- For most pollutants, the MMEDs of the individual pollutants are considerably lower than those of the TSP. This is typical for condensation type aerosols: during emission, pollutants adsorb from the gas phase preferentially to the small particles.

B2						P2					
fraction (%) below µm						fraction (%) below µm					
3	1.5	1	0.5	MMED	σ_g	3	1.5	1	0.5	MMED	σ_g
84	78	74	58	0.4	8.9	70	59	48	31	1.0	8.5
79	73	66	54	0.4	15.0	82	71	64	51	0.5	7.4
69	58	50	38	1.0	10.2	83	72	64	49	0.5	6.5
87	82	76	63	0.3	7.1	85	75	68	54	0.4	7.0
74	58	48	32	1.1	5.1	80	63	51	32	1.0	2.9
83	71	58	41	0.8	4.2	83	67	56	37	0.8	4.1
62	45	35	22	1.9	3.5	62	48	40	27	1.7	6.6
77	64	49	27	1.0	4.7	83	70	61	44	0.7	4.8
66	38	29	17	2.4	2.8	72	57	48	32	1.1	5.6
75	60	42	22	1.2	4.2	82	67	52	26	0.9	3.7
66	56	49	38	1.1	7.0	65	53	45	36	1.3	4.9
73	60	52	38	0.9	7.1	74	58	48	32	1.1	5.0
74	62	55	42	0.8	8.7	75	61	53	38	0.9	6.1
80	70	59	40	0.7	6.1	84	72	63	46	0.6	4.3
73	58	48	32	1.1	5.1	84	70	60	40	1.0	3.3
77	62	50	30	1.0	4.3	84	74	60	33	0.8	3.7
84	71	56	32	0.9	3.7	87	78	65	40	0.7	9.9
77	59	47	28	1.1	4.0	83	72	60	38	0.7	4.5
84	70	56	33	0.8	3.7	83	74	62	39	0.7	4.6
73	54	42	24	1.3	3.9	80	69	58	36	0.8	5.2
75	51	36	16	1.5	3.0	80	68	49	24	1.1	3.7
76	54	39	19	1.4	3.9	82	64	46	20	1.1	3.1
85	70	54	26	0.9	3.2	87	72	57	30	0.9	2.9
91	80	63	28	0.8	2.3	92	80	64	34	0.7	2.4
89	77	58	26	0.9	2.2	91	78	64	35	0.7	2.5
89	78	59	26	0.8	2.5	94	81	66	36	0.7	2.4
69	49	34	17	1.6	3.4	91	76	61	32	0.8	2.7

3. Lundgren Type Mass Distributions. In Figure 6 a summary of typical Lundgren type mass distributions is given, allowing visualization of the discussed size distribution shifts.

In the suburban samples, the maximum of the distribution for most pollutants spreads over 2 fractions between 0.5 and 1.5 µm. In the background stations, this changes into a distribution with a maximum for stage 4 and much less on stage 5, consistent with the shift of the fraction 0.5–1 to 1–1.5 µm as discussed earlier.

Between the suburban and background samples only little variations of the MMED are observed, in contrast to the clear shifts from fraction 0.5–1 to 1–1.5 µm. This is due to the fact that in the suburb the MMED of somewhat less than 1 µm lies about in the middle of fraction 5, and in the background stations, there is a transfer from fraction 5 to 4. Thus, half of the total mass will be found here at somewhat higher particle diameters, whereas this shift also implies an increased distribution width (increased σ_g).

The minor variations in σ_g for the suburban samples throughout the year can be understood with the aid of these figures. The width of the distribution is defined as the ratio of the diameter below which 84% (r_{84}) and 50% (r_{50} or MMED) is found. The suburban distributions always show a very similar pattern of relative abundances for the respirable fractions (<3 µm) and the r_{84} lies in the range of stage 3. Most differences over the year only affect the relative abundances of stage 6 vs. stage 5, and thus cause only minor changes within the shape of the Lundgren distribution (both fractions collect particles in a wide particle size range and the measured concentrations are divided by a relatively important factor). The r_{84} remains essentially constant and the MMED changes only slightly.

In the background stations, σ_g values increase, since the distributions are centered in only one fraction and drop more slowly with increasing particle size than for the suburban samples. This broadening of the distribution in the background areas, as seen in Figure 6, will be reflected in the σ_g values.

Conclusions

In order to fully characterize the differences in aerosol composition between suburban and background samples in a densely industrialized and populated country, it was necessary to supplement pollutant concentration data with size distribution measurements.

Although similar total suspended particulate concentrations (TSP) were found for the suburban and rural stations during the summer, a first indication for a size distribution shift toward higher aerodynamic diameters was detected in the TSP data of size-resolved samples. At the rural station (Botrange), the TSP distribution shifts toward larger particles. Near the seashore, an additional contribution of the fraction 3–7 µm to the total TSP concentration was found, due

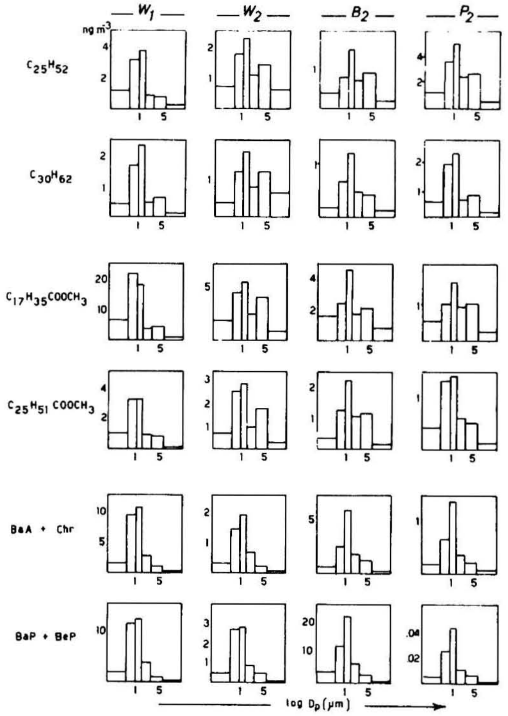


Figure 6. Summary of Lundgren type mass plots for individual compounds

to sand.

The total concentrations of individual pollutants showed the typical alternating pattern for the n-alkanes, probably related to selective volatilization of the even homologues during aerodynamic elution or blow-off from the filter substrate during sampling. Polyaromatic hydrocarbon levels show the well-known seasonal variations in the suburban samples and a further five- to tenfold dilution in the background stations.

To study the size distributions of individual pollutants, three different representations were used: concentration vs. stage number (raw data), cumulative mass distribution, and Lundgren type mass plots. Since each of these graphs has its specific sources of error, conclusions should be based on an integrated interpretation of all these data.

Compared to the suburban site, the background samples showed a depletion for all measured pollutants, in particular in the fraction between 0.5 and 1 μm, which is compensated to some extent by an increase on the next stage (1–1.5 μm). For the compounds with higher vapor pressure, volatilization from the smallest particles could account for a depletion in the submicron fractions. However, a similar distribution shift is also observed for the organic pollutants with negligible vapor pressure such as the higher molecular weight PAHs and carboxylic acids. It is believed that these size distribution shifts are the result of a particle growth process occurring with aging of the aerosol in relatively unpolluted background areas. For most pollutants the MMEDs are considerably lower than those for the TSP, as expected for a condensation aerosol. Also, the Lundgren plots, although less sensitive to variations in particle size distributions involving stages 5 and 6 (<1 μm), support the observation of a shifted distribution.

Acknowledgments

The authors wish to thank Dr. J. F. Van de Vate and coworkers at the Energy Research Center of the Netherlands (E.C.N.), Petten, Netherlands, for taking the seashore samples and the Royal Meteorological Institute (K.M.I.), Ukkel, Belgium, for permitting sampling in their meteorological observation station at Botrange.

Literature Cited

(1) Brown, J. H., Cook, K. M., Hatch, T., *Am. J. Public Health*, **40**, 450 (1950).
(2) Hatch, T., in Proceedings of the Pneumoconiosis Conference, Johannesburg, 1959, p 113.
(3) Van Vaeck, L., Van Cauwenberghe, K., *Atmos. Environ.*, **12**, 2229 (1978).
(4) Van Vaeck, L., Van Cauwenberghe, K., "Quantitative Mass Spectrometry in Life Sciences", Vol. II, Elsevier, New York, 1978, p 466.
(5) Willeke, K., *Am. Ind. Hyg. Assoc. J.*, **36**, 683 (1975).
(6) Rondia, D., *Int. J. Air Water Pollut.*, **9**, 113 (1965).
(7) de Wiest, F., Della Fiorentina, M., *Atmos. Environ.*, **10**, 951 (1975).
(8) Pupp, C., Lao, R. C., Murray, J. J., Pottie, R. F., *Atmos. Environ.*, **8**, 915 (1974).
(9) Van Vaeck, L., Broddin, G., Cautreels, W., Van Cauwenberghe, K., *Sci. Tot. Environ.*, **11**, 41 (1979).
(10) Cautreels, W., Van Cauwenberghe, K., *Atmos. Environ.*, **12**, 1133 (1978).
(11) Van Vaeck, L., Van Cauwenberghe, K., *Anal. Lett.*, **10**, 467 (1977).
(12) Fuchs, N. A., *Atmos. Environ.*, **9**, 697 (1975).
(13) Benarie, M., *Atmos. Environ.*, **11**, 527 (1977).
(14) Dams, R., Heindryckx, R., *Atmos. Environ.*, **7**, 319 (1973).
(15) Lippmann, M., *Am. Ind. Hyg. Assoc. J.*, **31**, 138 (1970).
(16) Lundgren, D. A., Paulus, H. J., *J. Air Pollut. Control Assoc.*, **25**, 1227 (1975).
(17) Natusch, D. F. S., Wallace, J. R., *Science*, **186**, 695 (1974).

Received for review May 22, 1979. Accepted September 4, 1979. The National Foundation for Scientific Research (N.F.W.O.) is thanked for according a grant to L. Van Vaeck as "aspirant-navorser".

Multielement Analysis of Municipal Sewage Sludge Ashes. Absorption of Elements by Cabbage Grown in Sludge Ash–Soil Mixture

A. Keith Furr and Thomas F. Parkinson

Office of Occupational Health and Safety, and Nuclear Reactor Laboratory, Virginia Polytechnic Institute and State University, Blacksburg, Va. 24061

Timothy Wachs

Department of Chemistry, Cornell University, Ithaca, N.Y. 14853

Carl A. Bache, Walter H. Gutenmann, Patricia C. Wszolek, Irene S. Pakkala, and Donald J. Lisk*

Pesticide Residue Laboratory, Department of Food Science, New York State College of Agriculture and Life Sciences, Cornell University, Ithaca, N.Y. 14853

■ An analytical survey of 42 elements and polychlorinated biphenyls (PCBs) was conducted on municipal sewage sludge ashes from 10 American cities. The concentrations of specific elements in the ashes varied widely. Calcium and iron content reflected the addition of lime and ferric chloride during sewage treatment. Elements such as cadmium, mercury, nitrogen, and selenium were low probably because of volatilization losses during incineration. PCBs were not detected in the ash samples. Although the total content of nickel and zinc in the ashes was high, absorption of these elements by cabbage grown on ash-amended soil was surprisingly low, possibly due to their presence in the ashes as insoluble compounds formed during incineration.

The annual production of sewage sludge in the United States presently is in the range of 5 million tons (*1*). Methods of disposal have included discarding in landfills, ocean dumping, incineration, and more recently its use as a soil amendment in horticulture and agriculture. There is much concern presently about elevated concentrations of Cd, Ni, Zn, Cu, Pb, Cr, and other elements in sludges resulting from industrial activities and their possible absorption by crops grown on sludge-amended soils. This area of research has been reviewed (*1, 2*).

Disposal of municipal sludges by incineration produces an odorless, sterile ash comprising from about 30 to 60% of the weight of the original sludge on a dry basis (*3*). Proper disposition of sludge ash thus constitutes an appreciable portion of the nation's total solid waste disposal problem. Farrell and Salotto (*4*) reported the content of 23 elements in sludge ashes from three small American cities, but extensive data have not been published on the elemental composition of municipal sludge ashes or the extent of absorption of elements by crops grown on sludge ash amended soil mixtures. In the work reported, 42 elements and polychlorinated biphenyls (PCBs) were determined in sludge ashes from 10 American cities. Cabbage was then grown in the greenhouse in potted soil amended with these sludge ashes, and the extent of specific elemental absorption by the plants was compared with the total content of the respective elements in the various ashes.

Experimental

In 1976 a description of our proposed study was sent to 16 cities with a request that they participate and return a representative sample of their sludge ash to us for analysis. The cities that responded and the data they provided pertaining to their sludge incineration process are given in Table I. The process may typically include addition of ferric chloride or aluminum sulfate to precipitate phosphates and the addition of polymer as a settling agent for the suspended solids and phosphate floc during primary sedimentation. Addition of lime may also be used to precipitate heavy metals and other solids. The resulting solids are largely dewatered by use of a centrifuge or vacuum filtration. The solids may then be fed into the top of the incinerator where they are further dried, incinerated, and cooled as they progress toward the bottom where the ash collects and is removed by trucking or sluicing. Exhaust scrubbers remove the fly ash, which may then be conveyed back and added (as a filtering aid) to incoming sewage prior to its primary sedimentation. In some cities the sludge that is incinerated is a mixture of dewatered primary and excess activated sludge.

The sludge ashes received were air dried, pulverized in a hammermill containing a 3-mm sieve, mixed by tumbling, and subsampled for analysis. A study was also made to determine if a crop grown on sludge ash amended soil would absorb elements in proportion to their concentration in the ash. The soil used was a Darian gravelly silt loam (fine loamy, mixed, mesic aeric ochraqualfs), pH 5.5, and with a determined cation exchange capacity of 20.8 mequiv/100 g. The soil was air-dried, sifted through a 2-mm screen, and thoroughly mixed. Five percent w/w of the various sludge ashes was mixed with portions of the soil using a cement mixer [or 111.2 metric tons/ha (50 tons/acre)]. For each sewage treatment plant, 7 kg of the respective sludge ash–soil mixture was used to fill each of three 7.6-L plastic pots. The pots were 21 cm i.d. and contained drain holes. Soil alone was used for growth of the control crop. Appropriate quantities of sulfur were mixed with the various sludge ash–soil mixtures so their resultant pH ranged from 5.2 to 5.7. The crop grown was "Golden Acre" cabbage (*Brassica oleracea* var. *capitata*). Cabbage was the crop chosen, since it has been found to be quite resistant to possible phytotoxic constituents in municipal sludge, yet actively absorbs heavy metals (*5*). One cabbage plant was grown to maturity in the greenhouse in each of four pots representing a given sewage treatment plant. The period of growth was from May to September. The plants were fertilized weekly with 1000 mL of a solution containing reagent grade KH_2PO_4 (0.001 M) and KNO_3 (0.005 M) (*6*). All plants were watered daily, care being taken to avoid splashing soil on the aerial portions of the plants.

At maturity the cabbage was harvested with only the edible leaf head portion taken for analysis. Prior to analysis the leaves were rinsed with distilled water to remove adhering dust. The respective replicated cabbage heads grown on sludge ash from a particular treatment plant were combined and subdivided in a food cutter. The plant material was mixed, freeze dried, milled to a powder, again mixed, and subsampled for analysis.

The ash and crop samples were analyzed for 32 elements using nondestructive neutron activation analysis as previously described (*3*). Arsenic was distilled as arsine and determined spectrophotometrically using the silver diethyldithiocarbamate procedure (*7, 8*). Boron was determined by the curcumin colorimetric procedure (*9*). Cadmium, lead, and zinc were determined by conventional stripping voltammetry (*10*).

0013-936X/79/0913-1503$01.00/0

Table I. Data Pertaining to Municipal Sewage Sludge Incinerator Ashes Studied

city	sewage treatment plant	ratio (%) industrial: domestic contribution	dewatering scheme	combustion unit	combustion temp, °C	feed rate, tons/h [a]	additives	ultimate ash disposal method
Dunkirk, N.Y.	Dunkirk Wastewater Treatment Plant	60:40	vacuum filtration	multiple (5) hearth	870	3	ferric chloride, lime	landfill
Grand Rapids, Mich.	Grand Rapids Wastewater Treatment Plant	30:70	vacuum filtration	multiple (7) hearth	up to 980	4	ferric chloride, lime	landfill
Greensboro, N.C.	North Buffalo Sewage Treatment Plant	30:70	vacuum filtration	multiple (5) hearth	870	2.5	polymer	landfill
Hilton, N.Y.	Northwest Quadrant Treatment Plant	2:98	vacuum filtration	multiple (6) hearth	775–870	4	aluminum sulfate	landfill
Indianapolis, Ind.	Dept. of Public Works	70:30	vacuum filtration	multiple (8) hearth	800–1000	5	dry sludge ash	landfill
Kalamazoo, Mich.	City of Kalamazoo Treatment Plant	50:50	vacuum filtration	multiple (7) hearth	775	7	none	landfill
Lorton, Va.	Lower Potomac Treatment Plant	10:90	vacuum filtration	multiple (6) hearth	775–870	5	ferric chloride, lime	landfill
Naugatuck, Conn.	Borough Naugatuck Wastewater Treatment Plant	50:50	vacuum filtration	multiple (7) hearth	775–870	6	ferric chloride, lime, aluminum sulfate, polymer	landfill
Saginaw, Mich.	Saginaw Wastewater Treatment Plant	heavily industrial	vacuum filtration	multiple (6) hearth	870–925	5	ferric chloride, lime	landfill
Youngstown, Ohio	Youngstown Wastewater Treatment Plant	25:79	vacuum filtration	multiple (7) hearth	800	6	ferric chloride, lime	landfill

[a] Moist sludge cake.

Mercury was measured by flameless atomic absorption analysis (*11*). Nickel was analyzed by the furnace atomic absorption method. Phosphorus was measured by the molybdivanadophosphoric acid spectrophotometric procedure (*12*). Selenium was measured by the fluorometric method of Olson (*13*). Nitrogen was assayed by the Kjeldahl method. The determination of pH was done by the method of Peech et al. (*14*). γ emission was measured with a Packard γ scintillation spectrometer equipped with a Model 9012 multichannel analyzer. Total γ radiation in the range of 5–505 keV was integrated and recorded for 10 g of each sample over a period of 1000 s. Relatively little γ radiation was recorded above 505 keV. Analytical precision in repetitive counting of duplicates of the same sample was within ±2%. PCBs were sought as Aroclor 1254 using electron-capture gas chromatography to analyze the supernatant solutions obtained from vigorously shaking 5 g of each ash sample with 25 mL of toluene for 2 h. A Tracor 220 gas chromatograph equipped with a ^{63}Ni detector and a glass column (180 cm × 4 mm i.d.) packed with 3% OV-17 on 100/120 mesh Gas-Chrom Q was used for these analyses. Flow rate through the column was 60 cm^3/min nitrogen and the column temperature was 185 °C. Detector and injector temperatures were 310 and 230 °C, respectively. Results were confirmed for selected ash samples using negative ion electron-capture chemical ionization mass spectrometry. Negative ions were formed by electron capture in a chemical ion source using methane as the reagent gas (*15*). These negative ions were detected using a modification of a conversion dynode system previously described (*16*).

Results and Discussion

The results of analysis of the sludge ashes are given in Table II. The concentrations of specific elements may vary widely depending on their concentration in the initial wastewater, those added during sewage treatment (aluminum, calcium, and iron), and losses during incineration. The calcium and iron contents of the ashes were reflective of the use of lime and ferric chloride in the treatment process (see Table I). Elements such as bromine, chlorine, cadmium, mercury, nitrogen, and selenium were probably lost by vaporization during incineration. Other elements such as barium, chromium, copper, and lead can be lost in small amounts as constituents of particulates in the stack gases (*4, 17*).

In an analytical survey of sludges from American cities conducted earlier (*3*), PCBs were detected in nearly all samples. No evidence was found for the presence of PCBs in the sludge ashes in this study. Farrell and Salotto (*4*) also found PCBs and chlorinated pesticides to be absent in ashes resulting from sludge incineration. As they point out, however, the absence of PCBs may not result entirely from thermal decomposition but also as volatilized condensates on escaping particulates. Others have shown the thermal decomposition of PCBs at elevated temperatures (*18, 19*).

The concentrations of selected toxic and nutrient elements in the cabbage are given in Table III. The errors in these elemental analyses were within ±10%. Whereas elements such as arsenic and lead tend to be excluded by plants, others such as nickel and zinc should expectedly have been absorbed to a much greater extent by the cabbage in the pH range (5.2 to 5.7) of the soil–sludge ash mixture based on the total nickel and zinc contents of the sludge ashes. It is possible that the formation of refractory, insoluble compounds of these elements occurred in the ash during incineration which reduced their equilibrium concentration in the soil solution and, therefore, availability for plant root absorption. Interestingly, elements such as iron, manganese, and lead were higher in the control cabbage than in any grown in the various sludge ashes. It is possible that a portion of these elements present natively in the soil was fixed in unavailable form by the sludge ash and this was reflected by a lower concentration in the cabbages. These observations could be important when considering sludge ash disposal in landfills where rainfall percolating through the landfill may dissolve heavy metals, which may ultimately reach water supplies. Also, the decomposition of

Table II. Element Concentration, pH, and Radioactivity in Sludge Ashes Surveyed

element	parts per million (dry wt) in sludge ash from (see Table I)									
	Dunkirk	Grand Rapids	Greensboro	Hilton	Indianapolis	Kalamazoo	Lorton	Naugatuck	Saginaw	Youngstown
Al	11 220	16 040	54 410	83 810	58 730	103 900	8 815	36 820	24 190	45 590
As	9.5	0.9	1.5	9.3	19	7.5	5.3	22	12	6.1
Au	*a*			3.0	5.0	0.5	1.0	0.4	0.3	7.8
B	48	56	17	40	17	8.4	61	17	40	38
Ba	5 439	295	5401	1 035	2 087	1 043	686	536	634	804
Br	8.1	2.7	1.2	2.9	0.8	0.5	10	5.0	3.7	10
Ca	274 900	273 500	42 390	84 970	102 800	29 800	337 400	203 400	173 900	142 500
Cd	3.8	10.9	22	1.5	31	0.7	1.3	5.6	127	4.8
Ce		77	403	36	160	117	132	73	46	71
Cl	14 610	11 270	563	1 044	1 050	954	29 210	6 365	6 212	6 587
Co	69	8.2	18	9.2	45	16	14	15	16	18
Cr	9 696	3 345	1 949	411	4 777	503	346	468	721	754
Cs	0.4	1.1	1.0	1.3	0.3	1.7	0.2	1.7	1.7	2.5
Cu	2 180	513	1 140	1 225	3 225	525	570	1 990	570	485
Dy	4.3	2.8	7.7	4.6	3.6	7.5	6.4	4.8	5.1	3.8
Eu	0.4	0.2	0.5		1.7	0.9	0.5	0.4	0.6	0.6
Fe	91 450	38 110	36 630	29 950	51 130	17 660	91 720	50 430	57 970	43 320
Hf		1.1	4.7	5.5	5.6	3.0	28	2.6	2.7	4.7
Hg	0.08	0.18	0.06	0.04	0.04	0.04	0.12	0.12	0.04	0.06
K	4 080	2 291	8 037	10 480	12 110	4 017	2 317	4 410	8 199	4 799
La	4.2	22	52	12	39	33	20	12	15	15
Lu					0.3	0.1	0.4	0.3	0.2	0.1
Mg	5 817	14 620	13 100	14 420	16 010	30 000	16 100	6 030	16 100	13 200
Mn	739	555	756	1 019	910	342	3 095	875	1 805	849
Na	1 473	1 671	6 006	5 959	7 217	3 940	846	2 704	2 713	2 185
N	600	1 200	800	800	1 000	600	1 000	800	800	800
Ni	4 200	2 660	350	89	680	55	40	700	209	480
P	10 000	20 000	27 000	65 000	52 000	38 000	34 000	21 000	21 000	37 000
Pb	120	277	559	248	1 333	406	82	156	412	123
Rb	7	5	13	31	73	34	18	44	41	23
Sb	5.5	163	69	8.8	21	15	4.0	11	10	13
Sc	0.9	0.8	4.9	2.2	4.3	6.6	13	2.0	2.5	2.7
Se	0.2	0.2	0.04	0.04	0.04	0.04	0.9	0.1	0.2	0.1
Sm	4.5	6.0	14	10	19	24	9.8	10	10	8.i
Sn	330	87	1 204	1 103	344	1 892	302	1 008	670	1 230
Sr	1 090	1 170	824	4 600	720	7 313	1 006		385	1 690
Ta	0.1	0.3	0.5	1.7	1.8	2.4	14	1.0	0.5	3.8
Ti	1 265	2 945	7 994	2 889	6 814	32 900	5 230	1 912	1 354	1 739
V	211	25	110	23	70	104	387	89	40	50
W	194	16	9.2	4.2	163	33	18	48	28	190
Yb					3.1	1.5	1.4	1.6	0.5	
Zn	700	5 050	740	400	1 070	2 250	1 040	8 000	3 700	1 650
pH	9.8	10.3	9.1	8.4	8.2	6.9	12.2	9.1	8.6	9.9
radioact.[b]	3.9	9.1	6.8	8.2	15.6	11.8	9.8	4.6	6.6	4.5

[a] Absence of data was due to analytical interference which prevented analysis. [b] γ radiation (cpm/g) above background.

Table III. Concentrations of Selected Elements in Cabbage Cultured on Soil Amended with the Various Sludge Ashes

element	parts per million (dry wt) in cabbage grown in soil amended with sludge ash from										
	control[a]	Dunkirk	Grand Rapids	Greensboro	Hilton	Indianapolis	Kalamazoo	Lorton	Naugatuck	Saginaw	Youngstown
As	0.4	0.4	0.4	0.2	0.6	0.2	0.4	0.4	0.6	0.4	0.4
Cd	0.5	0.2	0.2	0.7	0.3	0.7	0.2	0.2	0.1	0.9	0.2
Co	0.8	1.7	0.8	0.9	1.1	1.3	0.8	0.8	1.1	0.8	1.1
Cu	11.6	10.3	16.4	13.9	14.6	19.4	13.0	14.3	8.5	36.6	7.9
Fe	425	353	164	399	221	345	262	220	292	257	250
Mn	118	80	34	61	31	66	42	42	58	60	22
Ni	0.6	0.5	0.6	0.8	0.3	0.7	0.3	0.1	0.2	n.d.[b]	n.d.
Pb	1.4	0.6	0.7	1.0	0.5	0.7	0.5	0.6	0.6	0.6	0.6
Zn	31	18	16	41	13	23	37	12	16	17	12

[a] Soil with no sludge ash added. [b] Not detectable, i.e., less than 0.1 ppm.

PCBs and the loss of some volatile toxic elements during sludge incineration would serve to minimize contamination of leachates when the resulting ash is disposed in landfills.

Acknowledgments

The authors thank L. F. Armitage, H. J. Arnold, H. G. Corneil, J. G. Doss, T. H. Greweling, H. G. Knight, R. D. Lahr, J. H. Martini, R. Sheldrake, L. E. St. John, Jr., and D. R. Van Campen for their assistance during this investigation.

Literature Cited

(1) Cahill, H. P., Jr., "Application of Sewage Sludge to Cropland: Appraisal of Potential Hazards of the Heavy Metals to Plants and Animals", U.S. Environmental Protection Agency Publication No. EPA 430/9-76-013, 1976.
(2) Page, A. L., "Fate and Effects of Trace Elements in Sewage Sludge When Applied to Agricultural Lands", U.S. Environmental Protection Agency Publication No. EPA-670/2-74-005, 1974.
(3) Furr, A. K., Lawrence, A. W., Tong, S. S. C., Grandolfo, M. C., Hofstader, R. A., Bache, C. A., Gutenmann, W. H., Lisk, D. J., *Environ. Sci. Technol.*, **10**, 683 (1976).
(4) Farrell, J. B., Salotto, B. V., *Proc. Natl. Symp. Ultimate Disposal Wastewaters and Their Residuals*, 186–98 (1973).
(5) Babish, J. G., Stoewsand, G. S., Furr, A. K., Parkinson, T. F., Bache, C. A., Gutenmann, W. H., Wszolek, P. C., Lisk, D. J., *J. Agric. Food Chem.*, **27**, 399 (1979).
(6) Hoagland, D. R., Arnon, D. I., "The Water-Culture Method for Growing Plants Without Soil", *Calif. Agric. Exp. Stn. Circ.*, **No. 347** (1938).
(7) Evans, R. J., Bandemer, S. L., *Anal. Chem.*, **26**, 595 (1954).
(8) Fisher Scientific Co., "Reagents of Choice for Arsenic in Parts Per Billion", Technical Data Bulletin TD-142, Nov 1960.
(9) Greweling, H. T., "The Chemical Analysis of Plant Tissue", Mimeo No. 6622, Agronomy Department, Cornell University, Ithaca, N.Y., 1966.
(10) Gajan, R. J., Larry, D., *J. Assoc. Off. Anal. Chem.*, **55**, 727 (1972).
(11) Hatch, W. R., Ott, W. L., *Anal. Chem.*, **40**, 2085 (1968).
(12) Kitson, R. E., Mellon, M. G., *Ind. Eng. Chem., Anal. Ed.*, **16**, 379 (1944).
(13) Olson, E. O., *J. Assoc. Off. Anal. Chem.*, **52**, 627 (1969).
(14) Peech, M., Olsen, R. A., Bolt, G. H., *Soil Sci. Soc. Am. Proc.*, **17**, 214 (1953).
(15) Stafford, G. C., Reeher, J. R., Story, M. S., *Proc. Annu. Conf. Mass Spectrom. Allied Top., 26th*, 459–61 (1978).
(16) Hunt, D. F., Stafford, G. C., Crow, F. W., Russell, J. W., *Anal. Chem.*, **48**, 2098 (1976).
(17) Shen, T. T., *J. Environ. Eng. Div., Am. Soc. Civil Eng.*, **105** (No. EE1), 61–74 (1979).
(18) Ahling, B., Lindskog, A., *Sci. Total Environ.*, **10**, 51 (1978).
(19) Komamiya, K., Morisaki, S., *Environ. Sci. Technol.*, **12**, 1205 (1978).

Received for review June 8, 1979. Accepted September 4, 1979.

Estimating Rate Constants for the Uptake and Clearance of Chemicals by Fish

W. Brock Neely

Environmental Sciences Research, The Dow Chemical Company, Midland, Mich. 48640

■ With the increased need for predicting the movement and distribution of chemicals in an aquatic environment, knowledge of the rate constants governing the uptake and clearance of chemicals in fish is required. In the absence of experimental data, a method is proposed for making reasonable estimations of these two rate constants based on the physiology of the fish and the properties of the chemical. The credibility of the proposal is demonstrated by comparing predicted rate constants with values measured in the laboratory.

Hazard assessment on a chemical is based on the premise that hazard is a function of both the toxicity of the agent and its expected exposure to living organisms. As part of the exposure investigation in an aquatic ecosystem, the rates of uptake and clearance of chemicals from fish (*1, 2*) are important elements. In addition, the kinetic parameters are useful to predict the patterns of bioconcentration in fish resulting from episodic exposure. Without this knowledge, a meaningful analysis is very difficult. Ideally, the rates should be generated from experimental data (*3*). However, there are many times when the experimental information is lacking, and a need still exists to make an evaluation of the accumulation pattern that can be expected in aquatic organisms. It is this situation that will be discussed in the present study. The proposed method is an extension of the work described by Norstrom et al. (*4*) on the bioenergetics of chemical uptake by fish and the work of Neely et al. (*5*) showing the relationship between the octanol–water partition coefficient and bioconcentration in fish.

By combining these two studies it will be demonstrated that it is possible to make a reasonable estimate of the rates at which chemicals move in and out of fish.

The Uptake Model

Norstrom et al. (*4*) developed an uptake model. Essentially this was based on Equation 1:

$$\frac{\mathrm{d}C_{\mathrm{f}}}{\mathrm{d}t} = \frac{EC_{\mathrm{w}}R_{v}}{F} \qquad (1)$$

where E = efficiency of the chemical to transfer across the gill membrane, C_{f}, C_{w} = concentration of chemical in fish and water, R_{v} = volume of water flowing past the gills per unit time, and F = weight of fish.

This equation states that the rate of uptake of a chemical is equal to the efficiency with which the fish extracts the chemical from the volume of water flowing past the gill surface. The rate of uptake of a chemical is also given by Equation 2:

$$\frac{\mathrm{d}C_{\mathrm{f}}}{\mathrm{d}t} = k_1 C_{\mathrm{w}} \qquad (2)$$

where k_1 = rate constant for the uptake of chemicals in units of mL g^{-1} h^{-1} (mL of water (g of fish)$^{-1}$ h^{-1}). Accordingly, if values for E and R_{v} can be estimated, it will be possible to evaluate k_1.

Ventilation Volumetric Rate R_{v}. This parameter is a function of the oxygen concentration in the water and the amount of oxygen required to maintain the respiration rate of the fish. It was found (*4*) that R_{v} is given by Equation 3:

$$R_{v} = \frac{Q}{E_{\mathrm{ox}}C_{\mathrm{ox}}} \qquad (3)$$

where Q = total energy metabolism of the fish (mL of O_2 h^{-1}), E_{ox} = efficiency of oxygen transfer across the gills (this is re-

Table I. Standard (S) and Active (A) Metabolic Rate Coefficients (α) in Units of Milliliters of O_2 Hours^{-1} Gram$^{-0.8}$ for Various Species of Fish at Various Temperatures

	temp, °C									
	5		10		15		20		25	
fish	S	A	S	A	S	A	S	A	S	A
goldfish (*Carassius auratus*)	0.01	0.03	0.03	0.08	0.058	0.166	0.11	0.24	0.17	0.37
yellow perch (*Perca flavescens*)	0.03	0.15	0.05	0.22	0.08	0.29	0.14	0.34	0.22	0.37
Rainbow trout (*Salmo gairdneri*)	0.07		0.14 0.10[a]	(0.4–0.53)[a]	0.21		0.28			
brook trout (*Salvelinus fontinalis*)	0.14		0.20		0.32		0.39			
brown trout (*Salmo trutta*)	0.014	0.15	0.07	0.21	0.11	0.34	0.15	0.43	0.21	0.50
lake trout (*Salvelinus namaycush*)			0.03	0.22	0.08	0.33	0.10	0.33	0.14	0.28

[a] Data taken from Mayer et al. (*8*). Standard metabolism was determined at 11.9 °C. Active metabolism was measured at 9.6 °C. The range was based on the extent of water reuse, the greater the reuse the smaller the coefficient.

lated to the volume of water cleared of oxygen per unit time), and C_{ox} = concentration of oxygen in the water (mL of O_2 (mL of water)$^{-1}$). The total energy metabolism per gram of fish becomes smaller as fish grow. The empirical relation between Q and weight is given in Equation 4:

$$Q = \alpha F^{\gamma} \tag{4}$$

where $\gamma = 0.8$ (*4*), α = metabolic rate coefficient in units of mL of O_2 h^{-1} g$^{-0.8}$, F = weight of fish, and γ = growth exponent for fish.

Lloyd (*6*) estimated a value of 0.75 for E_{ox}, the efficiency with which oxygen is transferred across the gills. It is quite likely that E_{ox} varies with both temperature and the size of the fish; however, for the purposes of the proposed estimation it will be assumed to be a constant.

The metabolic coefficient (α) was obtained from the review by Fry (*7*). In this review, data were tabulated for both standard and active metabolism. Standard metabolism was defined as the resting state or respiration in the absence of any significant feeding. Active metabolism was the state when the fish was vigorously ingesting food under optimal conditions. The active rate of oxygen assimilation was found to be a few multiples of the standard rate. In fact, the greatest augmentation found by Fry (*7*) was about four times the standard rate. This is contrasted to man, where maximum work causes a 20-fold increase in oxygen consumption, and in insects, where the increase may be two orders of magnitude greater than the standard rate. The consequence of this observation (*7*) may be that in fish the respiratory surface rather than the absorptive surface of the digestive tract is the limiting factor in the rate of growth. It was also pointed out (*7*) that fish metabolism fluctuates widely under stimulation; for example, the handling of the fish will cause an increase in the rate that might last for several hours. Other factors that govern the rate of metabolism are the volume of the container where a confined space causes stimulation. On the other hand, some species of fish will be very quiet if they are in groups. Finally, a daily cycle is noticed where activity is higher during the daylight hours. These are but a few of the factors that need to be controlled for reproducible results in fish experiments.

However, the most important variables are temperature and the oxygen concentration in the water. Fry (*7*) presented data for the yellow perch (*Perca flavescens*) that demonstrated that as the oxygen level was lowered from the air saturation level to 4.3 and 3 mg/L, the level of active metabolism was correspondingly lowered until it finally was not sufficient to meet the standard metabolism requirements. Such a reduction obviously led to a lethal condition. From the graphs in this publication (*7*) the data in Table I were constructed. In order to make the conversion from mL of O_2 kg^{-1} h^{-1} (Fry's units) to mL of O_2 g$^{-0.8}$ h^{-1} (Norstrom's units), the following consideration must be understood. Fry based his results on a model where metabolic rate was a linear function of weight. As indicated in Equation 4, a better fit is obtained with an exponential model. The two models are similar when the weight of the fish is identical. Since most of the data reported by Fry were for a 5-g fish, the conversion to mL of O_2 g$^{-0.8}$ h^{-1} can only be made at that point. An illustration will make this clear. Fry (*7*) cites a value of 165 mL of O_2 kg^{-1} h^{-1} at 25 °C for a 5-g yellow perch (*Perca flavescens*). This is equivalent to (165/200) in units of (mL of O_2 (5 g fish)$^{-1}$ h^{-1}) or [165/(200 $\times$ 5$^{0.8}$)] in units of (mL of O_2 g$^{-0.8}$ h^{-1}). All of the data shown in Table I were calculated in a similar manner. The one exception is the values for rainbow trout that were based on the work of Mayer and Kramer (*8*). In this case the study was performed on trout that were in the weight range of 86–188 g. Mayer assumed a linear relation between weight and oxygen consumption and reported the latter in units of mg of O_2 (kg of fish)$^{-1}$ h^{-1}. Converting the mg of O_2 to mL of O_2 at the reported temperatures by means of the gas equation 5:

$$Q_2(\text{mL}) = \frac{Q_2(\text{g}) \times 82 \times \text{K}}{32} \tag{5}$$

(where K = absolute temperature, 82 = gas constant in units of mL atoms deg^{-1} mol^{-1}, and 32 = molecular weight of oxygen), and making the translation to Norstrom's units at a fish weight of 5 g, the values shown in Table I for rainbow trout were derived. The range for active metabolism was a function of the number of water reuses that were conducted with α decreasing as the frequency of water reuse increased. Thus, if the metabolic rate coefficient (α) is known, along with the oxygen concentration in the water and the weight of fish, then the ventilation volumetric rate (R_v) can be estimated from Equation 3.

The Efficiency Transfer Coefficient *E*. Once R_v has been estimated, it is necessary to have a value of E, the efficiency with which a chemical moves across the gill membrane. The process of transfer is most easily visualized as a partitioning phenomenon; hence the octanol–water partition coefficient (K_{oc}) is a likely candidate for testing the hypothesis that a relation exists between these two parameters, K_{ow} and E.

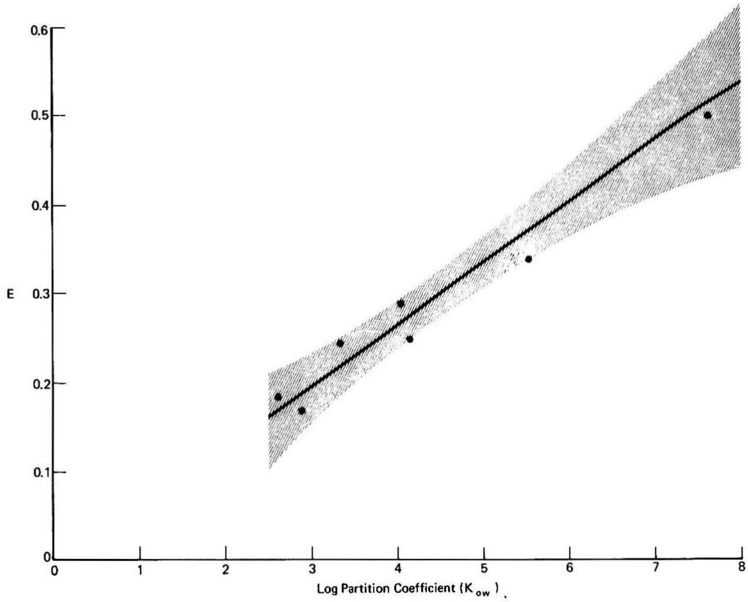


Figure 1. Relation between the efficiency of transfer (E) and the logarithm of the partition coefficient. The curved lines represent the 95% confidence region around the regression line

The data in Table II taken from Neely et al. (*5*) will be used to test the hypothesis. These data show the experimental rate of uptake of various chemicals by rainbow trout (*Salmo gairdneri*) at 10–12 °C. The weight of fish in these experiments was 9 g. The E values for the various chemicals were estimated by combining Equations 1 and 2 as shown in Equation 6:

$$E = \frac{k_1 F}{R_v} \tag{6}$$

In order to use Equation 6, the ventilation volumetric rate constant was determined as described in the previous section.

The oxygen concentration for the data in Table II was not reported. Since a flowing Lake Huron water supply was used in the reported experiments (*5*), the water was assumed to be saturated, and the oxygen concentration was estimated with Equation 7, Norstrom et al. (*4*):

$$C_{ox} = 14.45 - 0.413T + 0.00556T^2 \tag{7}$$

where T = °C between 0 and 25 °C and C_{ox} = oxygen concentration, mg of O_2 L^{-1} (ppm). This yields a value of 10.8 ppm. Combining Equations 5, 6, and 3 yields Equation 8 for estimating E for the various chemicals in Table II:

$$E = \frac{k_1 F \times 0.75 \times 82 \times T(\mathrm{K}) \times \text{mg of } O_2\ L^{-1} \times 10^{-6}}{\alpha F^{0.8} \times 32} \tag{8}$$

where α at 10 °C for standard metabolism = 0.14 and for active metabolism = 0.53 (the high value was chosen since a flowing water system was used where the reuse was zero), F = weight of fish (9 g), T = 283 K, and oxygen concentration = 10.8 mg L^{-1}.

The previously stated hypothesis was tested by plotting the average value of E between active and standard metabolism against the logarithm of the partition coefficient for the various chemicals in Table II as shown in Figure 1. The regression equation for these data is given in Equation 9:

$$E = 0.07 \log K_{ow} - 0.02 \tag{9}$$

The multiple correlation coefficient is 0.94 and the standard error above the regression line is 0.034. Figure 1 shows the 95% confidence line around the regression line for estimating E from the mean value for the partition coefficient. Knowing the values for the partition coefficient and R_v, a value for k_1 may be determined from Equation 10:

$$k_1 = \frac{(0.07 \log K_{ow} - 0.02) \times R_v}{F} \tag{10}$$

The variation in k_1 with both temperature and weight of fish is shown in Tables III and IV and shown graphically in Figure 2. For purposes of this comparison, the active metabolic data for yellow perch given in Table I were used for the various temperatures.

The Clearance Model

The bioconcentration factor for a neutral organic molecule in an aquatic organism by definition is the ratio of the two rate constants defining uptake and clearance as shown in Equation 11:

$$\mathrm{BCF} = k_1/k_2 \tag{11}$$

where BCF = bioconcentration factor and k_1, k_2 = rate constants for uptake and clearance of chemical by fish. Accordingly, if k_1 and BCF are known, a value for k_2 may be estimated.

If the actual BCF is not known, there are a number of correlation equations that have been established relating BCF to either the octanol–water partition coefficient or the water solubility of the chemical. These are shown in Equations 12–14:

$$\log \mathrm{BCF} = 0.76 \log K_{ow} - 0.23 \tag{12}$$

$$\log \mathrm{BCF} = 0.542 \log K_{ow} + 0.124 \tag{13}$$

$$\log \mathrm{BCF} = -0.508 \log S + 3.41 \tag{14}$$

where K_{ow} = parition coefficient between octanol and water and S = water solubility in μmol L^{-1}. Equation 12 was derived

Table II. Data for Establishing a Relationship between the Rate Constant for Uptake and the Efficiency of Chemical Transfer across the Gill Membrane of Trout at 10 °C

chemical	k_1, mL g^{-1} h^{-1}	log K_{ow} [a]	E [b] standard	E [b] active
tetrachloroethylene	3.24	2.88	0.21	0.05
carbon tetrachloride	4.05	2.64	0.26	0.07
p-dichlorobenzene	5.67	3.38	0.37	0.10
diphenyl oxide	5.50	4.20	0.36	0.10
diphenyl	6.79	4.09	0.44	0.12
2-biphenylyl phenyl ethers	8.06	5.55	0.52	0.14
tetrachlorobiphenyl	12.2	7.62	0.79	0.21

[a] Log K_{ow} = log of the partition coefficient between octanol and water. [b] Efficiency of transfer of chemical across the gill membrane during active and standard metabolism calculated from Equation 8.

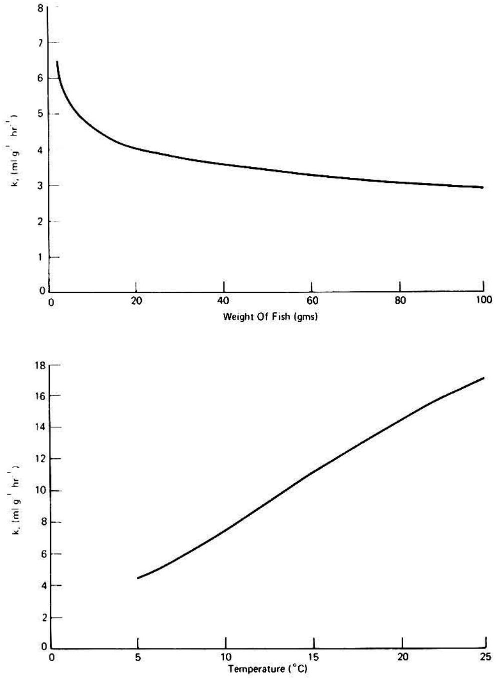


Figure 2. The relation between temperature and weight of fish with k_1, the rate constant for uptake. The data for yellow perch were used for the fish. In the lower diagram a constant weight of fish was used (1 g)

by Veith et al. (*9*) and represented the BCF as measured for whole fish. Equation 13 (*5*) was established on the basis of fish muscle as was Equation 14 (*10*). Consequently, in the absence of an experimental BCF, it is proposed that k_2 be estimated from the relation shown in Equation 15:

$$\log k_2 = \log k_1 - (a \log A + b) \qquad (15)$$

where $A = K_{ow}$ or S. The constants a and b are the appropriate values from Equations 12, 13, and 14. The selection is made on the basis of the type of experiment that is contemplated and the data available, i.e., is clearance being measured from whole fish or the muscle, and is water solubility or the partition coefficient being used for the estimation?

Table III. Rate Constant for Uptake in Yellow Perch as a Function of Weight [a]

wt of fish, g	k_1, mL g^{-1} h^{-1} [b]	wt of fish, g	k_1, mL g^{-1} h^{-1} [b]
2	6.47	50	3.40
10	4.69	100	2.96
25	3.91		

[a] A constant temperature of 10 °C was used and an E value of 0.20 for the chemical was assumed. [b] $k_1 = (E\alpha F^{0.8} \times 32)/[F \times 0.75 \times 82 \times T \times (\text{ppm of } O_2) \times 10^{-6}]$, where $E = 0.20$ and $\alpha = 0.22$ for yellow perch at 10 °C.

Table IV. Rate Constant for Uptake in Yellow Perch as a Function of Temperature [a]

temp, °C	ppm of O_2 [b]	α [c]	k_1, mL^{-1} g^{-1} h^{-1}
5	12.51	0.15	4.49
10	10.88	0.22	7.44
15	9.51	0.29	11.02
20	8.41	0.34	14.36
25	7.60	0.37	17.00

[a] A constant weight of fish of 1 g was used, and an E value of 0.20 for the chemical was assumed. [b] Estimated from Equation 7. [c] Active metabolism for yellow perch from Table I.

Test of the Model

Di-2-ethylhexyl Phthalate (DEHP). Mayer (*11*) investigated the residue dynamics of DEHP in fathead minnows (*Pimephales promelas*) at 25 °C. Unfortunately, the metabolic activity for this particular species is unknown. For our purposes it will be assumed that fathead minnows are similar to perch and goldfish from a bioenergetic point of view. Since the fish were actively growing, it will be further assumed that the metabolic coefficient is between the standard and active values (*4*) reported in Table I for these two species. Accordingly, a value of 0.27 was chosen for α. The average weight of fish used in the experiments was 1.24 g, and the oxygen concentration was estimated from Equation 7 (7.6 ppm). Substituting these values into Equation 3, the ventilation volumetric rate has a value of 73 mL of water h^{-1}. The log of the partition coefficient of DEHP is approximately 4 (*12*). The rate constant k_1 for uptake is then estimated from Equation 10 and has a value of 15.3 mL g^{-1} h^{-1}. The experimental number was 3.21 ± 0.3 mL g^{-1} h^{-1} (*13*).

The clearance rate constant was estimated for whole fish using Equation 15 with the constants developed in Equation 12. Using the appropriate numbers, a value of 2.37×10^{-2} h^{-1} is estimated for the clearance rate constant, which may be compared to the experimental number of 3.79×10^{-3} h^{-1} (*13*).

It is interesting to note that the calculated uptake and clearance constants are faster than what was observed; however, the bioconcentration factor (i.e., the ratio of k_1/k_2) is almost identical, 646 compared to the experimental value of 850 (*13*). The discrepancy between calculated and experimental rate constants may be due to several things: the assumption that fathead minnows are metabolically similar to perch and goldfish may be wrong, and DEHP may be metabolized by the fish.

Chlorpyrifos. Smith et al. (*14*) studied the uptake and movement of chlorpyrifos in an aquarium using goldfish (*Carassius auratus*) at 25 °C. The oxygen concentration was estimated as 7.6 ppm (5.8×10^{-3} mL of O_2 (mL water)$^{-1}$). Since the fish were being continually stimulated, it was assumed that the metabolic coefficient α would be 0.37 for active metabolism (Table I). The average weight of the fish used in the study was 1.2 g. Substituting into Equation 3, the ventilation volumetric rate has a value of 111 mL of water h^{-1}. The logarithm of the partition coefficient for chlorpyrifos is 4.6 (*15*). The uptake rate constant k_1 is then estimated from Equation 10 to be 28 mL g^{-1} h^{-1}. Experimentally, a value of 55 mL g^{-1} h^{-1} was determined (*2, 15*).

The clearance rate constant was estimated in a manner similar to that described for DEHP. A value of 1.5×10^{-2} h^{-1} for k_2 was derived from using Equations 12 and 15. The experimental value of 7.8×10^{-2} h^{-1} was much faster (*2*). This is probably related to the observation that the experimental number reflects not only the clearance of chlorpyrifos itself, but also the rate of metabolism and the clearance of the metabolite (a pyridinol derivative) (*14*), which is more water soluble and therefore more rapidly cleared than the parent material.

2,3,7,8-Tetrachlorodibenzo-*p*-dioxin (TCDD). In an effort to learn more about the movement and distribution of TCDD in an aquatic environment, experiments have been performed on the uptake and clearance of this chemical in fish (*16*).

Thirteen rainbow trout each weighing 35 g were placed in an aquarium containing 145 L of water. The aquarium was sealed in such a manner that the head space was negligible. For a period of 2 h the oxygen concentration was measured using a calibrated probe. During this time period the dissolved oxygen dropped from 9.0 mg h^{-1} to 6.6 mg h^{-1} for an estimated oxygen consumption of 174 mg of O_2 for the 455 g of trout in 1 h.

The metabolic coefficient (α) was determined by converting the 174 mg of O_2 to mL of O_2 using Equation 6 and a temperature of 13 °C (*16*). The conversion to mL of O_2 $g^{-0.8}$ h^{-1} was carried out as described in the text and generated a value for α of 0.39.

The value of 0.18 was assigned to α for standard metabolism for rainbow trout at 13 °C based on interpolation of the data in Table I between 10 and 15 °C. The experimental value of 0.39 would imply that the trout in the experiments were in a semiactive condition, which is not unreasonable considering the test conditions, i.e., starved for only 1 day prior to the experiment (*16*). However, by the time the trout had been placed in the aquarium to measure the uptake of TCDD, a further period of starvation had ensued. Accordingly, for purposes of estimating k_1, a value of α equal to 0.18 will be used.

In the uptake experiment (*15*), rainbow trout weighing 35 g were exposed at 13 °C where the oxygen concentration was 10.5 ppm (7.98×10^{-3} mL of O_2 (mL of water)$^{-1}$). The water solubility and the logarithm of the partition coefficient of TCDD were determined to be 200 ppt and 6.19, respectively (*16*).

A ventilation volumetric rate of 535 mL of water h^{-1} was estimated from Equation 3. The rate of uptake (k_1) was determined to be 6.3 mL g^{-1} h^{-1} (Equation 10). Experimentally, a value of 4.54 mL g^{-1} h^{-1} was found (*16*).

The clearance rate constant was determined experimentally on whole fish (*16*). Hence, Equations 12 and 15 will be used for estimating k_2. A value of 2.12×10^{-4} h^{-1} was derived by this method, which should be compared to the experimental number of 5×10^{-4} h^{-1} (*16*).

Summary

The proposed method has the ability for generating reasonable values for the rate constants controlling the uptake and clearance of neutral organic molecules by fish. The approach takes into account both the physiological characteristics of the fish and the properties of the chemical. In addition, the analysis indicates those parameters that need to be measured and considered when translating laboratory generated data to a real world situation.

Literature Cited

(1) Neely, W. B., *Int. J. Environ. Studies*, **13,** 101 (1979).
(2) Blau, G. E., Neely, W. B., *Adv. Ecol. Res.*, **9,** 133 (1975).
(3) Branson, D. R., Blau, G. E., Alexander, H. C., Neely, W. B., *Trans. Am. Fish. Soc.*, **104,** 785 (1975).
(4) Norstrom, R. J., McKinnon, A. E., DeFreitas, A. S. W., *J. Fish. Res. Board Can.*, **33,** 248 (1976).
(5) Neely, W. B., Branson, D. R., Blau, G. E., *Environ. Sci. Technol.*, **8,** 1113 (1974).
(6) Lloyd, R., *J. Exp. Biol.*, **38,** 447 (1961).
(7) Fry, F. E. J., "The Physiology of Fishes", Brown, M. E., Ed., Vol. 1, Academic Press, New York, 1957.
(8) Mayer, F. L., Kramer, R. H., *Prog. Fish-Cult.*, **35,** 9 (1973).
(9) Veith, G. D., Macek, K. J., Petrocelli, S. R., Carroll, J., *Fed. Regist.*, 15926 (March 15, 1979).
(10) Chiou, C. T., Freed, V. H., Schmedding, D. W., Kohnert, R. L., *Environ. Sci. Technol.*, **11,** 475 (1977).
(11) Mayer, F. L., *J. Fish. Res. Board Can.*, **33,** 2610 (1976).
(12) Takahashi, I., The Dow Chemical Co., Midland, Mich., 1977, unpublished data.
(13) Branson, D. R., Blau, G. E., Mayer, F. L., paper presented at the 91st Association of Official Analytical Chemists, Washington, D.C., Oct 17–20, 1977.
(14) Smith, G. N., Watson, B. S., Fisher, F. S., *J. Econ. Entomol.*, **59,** 1464 (1966).
(15) Neely, W. B., Blau, G. E., "Pesticides in the Aquatic Environments", Khan, M. A. Q., Ed., Plenum Publishers, New York, 1977, p 145.
(16) Branson, D. R., Takahashi, I., Parker, W. M., The Dow Chemical Co., Midland, Mich., 1979, unpublished data.

Received for review June 15, 1979. Accepted September 4, 1979. This paper is Dow Chemical Co. No. B-600-176-79.

Prediction of Removal of Vapors from Air by Adsorption on Activated Carbon

Eric B. Sansone*, Yadu B. Tewari, and Leonard A. Jonas

Environmental Control and Research Laboratory, Frederick Cancer Research Center, Frederick, Md. 21701

■ Carbon granules, packed to a reproducible bulk density in beds of uniform cross-sectional area, were subjected to constant inlet vapor concentrations, volume flow rate, and temperature. The breakthrough time of the vapor from the bed (t_b), at an exit concentration equal to 1% of the inlet concentration, was determined for several bed weights (W). Using carbon tetrachloride as the reference vapor, removal performance of the carbon was determined from the adsorption capacity (W_e) and adsorption rate constant (k_v) for the vapor, as calculated from the straight line curves obtained when t_b was plotted vs. W. From these properties, the kinetic adsorption equations for chloroform, benzene, *p*-dioxane, 1,2-dichloroethane, *sec*-butylamine, chlorobenzene, and acrylonitrile were predicted. Comparisons of predicted with experimental parameters revealed variations of from −1.8 to +7.7% for W_e and from −12.9 to +14.4% for k_v. This technique yields reliable predictions of the adsorption behavior of carcinogenic, or otherwise toxic vapors, on carbons.

Use of activated carbons for the removal of vapor phase potentially hazardous materials in air streams, e.g., in hood exhaust systems and respirator cartridges, raises an important risk-benefit problem: if the carbon is disposed of or regenerated too soon, the full benefit of the system is not realized; if its capacity is exceeded, risk to personnel and/or the environment may ensue. It is, of course, possible to test the capacity of a carbon for a particular adsorbate; however, not only does this require special equipment and precautions, but also it is hardly practical in view of the multitude of candidate adsorbates. In this paper, it is demonstrated that the adsorption capacity and the adsorption rate constant of a carbon for an adsorbate can be predicted using current adsorption theory and the data obtained from characterization of the carbon with a reference adsorbate. With this information it is possible accurately to predict the capacity of an activated carbon for a particular adsorbate.

Adsorption Model

Physical adsorption has been considered to be second order in kinetics, involving the reaction between an active site and a free vapor molecule (*1*, *2*). However, it has been shown (*3*) that the sigmoid curve, resulting from a plot of vapor concentration exiting a packed bed of activated carbon granules vs. time, exhibits second-order kinetics only in the linear or mid-portion of the curve where the exit concentration rises rapidly with time. The first portion of the sigmoid curve, with low concentrations of vapor penetrating the bed, is convex to the time axis; this portion of the curve represents an excess of active sites over free vapor molecules and displays pseudo-first-order kinetics with respect to vapor molecules. Analogously, the final portion of the curve, where the number of vacant sites is rapidly being depleted, and which is concave to the time axis, represents an excess of free vapor molecules over active sites, and therefore displays pseudo-first-order kinetics with respect to active sites. This study deals only with the adsorption characteristics of the carbon bed at low gas penetrations (≤1%), and is therefore characterized by pseudo-first-order kinetics with respect to gas molecules.

Kinetic Adsorption

The kinetic equation, applicable to the study of vapor adsorption by beds of activated carbon under dynamic flow conditions, was originally derived by Wheeler (*4*) from a continuity equation of mass balance between the vapor entering an adsorbent bed and the sum of the vapor adsorbed by plus that penetrating the bed. The Wheeler equation can be written (*5*):

$$t_b = (W_e/C_0Q)[W - \rho_B Q \ln (C_0/C_x)/k_v] \qquad (1)$$

where t_b = the vapor breakthrough time (min) at which the concentration C_x (g/cm^3) appears in the exit stream, C_0 = the inlet concentration (g/cm^3), Q = the volumetric flow rate (cm^3/min), ρ_B = the bulk density of the packed bed (g/cm^3), W = the absorbent weight (g), W_e = the kinetic adsorption capacity (g/g) at the arbitrarily chosen ratio of C_x/C_0, and k_v = the pseudo-first-order adsorption rate constant (min^{-1}). In Equation 1 the parameters C_0, C_x, and Q are set by the conditions of test, and ρ_B is measured. When breakthrough time (t_b) is plotted vs. carbon weight (W), a straight-line curve results, from whose slope and x-axis intercept the properties W_e and k_v can be calculated, respectively.

Equilibrium Adsorption

The Dubinin–Radushkevich (D–R) equation (*6*):

$$W_v = W_0 \exp[-B(T/\beta)^2 \log^2 (P_0/P)] \qquad (2)$$

describes the adsorption properties of fine-grained activated carbons for vapors under equilibrium conditions. W_v = the volume of condensed adsorbate (cm^3/g), W_0 = the maximum space available for condensed adsorbate (cm^3/g), P = the equilibrium pressure (atm) of the adsorbate vapor at T (K), P_0 = the saturated vapor pressure (atm) of liquid adsorbate at T, B = the structural constant of the adsorbent (K^{-2}), and β = the affinity coefficient (unitless), which compares the strength of the adsorptive interaction of the adsorbate to some reference adsorbate.

By taking the logarithm of both sides of Equation 2 and by setting:

$$B = (2.303)^2R^2k \qquad (3)$$

and

$$\epsilon = RT \ln (P_0/P) \qquad (4)$$

the D–R equation can be written:

$$\ln (W_v) = \ln (W_0) - k\epsilon^2/\beta^2 \qquad (5)$$

where R = the gas constant (1.987 cal/(mol·K)), k = a constant of the adsorbent (cal/mol)$^{-2}$, and ϵ = the adsorption potential (cal/mol). The affinity coefficient β can be obtained (*7*) from the ratio of the electronic polarization (P_e) of the test adsorbate to that of the reference adsorbate. P_e is related to n, the refractive index determined at the sodium D wavelength, by:

$$P_e = \frac{n^2 - 1}{n^2 + 2}(M/d_l) \qquad (6)$$

where M = the molecular weight (g/mol) and d_l = the liquid density (g/cm^3).

By characterizing an adsorbent with a reference adsorbate, setting β equal to unity, and calculating the parameters B and W_0 from Equation 2 or k and W_0 from Equation 5, the adsorption space W_v can be calculated for untested vapors from

0013-936X/79/0913-1511$01.00/0 © 1979 American Chemical Society

the above equations. To convert W_v (cm^3/g) to adsorption capacity (g/g), the concept of volume pore filling (*8*), wherein the adsorbed gas condenses to a liquid and fills the adsorption space of the micropore, can be used:

$$W_e = W_v d_l \tag{7}$$

where d_l is the liquid density of the condensed test gas.

It has been shown (*9*) that the adsorption capacity determined under kinetic conditions in a well-packed bed of carbon granules closely approximated that calculated under equilibrium conditions from the D–R equations. The only constraint was that the carbon had first to be characterized with a reference vapor before the equilibrium relationships could be used to calculate the carbon's adsorption capacity for other vapors.

Adsorption Rate Constant

The adsorption rate constant k_v has been found to be a function of temperature, linear flow velocity, adsorbent grain size, and the molecular weight of the adsorbate vapor (*10–12*). In this study, however, temperature, flow velocity, and adsorbent grain size were held constant. The only variable that affected k_v was the molecular weight of the vapors under test. After characterization of the carbon with the reference vapor, the rate constants for other vapors were predicted from the relationship (*12*):

$$(k_v M^{1/2})_i = (k_v M^{1/2})_{\text{ref}} \tag{8}$$

where ref indicates the reference vapor (i.e., carbon tetrachloride) and i is a test vapor.

Experimental

Materials. The vapors used in this study were: carbon tetrachloride, 99+%, Baker Chemical Co., Phillipsburg, N.J.; chloroform and benzene, Fisher certified, Fisher Chemical Co., Waltham, Mass.; *p*-dioxane and acrylonitrile, 99+%, and *sec*-butylamine, chlorobenzene, and 1,2-dichloroethane, 99%, Aldrich Chemical Co., Milwaukee, Wis.

The activated carbon adsorbent used was 6–10 mesh, BC-AC Lot 0993 granular carbon from Barnebey-Cheney Co., Columbus, Ohio. The mean diameter of the carbon granules was 0.268 cm.

Equipment. The kinetic adsorption tests were carried out on a vapor adsorption test apparatus connected with standard taper and ball and socket joints. The apparatus had three functional sections, one for vapor generation, another for vapor adsorption by the carbon, and the third for the detection of vapor penetration of the carbon bed. The apparatus has been described in detail (*3*).

The vapor penetrating the bed was passed into the 0.29-cm^3 gas sampling value of an HP 5830A gas chromatograph, then into the chromatographic column, and finally into the flame ionization detector. The response was recorded on an HP 18850A terminal. The column consisted of 4 ft of 1/8 in. (o.d.) stainless steel tubing packed with 3% silicone SE 30 on a Chromosorb W HP, 80–100 mesh support for use with the vapors of carbon tetrachloride, chloroform, benzene, chlorobenzene, and 1,2-dichloroethane. For *p*-dioxane the column consisted of 6 ft of 1/8 in. (o.d.) stainless steel tubing packed with 5% silicone DV 225 on a Chromosorb W HP, 100–120 mesh support. For *sec*-butylamine the column consisted of 6 ft of 1/8 in. (o.d.) copper tubing packed with 5% Carbowax 20M on a Chromosorb W HP, 80–100 mesh support. For acrylonitrile the column consisted of 6 ft of 1/8 in. (o.d.) copper tubing packed with 5% DEGS on a Chromosorb W HP, 80–100 mesh support.

Procedure. The air-flow rates of the apparatus were calibrated by a wet test meter. The adsorbate vapor was generated by the controlled passage of dried nitrogen over the liquid surface; the desired vapor concentration was obtained by diluting the vapor-laden nitrogen with an auxiliary source of dried nitrogen. Nitrogen was dried by passage through deep-bed columns of Drierite. A flow of 350 cm^3/min of the vapor–nitrogen mixture was directed into the reservoir of the apparatus, and samples were analyzed until the desired vapor concentration was obtained.

Table I. Coefficients of the Regression Equation $t_b = a + bW$, and the Correlation Coefficient of the Data, r

vapor	*a*	*b*	*r*
CCl_4	−27.41	31.78	0.987
chloroform	−19.29	23.73	0.989
benzene	−24.17	41.55	0.992
p-dioxane	−61.13	104.48	0.981
sec-butylamine	−13.58	19.90	0.987
1,2-dichloroethane	−36.24	59.88	0.982
chlorobenzene	−69.16	87.19	0.982
acrylonitrile	−33.10	60.49	0.992

The activated carbon was oven dried at 120 °C and stored in a desiccator until used. Adsorbent beds were prepared by gravity settling of the carbon granules in cylindrical glass sample holders (this procedure yielded uniform bulk densities). Eight to ten different adsorbent bed weights, ranging from 1 to 2.5 g, were exposed to the established vapor concentration drawn into the carbon bed at a volumetric flow rate of 285 cm^3/min, corresponding to a superficial linear velocity of 323 cm/min, at 23 °C. The inlet vapor concentrations represented a relative pressure (23 °C) of 0.0936 for carbon tetrachloride, chloroform, *p*-dioxane, benzene, *sec*-butylamine, and acrylonitrile. The relative pressure was 0.3448 for chlorobenzene. (The relative pressures were calculated assuming ideal gas behavior for each vapor.)

The exit air stream from the carbon bed was monitored continually by passage into a gas sampling valve. The breakthrough time t_b was the time in minutes when the exit stream vapor concentration was 1% of the inlet concentration (C_x/C_0 = 0.01).

Results and Discussion

Experimental values of gas breakthrough time t_b as a function of carbon bed weight W for the vapors tested were obtained. These data were subjected to linear regression analysis in the form of the polynominal $t_b = a + bW$. The results of these analyses, a and b, and the correlation coefficients of the data are shown in Table I. An examination of Equation 1 will show that:

$$a = -W_e \rho_B \ln (C_0/C_x)/C_0 k_v \tag{9}$$

$$b = W_e/C_0 Q \tag{10}$$

From the known values of C_0 and Q, the kinetic adsorption capacity, W_e, can be determined from Equation 10. With this value of W_e and the known values of ρ_B, C_0, and C_x, the pseudo-first-order adsorption rate constant can be determined from Equation 9. By setting $t_b = 0$ in the regression equations of Table I, and solving for W, the values for W_c, the critical weight of the carbon bed, were obtained, since $W = W_c$ when $t_b = 0$ and the inlet concentration is instantaneously reduced to the exit concentration by the carbon bed.

Considering carbon tetrachloride as the primary reference vapor, it was possible to calculate the adsorption capacity for vapors after initial characterization of the carbon, by using the set of equations 2 through 7. The characteristic properties of the BC-AC Lot 0993 activated carbon, derived from Equation 5, were a maximum adsorption space W_0 of 0.481

Table II. Comparison of Experimentally Determined with Calculated Adsorption Parameters

vapor	adsorption capacity, W_e (g/g) expti	calcd	% dev	adsorption rate constant, k_v (min^{-1}) expti	calcd	% dev
CCl_4	0.741			735		
chloroform	0.728	0.693	+5.1	780	834	−6.5
benzene	0.404	0.409	−1.2	1029	1031	−0.2
p-dioxane	0.476	0.483	−1.4	1083	971	+11.5
sec-butylamine	0.331	0.337	−1.8	928	1066	−12.9
1,2-dichloroethane	0.616	0.583	+5.7	1048	916	+14.4
chlorobenzene	0.545	0.527	−3.4	799	859	−7.0
acrylonitrile	0.404	0.375	+7.7	1160	1251	−7.3

cm^3/g and a structural constant k of 1.5×10^{-8} (cal/mol)$^{-2}$. Thus, at a relative pressure, P/P_0, of 0.0936 the adsorption space W_v was 0.467 cm^3/g, and at a P/P_0 of 0.3448, W_v was 0.478 cm^3/g.

Values for the kinetic adsorption capacity W_e were calculated for the various vapors by using Equation 7, inserting into it the known liquid densities and the W_v value for the relative pressure used in the test. Comparisons of experimental and calculated adsorption capacity values for the various vapors are shown in Table II. The experimental values deviated from those calculated over a range of from −1.8 to +7.7%, with a mean deviation of 3.8%.

Values for the adsorption rate constant k_v were calculated for the various vapors by using Equation 8, inserting into it the square root of the known molecular weight for the vapor. Comparisons of experimental and calculated adsorption rate constant values are also shown in Table II. The experimental values deviated from those calculated over a range of from −12.9 to +14.4%, with a mean deviation of 8.5%.

In summary, we have characterized a Barnebey-Cheney activated carbon using carbon tetrachloride as the reference vapor. Using these data, and applying the theories detailed above, the two basic adsorption parameters of the carbon were obtained. From these basic parameters the expected adsorption behavior of the carbon for seven other vapors was predicted. The mean deviation of the experimental from the predicted values was 8.5%. Insertion of the predicted values into the Wheeler adsorption equation (Equation 1) provides an estimate of the length of time an adsorbent can be expected to operate effectively in removing contaminant vapors from an air stream. On the basis of these results, we believe that the methodology described can be extended to other activated carbons and other vapors.

Literature Cited

(1) Hiester, N. K., Vermeulen, T., *Chem. Eng. Progr.*, **48**, 505–16 (1952).
(2) Masamune, S., Smith, J. M., *AIChE J.*, **10**, 246–52 (1964).
(3) Jonas, L. A., Svirbely, W. J., *J. Catal.*, **24**, 446–59 (1972).
(4) Wheeler, A., Robell, A. J., *J. Catal.*, **13**, 299–305 (1969).
(5) Jonas, L. A., Rehrmann, J. A., *Carbon*, **10**, 657–63 (1972).
(6) Dubinin, M. M., *Prog. Surf. Membr. Sci.*, **9**, 1–70 (1975).
(7) Reucroft, P. J., Simpson, W. J., Jonas, L. A., *J. Phys. Chem.*, **75**, 3526–31 (1971).
(8) Bering, B. P., Dubinin, M. M., Serpinsky, V. V., *J. Colloid Interface Sci.*, **21**, 378–93 (1966).
(9) Jonas, L. A., Rehrmann, J. A., *Carbon*, **11**, 59–64 (1973).
(10) Jonas, L. A., Boardway, J. C., Meseke, E. L., *J. Colloid Interface Sci.*, **50** (3), 538–44 (1975).
(11) Rehrmann, J. A., Jonas, L. A., *Carbon*, **16**, 47–51 (1978).
(12) Jonas, L. A., Tewari, Y. B., Sansone, E. B., *Carbon*, in press.

Received for review February 16, 1979. Accepted September 19, 1979. Research sponsored by the National Cancer Institute under Contract No. N01-CO-75380, with Litton Bionetics, Inc.

Atmospheric Fallout in the Vicinity of a Base Metal Smelter at Flin Flon, Manitoba, Canada

William G. Franzin*, Gordon A. McFarlane, and Andrew Lutz

Department of Fisheries and Oceans, Freshwater Institute, 501 University Crescent, Winnipeg, Manitoba, Canada R3T 2N6

■ Atmospheric fallout in the vicinity of a base metal smelter at Flin Flon, Manitoba, Canada, was monitored with bulk precipitation collections over 1 year (y) and by winter snow samples collected from the surfaces of frozen lakes. Simple correlation analysis of the data obtained from both types of collection indicated that the smelter was a major source of Zn, Cd, Pb, As, and Cu in bulk precipitation in the Flin Flon area. Metal deposition with respect to distance from the smelter fit curves of the type $y = ax^b$. Integration of the deposition curves to selected levels (1 mg·m^{-2}·y^{-1} for Zn, Pb, and Cu; 0.1 mg·m^{-2}·y^{-1} for As; and 0.01 mg·m^{-2}·y^{-1} for Cd) gave the following radii for affected zones: Zn, 131–264; Cd, 113–284; Pb, 44–87; As, 37–68; and Cu, 33–60 km. Total deposition within these zones was as follows: Zn, 850–1616; Cd, 2.0–8.0; Pb, 14–55; As, 0.4–4.0; and Cu, 14–48 t. Direct comparison of the two collection methods, possible for only one winter period, showed that bulk precipitation collections yielded estimates of metals deposition that were, on the average, only 55% of estimates determined from winter snow samples from the same location and time period.

Recognition that primary metal smelters and thermal electric plants can contribute significant amounts of various metals to the local terrestrial environment is long standing. Several authors in recent papers (*1–4*) have pointed out problems associated with contaminated soils and vegetation, while others, more concerned with human and animal health (*5–7*), have reported studies on air contamination. While there is a growing list of papers dealing with the mass balance of metals and environmental contamination associated with coal-fired power plants (e.g., *3–10*), there are few comprehensive studies on metal contamination in the vicinity of mines and smelters (e.g., *11*). Although there are a number of studies in the literature dealing with point source emissions, we found only one (*12*) that contained quantitative data on metal fallout in the vicinity of a point source (smelter) over a whole year. We found no case study that compared emission data with fallout catchment data in the vicinity of the source.

We have estimated the annual fallout of several metals and some other elements within an approximately 250-km radius of a base metal smelter located at Flin Flon, Manitoba, Can-

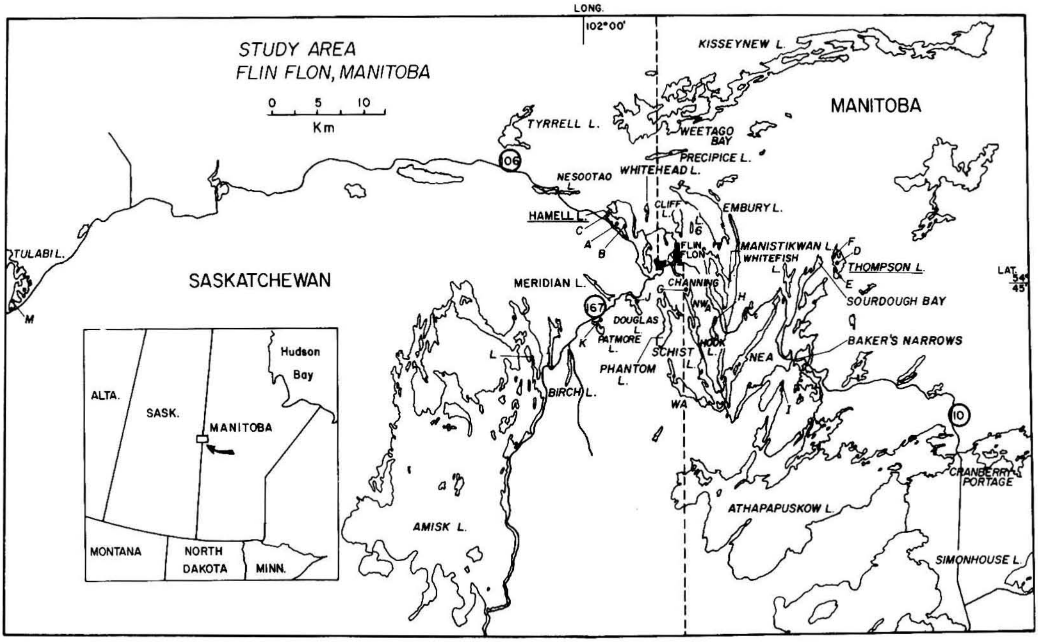


Figure 1. Study area, in the vicinity of Flin Flon, Manitoba, showing collection sites. Letters identify precipitation collector sites

ada. Previous work in the area (*13*) indicated probable contamination of many lakes in the Flin Flon area by airborne metals and potential for ecological disturbance. The present work reports the composition and quantity of atmospheric fallout in the Flin Flon environment including a comparison of two methods of collecting atmospheric deposition data. This paper is part of a study of the effects of fallout on lake ecosystems (*14*) and fish populations (*15*).

Materials and Methods

Study Area. Flin Flon is a city of approximately 10 000 people situated on the Manitoba–Saskatchewan boundary at approximately 55°N, 102°W (Figure 1). The city is the site of a base metal mining and smelting complex which processes approximately 7300 t per day of ore from Flin Flon area mines, producing, on-site, zinc, copper, and cadmium metals. Lead concentrates are produced and shipped off-site for further refining. Gold, silver, selenium, and tellurium are also recovered as byproducts of blister copper at off-site plants. Mining in this area began in 1927 and smelting commenced in 1930. Between 1930 and 1977, the smelter had processed approximately 77×10^6 t of ore (*16, 17*). In 1974 the low smelter stacks ($\sim$30 m) that had been in use for decades were replaced by a new super stack (251 m) for discharge of essentially uncontrolled smelter emissions.

The Flin Flon area has a low hilly topography containing many lakes and streams typical of the Precambrian Shield within which it is situated. A few kilometers south of Flin Flon, the shield rocks give way to the limestones common to the central part of the continent.

Sampling Methods. Annual deposition of metals in precipitation was estimated from amounts collected in samplers every 2 months from August 1976 through July 1977. The samplers consisted of 92-cm lengths of 20-cm diameter aluminum stovepipe set upright at ground level. Tight-fitting polyethylene bags ($\sim$30 cm × 60 cm) were placed in the open tops of the stovepipes providing a collection surface area of 0.032 m^2. Thirteen of these samplers (A–M, Figure 1) were operated during the collection period, including three at each of Hamell and Thompson lakes, three in each of SW and SE directions from the smelter stack, and one approximately 70 km west of the stack. Collection sites were chosen to provide comparative deposition rates on Hamell and Thompson lakes and two transects in a prevalent and a nonprevalent wind direction as well as a distant site at Tulabi Lake to estimate background deposition rates. Polyethylene containers (1.48 L, area 0.0085 m^2) were maintained for 4 months adjacent to two of the stovepipe samplers and at the same height, to provide an indication of a catchment efficiency. Each sampler was located in an open space with an angle of at least 45° from the top of the nearest tall vegetation to minimize the effect of wind on fallout distribution. However, it was not possible to locate samplers in a similar topographic situation in every case.

The amount of metals introduced directly into lakes from the atmosphere was estimated from snow samples collected in early February of 1976 and 1977 from the ice surfaces of 16 and 24 Flin Flon area lakes, respectively (Figure 1). In 1976, snow samples were taken with either a clean steel shovel or a clean plexiglass tube, while in 1977 only the plexiglass tube was used. Shovel samples collected a snow surface-to-ice level column of area 0.047 m^2, while the usual 8 cores taken with the plexiglass tube sampled 0.034 m^2. The core samples were obtained within about a 100-m^2 area in 1976, but in 1977 cores were taken about 100 m apart along the length of transects about 1 km long. Two transects were made on each lake so as to sample the windward and leeward sides of lakes relative to the direction of the smelter.

All precipitation collectors and snow sampling locations were at least 100 m from the nearest road, railway, or habitation.

Sample Handling and Preservation. At each sampling time, the sample bags were replaced with new bags and the precipitation samples transported to a field headquarters

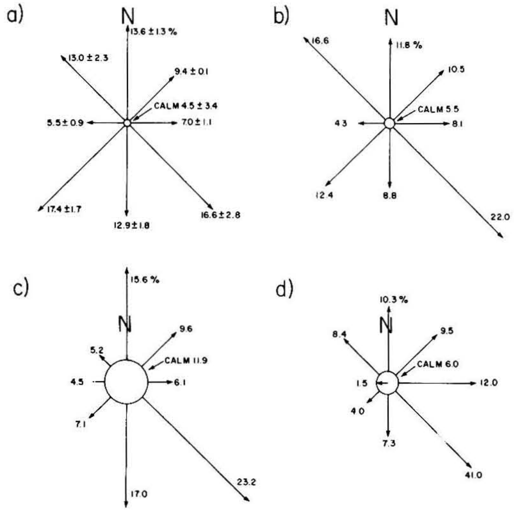


Figure 2. "Plume roses" for the Flin Flon smelter compiled from wind data obtained at Flin Flon Airport. Numbers on figures represent the percent time a direction was downwind of the smelter: (a) means and standard deviations for the five years, 1971–1975; (b) precipitation collection year, August 1976–July 1977; (c) winter snow collection period, November 1975–February 1976; (d) winter snow collection period, November 1976–February 1977

where they were thawed (if frozen) and the volumes measured. The samples were transferred to clean linear polyethylene (LPE) bottles; those for metals analyses were acidified with HNO_3 to 5 mL·L^{-1} and then transported to the Freshwater Institute for analysis. Snow samples were handled similarly.

Chemical Analyses. Major ions were determined by the methods of Stainton et al. (*18*). Metal analyses were as follows:

Arsenic. Two milliliters of concentrated H_2SO_4 was added with mixing to 20 mL (or a smaller aliquot) of sample followed by 1 mL of 10% KI. The sample was made to a 25-mL volume and aliquots were placed in sample cups. Analysis was by a modification of the semiautomated borohydride reduction method of Vijan and Wood (*19*), using a heated quartz cell constructed with a quartz window and an inlet tube at the same end. Standard equivalents from 10 to 40 μg of As·L^{-1} were similarly treated. The detection limit by this method was 1 μg of As·L^{-1}.

Cadmium, Copper, Iron, Lead, Manganese, and Zinc. Cadmium, copper, iron, lead, manganese, and zinc, when present in the sample at concentrations ≤30 μg·L^{-1}, were determined by flameless atomic absorption (carbon rod); otherwise they were determined by atomic absorption using an air-acetylene flame. A Varian AA-5 atomic absorption spectrophotometer equipped with a BC-6 simultaneous background corrector was used. Detection limits for Cd, Cu, Fe, Pb, Mn, and Zn by these methods were 0.1, 1, 2, 2, 0.5, and 0.1 μg·L^{-1}, respectively.

We define detection limit as a concentration of an element in solution that equals twice the peak-to-peak variability of the background signal of the measuring instrument.

Error. Analytical errors, determined from U.S. EPA check samples, were as follows: ±5% for Fe and Mn in the 400–700 and 40–400 μg·L^{-1} ranges, respectively; ±7% for Cu in the 70–100 μg·L^{-1} range; ±11.5% for Cd in the 20–75 μg·L^{-1} range; and ±9% for Zn in the 30–175 μg·L^{-1} range. Error was not determined for either As or Pb.

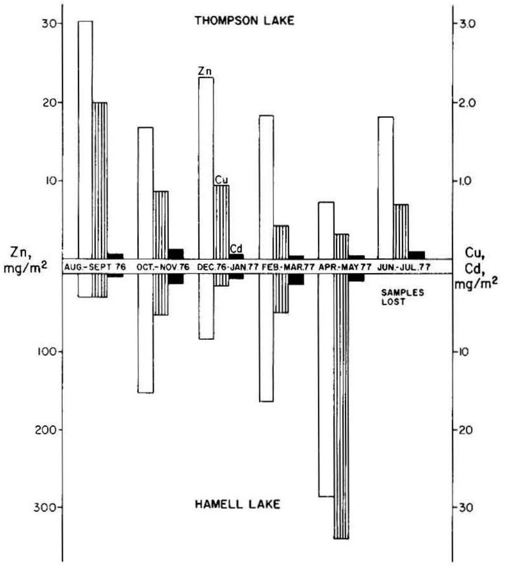


Figure 3. Seasonal pattern of deposition of Zn, Cd, and Cu on Thompson and Hamell lakes, August 1976–July 1977

Some overall error in metal deposition data was obtained from duplicate samplers located at Hamell and Thompson lakes. Deviations from the mean deposition for sampler pairs varied with time. Coefficients of variation for the metals at the two locations over the 4 months sampled (two collections) were: Fe, ±31–95%; Mn, ±13–85%; Pb, ±6–82%; As, ±3–107%; Cd, ±0–40%; Cu, ±27–92%; and Zn, ±8–69%.

We found no significant correlation between deposition of any metal with surface area of the samplers.

Weather Data. All weather data used in this study were recorded at Flin Flon Municipal Airport (*20*), which is located about 20 km SE of the smelter stack. These were the only regular monitoring data of weather conditions available for the Flin Flon area. Wind measurements at Flin Flon Airport are made near ground level, while stack emissions are discharged at a height of 251 m. Wind data for the airport ignoring the difference in height are summarized as directions of plume travel from the smelter stack in Figure 2, which compares long-term (Figure 2a) wind conditions with those of our study periods (Figures 2b–d). Precipitation data for the year of our study (1976–1977), measured at Flin Flon airport at the ends of bimonthly fallout collection periods, are shown in Table I.

Results

Precipitation Collector Data. Annual depositions of seven metals and sulfate for the period August 1976 through July 1977 are shown in Table II. The southeast and southwest transects were downwind of the smelter 22 and 12.4% of the

Table I

dates	mm precip as liquid
Aug–Sept 1976	54.1
Oct–Nov 1976	46.2
Dec 1976–Jan 1977	30.0
Feb–March 1977	19.8
April–May 1977	100.0
June–July 1977	143.6
total	394.5

Table II. Annual Deposition of Metals and Sulfate in Precipitation Near Flin Flon Estimated from Precipitation Collections for the Period August 1976–July 1977[a]

location and letter on Fig 1	distance from stack, km	deposition, $mg \cdot m^{-2}$								days collected
		Fe	Mn	Pb	As	Cd	Cu	Zn	SO_4	
Hamell Lake (3 stations; A, B, C)	4.5[b]	241	8.0	23	5.0	2.5	173	812	1606	254[d]
Thompson Lake (3 stations; D, E, F)	20[b]	36	4.5	4.5	0.6	0.4	5.4	119	657	358
SE transect										
Channing Hill (G)	4.3	164	7.9	42	6.2	4.5	57	1780	1935	358
Hook Lake (H)	8.6	74	4.4	27	3.2	2.1	27	813	310	239[c]
Baker's Narrows (I)	18.6	42	2.7	7.3	1.0	0.5	6.1	153	347	297[c]
SW transect										
Douglas Lake (J)	5.0	54	4.2	30	3.3	3.1	24	760	1022	240[c]
Patmore Lake (K)	9.5	28	1.4	5.3	0.5	0.6	6.8	182	314	241[c]
Amisk Lake (L)	18	34	4.1	3.4	0.3	0.2	3.0	49	339	295[c]
Tulabi Lake (distant station) (M)	71	15	2.4	1.7	0.04[e]	0.1	1.3	9.3		298[c]

[a] Note: Raw data from which Tables II, V, and VI are drawn are compiled in McFarlane et al. (*21*). [b] Mean distance for three stations. [c] Incomplete year's collections resulted from collectors being disturbed by wildlife or vandalized. [d] Mean number of days for three stations. [e] Calculated from 178 days collection, rest of period As was below detection.

Table III. Simple Correlation Coefficients of Metal Pairs and Annual Metal Deposition (1976–1977) with Distance from the Smelter Stack[a]

	corr coeff of distance (km)						
	Fe	Mn	Pb	As	Cd	Cu	Zn
Fe	−0.648	−0.515	−0.831**	−0.829**	−0.860**	−0.600	−0.782*
Mn		0.899**	0.610	0.851**	0.674	0.953**	0.672
Pb			0.683	0.852**	0.731*	0.770*	0.745*
As				0.934**	0.982**	0.438	0.961**
Cd					0.954**	0.709*	0.943**
Cu						0.511	0.964**
Zn							0.459

[a] Significant correlation at the 95% confidence level is indicated by * and at the 99% confidence level by **

Table IV. Total Metals Deposited within Circular Areas of Radius *x* around the Flin Flon Smelter for the Period August 1976–July 1977, as Determined by Integration of Curves $y = ax^b$

metal	*a*	*b*	*x*, km	metal deposited at distance *x*, $mg \cdot m^{-2}$	metal deposited in area $= \pi x^2$, t
Zn	15 371	−1.7285	264	1	1616
Cd	23	−1.3716	284	0.01	8.0
Pb	155	−1.1284	87	1	55
As	60	−1.6714	46	0.1	4.0
Cu	509	−1.5196	60	1	48

time, respectively, for this period compared with 17.4 and 16.6% for the previous 5 y (Figure 2 a,b,). Figure 3 shows mean seasonal deposition of Zn, Cu, and Cd on Hamell and Thompson lakes, which were downwind 16.6 and 8.1% of the time, respectively, during this period compared with 13.0 and 7.0% for the long term (Figure 2a,b). The variation in metal deposition from month to month is probably the result of fluctuations in wind speed and direction, and amounts of precipitation. Simple correlation coefficients between annual deposition of a metal and distance from the smelter (Table III) are significant for Pb, As, Cd, and Zn, which would indicate with reasonable certainty that these metals originated from the smelter stack. The other metals (Fe, Mn, Cu) may have originated partially from the stack and partially from dust and soil close to the collectors. Significant correlation exists between Fe and Mn, Cu and As; Mn and As, Cd and Cu; Pb and As, Cd and Zn; As and Cd, Cu and Zn; and between Cd and Zn. Month to month weather and deposition data show that the number of significant correlations among all metals is highest during winter when precipitation is light and in the form of snow and that the number of significant correlations between the metals linked to the smelter (Zn, Cd, As, Pb) in annual data with distance from the smelter is highest in summer when precipitation is heavier and as rain (*14*). Likewise, correlation between this group of metals and Fe and Mn, which are probably mainly of dust origin, is low at this time. Copper, which was more closely linked to Fe and Mn in annual data, showed significant correlation with distance from the smelter in summer collections. The highest numbers of significant correlations are found both between metals and distance from the smelter and among metals when winds are equitably distributed with respect to direction, i.e., both

Table V. Deposition of Selected Elements in Snow on Lake Surfaces Near Flin Flon for the Period November 20, 1975 to February 5, 1976

direction from smelter	lake[a]	km[b]	mm[c]	wind[d]	pH	mg·m^{-2}												
						Cl	SO_4	Na	K	Mg	Ca	Fe	Mn	Pb	As	Cd	Cu	Zn
N	WHI	5.6	50.5	15.6	6.59	40	162	4.5	3.5	7.1	30.0	15.0	1.00	16.0	2.80	1.9	21.0	873.0
	PRE	11.6	46.6	15.6	6.23	28	75	4.2	1.0	1.9	8.4	3.2	0.20	3.5	0.70	0.5	0.9	158.0
NE	CLI-A	4.0	62.7	9.6	6.68	88	213	17.0	3.1	5.0	23.0	16.0	0.90	20.0	2.30	3.1	8.1	718.0
	CLI-B	4.0	48.1	9.6	6.75	39	250	11.0	1.9	3.9	20.0	18.0	1.00	21.0	1.90	2.9	15.0	903.0
	CLI-C	4.0	54.3	9.6	6.92	43	250	5.4	2.2	4.3	33.0	39.0	1.20	40.0	0.60	4.5	48.0	2403.0
	LSIX-A	5.6	35.2	9.6	6.76	42	127	11.0	3.5	2.5	17.0	4.6	0.30	9.5	1.30	1.3	4.6	324.0
	LSIX-B	5.6	35.2	9.6	6.77	28	106	1.1	0.4	2.5	8.5	4.6	0.50	8.8	0.80	1.1	4.6	410.0
	LSIX-C	5.6	40.1	9.6	6.91	40	145	4.0	0.8	2.8	12.0	6.4	0.50	13.0	1.10	1.8	5.2	505.0
	EMB	7.2	53.6	9.6	6.68	54	97	6.4	1.6	5.4	23.0	4.7	0.30	5.0	1.10	0.9	1.6	221.0
E	BIL-A	5.6	53.6	6.1	6.48	43	75	2.1	0.0	3.8	16.0	11.0	0.50	7.7	1.00	0.9	9.1	413.0
	BIL-B	8.9	34.4	6.1	6.38	21	41	1.0	0.0	1.4	8.3	0.0	0.10	2.4	0.40	0.3	1.4	142.0
	SOU-B	18.5	45.9	6.1	5.83	37	37	6.0	2.3	3.2	14.0	3.4	0.20	0.0	0.20	0.0	0.0	60.0
	THO-A	20.0	44.0	6.1	5.89	52	26	6.6	2.6	1.8	16.0	0.0	0.10	0.0	0.10	0.0	0.0	22.0
	THO-B	20.0	27.9	6.1	5.68	22	17	1.7	0.0	0.8	3.4	0.0	0.04	0.0	0.10	0.0	0.0	30.0
	THO-C	20.0	36.3	6.1	6.20	44	15	15.0	8.3	2.2	15.0	0.0	0.20	0.0	0.10	0.0	0.0	25.0
SE	NWA-A	4.0	42.1	23.2	6.72	34	152	3.0	1.3	5.1	20.0	30.0	1.50	32.0	3.60	3.5	45.0	2185.0
	NWA-B	8.0	40.6	23.2	6.64	33	106	2.4	0.4	2.4	15.0	18.0	0.90	19.0	2.50	2.0	16.0	962.0
	SCH	12.9	51.9	23.2	6.32	42	104	3.1	0.5	2.1	9.3	4.4	0.40	7.5	1.10	0.7	1.1	263.0
	HOO-N	9.7	46.0	23.2	6.81	46	221	8.7	7.4	6.0	38.0	20.0	1.20	19.0	1.60	2.0	11.0	536.0
	NEA	13.7	57.3	23.2	6.05	46	138	5.7	0.6	4.0	28.0	20.0	0.90	15.0	1.90	1.1	4.9	334.0
	ATH	37.0	41.3	23.2	5.34	25	17	1.7	0.0	1.7	9.9	0.0	0.40	0.0	0.05	0.0	0.0	9.9
S	PHA-A	3.2	57.7	17.0	6.70	46	185	2.3	0.6	3.5	21.0	31.0	1.00	17.0	2.80	2.5	14.0	954.0
	PHA-B	8.9	46.3	17.0	6.47	37	83	7.0	1.4	9.3	25.0	4.5	0.40	6.9	0.90	0.7	1.0	278.0
	WA	12.0	41.3	17.0	6.22	33	58	4.1	0.8	1.7	9.9	4.9	0.20	6.2	0.90	0.7	0.8	124.0
SW	DOU	4.8	42.4	7.1	6.35	42	93	2.6	2.6	3.0	18.0	0.0	0.10	0.0	0.10	0.0	0.0	21.0
	BIR	13.7	49.6	7.1	5.73	40	30	2.0	0.0	2.5	8.9	3.6	0.20	0.0	0.20	0.2	0.0	43.0
	AMI	17.7	40.3	7.1	5.33	24	16	1.2	0.0	2.8	17.0	0.0	0.10	0.0	0.20	0.0	0.0	15.0
NW	HAM-A	4.8	43.8	5.2	6.64	35	123	3.9	1.3	1.8	11.0	21.0	0.70	14.0	2.00	1.4	13.0	782.0
	HAM-B	4.8	34.5	5.2	6.82	35	118	3.5	2.1	4.2	23.0	11.0	0.40	8.2	0.30	1.2	5.8	299.0
	HAM-C	7.2	48.1	5.2	6.94	48	67	3.4	1.4	3.9	20.0	11.0	0.30	5.7	1.70	0.6	1.0	172.0
	HAM-D	7.2	33.5	5.2	6.73	34	74	4.0	1.3	4.0	22.0	5.0	0.30	5.0	0.60	0.6	0.7	233.0
	NES-E	12.9	41.2	4.2	6.09	17	33	2.5	0.0	1.2	15.0	6.8	0.10	2.8	0.70	0.1	0.4	45.0

[a] Abbreviations used are: Amisk, AMI; Athapapuskow, ATH, BAK, SOU; Birch, BIR; Cliff, CLI; Douglas, DOU; Embury, EMB; Hamell, HAM; Hook, HOO; Kisseynew (Weetago Bay), WEB; Manistikwan, BIL; Meridian, MER; Nesootao, NES; Patmore, PAT; Phantom, PHA, POT; Precipice, PRE; Schist, SCH, NWA, WA, NEA; Simonhouse, SIM; Thompson, THO; Tulabi, TUL; Tyrrell, TYR; Whitefish, WHF; Whitehead, WHI; Lake 6, L-Six. [b] km = distance of sample site from smelter. [c] mm = water equivalent in millimeters of snow collected at sample site. [d] Wind = percent time that the smelter plume was in the direction of the sample site during the snow accumulation period.

smelter emissions and dust are well distributed in the air (*14*). No significant correlation was found between any single weather measurement and any of the metals.

For those five metals for which atmospheric deposition was significantly correlated with distance from the smelter (Zn, Cd, Pb, As, Cu), curves of the form $y = ax^b$ were fitted to the data (where y is metal deposition per unit area per unit time and x is the distance in kilometers from the smelter). The total quantity of a metal deposited within a circular area of specified radius x from the smelter was then calculated and is shown in Table IV.

These data are based essentially on nine data points, six of which are in two directions only, SE and SW from the smelter.

Winter Snow Samples. Atmospheric deposition of 11 metals, sulfate, and chloride, directly to Flin Flon area lakes for the periods November 20, 1975, to February 5, 1976, and November 8, 1976, to February 2, 1977, are shown in Tables V and VI, respectively. "Plume roses" for these two periods are shown in Figure 2c,d. Significant correlations among the data for each of these collections are indicated in Table VII.

The 1976 data are very irregular, probably due to sampling error. This is suggested by significant positive correlation between the measured water equivalent of samples (mm) and the deposition of Cl, SO_4, Ca, Fe, and Mn (Table VII). This correlation probably was caused by sampling too near to lake shores where snow accumulated and where there was a high availability of local particulate material. The more systematic, replicate sampling procedure undertaken in 1977 is evident, firstly, by the absence of significant correlation between water equivalent (millimeters) and the deposition of any material and, secondly, by reduction in the correlation between the alkali metal group (primarily from dust sources) and members of the heavy metal group, most of which have an obvious connection with the smelter (Table VII). The statistics in Table VII may be summarized as follows:

(1) Distance from the smelter, in 1976, was negatively correlated with pH, SO_4, Mg, Ca, Fe, Mn, Pb, As, Cd, Cu, and Zn. In 1977 only Zn, Pb, As, Cd, Cu, and pH were negatively correlated with distance. Only the deposition of Zn, Cd, Pb, As, and Cu consistently correlated with distance in both years, which indicates that these metals emanated from the smelter stack.

(2) The fraction of time that a sampling location was downwind of the smelter in 1976 was positively correlated with

Table VI. Deposition of Selected Elements in Snow on Lake Surfaces Near Flin Flon for the Period November 8, 1976 to February 2, 1977

direction from smelter	lake[a]	km[b]	mm[c]	wind[d]	pH	mg·m^{-2}												
						Cl	SO_4	Na	K	Mg	Ca	Fe	Mn	Pb	As	Cd	Cu	Zn
N	WHI-W	5.6	38.9	10.3	5.48	16.0	70.0	6.6	0.0	2.7	11.0	14.0	0.3	9.1	1.40	0.90	15.0	412.0
	WHI-E	5.6	49.7	10.3	5.73	30.0	109.0	7.0	0.0	3.5	11.0	25.0	0.4	14.0	1.70	1.40	16.0	586.0
	PRE-S	11.6	47.6	10.3	5.32	29.0	19.0	8.1	0.0	1.4	4.3	25.0	0.2	3.1	0.50	0.30	2.3	104.0
	PRE-N	11.6	43.8	10.3	5.64	18.0	35.0	5.3	0.0	3.9	16.0	14.0	0.2	4.1	0.60	0.40	2.7	142.0
	WEB-A	13.6	62.9	10.3	6.13	38.0	76.0	16.0	2.5	15.0	43.0	16.0	1.1	4.3	0.80	0.40	3.6	132.0
	WEB-B	13.6	56.2	10.3	5.46	34.0	45.0	16.0	0.0	6.2	21.0	13.0	0.2	3.2	0.70	0.30	2.7	77.0
NE	CLI-W	4.0	57.7	9.5	6.17	92.0	150.0	28.0	0.0	13.0	48.0	31.0	1.2	15.0	2.30	1.40	50.0	733.0
	CLI-E	4.0	57.3	9.5	5.22	34.0	115.0	9.2	0.0	5.7	24.0	26.0	0.9	17.0	1.90	1.30	34.0	619.0
	L-SIX	5.2	50.2	9.5	5.37	20.0	40.0	3.0	0.0	1.0	4.5	12.0	0.5	5.9	1.10	0.70	31.0	335.0
	EMB-S	8.0	66.9	9.5	5.90	27.0	67.0	8.0	0.0	5.4	25.0	6.8	1.1	6.0	0.90	0.50	8.3	203.0
	EMB-N	8.0	57.7	9.5	6.33	35.0	115.0	13.0	2.3	22.0	72.0	6.2	0.4	6.1	0.80	0.40	8.0	222.0
E	BIL-WW	6.2	40.6	12.0	7.36	33.0	219.0	13.0	5.3	38.0	135.0	9.5	0.9	10.0	1.30	1.10	23.0	467.0
	BIL-WN	6.2	33.9	12.0	6.60	20.0	115.0	6.5	0.0	17.0	53.0	8.6	0.5	11.0	1.20	0.90	22.0	482.0
	BIL-EW	8.6	34.6	12.0	6.64	21.0	118.0	8.0	1.4	16.0	59.0	9.0	0.4	8.5	0.90	0.80	12.0	360.0
	BIL-EE	8.6	43.0	12.0	6.69	43.0	138.0	14.0	1.7	21.0	70.0	9.2	0.6	11.0	1.20	0.90	15.0	428.0
	WHF-W	14.6	44.1	12.0	6.14	26.0	44.0	8.4	0.0	4.8	30.0	4.8	0.2	5.2	0.70	0.40	7.2	152.0
	WHF-E	14.6	56.9	12.0	6.74	46.0	80.0	22.0	4.6	22.0	79.0	5.0	0.3	4.5	0.70	0.40	5.5	124.0
	THO-W	20.2	50.9	12.0	5.32	20.0	41.0	11.0	0.0	3.6	14.0	5.2	0.2	2.8	0.30	0.20	2.4	63.0
	THO-E	20.2	51.5	12.0	6.30	31.0	41.0	12.0	0.0	13.0	57.0	3.1	0.2	2.0	0.30	0.10	1.7	44.0
SE	NWA-M	6.9	60.9	41.0	6.37	146.0	658.0	33.0	0.0	15.0	81.0	192.0	3.3	81.0	10.00	7.00	113.0	3735.0
	NWA-E	6.9	29.9	41.0	6.36	72.0	263.0	21.0	0.0	5.7	64.0	47.0	1.2	23.0	2.60	2.00	27.0	1039.0
	HOO-A	9.5	46.4	41.0	6.01	28.0	149.0	3.7	0.0	2.3	6.5	25.0	0.9	18.0	2.10	1.70	18.0	696.0
	HOO-B	9.5	76.4	41.0	6.21	46.0	245.0	6.9	0.0	4.6	18.0	78.0	1.5	36.0	4.00	3.10	35.0	1414.0
	BAK-M	19.4	40.5	41.0	7.19	81.0	154.0	19.0	0.0	11.0	71.0	12.0	0.4	6.1	0.90	0.50	5.6	174.0
	BAK-E	19.4	42.7	41.0	7.12	772.0	813.0	178.0	22.0	86.0	513.0	20.0	0.6	9.8	0.90	0.80	8.0	255.0
	ATH-A	38.0	58.3	41.0	4.90	47.0	23.0	19.0	0.0	2.9	8.2	3.5	0.2	1.5	0.30	0.10	0.9	19.0
	ATH-B	38.0	83.6	41.0	6.15	34.0	34.0	13.0	0.0	20.0	54.0	4.5	0.2	3.7	0.60	0.20	2.1	34.0
	SIM-A	54.0	75.9	41.0	5.39	30.0	15.0	4.6	0.0	6.1	18.0	4.1	0.2	1.2	0.30	0.01	1.0	16.0
	SIM-B	54.0	56.2	41.0	6.50	23.0	23.0	11.0	0.0	41.0	21.0	2.9	0.3	1.7	0.30	0.01	0.8	17.0
S	POT-W	4.5	44.8	7.3	6.20	27.0	296.0	9.0	0.0	8.5	33.0	104.0	1.6	28.0	3.60	3.70	36.0	1277.0
	POT-E	4.5	60.1	7.3	6.17	36.0	313.0	1.8	0.0	4.2	22.0	145.0	23.0	34.0	6.10	3.80	63.0	1347.0
	PHA-SW	8.5	53.6	7.3	5.84	32.0	118.0	1.6	0.0	2.7	9.6	40.0	1.8	18.0	2.40	1.70	16.0	825.0
	PHA-SE	8.5	56.5	7.3	8.04	57.0	362.0	36.0	18.0	66.0	203.0	58.0	1.6	25.0	4.00	2.00	21.0	1062.0
	WA-N	12.0	45.3	7.3	6.06	25.0	220.0	1.3	0.0	3.0	16.0	20.0	0.9	17.0	2.30	1.40	16.0	630.0
	WA-S	12.0	47.8	7.3	6.21	38.0	134.0	5.3	0.0	3.3	11.0	21.0	0.8	15.0	2.20	1.30	14.0	564.0
SW	DOU-E	5.0	55.0	4.0	6.68	44.0	66.0	11.0	0.0	9.9	79.0	25.0	0.5	6.8	0.90	0.60	13.0	261.0
	DOU-W	5.0	39.3	4.0	6.09	24.0	55.0	7.9	0.0	3.5	31.0	19.0	0.4	5.9	0.70	0.50	12.0	214.0
	PAT-E	9.5	44.7	4.0	5.45	27.0	27.0	10.0	0.0	4.0	14.0	19.0	0.4	2.6	0.50	0.30	4.9	114.0
	PAT-W	9.5	53.4	4.0	5.84	32.0	21.0	11.0	0.0	5.3	35.0	15.0	0.3	2.5	0.30	0.20	3.3	83.0
	BIR-E	14.0	40.8	4.0	4.95	33.0	8.2	5.7	0.0	4.1	15.0	8.0	0.3	0.7	0.20	0.10	1.0	26.0
	BIR-W	14.0	39.9	4.0	5.45	56.0	8.0	19.0	0.0	6.8	22.0	7.0	0.2	0.8	0.10	0.10	0.7	25.0
	AMI-E	17.5	59.7	4.0	5.00	36.0	12.0	22.0	0.0	3.6	11.0	5.1	0.1	1.0	0.10	0.05	1.0	14.0
	AMI-W	17.5	43.0	4.0	4.82	26.0	0.0	12.0	0.0	3.0	10.0	3.5	0.1	1.2	0.02	0.03	1.0	7.6
W	MER-E	7.0	48.6	1.5	5.24	29.0	19.0	16.0	0.0	2.4	6.8	5.2	0.1	4.1	0.40	0.20	1.8	97.0
	MER-W	7.0	62.1	1.5	5.26	37.0	25.0	19.0	0.0	5.0	20.0	5.3	0.2	2.7	0.40	0.20	2.4	109.0
	TUL-A	71.0	57.7	1.5	4.81	23.0	11.0	9.2	0.0	2.9	10.0	8.4	0.2	1.0	0.10	0.10	1.4	36.0
	TUL-B	71.0	37.2	1.5	4.91	22.0	0.0	10.0	0.0	1.9	3.3	27.0	0.1	0.2	0.10	0.01	0.1	1.8
NW	HAM-N	4.2	57.7	8.4	5.75	46.0	23.0	23.0	0.0	4.6	27.0	74.0	0.8	5.3	2.70	0.40	4.2	151.0
	HAM-S	4.2	49.3	8.4	5.27	39.0	20.0	18.0	0.0	2.0	8.9	25.0	0.4	4.0	0.60	0.40	3.1	181.0
	NES-E	12.5	69.8	8.4	5.08	61.0	26.0	36.0	0.0	3.1	6.1	19.0	0.2	0.9	0.30	0.10	0.5	13.0
	NES-W	12.5	46.6	8.4	5.18	24.0	0.0	11.0	0.0	2.4	5.6	5.5	0.4	1.2	0.20	0.10	0.8	20.0
	TYR-A	21.0	40.3	8.4	4.87	24.0	0.0	11.0	0.0	2.4	7.3	5.7	0.1	0.6	0.10	0.04	0.4	5.1
	TYR-B	21.0	47.0	8.4	4.75	9.4	0.0	3.8	0.0	1.4	4.2	5.0	0.2	3.0	0.04	0.02	0.2	4.2

[a–d] See corresponding footnotes in Table V.

Mn, Pb, and As, while in 1977 this parameter correlated positively with pH, Cl, SO_4, Na, Mg, Ca, Pb, Cd, and Zn.

(3) In both 1976 and 1977, pH and SO_4 were positively correlated with deposition of most elements, indicating a direct relationship of pH with amount of particulate material in a sample. The heavy metals were strongly correlated (positive) among themselves in both years.

(4) In both 1976 and 1977, Cl was positively correlated with

Table VII. Significant Correlations in Data from Winter Snow Collections; 1976 above Diagonal, 1977 below[a]

	km[b]	mm[c]	W[d]	pH	Cl	SO_4	Na	K	Mg	Ca	Fe	Mn	Pb	As	Cd	Cu	Zn
km				– –		– –			–	–	– –	–	– –	– –	– –	–	– –
mm					+ +	+ +			+	+ +	+ +	+ +	+	+	+		
W												+ +	+	+ +			
pH	–		+		+	+ +			+	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +
Cl			+ +	+		+ +	+ +	+	+	+ +					+		
SO_4			+ +	+ +	+ +		+			+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +
Na			+	+	+ +	+ +		+ +	+								
K				+ +	+ +	+ +	+ +			+ +							
Mg			+	+ +	+ +	+ +	+ +	+ +		+ +	+	+ +	+	+	+		
Ca			+	+ +	+ +	+ +	+ +	+ +	+ +		+ +	+ +	+ +	+	+ +	+ +	+ +
Fe						+ +						+ +	+ +	+ +	+ +	+ +	+ +
Mn											+ +		+ +	+ +	+ +	+ +	+ +
Pb	–		+	+ +		+ +					+ +	+ +		+ +	+ +	+ +	+ +
As	–			+ +		+ +					+ +	+ +	+ +		+ +	+ +	+ +
Cd	–		+	+ +		+ +					+ +	+ +	+ +	+ +		+ +	+ +
Cu	–			+		+ +					+ +	+ +	+ +	+ +	+ +		+ +
Zn	–		+	+ +		+ +					+ +	+ +	+ +	+ +	+ +	+ +	

[a] Signs indicate the direction and level of significance of corresponding correlation coefficients, e.g., + + refers to a positive correlation coefficient significant at the 99% confidence level, + refers to the 95% confidence level. Blank spaces are indicative of no significant correlation at the 95% confidence level. [b] km = distance from smelter. [c] mm = millimeters of precipitation recorded at sample location as liquid. [d] W = portion of collection period in which a sample location was downwind of smelter.

Table VIII. Total Mass of Elements Measured on Lake Surfaces Near Flin Flon on February 2, 1977, after 85 Days of Snow Accumulation[a]

		element loads, kg							metal	kg	
lake	area, km^2	Fe	Mn	Pb	As	Cd	Cu	Zn	Σ	SO_4^{2-}	H^+
Birch	1.66	12	0.36	1.3	0.24	0.13	1.4	42	57	13	0.50
Cliff	2.46	70	2.6	39	5.0	3.3	103	1663	1886	326	0.48
Douglas	1.22	27	0.54	7.7	0.93	0.68	15	290	342	74	0.02
Embury	13.12	85	10	79	11	6.2	105	276	572	1194	0.72
Hamell	2.33	115	1.4	10	3.7	0.8	8.5	387	526	50	0.42
Hook	0.90	46	1.1	24	2.7	2.2	24	950	1050	177	0.05
Meridan	1.23	6.5	0.18	4.2	0.53	0.26	2.6	127	141	27	0.38
Patmore	0.71	12	0.25	1.8	0.29	0.16	2.9	70	87	17	0.09
Phantom	4.78	315	8.7	125	19	4.4	163	5391	6026	1301	0.18
Precipice	1.45	22	0.25	5.2	0.82	0.58	3.6	178	210	39	0.24
Six	0.19	2.3	0.10	1.1	0.21	0.12	5.9	64	74	8[b]	0.21
Thompson	2.20	9.1	0.45	5.3	0.67	0.36	4.5	118	138	90	0.30
Tulabi	12.74	225	2.2	7.6	1.2	0.51	9.6	239	485	148[c]	10.2
Tyrrell	5.34	29	0.77	2.6	0.48	0.16	1.7	25	60	*d*	3.7
Whitefish	1.23	6.0	0.30	6.0	0.84	0.44	7.8	170	191	76	0.02
Whitehead	0.39	7.5	0.15	4.5	0.60	0.45	6.0	195	214	35	0.04

[a] Calculations are based on means of duplicate samples. [b] One sample only. [c] One sample only, second sample below detection limit of 0.2 ppm. [d] Below detection limit of 0.2 ppm.

SO_4, Na, K, Mg, and Ca, and, in 1976 only, with Cd.

(5) The alkali group of metals (Na, K, Mg, Ca) showed strong positive correlation among themselves in 1977, but in 1976 the relationships between Na and Ca and between K and Mg were not significant. In 1977, none of these metals correlated with As or any of the heavy metals (Fe, Mn, Pb, Cd, Cu, Zn), but in 1976 positive correlation was found between Mg and Fe, Mn, Pb, As, and Cd and between Ca and As and all the heavy metals.

Table VIII gives total fallout of As and heavy metals as well as SO_4 and H^+ on several Flin Flon area lakes at the time of 1977 winter sampling. These data illustrate the magnitude of chemical input to these lakes from airborne sources.

The significant negative correlations between fallout of Zn, Cd, Pb, As, and Cu with distance from the smelter for winter data allowed fitting of deposition curves to the data. Table IX gives the calculated annual deposition of the various metals within specified areas based on snow sample analyses for winter periods of 1975–1976 and 1976–1977. As before, the equation $y = ax^b$ was used in these calculations.

The 1976 data are based on 32 snow collections in 7 directions from the smelter (none from the west), while the 1977 data are based on 53 snow collections in all 8 major directions from the smelter. These metal depositions are calculated for a circular area of radius x, when in reality, the deposition zones were skewed to the south and southeast of the smelter in 1976 and strongly skewed to the southeast in 1977 due to prevailing winds during the snow accumulation periods (see Figure 2c and d). The actual deposition of metals in these directions is, therefore, probably higher than that given here for any given distance from the smelter.

Comparison of Deposition Estimates. Total fallout of the

Table IX. Total Metals Deposited within Circular Areas of Radius x around Flin Flon Smelter for the Winter Periods (a) November 20, 1975–February 5, 1976, and (b) November 8, 1976–February 2, 1977, as Determined by Integration of Deposition Curves ($y = ax^b$)

metal	a	b	x, km	metal deposited at distance x, mg·m^{-2}	metal deposited in area $= \pi x^2$, t
		(a) 1976			
Zn	12 252	−1.9301	131	1	1548
Cd	456	−3.5261	21	0.01	no fit
Pb	22 387	−4.6925	8.5	1	no fit
As	11	−1.2946	37	0.1	1.2
Cu	17 947	−4.9769	7	1	no fit
		(b) 1977			
Zn	7 269	−1.6534	217	1	850
Cd	15	−1.5349	113	0.01	2
Pb	72	−1.1299	44	1	14
As	1	−1.0600	68	0.1	0.4
Cu	190	−1.5048	33	1	14

five metals originating from the smelter, as estimated either by precipitation collections taken over 1 y or by snow collections extrapolated to a year as shown in Tables IV and IX, does not allow comparison of the relative efficacy of the methods of data collection. We were able to directly compare deposition data from precipitation collections with snow collections for the 1976–1977 snow collection period at five different lakes. The data, taken from Table VI and from McFarlane et al. (*21*) (raw data from which Table II was compiled), are compared in Table X. Although there is considerable variability in the ratios of precipitation:snow data, with the exception of Hamell Lake, snow collections yielded consistently higher deposition estimates for all metals at all lakes. Overall, estimates based on precipitation collections averaged only 55% of estimates determined from snow collections for the same time period.

Discussion

An assessment of the importance of the Flin Flon smelter as a source of atmospheric metal fallout requires comparison of the deposition in this area with that in the vicinity of other point sources as well as that recorded in urban areas and areas remote from human activity. This comparison is shown in Table XI. These data indicate that the smelter at Flin Flon is a significant source of atmospheric Zn, Cu, and Cd. The deposition of Pb, while high, is not higher than that found in large urban areas associated with high automobile use (see Copenhagen, Table XI).

The high degree of variation in time and space among our collections of precipitation has a number of explanations. The open-mouthed collectors that we used tend to underestimate precipitation (and presumably deposition) by 20% or more due to aerodynamic effects of the passage of wind across the mouth of the collector (*25*). This effect is influenced by the proximity of screening structures such as tall vegetation or the roughness of topography and by the height of the sampler above ground in areas where drifting snow is prevalent. Although we attempted to provide an unobstructed clearing around our samplers, errors arising from these sources could not be eliminated. Furthermore, sedimentation-type collectors do not trap effectively particles smaller than about 5 μm in still air (*26*) and with any wind at all are inefficient at collection of particles of <15 μm average diameter (*27*). Our estimates of metal deposition based on these samplers, therefore, may be too low. On the other hand, deposition based on snow collections from lakes may include fallout due to impaction, as well as sedimentation, and therefore may be more representative of the actual deposition, at least for the winter period. This possibility is reinforced by the data in Table X, which show that precipitation collections yielded estimates of metals deposition that averaged only 55% of estimates obtained from snow collections for the same time and place. This difference is in good agreement with the magnitude and direction of error expected on the basis of wind and site effects on precipitation collectors and on the variation in data obtained from duplicate collectors (see Error section in Methods), which, for the five metals linked to the smelter, had coefficients of variation averaging 44%. The discrepancy of Hamell Lake deposition ratios in Table X probably was caused by an upward bias in deposition data obtained from precipitation collectors. Only two of three precipitation collectors around the lake, the two

Table X. Comparison of Metals Deposition Estimated from Precipitation Collections with That from Snow Collections for the Same Time Period, November 8, 1976–February 2, 1977

		deposition, mg·m^{-2}					
		Thompson Lake[a]	Hamell Lake[b]	Patmore Lake	Hook Lake	Baker's Narrows	$\bar{x}$ ratio ± SD
Zn	precip.	30.2	167	19.7	390	86.9	
	snow	53.5	166	98.5	1055	215	
	ratio	0.57	1.01	0.20	0.37	0.40	0.51 ± 0.31
Cd	precip.	0.12	0.50	0.06	0.84	0.22	
	snow	0.15	0.40	0.25	2.4	0.65	
	ratio	0.80	1.25	0.24	0.35	0.34	0.60 ± 0.42
Pb	precip.	1.3	5.5	0.70	11.2	3.8	
	snow	2.4	4.7	2.6	27	8.0	
	ratio	0.54	1.17	0.27	0.41	0.48	0.57 ± 0.35
As	precip.	0.16	1.0	0.07	1.3	0.58	
	snow	0.30	1.7	0.40	3.1	0.90	
	ratio	0.53	0.59	0.18	0.42	0.64	0.47 ± 0.18
Cu	precip.	1.3	3.7	1.9	11.9	3.4	
	snow	2.1	3.7	4.1	27	6.8	
	ratio	0.62	1.00	0.46	0.44	0.50	0.55 ± 0.28
							$G\bar{x}$ = 0.54 ± 0.05
$\bar{x}$ ratios ± SD		0.61 ± 0.11	1.00 ± 0.26	0.27 ± 0.11	0.40 ± 0.04	0.47 ± 0.12	$G\bar{x}$ = 0.55 ± 0.28

[a] Precipitation average of three stations. [b] Precipitation average of two stations.

Table XI. Comparison of Metal Deposition at Flin Flon with That Recorded Elsewhere

location	deposition, $mg \cdot m^{-2} \cdot y^{-1}$					reference
	Zn	Cd	Pb	As	Cu	
Flin Flon, Channing (4.3 km from smelter)	1780	4.5	42	6.2	57	this work[a]
Wollongong, NSW, Australia (2.3 km from smelter)	130	2.0	36		80	Beavington (*12*)[a]
Copenhagen, Denmark (average of rural, suburban, and urban estimates)	82		50		7.3	Andersen et al. (*22*)[a]
Chadron, Neb. (nonindustrial town of 5000)	4.0	0.12	1.9		1.8	Streumpler (*23*)
New Hampshire (remote montane site)		0.87	19.6			Schlesinger et al. (*24*)

[a] Similar sampling apparatus used.

closest to the smelter, yielded data complete enough for comparison with snow collection data. Since snow collections were obtained from two transects over the length of the lake, the results obtained are credible.

The lack of fit of Cd, Pb, and Cu deposition data in the 1976 snow collections to the $y = ax^b$ model probably is due to the use of higher analytical detection limits for these metals in that year. The limits in 1976 were Cd, 3 $\mu g \cdot L^{-1}$; Pb, 30 $\mu g \cdot L^{-1}$; and Cu, 10 $\mu g \cdot L^{-1}$, compared with 0.1, 2, and 1 $\mu g \cdot L^{-1}$, respectively, in 1977. The higher limits in 1976 put many samples collected distant from the smelter below detection. This has the effect of increasing the slope and intercept of deposition curves and significantly raising estimates of total deposition while at the same time reducing x, the radius of the affected zone. It is obvious that this is the case in the data presented in Table IX. Zinc and arsenic data for the 2 y are not so affected because the amount of zinc deposited is very high (never below detection) and similar detection limits for arsenic were employed in the 2 y.

Although particle sizes were not measured in this study, large "rust" particles were observed in both precipitation collections and in snow samples taken near the smelter along the SE transect. These particles contained considerable amounts of iron. Gladney et al. (*28*) found that Fe became concentrated preferentially on large particles in the fly ash from a coal-fired plant; a similar process may occur here.

We made no attempt to determine particulate mineralogy in this study. However, melted snow samples invariably contained considerable amounts of sulfate, suggesting that some metals are deposited as sulfates (*14*) as described by Haagen-Smit and Wayne (*29*). Allen et al. (*30*), in studies of particles collected near a smelter complex at Avonmouth, U.K., found evidence that Zn may exist in some particles as a sulfide or sulfate or in others as a silicate. Pb, on the other hand, apparently existed as an oxide in the particles examined. Probably the volatile metals As, Cd, Pb, and Zn are emitted as very fine particles of their oxides (*31*). The oxides may catalyze the oxidation of SO_2 in the stack gases to SO_3, which subsequently forms droplets of H_2SO_4 that may in turn react with the metal oxides and other elements to form $PbSO_4$, $CdSO_4$, $ZnSO_4$, and other sulfate salts (*29*). The differences in behavior of the nonvolatile elements Cu, Mn, and Fe vs. the volatile elements Cd, Pb, Zn, and As in stack emissions may explain partially the results of simple correlation analysis of precipitation collections (Table III), where it was shown that these elements were correlated within groups but, with the exception of As, not correlated between groups. Perhaps As is associated with both volatile and nonvolatile components of the emissions.

Conclusions

We have documented here, by two methods, the deposition of metals in atmospheric fallout in the vicinity of a base metal smelter. Comparison of the figures with those for other areas indicates that the Flin Flon smelter is a significant source of airborne Zn, Cd, Pb, As, Cu, and possibly SO_4 to as much as 250 000 km^2 of the environment in the vicinity of the smelter. Use of these two methods suggests that a carefully planned winter survey of snow on lake ice could provide a fair assessment of fallout of airborne metals in the Flin Flon area for the winter period of approximately 135 days. Such a survey, taking only about four man-days on site to complete, would utilize multiple snow core samples from snow surface to ice level along two or more transects of at least 1 km length on each lake sampled. In the Flin Flon area, the abundance of lakes in all directions from the smelter would allow two persons, each equipped with a snowmobile to sample approximately 25 to 30 lakes in about 2 days near the end of winter. This type of sampling compares favorably with the more time-consuming collection of precipitation with monitoring equipment, which, to be economically feasible, is fraught with unmanageable errors. Although annual deposition of metals may not be determined from winter snow samples with reasonable confidence, year-to-year assessment of deposition during the winter could be monitored, for example, as an adjunct to short-term in-stack monitoring in an emission control compliance schedule.

Further work in this area and elsewhere should aim at discovering the sizes and mineralogy of fallout particles to aid in determining the availability of constituents to biota.

Acknowledgments

D. G. Alexander, S. Franzin, G. Kendall, and J. K. McFarlane assisted in the field. I Borys, M. Capel, B. Hauser, R. Hunt, M. Pitze, R. Schade, K. Supeene, and C. Tam assisted with chemical analyses. D. Abrams assisted with computations. The manuscript was reviewed critically by F. A. J. Armstrong and R. Wagemann.

Literature Cited

(1) Hutchinson, T. C., Whitby, L. M., *Environ. Cons.*, **1**, 123–32 (1974).
(2) Buchauer, M. J., *Environ. Sci. Technol.*, **7**, 131–6 (1973).
(3) Little, P., Martin, M. H., *Environ. Pollut.*, **3**, 251–4 (1972).
(4) Beavington, F., *Environ. Pollut.*, **9**, 211–7 (1975).
(5) Ragaini, R. C., Ralston, H. R., Roberts, N., *Environ. Sci. Technol.*, **11**, 773–81 (1977).
(6) Djuric, D., Kerin, Z., Graovac-Leposavic, L., Novak, L., Kop, M., *Arch. Environ. Health*, **23**, 275–9 (1971).
(7) Dorn, C. R., Pierce, J. O., Philips, P. E., Chase, G. R., *Atmos. Environ.*, **10**, 443–6 (1976).
(8) Kaakinen, J. W., Jorden, R. M., Lawasani, M. H., West, R. E., *Environ. Sci. Technol.*, **9**, 862–9 (1975).
(9) Klein, D. H., Russell, P., *Environ. Sci. Technol.*, **7**, 357–8 (1973).
(10) Lee, R. E., Jr., Crist, H. L., Riley, A. E., MacLeod, K. E., *Environ. Sci. Technol.*, **9**, 643–7 (1975).
(11) Wixson, R. G., Ed., "Missouri Lead Study; an Interdisciplinary Investigation of Environmental Pollution by Lead and Other Heavy Metals from Industrial Development in the New Lead Belt of Southeastern Missouri", University of Missouri–Columbia, 1977.
(12) Beavington, F., *Environ. Pollut.*, **13**, 127–31 (1977).
(13) Van Loon, J. C., Beamish, R. J., *J. Fish. Res. Board Can.*, **34**, 899–906 (1977).

(14) Franzin, W. G., McFarlane, G. A., Department of Fisheries and Oceans, Freshwater Institute, Winnipeg, Manitoba, Canada, 1978, unpublished data.
(15) McFarlane, G. A., Franzin, W. G., *J. Fish. Res. Board Can.*, **35**, 963–70 (1978).
(16) Rowley, W. J., Environment Canada, Environmental Protection Service Survey Report EPS 5-NW-75-7, 1975, 129 pp.
(17) Sergy, G. A., Fallis, B. W., Environment Canada, Environmental Protection Service Survey Report EPS 5-NW-78-6, 1978.
(18) Stainton, M. P., Capel, M. J., Armstrong, F. A. J., *Fish. Res. Board Can. Misc. Spec. Publ.*, **25** (1974).
(19) Vijan, P. N., Wood, G. R., *At. Absorpt. Newsl.*, **13**, 33–7 (1974).
(20) Monthly Record of Meteorological Observations, Atmospheric Environment Service, Department of Fisheries and Environment, Canada, 1971–1977.
(21) McFarlane, G. A., Franzin, W. G., Lutz, A., Canada Fisheries and Marine Services MS Report 1486, 1979.
(22) Anderson, A., Horman, M. F., Johnson, I., *Environ. Pollut.*, **17**, 133–51 (1978).
(23) Streumpler, A. W., *Atmos. Environ.*, **10**, 33–7 (1976).
(24) Schlesinger, W. H., Reiners, W. A., Knopman, D. S., *Environ. Pollut.*, **6**, 39–47 (1974).
(25) Rasmussen, K. R., Halgreen, D., *Nordic Hydrol.*, **9**, 145–60 (1978).
(26) Corn, M., in "Air Pollution", 3rd ed., Vol. I, Stern, A. C., Ed., Academic Press, New York, 1976, pp 78–158.
(27) Hendrickson, E. R., in "Air Pollution", 2nd ed., Vol. II, Stern, A. C., Ed., Academic Press, New York, 1968, pp 3–51.
(28) Gladney, E. S., Small, J. A., Gordon, G. E., Zoller, W. H., *Atmos. Environ.*, **10**, 1071–7 (1976).
(29) Haagen-Smit, A. J., Wayne, L. G., in "Air Pollution", 3rd ed., Vol. I, Stern, A. C., Ed., Academic Press, New York, 1976, pp 235–85.
(30) Allen, G., Nickless, G., Wibberly, B., *Nature (London)* **252**, 571–2 (1974).
(31) Nelson, K. W., in "Air Pollution", 2nd ed., Vol. III, Stern, A. C., Ed., Academic Press, New York, 1968, pp 235–86.

Received for review May 18, 1979. Accepted September 19, 1979.

NOTES

Particulate Matter. Its Association with Microorganisms and Trace Metals in an Estuarine Salt Marsh Microlayer

Leonard W. Lion, Ronald W. Harvey, Lily Y. Young, and James O. Leckie*

Environmental Engineering and Science, Department of Civil Engineering, Stanford University, Stanford, Calif. 94305

■ Water samples collected from the air–water interface in a salt marsh were analyzed for particulate numbers and size range, viable heterotrophic bacteria, cadmium, and lead. Comparison of the results with those from bulk water samples indicated significantly elevated levels of particulates, plate count bacteria, and lead in all samples examined. Data suggest elevated concentrations of bacteria and lead at the interface are a consequence of high concentrations of particulates that may serve as a site for accumulation.

A significant portion of the net planktonic photosynthesis in salt marsh systems has been stated to occur within the surface microlayer (*1*). The air–water interface has been shown to contain elevated concentrations of toxic trace metals (*2*), chlorinated hydrocarbons (*3*), and microorganisms (*4*). Several heavy metals in the marine microlayer, most notably lead, have been found to associate with particulate matter (*5*). Particulate surfaces may significantly enhance microbial metabolic activity (*6, 7*). These data suggest that particulate surfaces within the salt marsh microlayer may be an important site for the introduction of toxic pollutants into the marine food web.

The authors have sampled bulk water and surface water microlayers in a San Francisco Bay salt marsh to determine microlayer enrichment of plate count bacteria, particulate material, cadmium, and lead. Determination of all these entities on single samples allows a better understanding of particulate, microorganism, and trace metal interrelationships within the salt marsh microlayer.

Experimental

Surface microlayer samples were taken with a 20-mesh polyethylene screen, using the screen dip method of Garrett (*8*). This technique samples the top 150 to 300 μm of the water surface (*9*). Bulk subsurface samples were collected by opening an acid-cleaned sampling bottle at an approximate 0.2 m depth and resealing the bottle at depth to avoid contamination by interfacial materials.

All samples for bacterial analysis were collected in sterilized, glass-stoppered bottles and kept on ice until processed. Sample aliquots were cultured within 6 h upon return to the laboratory. Plate count bacteria were determined using a Quebec colony counter 48 h after plating on seawater nutrient agar and incubating at 30 °C (*10*).

Analysis for concentration and size distribution of particulates was performed using a Coulter Electronics, Inc., Model TA II Coulter Counter. All analyses of particles were performed using a 70-μm aperture, which is applicable to the 1 to 40 μm particle diameter size range. The particle size range examined is well below the 930-μm mesh opening in the sample screen, so it is unlikely that the observed distributions were biased by the sampling procedure. The Coulter counter was calibrated using 2.0- and 9.7-μm latex spheres. Where appropriate, samples were diluted with 0.05-μm filtered artificial seawater or 0.2-μm filtered isoton. Particle size distributions were corrected for dilution water contributions. At salt marsh salinities (11–30‰), coagulation of colloidal particles is likely to have already occurred. Therefore, salinity changes on sample dilution are not expected to have produced particle flocculation. All glassware used to handle samples was acid-cleaned in 10% HNO_3 and rinsed with distilled water.

Particulate materials were examined by light and scanning electron microscopy (SEM). SEM was performed using an AMR 900 SEM equipped for elemental analysis with a KEVEX X-ray energy spectrometer. Samples for SEM analysis were air-dried onto glass cover slides under a laminar-flow hood and rinsed with distilled water to remove dried salts.

Acid exchangeable (pH ~2) cadmium and lead were determined by differential pulse anodic stripping voltammetry (DPASV) using a polarographic analyzer (Princeton Applied Research Model 174A) equipped with an automatic electro-

0013-936X 79/0913-1522$01.00/0

analysis controller (Model 315). All DPASV analyses were performed on 50-mL sample aliquots acidified with 1 μL of concentrated HCl/mL (BDH Aristar grade). Samples for dissolved trace metal analysis were acidified after filtration through 0.4-μm polycarbonate membrane filters (Nuclepore Corp., Pleasanton, Calif.). Typical settings for DPASV analysis were as follows: 50-min N_2 purge; 3-min preconditioning of the hanging mercury drop electrode at −0.05 V; 999-s stirred metal deposition at −0.8 V and 30-s quiescent equilibration at −0.8 V. Scans were performed at 2 mV/s to a final potential of −0.05 V. Concentrations were measured by the method of standard additions. All glassware for DPASV analyses was sequentially cleaned in 10% reagent grade HNO_3 in deionized water followed by 10% redistilled HNO_3 in distilled water, and 10% HNO_3 (BDH Aristar grade) in quartz-distilled water. These analyses were performed under a laminar-flow hood, in a clean room. Analyses by DPASV and an ammonium pyrrolidinedithiocarbamate (APDC)/diethylammonium diethyldithiocarbamate (DDDC) chelation, methyl isobutyl ketone (MIBK) solvent-extraction procedure give comparable results on field samples. Ongoing research utilizes the APDC/DDDC–MIBK technique as the primary trace metal analytical procedure.

Results and Discussion

Distributions of particulate size, surface area, and volume for three different pairs of surface microlayer and bulk water samples are shown in Figure 1. Microlayer particulate concentrations are consistently greater than those in the bulk water over virtually the entire size range measured. Consequently, particulate surface area and volume are also enhanced over levels in the bulk water samples.

Microlayer particles appear to have a relatively larger component in large-sized categories (4 to 20 μm diameter) than corresponding bulk water samples. Although the cause for this distribution is unknown, we may speculate that it could occur in part from fallout of large-sized material from marsh vegetation. Such particles may be temporarily held at the microlayer by surface tension, but when disturbed, sink to the sediment and consequently are not found in great numbers in the bulk water.

The particulate volumes, diameters, and surface areas shown in Figure 1 should be viewed as conservative estimates of the true sample particulate characteristics, since Coulter counter response is directly proportional to particle volume for coalesced solids (treated as spheres). For particle aggregates or porous particles, instrument response is reduced with respect to the actual particle size. For example, a particle aggregate with porosity of 0.69 would have a diameter 25% above that recorded by the Coulter counter (*11*). Underestimation of porous particle surface area, which is calculated assuming a spherical particle morphology, would be even more severe than the underestimation of particle volume and diameter. SEM and light microscopic examination of microlayer particulates revealed that, in general, they are nonspherical in shape and dominated by detrital material, which would be expected to be of a porous nature (Figure 2).

Plate count bacteria, particulate data, and respective partitioning for salt marsh samples are summarized in Table I. Elevated surface concentrations of plate count bacteria and particulates occurred in all three samples presented, with a clear linear correlation between these two moieties. It must be noted that plate count techniques grossly underestimate actively respiring and total numbers of bacteria. However, strong linear correlations have been found in other sample sets between fractionation (surface to subsurface concentration ratios) of particulates and fractionation of both plate count bacteria and total numbers of bacteria (determined by epifluorescence) (*12*). Observation of additional salt marsh surface samples by epifluorescent microscopy has shown that a high percentage of organisms at the air–sea interface are actually attached to particulate surfaces (*12*). These observations indicate that microlayer particulates may provide a

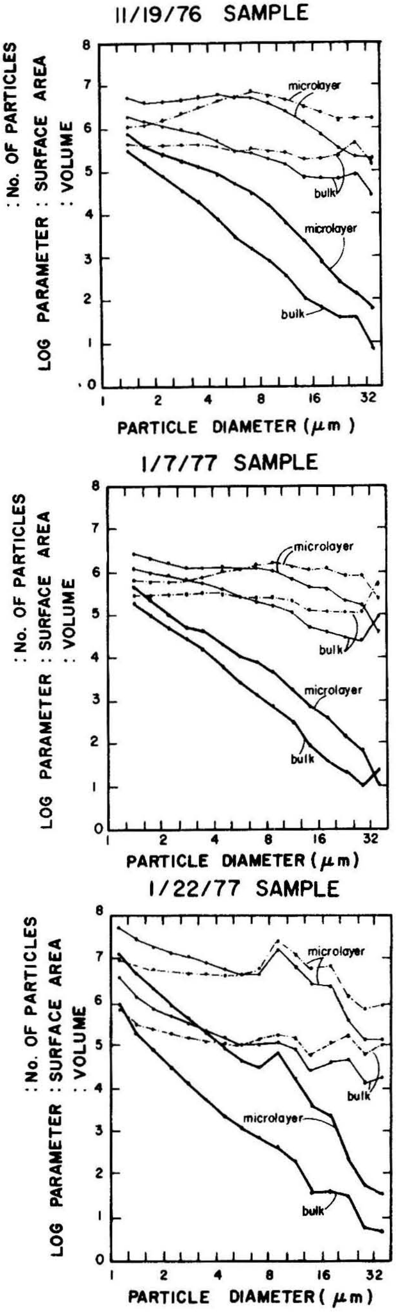


Figure 1. Coulter counter data for three San Francisco Bay salt marsh samples. Surface and subsurface particulate numbers, surface areas and volumes vs. mean particle diameter in three salt marsh samples: (—) number of particles/mL; (—) surface area, μm^2/mL; (–·–·) volume, μm^3/mL

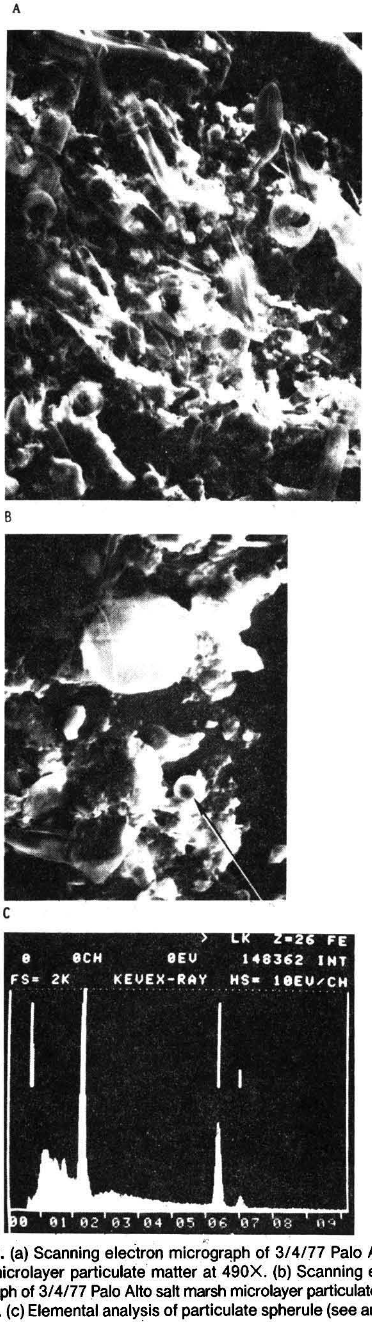


Figure 2. (a) Scanning electron micrograph of 3/4/77 Palo Alto salt marsh microlayer particulate matter at 490X. (b) Scanning electron micrograph of 3/4/77 Palo Alto salt marsh microlayer particulate matter at 980X. (c) Elemental analysis of particulate spherule (see arrow) by X-ray energy spectrometry. Elevated bars show positions of Fe spectral bands; the large undesignated band corresponds to S

Table I. Surface and Subsurface Bacteria (Plate Count) and Particulate Counts in a San Francisco Bay Salt Marsh

	date of sample		
	11-19-76	1-7-77	1-22-77
bacteria[a]			
B_s, surface counts/mL	590	14.2	230
B_b, subsurface counts/mL	77	3.2	6.1
fractionation factor, $f_b = B_s/B_b$	7.7	4.4	38.3
particulate			
P_s, surface no./mL	2020	830	20100
P_b, subsurface no./mL	580	370	1290
fractionation factor, $f_p = P_s/P_b$	3.5	2.2	15.7
particulate surface areas[b]			
A_s, surface (μm^2/mL) × 10^6	52.2	15.3	173
A_b, subsurface (μm^2/mL) × 10^6	8.00	5.44	7.54
fractionation factor, $f_a = A_s/A_b$	6.53	2.81	22.9

[a] Bacterial counts are the averages of duplicate plate counts run on the same series dilution (particulate and bacteria counts × 10^3/mL). [b] Particulate surface areas were computed using particle size distribution data assuming spherical particulate morphologies.

surface area upon which the bacterial populations attach and that the observed correlation of microorganisms and particle fractionation is not merely coincidental. High particulate concentrations in the microlayer may ameliorate some stress factors found in this environment, most notably UV radiation (*13, 14*). Predator-prey interactions are suggested to be interrupted by adsorption of microorganisms to colloidal materials (*15*). In addition, particulate-associated organics can serve as a source of nutrients for the bacterioneuston (*16*). Particulate-microorganism interactions, therefore, may alter microbial population levels in marine ecosystems, and the elevated bacterial populations found at the salt marsh microlayer may result directly from the simultaneous presence of high concentrations of particulate matter.

Observations by light microscopy have shown particulate material in the salt marsh to be dominated by diatomaceous debris, plant detritus, green algae, and aggregates of small crystalline-appearing minerals. SEM photomicrographs of surface particulates are shown in Figure 2. The stoichiometry of the small spherule (Figure 2b) was established as FeS_2 by comparing the iron to sulfur X-ray peak area ratios (Figure 2c) to iron solids of known mineralogy, i.e., pyrite (FeS_2) and pyrrhotite ($Fe_{1-x}S$). The crystalline structure of the spherule was not determined. The particle probably originated from reduced marsh sediments. During periods of water movement within the salt marsh, large-sized pieces of sediment have been observed to break off and float to the surface. Some materials that have settled from the microlayer and bulk water to the marsh sediments are, therefore, returned to the surface by this process. Presumably, flotation occurs via trapped gas bubbles (CH_4) from anaerobic sediments. The production of CH_4 and CO_2 in marsh sediments has been well documented (*17, 18*), and the concentration-depth profiles of CH_4 indicate the loss of CH_4 from sediments in the form of bubbles (*18, 19*).

Flotation of sedimentary materials could conceivably provide a transport route for trace metals, present in the reducing sediments as solid sulfides, to the surface microlayer. Another important transport route of trace metals to the microlayer would result from atmospheric fallout. Plants have recently been shown to release trace metals, taken up from solids and sediments, as small-sized aerosol particulates (*20*). This process represents a potential for vegetation-derived atmospheric input of particulate trace metals in the marsh microlayer. Atmospheric input of particulate trace metals to the microlayer must also include that of anthropogenic origin, such as lead from automotive emissions. The flux of lead into the South San Francisco Bay from the atmosphere can be

Table II. Trace Metal Analysis of Field Samples[a]

sample	metal	mean total microlayer concn ($C_{microlayer}$) ± *S*, μg/L	mean dissolved microlayer concn ± *S*, μg/L	% particulate trace metal[b] where statist signif	mean bulk concn (C_{bulk}) ± *S*, μg/L	partitioning where statist signif, $C_{microlayer}/C_{bulk}$
11/19/76						
Palo Alto salt marsh	Cd	0.47 ± 0.17	0.36 ± 0.12		0.49 ± 0.13	
	Pb	10.24 ± 5.09	0.31 ± 0.13	97	0.75 ± 0.08	13.7
1/7/77						
Palo Alto salt marsh	Cd	0.29 ± 0.08	0.22 ± 0.11		0.29 ± 0.003	
	Pb	3.87 ± 0.13	0.66 ± 0.43	83	0.69 ± 0.16	5.61

[a] The 1/22/77 San Francisco Bay salt marsh sample was not analyzed for trace metals. [b] (Mean total microlayer concentration − mean dissolved microlayer concentration)/mean total microlayer concentration(100).

roughly estimated at 9×10^{-3} μg/(m^2·s) using an aerosol Pb content of 0.93 μg/m^3 (Bay Area Pollution Control District, 1977, average figures) and a deposition velocity of 1 cm/s (*21*). Regardless of source, trace metals that are delivered to the marine microlayer will have their microlayer residence times largely controlled by the tendencies of individual metal species to adsorb to available solid surfaces or to complex with surface active microlayer organic compounds.

It may be seen from Table II data that enrichment of lead at the surface microlayer occurred during both sampling dates. Cadmium, however, was not significantly partitioned. Significance of differences was determined by using the Student's *t* test for inferences concerning the difference between the means of two small sample populations (*22*). A significant portion of microlayer lead was determined to be associated with particulate matter, while this was not the case for cadmium. Different affinities of these two metals for organic complexation and solid surface adsorption may explain the differences in observed behavior (*23*).

Conclusion

The data indicate that the salt marsh microlayer contains elevated concentrations of particulates, microorganisms, and lead. Microlayer plate count bacteria appear to be closely correlated with particulate matter, perhaps due to an increased availability of organic substrates at these surfaces. An amelioration of surface stress factors by particulates may allow microbial utilization of elevated microlayer organics. Particulate surfaces may, in fact, serve as important sites for heterotrophic activity in the microlayer. Lead is also seen to be associated with microlayer particulates. The analysis for microorganisms, particulates, and trace metals performed on single samples shows concurrent enrichment of all three entities at the air–sea interface. The presence of lead and microorganisms at particulate surfaces leads to speculation that microlayer particulate surfaces may function as a site for uptake of lead into the marine biomass. Our future research efforts will investigate this possibility. Any biological uptake of lead would depend, in part, on lead concentration and speciation. Lead on particulate surfaces may be directly adsorbed or complexed with adsorbed organic ligands. The biological availability of these forms of lead is not yet understood and requires further study.

Literature Cited

(1) Gallagher, J. L., *Limnol. Oceanogr.*, **20**, 120 (1975).
(2) Barker, D. R., Zeitlin, H., *J. Geophys. Res.*, **77**, 5076 (1972).
(3) Bidleman, T. F., Olney, C. E., *Science*, **183**, 516 (1974).
(4) Sieburth, J. M., *Deep Sea Res.*, **18**, 1111 (1971).
(5) Piotrowicz, S. R., Ray, B. J., Hoffman, G. L., Duce, R. A., *J. Geophys. Res.*, **77**, 5243 (1972).
(6) Pomeroy, L. R., Johannes, R. E., *Deep Sea Res.*, **15**, 381–91 (1968).
(7) Hargrave, B. T., *Limnol. Oceanogr.*, **17**, 583 (1972).
(8) Garrett, W. D., *Limnol. Oceanogr.*, **10**, 602 (1965).
(9) Hatcher, R. F., Parker, B. C., *Limnol. Oceanogr.*, **19**, 162 (1974).
(10) Meynell, G. G., Meynell, E., "Theory and Practice in Experimental Bacteriology", Cambridge University Press, New York, 1965, pp 12–24.
(11) Treeweek, G. P., Morgan, J. J., *Environ. Sci. Technol.*, **11**, 707 (1977).
(12) Harvey, R. W., Young, L. Y., submitted for publication in *Appl. Environ. Microbiol.*
(13) Dietz, A. S., Albright, L. J., Tuominen, T., *Can. J. Microbiol.*, **22**, 1699 (1976).
(14) Marumo, R., Taga, N., Nakai, T., *Bull. Plankton Soc. Jpn.*, **18**, 36 (1971).
(15) Marshall, K. C., "Interfaces in Microbial Ecology", Harvard Press, Boston, 1976.
(16) Paerl, H., *Science*, **180**, 496 (1973).
(17) King, G. M., Wiebe, W. J., *Geochim. Cosmochim. Acta*, **42**, 343 (1978).
(18) Whelan, T., in "Natural Gases in Marine Sediments", Kaplan, I. R., Ed., Plenum Press, 1974, pp 47–61.
(19) Reeburgh, W. S., Heggie, D. T., in "Natural Gases in Marine Sediments", Kaplan, I. R., Ed., Plenum Press, 1974, pp 27–45.
(20) Beauford, W., Barber, J., Barringer, A. R., *Science*, **195**, 571 (1977).
(21) Wallace, G. T., Jr., Duce, R. A., *Mar. Chem.*, **3**, 157 (1975).
(22) Mendenhall, W., "Introduction to Probability and Statistics", Wadsworth Publishing Co., Belmont, Calif., 1964.
(23) Lion, L. W., Leckie, J. O., Civil Engineering Department, Stanford University, 1979, in preparation.

Received for review December 11, 1978. Accepted July 30, 1979. Research on this project was supported in part by National Science Foundation, Grant No. OCE-76-11613.

Association of Hydrophobic Organic Compounds with Dissolved Organic Matter in Aquatic Systems

John P. Hassett[1]* and Marc A. Anderson

Water Chemistry Program, University of Wisconsin, Madison, Wis. 53706

■ Radiolabeled cholesterol added to water samples was recovered less efficiently from river water than from distilled water by solvent extraction. However, if organic matter in river water was destroyed with UV radiation prior to cholesterol addition, recovery was equivalent to that from distilled water. This demonstrated that cholesterol could be bound by dissolved organic matter and stabilized in the aqueous phase. Water samples containing radiolabeled cholesterol or the PCB isomer 2,2′,5,5′-tetrachlorobiphenyl were fractionated by gel permeation chromatography. Results indicated that these compounds were associated with high molecular weight organic matter present in the samples.

Several studies have demonstrated that dissolved organic matter can increase the apparent aqueous solubility of hydrophobic organic compounds. Wershaw et al. (*1*) found that 500 mg/L of humic material extracted from soil increased the solubility of DDT 20 to 40 times. Poirrier et al. (*2*) found that DDT associated with iron-organic colloids in water and that it was concentrated in the colloids by a factor of 16 000. Matsuda and Schnitzer (*3*) showed that fulvic acid fractions of soil extracts increased the solubility of phthalate esters, but the effect decreased with decreasing molecular weight of the phthalate ester. Boehm and Quinn (*4*) demonstrated that the fulvic acid fraction of a marine sediment increased the solubility of the alkanes hexadecane, eicosane, and pristane but did not affect the behavior of the aromatic hydrocarbons phenanthrene and anthracene, which in pure water are more soluble than the alkanes studied. They also found that the alkanes were more soluble in untreated natural water than in water that had been treated to remove organic matter by either carbon adsorption or ultraviolet irradiation. Again, this effect was not observed for the aromatic hydrocarbons.

The increased solubility of hydrophobic organic compounds in the presence of dissolved natural organic matter is probably a result of surfactant characteristics of this material. The organic compound would associate with hydrophobic sites such as alkyl chains on the natural organic matter and the resulting complex would be held in solution or colloidal dispersion by hydrophilic sites such as carboxylic acid and phenolic and hydroxyl groups. Hydrophobic compounds held in such associations might then be expected to show behavior characteristic of the natural organic matter rather than the behavior they themselves normally exhibit in pure water systems.

A study of the behavior of the sterols coprostanol and cholesterol in the Menomonee River near Milwaukee, Wis., revealed that dissolved sterols entering the river from a municipal sewage discharge remained unchanged for at least 8 miles downstream (*5*). One explanation for this behavior was that the sterols were bound by dissolved organic matter and thus unavailable for adsorption. Experiments described here were designed to demonstrate whether a sterol (cholesterol) and a polychlorinated biphenyl (2,2′,5,5′-tetrachlorobiphenyl) were bound by indigenous organic matter in Menomonee River water and in sewage. Results reported elsewhere (*6*) describe effects of dissolved organic matter on adsorption of these compounds.

Experimental

Water samples were collected from the Menomonee River upstream, downstream, and from the Memonomee Falls municipal sewage outfall. Organic matter in selected samples was concentrated by ultrafiltration using an Amicon UM05 ultrafilter (nominal molecular weight cutoff = 500). Sample volumes were reduced fivefold by this method.

Samples collected upstream of the sewage outfall were pretreated to remove particulate matter by continuous flow centrifugation at a force of 31 000*g* and a flow rate of 100 mL/min using a Sorvall Superspeed RC2-B refrigerated centrifuge. Some centrifuged samples were further treated to destroy organic matter by irradiating them in 2.7 cm (i.d.) quartz tubes for 6 h at a distance of 8 cm from a 450-W high-pressure mercury vapor ultraviolet light source (Englehard Hanovia, Inc.). These samples were passed through glass fiber filters (Reeve Angel 935 AH) before use. Ultraviolet oxidation has been found effective in destroying a variety of organic compounds, including humic material, in water (*7*).

[4-^{14}C]Cholesterol (ICN Pharmaceuticals, Inc.) was added to the water samples by placing benzene solutions containing 3.83×10^3 cpm of cholesterol in 2-L Erlenmeyer flasks, evaporating the solvent with a stream of nitrogen, adding 1.5 L of water sample to each flask, and stirring for 20 h on a magnetic stirrer at 4 or 20 °C. All samples were then acidified to pH <3.0 with 2.0 mL of concentrated HCl and extracted three times with 100-mL portions of glass-distilled carbon tetrachloride. The flasks were also rinsed with acetone and carbon tetrachloride to recover any adsorbed cholesterol. The extracts were evaporated to dryness and transferred to scintillation vials, and the ^{14}C activity was determined by liquid scintillation spectrometry. Radiolabeled cholesterol could be recovered quantitatively from flasks to which no water was added. The coefficient of variance for recovery efficiency from river water was 0.11.

Selected water and sewage samples were fractionated by gel permeation chromatography (GPC) using columns packed with Sephadex G-15, G-50, or G-75. Distilled water was pumped through the column in an ascending mode by an Isco Model 312 metering piston pump. Column effluent was monitored for UV absorbance at 254 nm with an Isco Type 6 optical unit and an Isco Model UA-5 absorbance monitor. The effluent was collected in 10.0-mL fractions by a Gilson Model V-10 volumetric fraction collector. Characteristics of the columns are listed in Table I. Void volume (V_0), the volume of water required to elute a compound completely excluded from the gel matrix, was determined for soluble starch. Interstitial volume plus void volume ($V_i + V_0$), the volume required to elute a compound that can enter all pores in the gel, was determined for potassium dichromate.

Radiolabeled [^{14}C]cholesterol and 2,2′,5,5′-tetrachlorobiphenyl (TCB) were added to water samples to be fractionated by placing one of the labeled compounds dissolved in benzene into a glass vial with Teflon-lined cap, evaporating the solvent with a nitrogen stream, adding 10.0 or 5.0 mL of filtered (0.4-μm Nuclepore filter) sample, and shaking for 48 h. These spiked samples were filtered again (0.4-μm Nuclepore), a 3.0-mL aliquot was injected onto the Sephadex column, and another 3.0-mL aliquot was extracted to determine the amount of radioactive material injected. This aliquot and

---

[1] Present address, Environmental Studies Institute, Drexel University, Philadelphia, Pa. 19104.

Table I. Gel Permeation Column Characteristics

Sephadex gel	mol wt fractionation range	i.d., cm	length, cm	flow rate, mL/h	V_0, mL	$V_0 + V_i$, mL
G-15	<1500	2.7	21	80	45	
G-50 fine	1500–30 000	1.6	63	60	35	95
G-75	3000–70 000	1.6	67	40	35	125

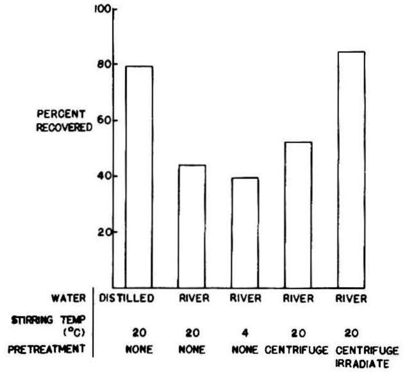


Figure 1. Extraction efficiencies of cholesterol from water

fractions eluted from the column were acidified (pH <3.0) with concentrated HCl and extracted three times with 5.0-mL portions of carbon tetrachloride (cholesterol-containing samples) or dichloromethane (TCB-containing samples). Extracts were placed in 20-mL glass scintillation vials, 100 μL of mineral oil was added to TCB-containing samples, the solvent was evaporated in an air stream, and the residue was redissolved in scintillation cocktail. Mineral oil was added to samples containing TCB in order to minimize evaporative losses of TCB during solvent evaporation. This approach was found to reduce such losses to negligible amounts. ^{14}C activity in each sample was determined by liquid scintillation spectrometry.

Dissolved, high molecular weight organic matter in selected samples was concentrated by membrane ultrafiltration. Samples were centrifuged (continuous flow method), filtered (0.4-μm Nuclepore filter), and passed through an Amicon UM05 ultrafilter membrane using nitrogen pressure. This membrane has an average pore diameter of 10 Å and retains globular molecules with molecular weights greater than 500. Samples were passed through this membrane at a nitrogen pressure of 70 psi and concentrated by a factor of 5; that is, 2000-mL samples were reduced to a volume of 400 mL.

Results and Discussion

Solvent Extraction. Efficiencies of solvent extraction of [^{14}C]cholesterol from distilled and river water are presented in Figure 1. Cholesterol was recovered with an efficiency of 79% from distilled water, but only 44% from unfiltered river water. Initially it was felt that the poor recovery from river water was due to biological degradation; however, this possibility was eliminated when repetition of the experiment at a lower temperature (4 °C) gave similar results. This conclusion was further confirmed by using sodium azide as a disinfectant in some samples (not shown). Another possible explanation was that cholesterol was adsorbed by suspended solids and was therefore not as readily available to the solvent phase. This explanation was also eliminated, however, when no significant improvement in recovery was achieved by filtering samples before spiking them with cholesterol. The final possibility considered was that dissolved material in river water affected recovery. This might be due to either an ionic strength effect of inorganic ions or binding of cholesterol to dissolved polymeric organic acids, commonly referred to as humic material, which are themselves not readily extracted by chloroform. This question was resolved by destroying organic material in river water with UV radiation prior to the addition of cholesterol. As can be seen in Figure 1, recovery from irradiated river water was equivalent to recovery from distilled water. This experiment therefore demonstrates that natural organic matter in river water can indeed bind hydrophobic organic compounds such as cholesterol and thereby increase their affinities for the aqueous phase.

Extraction efficiencies reported here for cholesterol are considerably lower than those reported for other investigations. Hassett and Lee (*8*) obtained 90% recovery from lake water spiked with 100 μg/L of cholesterol and Wun et al. (*9*) recovered 97% of 200 μg/L added to sewage. The high concentrations of cholesterol used in these studies probably exceeded the binding capacity of dissolved organic matter in the sample, thus facilitating recovery. Results reported here therefore demonstrate the importance of performing recovery studies at realistic concentrations. This conclusion is supported by data presented by Dutka et al. (*10*), who found 75% recovery of cholesterol at 0.5 μg/L, but 91% at 100 μg/L.

Gel Permeation Chromatography. The preceding experiments indicate that cholesterol can form associations with dissolved natural organic matter. These associations were investigated further using gel permeation chromatography (GPC). GPC separates compounds on the basis of molecular size. Assuming no adsorption–desorption interaction with the gel, molecules too large to enter any pores of the gel matrix will elute at the void volume (V_0), and compounds small enough to penetrate all pores of the matrix will elute at the void plus interstitial volume ($V_0 + V_i$). Compounds of intermediate molecular size will elute between these extremes. Fractionation may also result from adsorption–desorption interactions with the gel, and molecules eluting after $V_0 + V_i$ are assumed to undergo adsorption on the column as well as physical size fractionation. Cholesterol (mol wt 387) or 2,2′,5,5′-tetrachlorobiphenyl (TCB, mol wt 292) associated with dissolved organic matter would behave as higher molecular weight compounds than they would if dissolved by themselves. Thus, it might be possible to distinguish between bound and unbound aqueous cholesterol and TCB.

Figures 2 and 3 are Sephadex G-15 chromatograms of unconcentrated and concentrated (ultrafiltration) river water containing [^{14}C]cholesterol from upstream and downstream of a sewage treatment plant. In all chromatograms shown here, ^{14}C activity in each 10-mL fraction is represented by bar graphs and UV absorbance by dotted lines. UV absorbance is used as a qualitative indication of the presence of organic matter. In each of the chromatograms in Figures 2 and 3, the major cholesterol peaks occur in fractions 4 and 5, which correspond to fractions where high molecular weight material should elute. Since the molecular weight exclusion limit of the gel (1500) is greater than the molecular weight of cholesterol, cholesterol eluting in these fractions is mostly likely bound by other organic matter. This is supported by the observation

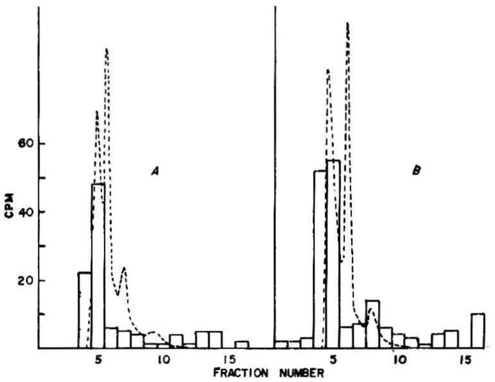


Figure 2. Sephadex G-15 molecular sieve chromatograms of river water containing [^{14}C]cholesterol: (A) river water upstream of sewage plant, UV attenuation × 1; (B) concentrated river water (UM05), UV attenuation × 5. Dotted line is UV absorbance

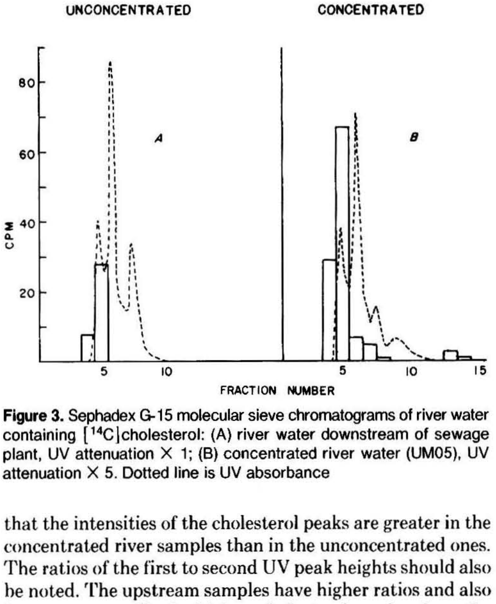


Figure 3. Sephadex G-15 molecular sieve chromatograms of river water containing [^{14}C]cholesterol: (A) river water downstream of sewage plant, UV attenuation × 1; (B) concentrated river water (UM05), UV attenuation × 5. Dotted line is UV absorbance

that the intensities of the cholesterol peaks are greater in the concentrated river samples than in the unconcentrated ones. The ratios of the first to second UV peak heights should also be noted. The upstream samples have higher ratios and also have correspondingly higher cholesterol peaks than the downstream samples. Thus, it appears that the highest molecular weight material is principally responsible for binding cholesterol.

Figure 4 is a Sephadex G-75 chromatogram of cholesterol in river water and river water concentrated by ultrafiltration. With this gel cholesterol again elutes in the fraction containing the highest molecular weight material, although UV absorbing material elutes for the most part in later, lower molecular weight fractions. The greater intensity of the cholesterol peak in the concentrated sample indicates that dissolved, high molecular weight organic matter is binding cholesterol and causing it to elute as a high molecular weight species. Burns et al. (*11*) have shown by GPC that humic material from soil binds the pesticide paraquat. To determine if similar base soluble material in Menomonee River sediment can bind cholesterol, a sediment sample was extracted with 0.5 N NaOH and the extract was spiked with [^{14}C]cholesterol. Figure 5 is the Sephadex G-50 chromatogram of this sample. Cholesterol elutes in several peaks, each associated with a UV absorption peak. The first peak elutes in the highest molecular weight fraction and the second in the lowest molecular weight fraction. The last two peaks elute after $V_0 + V_i$, indicating that these fractions are associated with material undergoing adsorption–desorption interactions on the columns. It should be noted that fractions 21–25 were collected as a composite fraction and that the cholesterol peak they contain may actually be much higher and narrower.

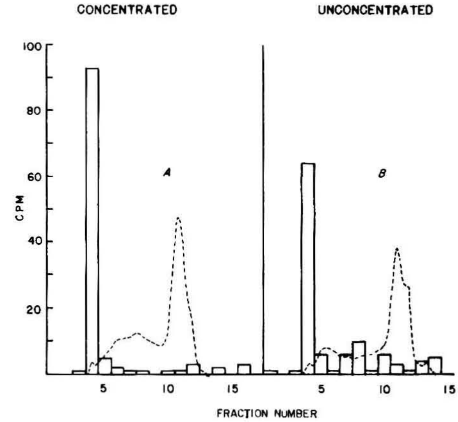


Figure 4. Sephadex G-75 molecular sieve chromatograms of river water containing [^{14}C]cholesterol: (A) concentrated river water (UM05), UV attenuation × 5; (B) river water, UV attenuation × 1. Dotted line is UV absorbance

A number of water samples were also spiked with the TCB isomer and subjected to GPC. In the case of this compound, however, no radioactive material was detected in the eluants with the exception of one sample, a concentrated river sample that eluted a very small amount of TCB. TCB is a more hydrophobic compound than cholesterol and should be more readily adsorbed from water. In these experiments, TCB was apparently adsorbed by the column material. It is unknown if adsorption was irreversible or if TCB eluted in low, broad, undetectable peaks.

A peak that could be regarded as free dissolved cholesterol or TCB was not detected for any of the natural water samples. To determine how the free compounds would elute, several distilled water samples were chromatographed. For samples containing TCB, no ^{14}C activity was detected in the column effluent. Cholesterol was eluted, but the fractionation pattern was not reproducible from sample to sample (Figure 6). Most samples contained a cholesterol peak in the highest molecular weight fraction plus other apparently randomly distributed peaks. It is likely that in these samples cholesterol is forming self-aggregates or micelles that elute as high molecular weight species. This may also occur to some extent in river samples, but the increased amount of cholesterol eluted in high molecular weight fractions of concentrated samples relative to nonconcentrated ones indicates that cholesterol is also bound by organic matter. Unbound, truly dissolved cholesterol in river or distilled water samples is probably adsorbed by the gel matrix and does not elute.

An interesting sidelight of the GPC studies was that a greater percentage of injected ^{14}C-labeled material was recovered from the columns for concentrated samples than for unconcentrated ones, indicating that dissolved organic matter affects the adsorption of these compounds. This phenomenon was investigated further in adsorption experiments using river and sewage solids. It was indeed found that dissolved organic matter inhibited adsorption of cholesterol and TCB, probably by binding these compounds and holding them in solution (*6*).

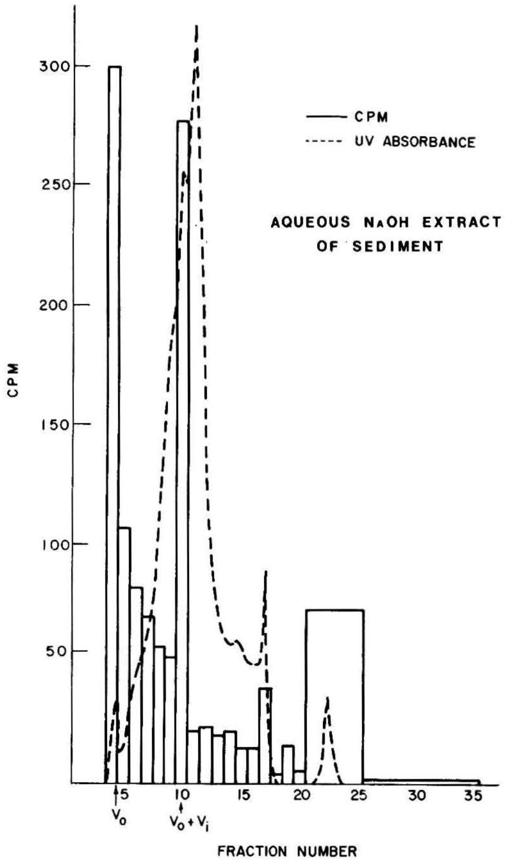


Figure 5. Sephadex G-50 molecular sieve chromatogram of an aqueous NaOH sediment extract containing [^{14}C]cholesterol. Dotted line is UV absorbance

The mechanism of binding between hydrophobic compounds and dissolved high molecular weight organic matter is at present unknown. A possible explanation may be derived, however, by considering the nature of dissolved organic matter, which is believed to be similar to humic substances in soil. This material contains hydrophobic sites such as alkyl chains and hydrophilic sites such as carboxylic acid and hydroxyl groups and could therefore have surfactant properties. Hydrophobic compounds would associate with hydrophobic sites in the organic matter and the complex held in solution or colloidal dispersion by hydrophilic sites. Compounds held in such associations might then be expected to show solubility and adsorption behavior characteristic of the natural organic matter rather than the behavior they themselves exhibit in pure water systems.

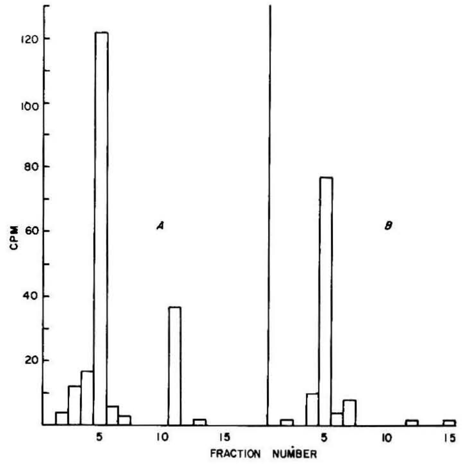


Figure 6. Sephadex G-15 molecular sieve chromatograms of distilled water containing [^{14}C]cholesterol. Counts per minute vs. fraction number. (A and B) Distilled water

If such associations exist in natural water, there may be several environmental implications related to stabilization of hydrophobic compounds in the aqueous phase. As demonstrated here, extraction methods used in analytical schemes may be affected, and the importance of performing recovery studies at realistic concentrations should be recognized. Solubility may be enhanced and adsorption decreased, thus increasing the mobility of these compounds in the aquatic environment. On the other hand, direct biological uptake from water and concentration in fatty tissue for compounds such as DDT and PCBs might be decreased. At present, the existence and importance of these associations in the aqueous environment are unknown.

Conclusions

Solvent extraction studies indicate that cholesterol is bound by dissolved organic matter and stabilized in the aqueous phase. Comparison of GPC elution patterns for cholesterol and TCB in concentrated vs. nonconcentrated river and sewage samples demonstrates that increasing DOC concentrations by ultrafiltration results in enhanced recovery of these compounds in high molecular weight fractions, thus indicating that they are bound by high molecular weight compounds in water. Further work is necessary to establish the nature of these bonds as well as the existence and significance of the resultant aggregates in aquatic environments.

Acknowledgment

We thank Aileen Keith and Susan Barta for their technical assistance.

Literature Cited

(1) Wershaw, R. L., Burcar, P. J., Goldberg, M. C., *Environ. Sci. Technol.*, **3**, 271–3 (1969).
(2) Poirrier, M. A., Bordelon, B. R., Laseter, J. L., *Environ. Sci. Technol.*, **6**, 1033–5 (1972).
(3) Matsuda, K., Schnitzer, M., *Bull. Environ. Contam. Toxicol.*, **6**, 200–4 (1971).
(4) Boehm, P. D., Quinn, J. G., *Geochim. Cosmochim. Acta*, **37**, 2459–77 (1973).
(5) Hassett, J. P., Anderson, M. A., in "Chemistry of Wastewater Treatment", Rubin, A. J., Ed., Ann Arbor Press, Ann Arbor, Mich., 1978.
(6) Hassett, J. P., Ph.D. Thesis, Water Chemistry, University of Wisconsin—Madison, 1978.
(7) Armstrong, F. A. J., Williams, P. M., Strickland, J. D. H., *Science*, **211**, 481–3 (1966).
(8) Hassett, J. P., Lee, G. F., *Water Res.*, **11**, 983–9 (1977).
(9) Wun, C. K., Walker, R. W., Litsky, W., *Water Res.*, **10**, 955–9 (1976).
(10) Dutka, B. J., Chau, A. S. Y., Coburn, J., *Water Res.*, **8**, 1047–55 (1974).
(11) Burns, I. G., Hayes, M. H. B., Stacey, M., *Pestic. Sci.*, **4**, 629–41 (1973).

Received for review December 26, 1978. Accepted August 3, 1979. Financial support was provided by EPA Grant No. R00514201, administered by the University of Wisconsin Water Resources Center. Additional support was delivered by the University of Wisconsin Department of Civil and Environmental Engineering and the Engineering Experiment Station.

Chemical Heterogeneity of Aerosol Samples as Revealed by Atomic Absorption and X-ray Photoelectron Spectroscopy

Brigitte Barbaray, Jean-Pierre Contour, and Gérard Mouvier*
Laboratoire de Physico-Chimie Instrumentale, Université Paris VII, 2, place Jussieu-75221 Paris Cedex 05, France
René Barde, Gérard Maffiolo, and Bernard Millancourt
Département Environnement Aquatique et Atmosphérique, E.D.F., 6, quai Watier-78400 Chatou, France

■ Atmospheric particles collected by sedimentation or filtration have been analyzed by photoelectron spectroscopy (XPS) and by atomic absorption spectroscopy. The lack of correlation between the results has led us to discern problems of sample composition heterogeneity. Three types of heterogeneity have been noted: localization heterogeneity, thickness heterogeneity, and heterogeneity of particle composition. These effects are emphasized in XPS, which only takes into account the first layers of the samples, in contrast to atomic absorption, which constitutes an overall analysis.

The properties of atmospheric aerosols have been widely studied, and numerous publications dealing with particle size distribution, mechanisms of formation, lifetime, and transport have appeared in recent years (*1*). The chemical analysis of samples has only rarely been undertaken, although this information is essential to the understanding of the mechanisms by which particles are formed from atmospheric pollutants (*2*).

Several publications report interesting results concerning the use of X-ray photoelectron spectroscopy (XPS) in the analysis of atmospheric particle samples (determination of the nature of the elements and of their chemical state (*3*).

Quantitative analysis by photoelectron spectroscopy has already been reported (*4*), but XPS gives only the surface composition of the samples. We have therefore compared the results with those obtained by atomic absorption spectroscopy, which provides the overall analysis, in order to reveal heterogeneity in the chemical composition as reported by Linton et al. with their ion microprobe experiments (*5*).

Analytical Techniques

Photoelectron Spectroscopy. The spectra were recorded on an AEI ES 200 B photoelectron spectrometer. The excitation is provided by the $K\alpha$ radiation of magnesium ($\text{Mg } K\alpha = 1253.65$ eV). The pressure in the neighborhood of the sample is 10^{-8} Torr when the spectra are recorded. The sample area is 0.75 cm^2.

The electron binding energy is determined by taking that of the 1s electrons of carbon contamination as an internal standard. This energy is set at 285 eV relative to the Fermi level of the spectrometer.

Atomic Absorption Spectroscopy. Before they can be analyzed by atomic absorption spectroscopy, the aerosol samples must be dissolved either by acid (analysis of all the elements except silicon) or by base (silicon analysis).

The apparatus used is a PYE UNICAM SP 1900 double beam instrument operating with an air–acetylene or nitrous oxide–acetylene flame, depending on the elements to be analyzed.

Collection of Atmospheric Aerosols

Plate Method. Sampling was performed in three industrial areas: Rouen, Dunkerque, and Blenod, by the "plate deposit" method (*6*).

Sedimentable dust carried by the air is deposited on metal plates covered with an appropriate coating. After a predetermined exposure time, the plates are washed with benzene. The suspension obtained is subjected to a series of rinses (benzene) and centrifugations. The particles are then obtained directly.

Filtration over Cellulose Ester Membranes. The aerosols were trapped on Millipore cellulose ester MF filters (reference AA WP 04700, 0.8 μm); samples were collected in Paris. The air flow rate is 500 $\text{L}\cdot\text{h}^{-1}$, and the sampling time varies from 1 to 4 days.

Generally, the samples were divided into two parts: one for analysis by XPS, the other for atomic absorption analysis. This treatment is obligatory, since the same part of a sample cannot be used successively for the two analyses. Firstly, analysis by atomic absorption spectroscopy is destructive and, secondly, a sample that has already been analyzed by XPS can only be reused with difficulty because of the fixing process.

Comparison of the Results of the Analysis Obtained by X-ray Photoelectron Spectroscopy and by Atomic Absorption Spectroscopy

The results of XPS have been expressed as the atomic concentration relative to sodium, since it is impossible to reproduce exactly the experimental conditions for the analysis of each sample (*7, 8*).

Sedimentable Particles Collected on Deposit Plates. The results of the analyses of sedimentable particles collected by the plate method are given in Figure 1 for the Ca/Na concentration. Similar dispersion is observed for iron, zinc, and lead. It is quite clear that there is no correlation between the results obtained by these two techniques. The absence of correlation could be due in part to the fact that photoelectron spectrometry only reaches the first layers of the samples.

Furthermore, the sedimentable particles are large (several microns) and can therefore show more marked heterogeneity of composition than the fine particles. XPS analyses of

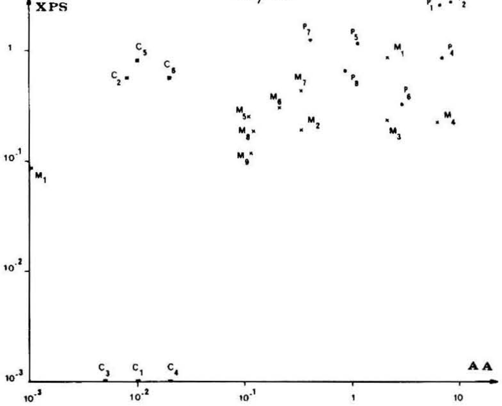


Figure 1. Comparison of the concentrations of Ca relative to Na determined by XPS and AA (P_i, plate sampling; M_i, Millipore sampling)

0013-936X/79/0913-1530$01.00/0 © 1979 American Chemical Society

Table I. Study of Particle Composition Heterogeneity Analysis by X-ray Photoelectron Spectroscopy

rel comp	Dunkerque 2 (P5) primary	Dunkerque 2 (P5) crushed	Dunkerque 3 (P6) primary	Dunkerque 3 (P6) crushed	Dunkerque 4 (P7) primary	Dunkerque 4 (P7) crushed	Dunkerque 5 (P8) primary	Dunkerque 5 (P8) crushed
Ca/Na	0.81	2.1	2.7	2.1	1.7	2.4	2.6	3.0
Zn/Na	0.35	0.19	0.32	0.19	0.77	0.68	0.54	0.59
Fe/Na	0.81	0.97	1.3	0.97	1.2	1.4	1.6	2.0
Si/Na	3.9	3.3	5.9	3.3	4.4	5.0	7.1	6.8

Table II. Study of Localization Heterogeneity Analyses by Atomic Absorption Spectroscopy[a]

element	filter no. 1 for piece a	b	c	d	mean value, $\mu g\ cm^{-2}$	filter no. 2 for piece a	b	c	mean value, $\mu g\ cm^{-2}$	filter no. 3 for piece a	b	c	mean value, $\mu g\ cm^{-2}$	blank, $\mu g\ cm^{-2}$
Na	+17	−21	0	+2	1.33	+1	−25	+9	1.40	−36	−26	+23	2.43	0.22
Fe	+28	−49	+17	−25	0.63	−11	−25	+14	1.61	−28	−19	−3	1.80	0.19
Ca	−36	+38	+17	−48	0.42	−44	0	+16	0.61	−36	+14	+8	0.91	0.15
K	−19	−30	+30	−14	0.70	+24	−18	−2	0.55	−3	−17	+7	1.20	0.11
Zn	−25	+3	+16	−13	3.46	−58	+173	−43	0.99	−46	−13	+21	0.63	0.10
Mg	−72	−67	+91	−70	0.43	−68	−64	+50	0.44	−69	−66	+50	0.62	
Al	−6	+6	−3	+6	0.33	−9	−12	+9	0.43	−5	+2	0	0.59	
mean of the abs devs per filter			27%				32%				23%			

[a] The areas of the pieces are not equal; the results are expressed as the deviation relative to the mean value.

Table III. Study of Localization Heterogeneity Analyses by X-ray Induced Photoelectron Spectroscopy

element/Na	filter no. 8 for piece a	b	c
Ca/Na	+15	−4	−11
Zn/Na	−55	+18	+36
N/Na	−22	+11	+10
Pb/Na	−31	+15	+15
S/Na	−28	+3	+25
Si/Na	+25	+1	−27
C/Na	−9	+9	0
mean of the abs dev per filter		18%	

[a] The results are expressed as the deviation relative to the mean value.

crushed and noncrushed samples confirm this result (Table I).

Particles Collected on Filter Membranes. Once again, no correlation between the results obtained by the two techniques is possible; the same dispersion is recorded for the other elements. The analytical results for Ca are given in Figure 1.

Study of Sample Composition Heterogeneity

Three types of heterogeneity need to be considered: localization heterogeneity, which corresponds to nonuniform distribution of the particles on the filter; thickness heterogeneity due, for example, to the deposition of layers of variable composition (changes in the meteorological conditions during sampling can in particular explain this sort of heterogeneity); heterogeneity of particle composition due to the fact that a particle can have a core composition different from that of the surface.

Whereas atomic absorption spectroscopy constitutes an overall analysis, XPS is affected by these three types of heterogeneity, since it takes into account only the superficial layers (≃50 Å) (*4*). Among these three types of heterogeneity, two have been studied experimentally.

Study of Localization Heterogeneity by Atomic Absorption Spectrophotometric and XPS Analysis. Three filters impregnated with aerosols were cut into three or four parts that were analyzed separately by atomic spectroscopy for sulfur, iron, calcium, potassium, zinc, magnesium, and aluminum. The areas of the different pieces were not equal. Table II gives the relative differences between the concentrations for each of the elements.

These results show that localization heterogeneity is important, on the average of the order of 30%. It must be noted that reproducibility of the method cannot explain the size of such errors. Another series of measurements carried out by X-ray fluorescence spectroscopy on two pieces of the same filter showed deviations of 40% relative to the mean value.

The same experiments were carried out by XPS, but we would remark at the outset that the figures determined by photoelectron spectroscopy concerning heterogeneity cannot be rigorously compared to those found by atomic absorption, since the latter takes into account all the thickness of the deposit, in contrast to photoelectron spectroscopy.

Three pieces of about 0.75 cm^2 were cut out from a Millipore filter. In contrast to the atomic absorption analysis, the whole filter is not analyzed; the mean concentration of each element (relative to sodium) on the filter was estimated from the mean of the concentrations of the parts analyzed.

As in the case of atomic absorption, the relative deviations in Table III are calculated from the concentration of each element (relative to sodium), determined on each of the pieces, and the mean value. These deviations, of the order of 20%, cannot be entirely explained by the reproducibility of the analytical technique, which is about 10%.

Study of the Heterogeneity of Particle Composition by XPS. A fraction of the sedimentable particles collected over the Dunkerque sites was analyzed directly by XPS; another fraction was first finely crushed. The relative atomic concentrations of Ca, Fe, Zn, and Si of four samples are given in Table I and reveal marked heterogeneity in the particle composition, especially for Zn and Ca, but no surface predominance of any element clearly appears.

In conclusion, these results reveal that aerosol samples show a triple heterogeneity: heterogeneity of particles whose surface composition is different from that of the core, this being detected by photoelectron spectroscopy; heterogeneities of samples trapped on filters (localization and thickness).

It is implicitly assumed in most work published that a piece of filter has the same composition as the mean composition of the whole filter. This does not at all correspond to what we have been able to observe in cases where the density is of the order of 1 $\mu g \cdot cm^{-2}$. Errors of 30–40% relative to the mean composition are possible. For this reason, the technique of cutting filters must be used the least, contiguous and simultaneous samples having a better chance of being comparable.

Acknowledgments

The authors are grateful to Mr. A. Salesse (Centre de Spectrochimie du Goupement Régional de Mesures) for technical assistance in XPS.

Literature Cited

(1) Saltzman, B. E., Cuddeback, J. E., *Anal. Chem.*, **47**, 1R (1975).
(2) Finlayson, B. J., Pitts, J. N., *Science*, **192**, 111 (1976).
(3) Novakov, T., Chang, S. G., Dod, R. L., *Contemp. Top. Anal. Clin. Chem.*, **1**, 249 (1977).
(4) Brion, D., Escard, J., *J. Microsc. Spectrosc. Electron*, **1**, 227 (1976).
(5) Linton, R. W., Loh, A., Natusch, D. F. S., Evans, C. A., Williams, P., *Science*, **191**, 852 (1976).
(6) "Fallout Measurements by the Deposition Plaquette Method", Standard NF X 43-007, Dec 1973.
(7) Carlson, T. A., Carter, W. J., Schweitzer, G. K., *J. Electron. Spectrosc.*, **5**, 827 (1974).
(8) Barbaray, B., Contour, J. P., Mouvier, G., *Analusis*, **5**, 413 (1977).

Received for review May 31, 1978. Resubmitted March 13, 1979. Accepted August 17, 1979. One of the authors (B. Barbaray) thanks the Electricité de France for financial support.

Cyanoarenes in Soot: Synthesis and Mutagenicity of Cyanoacenaphthylenes

S. Krishnan, Debra A. Kaden, William G. Thilly, and Ronald A. Hites[1]*
Massachusetts Institute of Technology, Cambridge, Mass. 02139

■ Two cyanoacenaphthylene isomers were synthesized and used to verify the presence of these compounds in soots generated by the combustion of aromatic hydrocarbon fuels doped with pyridine. Charge exchange–chemical ionization mass spectrometry (CE–CI MS) was utilized in differentiating between the other two cyanoacenaphthylene isomers. The mutagenic activity of the synthesized compounds was measured using a forward bacterial assay.

Several polycyclic aromatic hydrocarbons (PAHs) have been identified as carcinogenic compounds associated with soot (*1*). Nitrogen-containing aromatic compounds (azaarenes) are also present in soot (*2*), and some are known to be carcinogenic (*3*). However, since azaarenes are much less abundant than PAHs, they have received less attention, and their environmental abundances and biological activities are not well known. This is unfortunate since the environmental occurrence of azaarenes is likely to increase as fuels higher in organic nitrogen content are burned.

Dubay and Hites (*4*) have recently burned a model fuel containing 1–6% nitrogen and have identified the major azaarenes associated with this soot. The procedure involved Soxhlet extraction of the compounds from soot with CH_2Cl_2, the separation of the azaarenes from the bulk of the PAH by column chromatography, and the separation and identification of the individual azaarenes using gas chromatography (GC) and gas chromatographic mass spectrometry (GC–MS).

Figure 1 shows the gas chromatogram of the azaarene fraction obtained with a nitrogen-specific GC detector. The major nitrogen-containing compounds in the soot were identified as 1- and 2-cyanonaphthalene (peaks 1 and 2, respectively) and as the four isomers of cyanoacenaphthylene (peaks 3–6, isomers unspecified). The cyanonaphthalenes were identified by comparison of their mass spectra and exact gas chromatographic retention times with those of available standard materials. Cyanoacenaphthylene standards were not available; therefore, the identification of these compounds was considered tentative (*4*).

The purpose of the present study was to verify the identification of peaks 3–6 as cyanoacenaphthylenes, to specify which peak is which isomer, and to assess the mutagenic activity of these compounds. This has been done by a combination of chemical synthesis of reference compounds and charge exchange–chemical ionization mass spectrometry. The synthesized compounds were tested by a quantitative, forward mutation assay using 8-azaguanine resistance in *Salmonella typhimurium*. For the reader's reference, the numbering system of acenaphthylene is shown here:

Experimental

Instrumentation. A Hewlett-Packard 5730A gas chromatograph equipped with dual nitrogen–phosphorus flame ionization detectors was used for GC analyses. A Hewlett-Packard 5982A mass spectrometer interfaced to a 5933A data system was used for gas chromatographic mass spectrometry. Melting points were measured using an Electrothermal melting point apparatus and are uncorrected. NMR spectra were run on a Varian T-60 instrument. Clones arising on the mutation plates were counted with an Artek Systems automatic colony counter.

Synthesis of 1-Cyanoacenaphthylene. Acenaphthylene (1 g) was added to a stirred suspension of 5 g of anhydrous aluminum chloride in 150 mL of hexane; this was followed by 1 mL of bromine dropwise over a 5-min period. The mixture was stirred at room temperature for 1 h under anhydrous conditions ($CaCl_2$ drying tube). At the end of this period, a 0.2-mL aliquot of the reaction mixture was quenched with water and extracted with 1 mL of hexane. Gas chromatographic analysis of the hexane extract showed the absence of acenaphthylene, and GC–MS analysis showed the major

---

[1] Present address, School of Public and Environmental Affairs, Indiana University, Bloomington, Ind. 47405.

0013-936X/79/0913-1532$01.00/0 © 1979 American Chemical Society

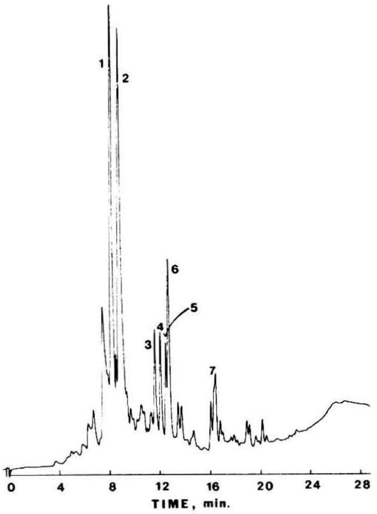


Figure 1. Gas chromatogram of azaarene mixture produced by combustion of 32% pyridine in *o*-xylene. GC conditions: 1.8 m × 2 mm i.d. glass column packed with 3% OV-17 on 80–100 mesh Supelcoport, programmed from 100 to 300 °C at 8 °C/min, nitrogen-specific FID. Peak identities as established in this study (see below): 1, 1-cyanonaphthalene; 2, 2-cyanonaphthalene; 3, 4-cyanoacenaphthylene; 4, 5-cyanoacenaphthylene; 5, 3-cyanoacenaphthylene; 6, 1-cyanoacenaphthylene; 7, isomers of cyanophenanthrene

product to be 1-bromoacenaphthylene [*m/e* (relative abundance) 233 (14), 232 (97), 231 (14), 230 (94), 151 (100), 150 (51)]. The reaction mixture was poured into 300 mL of ice-cold water in a separatory funnel and extracted with three 100-mL portions of hexane. The hexane extracts were combined, dried ($MgSO_4$), and evaporated in vacuo to remove the solvent. The residue, which contained the 1-bromoacenaphthylene, was treated with CuCN (1 g) in refluxing DMF (25 mL) for 14 h (*5*) to form 1-cyanoacenaphthylene. Final purification of the product was achieved by alumina column chromatography using hexane as the eluent. The yield was 250 mg (overall yield 22%): mp 91–95 °C dec; GC retention index, 2138; *m/e* (relative abundance) 178 (12), 177 (100), 176 (6), 151 (5), 150 (15).

Synthesis of 5-Cyanoacenaphthylene. 5-Bromoacenaphthene (4 g), available from Aldrich, was converted into 5-cyanoacenaphthene [2.5 g; 82% yield; mp 109–110 °C; NMR δ 3.39 (s, 4 H), 7.0–8.0 (m, 5 H); *m/e* (relative abundance) 181 (1), 180 (14), 179 (97), 178 (100), 177 (21), 153 (4), 152 (14), 151 (34), 150 (17)] by treatment with CuCN (2.5 g) in refluxing DMF (50 mL) for 6 h (*5*).

Dehydrogenation of 5-cyanoacenaphthene (0.15 g) was carried out in refluxing chlorobenzene (10 mL) with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 0.8 g) for 6 h under nitrogen. After this period, the mixture was cooled to room temperature and filtered through a small column of Al_2O_3 (25 g). The column was washed with 200 mL of 1:1 benzene–petroleum ether. The filtrate and washings were collected together and concentrated in vacuo. Chlorobenzene was removed from the residue by stream distillation, and the 5-cyanoacenaphthylene solid was recrystallized from methanol–water. The yield was 95 mg (63%): mp 82–83 °C; GC retention index, 2083; *m/e* (relative abundance) 178 (15), 177 (100), 176 (7), 151 (6), 150 (14).

Bacterial Mutation Assay. The compounds were assayed individually for their ability to induce mutations to 8-azaguanine resistance in *Salmonella typhimurium* as described by Skopek et al. (*6, 7*). Exponentially growing cultures of *S. typhimurium* were incubated for 2 h at 37 °C with several concentrations of each compound dissolved in dimethyl sulfoxide. To allow for the possible metabolic activation of the compounds, a drug metabolizing system derived from Aroclor 1254 induced rat livers (*7*) was added to the cultures. Following the incubation, bacteria were centrifuged (2000 rpm × 15 min), resuspended in phosphate-buffered saline, and plated under selective (50 μg/mL 8-azaguanine) and permissive conditions. Colonies were counted after 2 days' growth at 37 °C, and the mutant fraction for each culture was calculated (the number of colonies observed under selective conditions divided by the number of colonies observed under permissive conditions times the appropriate dilution factors).

Results and Discussion

The four cyanoacenaphthylenes may be divided into two classes: (i) bridge substituted and (ii) ring substituted. The two compounds synthesized represent an example from each category. Peaks 4 and 6 were identified as 5- and 1-cyanoacenaphthylene isomers, respectively, by coincidence of their exact GC retention times (through co-injection) and of their electron-impact mass spectra. The 1-cyanoacenaphthylene isomer decomposes on melting. In GC experiments, solutions containing equal concentrations of 1- and 5-cyanoacenaphthylene gave a lower response for the 1 isomer, probably due to its partial decomposition in the injection port (300 °C). This factor must be taken into account in the quantitation of 1-cyanoacenaphthylene in environmental samples using gas chromatography.

Peaks 3 and 5 (Figure 1) represent either 3- or 4-cyanoacenaphthylene. It is possible to differentiate between these isomers based on the (M + 1)/M ratios obtained from charge exchange–chemical ionization mass spectrometry (*8, 9*). This method involves the creation of a plasma containing $C_2H_5^+$ and Ar^+ by using 5–10% methane in argon as a reagent gas. A molecule reacts with the strongly acidic $C_2H_5^+$ to give the protonated molecular ion $(M + 1)^+$ or with an Ar^+ ion to give the molecular ion $(M)^+$. The intensity ratio of these two ions depends on their relative rates of formation. A high, positive correlation has been observed between the ionization potential of the molecule and the (M + 1)/M ratio derived from CE–CI mass spectrometry (*8*).

An examination of data previously reported from this laboratory (*4*) shows that the (M + 1)/M ratios are: 2.33 (peak 3), 2.10 (peak 4), 2.49 (peak 5), and 2.27 (peak 6). With the current knowledge of the identity of peaks 4 and 6 as 5- and 1-cyanoacenaphthylene, respectively, a prediction of the relative ionization potentials of the other two isomers would lead, through the correlation with the (M + 1)/M ratios from CE–CI MS, to the assignment of identities for peaks 3 and 5.

Charge exchange induced ionization by Ar^+ is an electrophilic reaction. Based on reactions of other electrophilic reagents, ionization of simple acenaphthylenes may be expected to occur at the ethylene bridge. Electron-withdrawing substituents on the aromatic ring would act to decrease the loss of an electron by this process, thereby increasing the ionization potential of the molecule. Such an inductive effect would decrease as the substituent is moved farther away from the reaction site (*10*). On this basis, one would predict that the ionization potentials would increase in the order 5-cyanoacenaphthylene < 4-cyanoacenaphthylene < 3-cyanoacenaphthylene. Experimentally observed CE–CI MS values of (M + 1)/M increase in the order peak 4 < peak 3 < peak 5. Based on the expected positive correlation between these two sets of parameters, it is predicted that peaks 3 and 5 are 4- and 3-cyanoacenaphthylene, respectively.

Acenaphthene, 1-cyanoacenaphthylene, 5-cyanoacenaph-

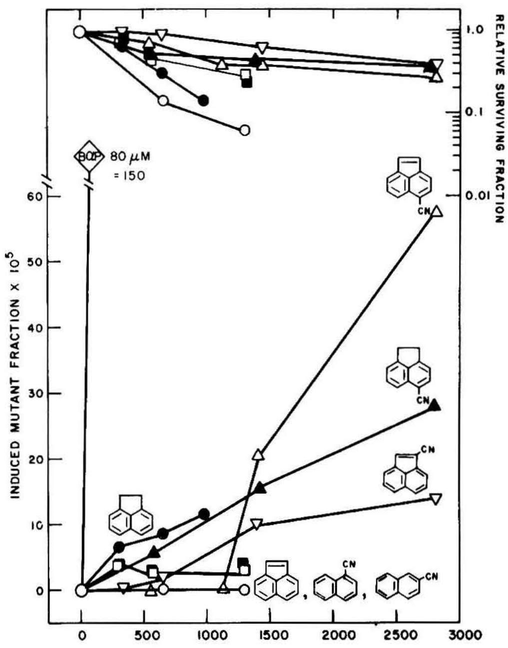


Figure 2. Dose-dependent mutagenicity (induced mutant fraction vs. concentration) and toxicity (relative surviving fraction vs. concentration) of acenaphthene (●), acenaphthylene (○), 1-cyanonaphthalene (□), 2-cyanonaphthalene (■), 1-cyanoacenaphthylene (▽), 5-cyanoacenaphthene (▲), and 5-cyanoacenaphthylene (△). All compounds were assayed in the presence of Aroclor-induced postmitochondrial supernatant. Each point represents the average of two independent determinations

thene, and 5-cyanoacenaphthylene induced significant mutation (Figure 2) to 8-azaguanine resistance in *S. typhimurium* at concentrations as low as 1000, 2800, 1100, and 1250 μM, respectively. Acenaphthylene and 1- and 2-cyanonaphthalene did not induce significant mutation at concentrations up to 1300 μM, their limit of solubility under the assay conditions. Benzo[*a*]pyrene, run as a positive control in each mutation assay, consistently induced mutation at concentrations as low as 4 μM. Although our results indicate that the active compounds have less than 1% of the activity of benzo[*a*]pyrene on a molar basis, the significant amounts of cyanoarenes produced by the combustion of nitrogen-containing fuels imply a need for concern. On the other hand, it is not known whether the cyanoarenes are environmentally persistent. Air particulate samples have been shown to contain the cyano functionality (*11*), but specific cyanoarenes have not been detected in the environment.

Acknowledgment

The authors thank Joanne Donovan for the exploratory work concerning 5-cyanoacenaphthylene.

Literature Cited

(1) Hoffman, D., Wynder, E. L., *ACS Monogr.*, **No. 173,** 324–65 (1976).
(2) Sawicki, E., McPherson, S. P., Stanley, T. W., Meeker, J., Elbert, W. C., *Int. J. Air Water Pollut.*, **9,** 515 (1965).
(3) Dipple, A., *ACS Monogr.*, **No. 173,** 245–314 (1976).
(4) Dubay, G. R., Hites, R. A., *Environ. Sci. Technol.*, **12,** 965 (1978).
(5) Friedman, L., Shechter, H., *J. Org. Chem.*, **26,** 2522 (1961).
(6) Skopek, T. R., Liber, H. L., Krolewski, J. J., Thilly, W. G., *Proc. Natl. Acad. Sci. U.S.A.*, **75,** 410 (1978).
(7) Skopek, T. R., Liber, H. L., Kaden, D. A., Thilly, W. G., *Proc. Natl. Acad. Sci. U.S.A.*, **75,** 4465 (1978).
(8) Lee, M. L., Hites, R. A., *J. Am. Chem. Soc.*, **99,** 2008 (1977).
(9) Hites, R. A., Dubay, G. R., in "Carcinogenesis", Jones, P. W., Ed., Vol. III, Raven Press, New York, 1978, pp 85–7.
(10) Ingold, C. K., in "Structure and Mechanism in Organic Chemistry", Cornell University Press, Ithaca and London, 1969, pp 71–83, 280–1.
(11) Chang, S. G., Novakov, T., *Atmos. Environ.*, **9,** 494 (1975).

Received for review June 18, 1979. Accepted August 20, 1979. Work supported by the Department of Energy (Grant No. EE-77-S-02-4267).

An Estimate of the NO_x Removal Rate in an Urban Atmosphere

Tai Yup Chang*, Joseph M. Norbeck, and Bernard Weinstock
Engineering and Research Staff, Research, Ford Motor Company, Dearborn, Mich. 48121

■ A formulation for estimating the NO_x removal rate by chemical reaction in an urban area is presented. Using the $(NO_x)/(CO)$ ratio from data obtained in the Los Angeles (LA) Basin, a lower bound for the yearly average removal rate of NO_x during daylight hours is found to be 4% h^{-1}. Using the $(PAN + HNO_3)/(NO + NO_2 + PAN + HNO_3)$ ratio from data obtained during the summer months at West Covina (LA Basin) and St. Louis by Spicer et al., the average NO_x removal rate during the daytime is also found to be 4% h^{-1}. From this analysis, the average residence time for NO_x in the LA Basin (all year) and St. Louis (summer) is estimated to be less than 2 days.

Nitrogen oxides ($NO_x \equiv NO + NO_2$) are involved in virtually every aspect of photochemical smog formation and tropospheric chemistry. Smog chamber studies and field monitoring reveal that the NO_x removal rate depends primarily on the degree of photochemical activity. A quantitative understanding of the NO_x removal rate is of some importance since the longer the residence time the greater the impact urban NO_x has on downwind areas. Despite recent studies, the NO_x removal rate in an urban atmosphere is not well understood quantitatively (*1*). The purpose of this note is to obtain an estimate of the NO_x removal rate in an urban atmosphere using available aerometric data.

Tracer and Reactive Species

The concentrations of the reactive species in the polluted atmosphere change with time as a result of chemical reaction, changes in pollutant sources, and dispersion/dilution. One may isolate somewhat the effects of chemical reaction and dispersion/dilution by using the concentration of some relatively inert compound as a normalizing factor. If the concentrations of a reactive species and an inert tracer in an air mass

Table I. Estimated Lower Bound for NO_x Removal Rate, k_r (h^{-1}), during Daytime

	West Los Angeles (800–1600 h)			Downtown Los Angeles (800–1600 h)			Azusa[a] (900–1300 h)		
year	annual	May–Oct	Nov–April	annual	May–Oct	Nov–April	annual	May–Oct	Nov–April
1970	0.066	0.088	0.049	0.051	0.042	0.062			
1971	0.053	0.068	0.041	0.040	0.051	0.037			
1972	0.050	0.063	0.041	0.052	0.050	0.050	0.084	0.095	0.073
1973	0.044	0.070	0.023	0.048	0.054	0.040	0.082	0.107	0.047
1974	0.023	0.039	0.007	0.032	0.030	0.031	0.085	0.111	0.051
1975	0.037	0.060	0.017	0.029	0.023	0.038	0.089	0.133	0.046
av	0.046	0.065	0.030	0.043	0.042	0.043	0.086	0.112	0.054

[a] Insufficient data for the years 1970–1971.

are designated by A and T, respectively, the rate equations for A and T may be written as:

$$\frac{dA}{dt} = S_A - (k_d + k_r)A \qquad (1)$$

and

$$\frac{dT}{dt} = S_T - k_d T \qquad (2)$$

where dA/dt and dT/dt are time derivatives, S_A and S_T are source strengths for the reactive and tracer species, respectively, k_d is the dispersion/dilution rate coefficient, and k_r is the pseudo-first-order reaction rate coefficient for the reactive species. S_A, S_T, k_d, and k_r are, in general, functions of time, t. By use of Equations 1 and 2, the rate equation for the ratio, $B = A/T$, is found to be:

$$\frac{dB}{dt} = (S_A - BS_T)/T - k_r B \qquad (3)$$

or

$$\frac{1}{B}\frac{dB}{dt} = \left(\frac{S_A}{A} - \frac{S_T}{T}\right) - k_r \qquad (4)$$

For the case when $|(S_A/A) - (S_T/T)| \ll k_r$:

$$k_r \simeq -\frac{1}{B}\frac{dB}{dt} = -\frac{d(\ln B)}{dt} \qquad (5)$$

Since $S_A/A \geq S_T/T$ for common sources of A and T, Equation 5 can be used to derive a lower bound for k_r even when $(S_A/A - S_T/T)$ is not negligible compared to k_r. It is also worth noting that when $(S_A/A - S_T/T) > k_r$, dB/dt becomes positive, i.e., B increases as t increases.

Although in general, S_A, S_T, k_d, and k_r are complicated functions of t, the steady-state approximation may be applied when t is large. The steady-state approximation for Equations 1 and 2 gives:

$$B = \frac{S_A}{S_T}\frac{k_d}{k_d + k_r} \qquad (6)$$

Rigorously, the relationships derived above apply only to a Lagrangian air mass. However, if relatively long time averaged quantities are obtained, ground level monitoring data can be used to approximate an average value for k_r. The assumption is that long-term, average aerometric data measured at a fixed ground location represent the average air quality of a relatively large air mass (mixed layer) surrounding the site. Aerometric data obtained from the Los Angeles Basin are used here.

Annual average, May–October (summer) and November–April (winter) $(NO_x)/(CO)$ ratios for West Los Angeles (WLA), Downtown Los Angeles (DOLA), and Azusa (AZ) for the years 1970–1975 have been used to estimate an average k_r. (The NO_x data used here were obtained by the Saltzman reagent wet-chemical method, which is known to be specific to NO and NO_2. Since the chemical residence time of CO is two orders of magnitude larger than that of NO_x, CO can be treated here as an inert species.) At these sites, ambient NO_x and CO are expected to result mainly from motor vehicles. (The 1970–1975 NO_x source inventory in LA County shows that the ratio of mobile to stationary sources is about 2–3. However, major stationary sources are located relatively far away from the sites WLA, DOLA, and AZ. The stationary source contribution to NO_x concentrations observed at the WLA, DOLA, and AZ sites is likely to be less than 10% (2).) The diurnal variations of the $(NO_x)/(CO)$ ratio at DOLA and WLA for 1970 are shown, for example, in Figures 1 and 2, respectively. The diurnal trend is consistent with the photochemical removal of NO_x during the daytime. For the years 1970–1975, the $(NO_x)/(CO)$ minimum occurs around 1600 h at the DOLA and WLA sites and 1300 h at the AZ site. For the period between 800 and 1600 h at DOLA and WLA, and between 900 and 1300 h at AZ, Equation 7 is used to estimate k_r:

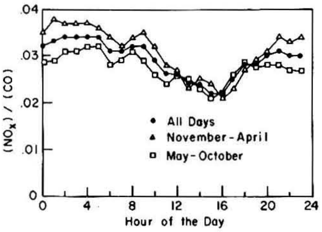


Figure 1. Diurnal variation of $(NO_x)/(CO)$, Downtown Los Angeles, 1970

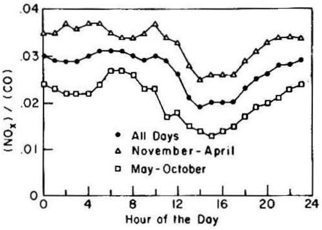


Figure 2. Diurnal variation of $(NO_x)/(CO)$, West Los Angeles, 1970

$$k_r \simeq -\frac{\Delta(\ln B)}{\Delta t} \qquad (7)$$

where B is the $(NO_x)/(CO)$ ratio. The results are shown in Table I. The average removal rate of NO_x in the LA Basin, for the time periods considered, is at least 4% h^{-1}. Furthermore, the removal rate at the WLA and AZ sites is much larger during the summer (May–October) than during the winter (November–April).

The diurnal variation of $(NO_x)/(CO)$ observed at AZ was quite different from those at WLA and DOLA. This may be the result of an influence of upwind sources, as may be seen

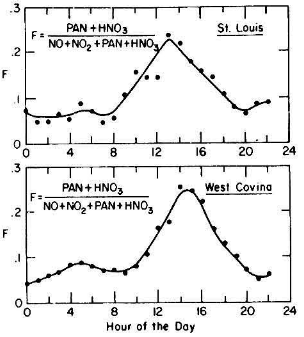


Figure 3. Composite profiles of F in St. Louis and West Covina (reprinted, with permission, from ref *1b*)

from the fact that the $(NO_2)/(NO_x)$ ratio at AZ is substantially higher than that observed at DOLA (*2*). The computed removal rate of DOLA is slower than that at AZ since freshly emitted NO_x has a relatively greater influence at DOLA than at AZ.

Reactant and Product

If a reactant concentration, R, and its product concentration, P, are monitored simultaneously, the sum, $R + P$, can be used as a tracer. Thus:

$$\frac{dR}{dt} = S_R - (k_d + k_r)R \tag{8}$$

$$\frac{d(R + P)}{dt} = S_R - k_d(R + P) \tag{9}$$

By defining the ratio:

$$F = P/(R + P) \tag{10}$$

F satisfies the rate equation:

$$\frac{dF}{dt} = - S_R F^2/P + k_r(1 - F) \tag{11}$$

When $S_R F^2/P \ll k_r(1 - F)$:

$$k_r \simeq \frac{1}{1 - F}\frac{dF}{dt} \tag{12}$$

It is noted that, if $S_R \neq 0$, Equation 12 underestimates k_r. Consequently, Equation 12 can also be used to estimate a lower bound for k_r.

Occasionally, all of the products are not measured or identified, and some portions of the identified products are lost from the air mass, e.g., dry deposition. When this occurs the measured value of F is less than the true value. In addition, since the loss of products increases as the product concentrations increase, the measured value of dF/dt is less than its true value. Since the effects of product loss and unidentified products are in the direction of underestimating k_r, in general, Equation 12 can be used to obtain a lower bound for k_r.

Spicer et al. (*1*) measured NO_x, HNO_3, and peroxyacetyl nitrate (PAN) at St. Louis and West Covina, in the LA Basin, for a 5-week period during the summer of 1973. They showed that the major reaction products of NO_x are PAN and HNO_3. The average diurnal variation of the ratio:

$$F = (PAN + HNO_3)/(NO_x + PAN + HNO_3) \tag{13}$$

obtained by Spicer et al. (*1*) is shown in Figure 3. For West Covina for the period 1000–1400 h, k_r was calculated, using Equation 12, to be 0.047 h^{-1}. This value is in good agreement with k_r obtained for LA using the $(NO_x)/(CO)$ ratio (see Table I). For St. Louis, for the period 800–1300 h, k_r is calculated to be 0.036 h^{-1}.

Discussion

An estimate of the average NO_x removal rate during daylight has been found to be greater than 4% h^{-1} for the yearly average in the LA Basin and greater than 3.6% h^{-1} during the summer months in St. Louis. If the NO_x removal rate is assumed to be 4% h^{-1} for 12 daylight hours and 0% h^{-1} for the 12 nighttime hours, the average NO_x residence time is 2.1 days. Since a lower bound for k_r was used, the average residence time is shorter than this. Also, it should be noted that the actual NO_x removal rate will vary greatly from day to day since it is dependent on the degree of photochemical activity.

From the lower bound of 4% h^{-1} for k_r, a lower bound for the average OH radical concentration, (OH), may be obtained. If the majority of NO_x is assumed to be removed via the reaction $NO_2 + OH = HNO_3$, with a rate constant equal to 1.1×10^{-11} cm^3 $molecule^{-1}$ s^{-1} (*3*), then the estimate of a lower bound for daytime (OH) is 1.0×10^6 molecule cm^{-3}. On the other hand, since the average (PAN) to (HNO_3) ratio measured by Spicer et al. (*1*) is approximately 3 to 1, the NO_x removal rate via the reaction $NO_2 + OH = HNO_3$ could be as low as 1% h^{-1}. This would yield a lower bound for daytime (OH) of 2.5×10^5 molecules cm^{-3}. The range of lower bounds for daytime (OH), 2.5×10^5–1.0×10^6, is consistent with the current range of estimates of average (OH), 5.0×10^5–2.0×10^6 molecule cm^{-3} (*4*). An additional removal of NO_x is via dry deposition, which has not been considered explicitly in this note. Hill (*5*) showed that for vegetation the uptake rate of NO_x is smaller than that of SO_2. The dry deposition velocity for SO_2 is approximately 1 cm s^{-1} (*6*). Thus, the dry deposition velocity for NO_x is expected to be less than 1 cm s^{-1}. The deposition coefficient, k_d, in h^{-1} can be estimated by means of a box model to be:

$$k_d = 36\nu_d/H \tag{14}$$

where ν_d is the deposition velocity (cm s^{-1}) and H is the mixing depth (m). If H is assumed to be 2000 m and ν_d is between 0.1 and 1 cm s^{-1}, the range of k_d is 0.002 to 0.018 h^{-1}. Since the estimate of k_d for NO_x is very uncertain, the effect of k_d will not be considered here.

Equations 5 and 12 can be rigorously applied to a Lagrangian air mass. A Lagrangian-type experiment was performed during the Los Angeles Reactive Pollutant Program (LARPP) (*7*). Calvert (*8*) used the LARPP data (operation 33, Nov 5, 1973) to estimate k_r for NO_x using C_2H_2 and CH_4 as tracers. Calvert obtained $k_r \simeq 9\%$ h^{-1} during the 800–1300 h period. During the LARPP operation 33, the degree of photochemical activity was moderate, with the O_3 concentration rising above 0.1 ppm by 1300 h.

Equation 5 cannot be applied for every LARPP operation since the relative contribution of the source-related term $(S_A/A - S_T/T)$ in Equation 4 varies significantly from operation to operation. The uncertainty in the measurement of low pollutant concentrations introduces an additional difficulty in deriving the NO_x removal rate from an individual experiment. To derive the NO_x residence time from an individual experiment, accurate measurements of various pollutant concentrations are needed. In addition, a detailed photochemical-dispersion model that explicitly includes sources and boundary conditions should be used.

Currently the influence of urban NO_x and hydrocarbon transport on high O_3 levels observed in nonurban areas has not been quantified (*9*). The removal rate and residence time for NO_x presented here are for an air mass near the ground in a well-mixed layer under average meteorological conditions.

During periods of very high photochemical activity, the NO_x residence time should be less than average, perhaps of the order of a few hours. Thus, urban NO_x emitted at ground levels would be consumed in less than 1 day under conditions conducive to high oxidant formation; consequently, under these conditions, the direct influence of urban NO_x emitted at ground levels to ozone formation at downwind areas may be minimal. On the other hand, plume NO_x from elevated sources, which is trapped in the inversion layer, may have a considerably longer residence time. Reliable Lagrangian-type air quality data (particularly, the ratios A/T and $P/[R + P]$) from the urban mixed layer and from power plant plumes during days conducive to photochemical oxidant formation are needed to clarify this issue.

Literature Cited

(1) (a) Spicer, C. W., *Adv. Environ. Sci. Technol.*, **17**, 163–261 (1977); (b) Spicer, C. W., Gemma, J. L., Schumacher, P. M., Ward, G. F., "Second Year Report: The Fate of Nitrogen Oxides in the Atmosphere to Coordinating Research Council, Inc. (CAPA-9-71)", Battelle Columbus Laboratories, Columbus, Aug 1976.
(2) Chang, T. Y., Norbeck, J. M., Weinstock, B., "NO_2 Air Quality–Precursor Relationship: An Ambient Air Quality Evaluation in the Los Angeles Basin", Air Pollution Control Association, Cincinnati, June 1979, Preprint 79-51.6.
(3) Hampson, R. F., Jr., Garvin, D., *Natl. Bur. Stand. (U.S.), Spec. Publ.*, **No. 513** (1978).
(4) Weinstock, B., Niki, H., Chang, T. Y., *Adv. Environ. Sci. Technol.*, in press.
(5) Hill, A. C., *J. Air Pollut. Control Assoc.*, **21**, 341–6 (1971).
(6) Garland, J. A., *Atmos. Environ.*, **12**, 349–62 (1978).
(7) Black, J. F., "Background on LARPP", Los Angeles Reactive Pollutant Program Symposium, Santa Barbara, Calif., 1974.
(8) Calvert, J. F., *Environ. Sci. Technol.*, **10**, 256–62 (1976).
(9) "Air Quality Criteria for Ozone and Other Photochemical Oxidants", Vol. I (preprint), U.S. Environmental Protection Agency, Washington, D.C., April 1978, EPA-600/8-78-004.

Received for review April 27, 1979. Accepted August 27, 1979.

Effects of Organic and Inorganic Binding on the Volatilization of Trace Elements during Coal Pyrolysis

Bill T. G. Ting and Stanley E. Manahan*

Department of Chemistry, 123 Chemistry Building, University of Missouri, Columbia, Mo. 65211

■ Volatilities were determined for eight environmentally important trace elements in coal subjected to pyrolysis in an inert atmosphere, using instrumental neutron activation analysis as the primary analytical tool. The elements studied were bromine, chlorine, selenium, arsenic, vanadium, manganese, chromium, and cobalt. In addition to observing these elements in the coal as received, they were added to the coal in both inorganic and organic forms. Both hydrogenated and nonhydrogenated coal were pyrolyzed. Striking differences in volatility were observed as a function of the element and as a function of the form of the element added to the coal. The metals incurred insignificant losses and were retained entirely in the coke. Bromine, chlorine, selenium, and arsenic were quite volatile. Losses of the latter two elements were much lower when they were added to the coal as a coal humic acid complex than when they were added as the inorganic sulfides.

Both pyrolysis and hydrogenation can be employed to obtain liquid hydrocarbon fuels from coal (*1*). A major environmental consideration in these processes is the fate of trace elements in the coal (*2*). The occurrence of trace elements in coal is illustrated by published studies involving 101 coals, primarily bituminous coals from the Illinois Basin region (*3, 4*). Among selected environmentally significant trace elements at levels of 1–10 ppm (mean values for all 101 coals analyzed) were beryllium, cadmium, cobalt, gallium, germanium, molybdenum, antimony, selenium, and tin; those present at 10–100 ppm were arsenic, bromine, chromium, copper, fluorine, manganese, nickel, phosphorus, lead, vanadium, and zirconium; and those present above 100 ppm were chlorine, boron, and zinc. In addition, pyritic and organic sulfur are normally present in coal at levels of at least 1%, and aluminum, calcium, iron, potassium, magnesium, sodium, silicon, and titanium are major components of mineral matter associated with coal. It is obvious that many elements are available to undergo reactions leading to their mobilization as soluble or volatile forms during coal conversion processes. For example, high-pressure hydrogen or carbon monoxide present during some coal conversion processes may well react with trace elements to form volatile hydrides, such as AsH_3, or volatile carbonyls, such as $Ni(CO)_4$ (*2*).

It is reasonable to believe that the forms of trace elements in coal subjected to coal conversion could strongly influence the fates and mobilization of these elements; organic vs. mineral binding is of particular importance. Although the speciation of trace elements in coal is largely unknown and difficult to study, it is possible to use known chemical properties to assign likely forms of the elements in coal (*5*). Following this approach, the elements likely to be present as oxides are arsenic, chromium, iron, scandium, silicon, and zirconium; as sulfides are antimony, arsenic, bismuth, cadmium, cobalt, copper, iron, lead, mercury, molybdenum, nickel, selenium, silver, sulfur, tin, and zinc; as sulfates are barium, calcium, and sulfur; as carbonates are calcium, magnesium, and iron; as silicates (clay, quartz) are lithium, magnesium, aluminum, manganese, samarium, silicon, silver, thorium, titanium, ytterbium, and zirconium; as an organic form are beryllium, boron, chlorine, chromium, cobalt, germanium, magnesium, manganese, mercury, nitrogen, selenium, sodium, strontium, sulfur, titanium, and vanadium; and as other forms are CaF_2, Hg (element), KCl, NaCl, iron selenides, and iron tellurides. Some elements are seen as possibilities in more than one classification.

This investigation was undertaken to determine the volatilities of selected trace elements during the pyrolysis of coal and hydrogenated coal, both unspiked and spiked with inorganic and organic forms of the trace elements. Coal pyrolysis was chosen because it represents a useful coal conversion process (*1*) that was relatively amenable to study with the apparatus available. Halides were added as sodium salts, the most likely form of these elements in coal. Inorganic forms of the other trace elements were spiked into the coal as sulfides, a possible form of a number of trace elements in coal. Coal humic acid was chosen as the medium for the addition of organically bound trace elements. This material has a strong affinity for a number of trace elements that can be bound to

0013-936X/79/0913-1537$01.00/0 © 1979 American Chemical Society

it by chelation and other means (6). Furthermore, some of the lower rank coals have a strong humic acid component, which is probably involved in the binding of trace elements in the coal.

Experimental

Sources and Characterization of Coal and Hydrogenated Coal. The coal employed in this study was originally obtained as a 10-kg fresh sample of raw coal from the Bruceton mine in Allegheny County, Pittsburgh, Pa. A 500-g portion of coal was randomly selected from the 10-kg sample, ground to a 100-mesh coal powder, homogenized on a shaker for 4 h, and dried at room temperature under vacuum for 1 week. In addition to studies performed directly on it, this product was used to prepare hydrogenated coal (H-coal) by treatment with hydrogen-donor tetralin solvent. A total of 100 g of coal powder was suspended in 500 mL of double-distilled tetralin contained in a 1-L round-bottomed flask and refluxed for 7 days, followed by vacuum evaporation of the remaining solvent for 2 days at 60–70 °C. The same basic procedure was used to hydrogenate coal *after* spiking with inorganic forms of trace elements.

Elemental Sulfides. Selenium sulfide (SeS_2), cobaltous sulfide (CoS), and chromium sulfide (Cr_2S_3) were obtained as commercial reagent-grade materials. Arsenious sulfide (As_2S_3), vanadium sulfide (V_2S_5), and manganous sulfide (MnS) were prepared by standard inorganic synthetic methods (7).

Trace Element Coal Humates. Coal humic acid was prepared by treating the coal with nitric acid oxidant (a necessary step for the extraction of significant quantities of humic material from bituminous coal), extracting with base, and purifying by methods previously described (8). Moist humic acid was dissolved in 0.1 M NaOH. Humate compounds were prepared by mixing this solution with acidic solutions of V(V), Mn(II), Cr(III), Co(II), As(V), and Se(−II) until a precipitate persisting in acidic solution was formed (7). These precipitates were removed by centrifugation, washed with water, and dried under vacuum for 24 h.

Spiked Coal and H-Coal. Coal and H-coal were spiked with desired amounts of pulverized trace-element species and mixed by agitation on a shaker for 32 h in glass sample bottles.

Pyrolysis of Spiked and Unspiked Coal and H-Coal. Samples were pyrolyzed in a 16 in. × 1 1/8 in. o.d. quartz reaction tube heated in a voltage-regulated tube furnace (Figure 1). Volatile products were transported to the traps with helium gas. The tube leading to the first trap was heated externally to minimize condensation in that tube. The first and second traps each contained 50 mL of double-distilled methyl isobutyl ketone (MIBK) to trap chelatable metal species, the third trap contained 50 mL of 0.5 M HNO_3 to trap acid-soluble volatile species, and the fourth trap contained 50 mL of 0.01 M EDTA at pH 10 to trap base-soluble volatile species and chelatable metals. An accurately weighed 5-g sample in a quartz boat was placed in the quartz tube preheated to 100 °C, following which the pyrolysis was carried out according to Table I at a helium flow rate of 0.12 standard L/h.

After pyrolysis was complete, the coke mass was removed, weighed, and saved for analysis. In addition, solution was sucked back into the tube leading to the first trap to wash residue from that tube.

Instrumental Neutron Activation Analysis (INAA). INAA was used for the determination of trace elements in the solid, and most of the liquid samples. Bromine, vanadium, chlorine, and manganese were analyzed with a 1-min irradiation at a neutron flux of 8×10^{13} n cm^{-2} s^{-1}, a 20-min decay period, and a 500-s counting time. Selenium, chromium, arsenic, and cobalt were analyzed with a 10-h irradiation at 3.5×10^{13} n cm^{-2} s^{-1}, a 3-day decay time for arsenic, a 14-day decay time for the other three elements, and a 500-s counting time. Details regarding the analysis procedure are given in a thesis dealing with the subject (7).

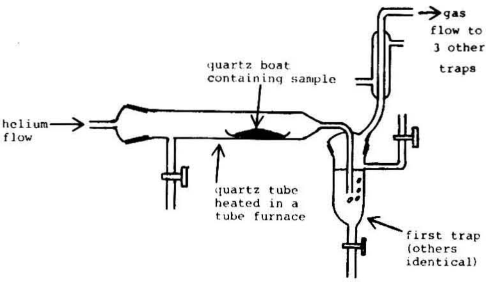


Figure 1. Apparatus for coal pyrolysis

Table I. Times and Temperatures for Coal and H-Coal Pyrolysis

time since sample insertion, min	T, °C	changes in coal during pyrolysis at the designated temp
0–10	100	loss of absorbed H_2O, CO_2, CH_4
10–25	250	evolution of lighter aromatics, alkyl-substituted aromatics, and aliphatics loosely bound to the coal structure
25–55	400	drastic decomposition, softening, evolution of NH_3
55–85	600	shrinking and hardening of coal mass
85–120	1000	evolution of H_2, CH_4, CO, and CO_2 leaving a char (coke) residue

Table II. Elemental Concentrations in Coal and H-Coal

element	concn in coal, µg/g	concn in H-coal, µg/g	
		uncorrected[a]	corrected[b]
Br	17.4 ± 0.8	14.7 ± 1.4	16.8 ± 1.6
Cl	835 ± 18	598 ± 53	682 ± 60
V	16.0 ± 0.3	13.2 ± 1.1	15.1 ± 1.3
Mn	9.45 ± 0.12	6.95 ± 0.65	7.92 ± 0.74
Se	1.42 ± 0.11	1.58 ± 0.03	1.80 ± 0.03
As	6.01 ± 0.86	5.32 ± 0.45	6.07 ± 0.51
Cr	10.4 ± 0.2	9.5 ± 0.1	10.8 ± 0.1
Co	2.83 ± 0.16	2.29 ± 0.22	2.61 ± 0.25

[a] Concentration of element in hydrogenated coal, not corrected for weight gain due to hydrogenation. [b] Concentration of element in hydrogenated coal corrected for 14% weight gain due to hydrogenation.

Atomic Absorption Analysis of Cobalt and Chromium in Liquids. Because of insufficient sensitivity by INAA, cobalt and chromium were determined in some of the liquid samples employing atomic absorption analysis following preconcentration by coprecipitation. Pyrrolidine carbodithioate, commonly abbreviated as APCD, and iron(III) were used to coprecipitate cobalt and chromium from acid-digested liquid samples. The precipitate was dissolved in HNO_3 and analyzed by graphite furnace atomic absorption (7).

Results and Discussion

The results of the trace element analyses of coal and H-coal are summarized in Table II. Lower concentrations of the elements in H-coal reflect an observed average weight gain of 14% due to hydrogenation. Although volatilization of trace elements during hydrogenation cannot be ruled out from the data available, chlorine is the only element that exhibits convincing evidence of volatilization as shown by a significantly lower Cl content in H-coal compared to the parent coal.

Table III. Trace Element Loss and Recovery during Pyrolysis

sample[a]	% wt loss[b]	wt, µg, of element in sample[c]		% volatile[d]	wt, µg, recovd[e]	% recovy[f]
		coal sample	coke			
bromine						
coal	32.6	75.6 ± 3.7	24.4 ± 4.2	67.7	29.6 ± 0.7	71.4
H-coal	46.0	74.6 ± 7.1	27.6 ± 3.9	63.0	20.4 ± 0.5	64.3
in/coal	32.1	$4.13 \times 10^3 \pm 0.38 \times 10^3$	$1.70 \times 10^3 \pm 0.16 \times 10^3$	58.8	430 ± 12	51.6
in/H-coal	46.4	$2.82 \times 10^4 \pm 0.25 \times 10^4$	$1.03 \times 10^4 \pm 0.04 \times 10^4$	63.4	$3.33 \times 10^3 \pm 0.06 \times 10^3$	48.3
chlorine						
coal	32.6	$3.63 \times 10^3 \pm 0.08 \times 10^3$	191 ± 16	94.7	$2.25 \times 10^3 \pm 0.05 \times 10^3$	67.2
H-coal	46.0	$3.03 \times 10^3 \pm 0.27 \times 10^3$	224 ± 20	92.6	$2.16 \times 10^3 \pm 0.08 \times 10^3$	78.7
in/coal	32.0	$2.48 \times 10^4 \pm 0.12 \times 10^4$	$1.30 \times 10^4 \pm 0.05 \times 10^4$	47.6	$3.49 \times 10^3 \pm 0.07 \times 10^3$	66.5
in/H-coal	46.2	$1.58 \times 10^4 \pm 0.07 \times 10^4$	$6.07 \times 10^3 \pm 0.04 \times 10^3$	61.6	$4.6 \times 10^3 \pm 0.08 \times 10^3$	67.6
vanadium						
coal	32.6	69.4 ± 1.1	74.3 ± 5.1		<0.03	
H-coal	46.0	66.8 ± 5.5	63.7 ± 5.5		<0.03	
in/coal	33.0	$4.18 \times 10^3 \pm 0.15 \times 10^3$	$3.72 \times 10^3 \pm 0.18 \times 10^3$		<0.03	
in/H-coal	46.3	$1.45 \times 10^3 \pm 0.08 \times 10^3$	$1.37 \times 10^3 \pm 0.04 \times 10^3$		<0.03	
org/coal	35.7	$9.05 \times 10^3 \pm 0.62 \times 10^3$	$8.63 \times 10^3 \pm 0.74 \times 10^3$		<0.03	
org/H-coal	46.3	$1.36 \times 10^3 \pm 0.13 \times 10^3$	$1.23 \times 10^3 \pm 0.04 \times 10^3$		<0.03	
manganese						
coal	32.6	41.1 ± 0.5	40.9 ± 1.1		<0.6	
H-coal	46.0	35.3 ± 3.3	30.9 ± 3.6		<0.6	
in/coal	31.7	$1.96 \times 10^3 \pm 0.16 \times 10^3$	$2.32 \times 10^3 \pm 0.29 \times 10^3$		<0.6	
in/H-coal	46.1	$2.14 \times 10^3 \pm 0.46 \times 10^3$	$2.09 \times 10^3 \pm 0.05 \times 10^3$		<0.6	
org/coal	33.8	$1.87 \times 10^4 \pm 0.22 \times 10^4$	$1.80 \times 10^4 \pm 0.10 \times 10^4$		<0.6	
org/H-coal	46.0	$6.20 \times 10^3 \pm 0.71 \times 10^3$	$6.40 \times 10^3 \pm 0.24 \times 10^3$		<0.6	
selenium						
coal	32.6	6.21 ± 0.52	2.31 ± 0.20	62.8	4.54 ± 0.28	110
H-coal	46.0	8.03 ± 0.16	3.31 ± 0.52	58.8	4.83 ± 0.20	101
in/coal	32.0	$2.18 \times 10^3 \pm 0.07 \times 10^3$	414 ± 21	81.0	$1.89 \times 10^3 \pm 0.03 \times 10^3$	105
in/H-coal	45.7	$2.23 \times 10^3 \pm 0.05 \times 10^3$	281 ± 2	87.4	$2.01 \times 10^3 \pm 0.13 \times 10^3$	102
org/coal	32.9	$2.76 \times 10^3 \pm 0.17 \times 10^3$	$2.18 \times 10^3 \pm 0.14 \times 10^3$	21.0	606 ± 18	101
org/H-coal	46.9	$2.57 \times 10^3 \pm 0.09 \times 10^3$	$1.57 \times 10^3 \pm 0.06 \times 10^3$	38.9	974 ± 27	99
arsenic						
coal	32.6	26.1 ± 3.7	13.2 ± 0.5	49.4	0.41 ± 0.14	52.3
H-coal	46.0	26.9 ± 2.3	16.7 ± 0.2	37.9	0.63 ± 0.26	64.3
in/coal	32.1	$5.01 \times 10^3 \pm 0.32 \times 10^3$	$2.58 \times 10^3 \pm 0.02 \times 10^3$	48.4	853 ± 57	68.5
in/H-coal	46.6	$3.04 \times 10^3 \pm 0.08 \times 10^3$	$1.75 \times 10^3 \pm 0.12 \times 10^3$	42.3	362 ± 23	69.5
org/coal	33.1	$1.65 \times 10^3 \pm 0.10 \times 10^3$	$1.53 \times 10^3 \pm 0.08 \times 10^3$	7.5	35.8 ± 3.3	94.6
org/H-coal	47.1	$1.90 \times 10^3 \pm 0.14 \times 10^3$	$1.73 \times 10^3 \pm 0.12 \times 10^3$	8.1	28.5 ± 0.9	93.3
chromium						
coal	32.6	45.3 ± 0.8	47.0 ± 7.5		<0.03	
H-coal	46.0	47.9 ± 0.3	45.2 ± 0.8		<0.03	
in/coal	31.0	$3.54 \times 10^3 \pm 0.17 \times 10^3$	$3.86 \times 10^3 \pm 0.35 \times 10^3$		<0.03	
in/H-coal	46.4	$4.46 \times 10^3 \pm 0.45 \times 10^3$	$4.75 \times 10^3 \pm 0.37 \times 10^3$		<0.03	
org/coal	32.5	$1.50 \times 10^4 \pm 0.02 \times 10^4$	$1.44 \times 10^4 \pm 0.07 \times 10^4$		<0.03	
org/H-coal	47.1	$1.80 \times 10^4 \pm 0.02 \times 10^4$	$1.81 \times 10^4 \pm 0.06 \times 10^4$		<0.03	
cobalt						
coal	32.6	12.3 ± 0.7	12.4 ± 1.4		<0.02	
H-coal	46.0	11.6 ± 1.1	10.8 ± 0.2		<0.02	
in/coal	31.6	$2.04 \times 10^3 \pm 0.22 \times 10^3$	$2.02 \times 10^3 \pm 0.30 \times 10^3$		0.23 ± 0.03	
in/H-coal	46.4	$5.28 \times 10^3 \pm 0.33 \times 10^3$	$5.40 \times 10^3 \pm 0.64 \times 10^3$		0.07 ± 0.01	
org/coal	32.5	$2.15 \times 10^3 \pm 0.05 \times 10^3$	$2.16 \times 10^3 \pm 0.03 \times 10^3$		0.26 ± 0.03	
org/H-coal	47.0	$2.78 \times 10^3 \pm 0.41 \times 10^3$	$3.04 \times 10^3 \pm 0.02 \times 10^3$		0.05 ± 0.01	

[a] Type of sample pyrolyzed for the immediately preceding element in italics. Coal designates unspiked original coal, H-coal designates unspiked coal hydrogenated with tetralin, in/coal designates original coal spiked with the inorganic form of the element (NaBr, NaCl, sulfides of the other elements), in/H-coal designates hydrogenated coal spiked with trace element after hydrogenation, org/coal designates original coal spiked with trace element humate, and org/H-coal designates hydrogenated coal spiked with trace element humate after the coal had been hydrogenated. [b] Percent total weight loss from the sample as volatile matter. [c] Total weight of the specified trace element in the sample prior to pyrolysis and after pyrolysis. [d] Percent of the trace element volatilized = [(wt trace element in sample − wt trace element in coke)/wt trace element in sample] × 100. [e] Total weight of trace element recovered in the four traps. In general, most of the recovery is in the first trap. Significant anomalies in this pattern are noted in the text. [f] Percent recovery = [(wt in traps + wt in coke)/wt in sample] × 100.

The most meaningful estimate of trace element mobilization during pyrolysis may be obtained by examining the mass of element lost from a particular sample during pyrolysis and the mass of the element recovered in the traps. These data are given in Table III and explained in the table footnotes. The percentage of total weight lost is higher for the more volatile

Table IV. Trace Element Loss and Recovery during Pyrolysis of Coal Hydrogenated after Spiking with Inorganic Forms of Trace Elements

element	wt, μg, of element in sample[a] coal sample	 coke	% volatile[a]	wt, μg, recovd[a]	% recovy[a]
Br	$1.70 \times 10^3 \pm 0.47 \times 10^3$	660 ± 42	61.1	126 ± 11	46.4
Cl	$3.23 \times 10^3 \pm 0.39 \times 10^3$	462 ± 95	85.7	820 ± 149	39.7
V	133 ± 11	113 ± 20		0.085 ± 0.08	
Mn	$1.16 \times 10^3 \pm 0.02 \times 10^3$	$1.11 \times 10^3 \pm 0.02 \times 10^3$		1.06 ± 0.09	
Se	380 ± 8	140 ± 6	63.2	216 ± 4	93.7
As	546 ± 22	527 ± 18	3.5	20.4 ± 0.6	100
Cr	$1.09 \times 10^3 \pm 0.17 \times 10^3$	$1.00 \times 10^3 \pm 0.08 \times 10^3$		none det.	
Co	662 ± 43	649 ± 28		none det.	

[a] Headings have the same meanings as the corresponding headings in Table III.

hydrogenated coal (H-coal) than for nonhydrogenated coal.

Both bromine and chlorine show a high percentage loss during pyrolysis. This holds true of the halides originally present in the coal, as well as those added as dry sodium salts. Although the maximum pyrolysis temperature of 1000 °C is lower than the boiling temperature of sodium bromide (1390 °C) and sodium chloride (1413 °C), complete loss of sodium chloride has been observed from an atomic absorption graphite furnace at 1000 °C (*9*). Therefore, it is likely that these salts were lost largely as volatile hydrogen halides or ammonium halides. Very small quantities of volatile organohalide compounds may have been formed. It is possible that sodium halide fumes were produced that were carried through the trapping system as very small aerosol particles. This possibility is consistent with the observation that halides were found in all four traps indicating transport through the trapping system.

Vanadium and manganese exhibited generally similar behavior during pyrolysis. For all samples pyrolyzed, these elements were quantitatively retained in the coke, and the levels of vanadium and manganese were below detection limits in all of the traps. It may be concluded, therefore, that no volatile chemical species of these two elements were produced by pyrolysis. Significant selenium losses were observed for all samples, especially those spiked with selenium sulfide, SeS_2. Selenium organically bound to coal humic acid was markedly less volatile. The nature of the binding of selenium to coal humic acid is not known. The selenium(IV) reacting with coal humic acid to form a selenium humate complex was in the form of $HSeO_3^-$. It is possible that this entity could be held by ion exchange on $-NH_3^+$ groups on the coal humic acid molecule or bound directly in the form, {coal humic acid}–SeO_3^-. The behavior of arsenic during pyrolysis parallels that of selenium. Like selenium, organically bound arsenic is strikingly nonvolatile.

No evidence was observed for the formation of volatile chromium compounds. Within the experimental error of the analysis method employed, all chromium was recovered in the coke product. No evidence of chromium was found in the traps. Detectable levels of cobalt were found in the first trap from pyrolysis of spiked samples. However, the detection limit of Co as applied to the medium in this trap is so low that the cobalt detected could well be from traces of the element carried over mechanically from the spiked samples rather than from formation of volatile cobalt-containing compounds.

Table IV presents data for the volatility and recovery of trace elements spiked into coal as the sulfides and sodium halides prior to hydrogenation by refluxing with tetralin. After hydrogenation, these samples were pyrolyzed and the degree of loss of each element determined. Substantial losses of bromine, chlorine, and selenium were observed. Surprisingly, relatively little arsenic was lost, suggesting that this element may have become bound to the organic coal matrix during the hydrogenation step preceding pyrolysis. However, measurable quantities of arsenic were recovered in the traps, so that some volatilization of this element did occur. Vanadium, chromium, and cobalt were not significantly volatilized. Very small but measurable levels of manganese were recovered in the first three traps. Thus, it is plausible that a very small fraction of manganese was converted to volatile manganese organometallic compounds by hydrogenation and subsequent pyrolysis of coal.

In summary, the volatilities of eight environmentally significant trace elements during laboratory pyrolysis have been determined for samples of coal and hydrogenated coal, both spiked and unspiked with the trace elements in question. Very significant differences were observed in that the halides and metalloids (Se, As) were quite volatile, whereas the metals were not. Organically bound selenium and arsenic were much less volatile than these elements in the form of sulfide salts. These results suggest that the chemical forms of elements are quite important in determining their mobilization during coal conversion processes, and that in some cases organic forms may be *less* volatile than inorganically bound trace elements. Although caution should be employed in extrapolating the results of laboratory studies to pilot plant and commercial scale coal conversion facilities, the results of this research imply that knowledge of the form of a trace element, as well as its quantity, may be necessary to evaluate potential problems from trace element mobilization in coal conversion processes.

Acknowledgments

The assistance of David McKown, Edward E. Pickett, and James R. Vogt in performing the chemical analyses and interpreting some of the data is acknowledged.

Literature Cited

(1) White, Jack W.; Sprague, Rita; McGrew, Wilma "Clean Fuels from Coal II"; Institute of Gas Technology: Chicago, 1975.
(2) Koppenaal, David W.; Manahan, Stanley E. *Environ. Sci. Technol.* **1976,** *10,* 1104-7.
(3) Ruch, R. R.; Gluskoter, H. J.; Shimp, N. F. *Environ. Geol. Notes, Ill. State Geol. Surv.* **1974,** *72.*
(4) Gluskoter, H. J. *Ill. State Geol. Surv., Circ.* **1977,** *No. 499.*
(5) Attari, A.; Mensinger, M.; Pau, J. Washington, D.C., 1976, U.S. Environmental Protection Agency Report EPA-600/2-76-259.
(6) Manahan, Stanley E. "Environmental Chemistry", 3rd ed.; Willard Grant Press: Boston, 1979; Chapter 4.
(7) Ting, Bill T. G. Ph.D. Thesis, University of Missouri, Columbia, 1979.
(8) Manahan, S. E.; Poulson, R. E.; Green, J. B.; Farrier, D. S. USDOE Technical Information Center, Oak Ridge, 1978, LETC/RI-78/5.
(9) Ediger, R. D.; Peterson, G. E.; Kerber, G. E. *At. Absorpt. Newsl.* **1974,** *13,* 3.

Received for review April 23, 1979. Accepted September 11, 1979. This research was supported in part by United States Department of the Interior Office of Water Research and Technology Allotment Grant A-110-MO and by the facilities of the University of Missouri Research Reactor.

INDUSTRY TRENDS

Los Angeles By-Products Co. (BYPRO, Pasadena, CA) has named Material Recovery Ltd. (Britain) as its international distributor. BYPRO manufactures refuse handling and resource recovery equipment.

Westinghouse has a $1.6 million contract to continue development of a unique solar reflector system, using 4300 heliostats, to produce 50 MW of electricity. The funding is from the Dept. of Energy.

The Babcock & Wilcox Co., now a subsidiary of J. Ray McDermott & Co., Inc., has a $13.5 million order from Westinghouse for the fabrication of nuclear components. A complete fabrication.

Gilbert/Commonwealth (Reading, PA) is providing engineering services to upgrade water supply/distribution for Empresa Municipal de Agua Potable Guayaquil (Ecuador). This will include one 100-mi, 24–28 in. pipeline.

Tower Systems Inc. (Tacoma, WA) announces success in tests of a method, tried in Nevada, to reduce wastewater volume at power plants and other facilities by as much as 96% through a patented waste heat transfer technology.

Stone & Webster Engineering Corp. (Boston, MA) is subcontracting for El Paso Electric Co. to evaluate use of solar energy to replace natural gas or oil in many of the Southwest's power plants. Funding is from the Dept. of Energy.

Envirotech/Air Quality Control Group says that the Buell division will install am 825 000-acfm "comprehensive" air pollution control system for Public Service Co. of Colorado. The 290-filter bag system should start up next November.

Reynolds Metals Co. will build a multimillion-dollar plant to separate aluminum and other nonferrous metals from automobile shredder residues, and will thus have the first U.S. facility using the Dutch "dense media" Stamicarbon process.

Messrs Cremer and Warner Ltd. (Britain) will assist the Singapore Ministry of the Environment in the control of environmental pollution from a proposed petrochemical complex, and will advise as to design through initial operations of the complex itself.

Sverdrup Corp. (St. Louis, MO) has expanded environmental services to include assistance with trace toxics and hazardous wastes.

Total Energy Corp. (Bohemia, NY), maker of solar-energy products, has started construction of a new 10 000-ft^2 plant whose completion is expected early next year.

Fuller Co. (Bethlehem, PA) has a fly ash conveying contract in excess of $1.5 million for the Chalk Point plant of Potomic Electric Power Co., to be installed at Aquasco, MD.

Goodyear (Akron, OH) estimates that the 200 million auto and light truck tires scrapped each year could, instead, be a source of energy to heat and light factories and office buildings.

LFE Environmental Analysis Laboratories (Richmond, CA) has a $495 000 contract from Lawrence Livermore Laboratory to analyze samples from the Marshall Islands for radioactivity levels. Among substances to be measured are americium, plutonium, and strontium.

Martin Marietta Data Systems will provide computer teleprocessing services to the Solar Energy Research Institute. Actual processing will be done at Martin Marietta's Orlando, FL facility.

Hydranautics Water Systems (Santa Barbara, CA) has provided a 150 000-gpd reverse osmosis (RO) system to furnish drinking water for phosphate miners in the Western Desert of Egypt.

Pollutronics, Inc. (Cleveland, OH) will make and market a complete filter-press line for F. H. Schule GmbH (Hamburg, W. Germany). This agreement is estimated to create 35–60 new jobs for the Cleveland area.

Wiley & Wilson, Inc. (Lynchburg, VA) was the designer of a waste-to-energy plant for NASA and the City of Hampton, VA, that cost $10 million, and will become operational next year. It will save more than 12 000 gpd of fuel oil, and confer other benefits.

York Research Corp. (Stamford, CT) is offering a service to check workplace environments for 400 contaminants for which OSHA has established exposure limits.

AIG Energy, Inc. has been formed at New York, NY, to furnish property and casualty coverages for energy-related industries, not including offshore oil or nuclear risks; these have other coverage channels.

Wastesaver Corp. (Bristol, CT) is to provide its evaporative recovery system to decontaminate radioactive water at the Three Mile Island nuclear power plant.

Milam Engineering, Inc. (Dunbar, WV) and its subsidiary have merged with Betz·Converse·Murdoch, Inc. The new firm will be Milam/BCM Engineering Inc. BCM is a supplier of environmental engineering services.

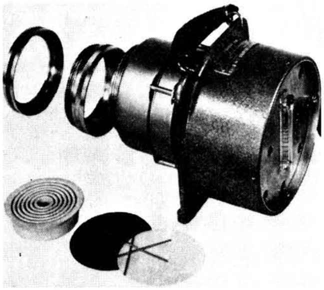
Acurex Corp. (Mountain View, CA) has opened a Chicago office of the company's Energy and Environmental Division. This office will offer full emissions sampling and particulate analysis services.

Air Resources, Inc. (Palatine, IL) has acquired Miscoliner Division of Misco United Supply, Inc. Miscoliner supplies and installs liners for ponds and tanks to prevent ground water contamination.

Columbia Chase Corp. (Braintree, MA) and **Surftex Inc.** have formed a joint venture to further fluidized-bed combustion of coal. A unique water process enhances the coal combustion.

Environmental Analysis and Design, Inc. (Orlando, FL) is gathering data for environmental impact statements in connection with proposed phosphate mine development in Polk County, FL.

ES&T PRODUCTS



Filter papers for air
New sampling filter papers for Model TFIA High Volume Air Sampler are now available. They allow sampling of particulate matter down to 0.01 μ, and alpha and beta particles at flow rates of 0–70 cfm. The Staplex Co. **101**

Tubing for water analysis
Stable tubing, marketed as Bev-A-Line®, consists of materials which do not interfere with highly sensitive water analysis. Tubing can tolerate temperatures from −60–160 °F, and for the V HT type, up to 250 °F. Many applications. Thermoplastic Scientifics Inc. **102**

Energy-saving fuel systems
Proprietary emulsion system allows fuel oil to be mixed with measured quantities of water before burning. Combustion is complete. Capacities up to 1900 gph of fuel oil now available; larger capacities may come soon. Folland Corp. **103**

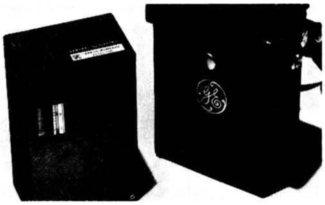
Air sampling pump
Hand-held pump can measure noncorrosive gases at 1–20 L/h, or at a fixed high rate of 1.5 L/min. Works on batteries, and can measure carbon monoxide (CO), other urban pollutants, and many industrial pollutants and components of mine atmospheres. Uses Tedlar® bags for gas sampling. Horizon Ecology Co. **104**

***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*

Fume scrubber/absorber
The Aerosorb® fume scrubber/absorber is designed to simplify removal of small particles and control fumes in laboratory exhaust, and low-capacity gas streams. Capacities 500–4000 cfm. Made of reinforced plastic, and equipped with a recirculating pump when necessary. Buffalo Forge Co. **105**

Portable pH meter
This portable and automatic pH meter has no adjustment rods, controls, or switches. Temperature compensation is built into the single combination pH electrode. Calibration is automatic. Measures pH 0–14 with temperatures of 0–90 °C and has a liquid-crystal display. Scientific Glass & Instruments, Inc. **106**

Land reclamation/revegetation
Reclamation equipment of new design helps to prepare land to be reclaimed for revegetation. LAND IMPRINTER crushes old plant material, brush, and soft rock, forms rough seed beds for planting, and inhibits erosion while promoting porosity and water infiltration into soil. EROCON **108**



CO detector
Carbon monoxide (CO) detector is compact and self-contained. It can measure 0–1000 ppm on a liquid-crystal display, and show the cumulative amount of CO to which a person may have been exposed. Alarms are built in. General Electric **107**

Inhalation chamber
A 200-L inhalation chamber is used for research and toxicity testing for various test-animal species, and uses pulmonary exposure techniques now available. Animal cages and racks are easily removable. Equipped with blowers, filters, and viewing ports. Wahmann Manufacturing Co. **109**

pH/mV meter
Model 18800 pH/mV meter has LCD digital display, and operates on single 9-V battery. Readings to 0.01 pH or 1 mV without guesswork or parallax error. Weight 1.6 lb. Battery life 100–260 h. Automatic or manual temperature compensation. Hach Chemical Co. **110**

Coke pushing emission control
Mobile coke oven pushing emission control system is now on line in Texas. Can capture outlet particulate down to 0.02 gr/dscf, as measured at 20% opacity or less. System on line processes 55 000 scfm. Hydro-Sonic Systems **113**

Water purification with RO
Water can be purified with reverse-osmosis (RO) systems up to 1000 L/h (4.4 gpm). That comes to 6400 gpd. Removes 90–95% dissolved inorganics; all organics over 300 molecular weight; 99% of particles and microorganisms. Operating cost about 0.5¢/gal. Millipore Corp. **111**

Non-PCB transformers
Transformers use dimethyl silicone as cooler/insulator. In addition, new features promote efficiency in transformer/rectifier sets. NWL Transformers **112**

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

Oil skimmers
Oil skimmers, Class V, 36 ft, are used in the Gulf of Mexico to defend against oil from the catastrophic Ixtoc I oil spill from Mexico. Major protection potential is in bays, harbors, and lagoons, to prevent oil from coming in. Marine Construction & Design Co. **114**

Comminutor
PIPELINE DELUMPER® comminutor breaks up solids, rags, or stringy materials in wastewater streams in pipes. Can work in 2–48 in. pipe sizes. Pressure rated, gas-, odor-, and watertight, fully enclosed and self-contained. Franklin Miller, Inc. **115**

$NO/NO_2/NO_x$ analyzer
The CSI 1600 analyzer can detect these oxides of nitrogen from 2 ppb to 5 ppm. Guaranteed over temperatures 10–40 °C. Easily maintained. Rapid cycling. Extremely low zero drift and span drift specifications. Columbia Scientific Instruments Corp. **116**

Welding fume removal
Nonelectronic collector, no special hoods or inlets needed, removes smoke and fumes from 2 spot-welding operations simultaneously. Fine particles in submicron range are removed. The Aget Manufacturing Co. **117**

Gas monitor
The ENMET CGS-10M gas monitor detects toxic and combustible gases in confined spaces, or other potentially hazardous areas. Has audio and visual hazard alarms. Determines actual gas concentrations, as well as oxygen deficiency. ENMET Corp. **118**

pH/temperature meter
Model 102B pH/temperature meter is used in the field, and can measure to 0.1 pH unit, and plus or minus 1 °C. Runs on 9-V carbon-zinc batteries (2 needed). Drew Chemical Corp. **119**

Clarifier
Collector tubes containing bacteria that convert organic nitrogen to nitrates have been developed to cleanse facultative lagoon effluent of algae and other suspended solids. The product is called D-CAN-TOR™. Schramm **120**

Level control/alarm
The complete unit consists of the all-plastic Model LL74 liquid level control and the Model 600 remote alarm package in one enclosure. The unit offers the means of monitoring high and/or low tank liquid levels in the same package. The Jobar Corp. **121**

IR spectrophotometer
The company is offering "a low cost ratio recording IR spectrophotometer", which features transmittance accuracy and repeatability. Options include microprocessor control and on-line computer interfacing. Sargent-Welch Scientific **122**

Fabric filter
The filter is designed for shaker and reverse air dust collectors. The fabric is constructed of heavy weight, abrasion resistant material. Baghouse Accessories **123**

Chemical feed systems
The custom designed, skid mounted feed systems are designed for use in water and wastewater treatment applications. The systems can be prewired and prepiped to any requirements. Systems include tanks, pumps, mixers, piping, wiring and controls. Neptune Chemical Pump **124**

Microbial sampler
The six-stage sampler collects airborne microorganisms, and differentiates between respirable and nonrespirable particles. Andersen Samplers **125**

Thyristor controller
The controller is developed for use with electrostatic precipitators; it maintains high precipitator efficiency by assuring that the T/R set's output voltage is maintained as close to the flashover point as desired. NWL Transformers **126**

Biocide for cooling towers
The "bromicide" is purported to be more effective than chlorine in controlling the common species of algae, fungi, and slime-producing bacteria found in industrial cooling towers. The product comes in solid form, for ease of handling and feeding. Western Chemical **130**

Weir oil skimmer
The manufacturer claims that this is the smallest stationary skimmer on the market: 8.2 kg, and measuring only 71×71×20 cm. It can recover up to 15 900 L of oil-fouled water per hour. Douglas Engineering **127**

Wastewater antifoam
EXFOAM® eliminates foam at waste treatment facilities, the manufacturer claims. The antifoam is available as a liquid in 5-gal pails, or 30- and 55-gal drums. Dearborn Chemical **128**

X-ray spectrometry system
The system offers rapid, simultaneous analysis of multiple elements, without the limitation of a fixed number of measuring channels. Measurements of a few ppm are possible. Philips **129**

Organic carbon analysis
Automatic sample introduction system is available as optional equipment for the PHOTOchem™ Organic Carbon Analyzer. Can work unattended, and handle 20 000 ppm down to 50 ppb, and even lower. Sampling error possibilities virtually eliminated. Sybron/Barnstead **131**

Water treater
Electronic water treater protects against corrosion and controls biological fouling in boilers, heat exchangers, cooling towers, chillers, and steam generators. Meets ASTM requirements for boiler piping, and is approved by the Canadian Standard Association. Progressive Equipment Co. **132**

Odor controller
Odor controller uses a prefabricated granular activated carbon filter. Phenolic material construction protects from corrosion. Can stop many obnoxious industrial odors from organic substances. Hoyt Mfg. Corp. **133**

Oxygen analyzer
Portable oxygen sampler/analyzer takes direct stack samples, reads oxygen content in percentages, 0–200 mV input, 1/10th increments. Weight is 4 lbs, accuracy 0.1% with instant response. Thermal Con Serv **136**

LITERATURE

Particulate analysis. Brochures tell how to collect and analyze both radioactive and nonradioactive particulates, as well as asbestos fibers and free silica. Paper prepared by certified industrial hygienists. LFE Environmental Analysis Laboratories **151**

HPLC sample injection. Technical note reports experiments showing effects of various sample-injection techniques on high-performance liquid chromatography (HPLC). Best techniques are explained. Rheodyne, Inc. **152**

Chemical-waste pumps. Technical bulletin TL-42 describes uses of Sump-Gard® SG plastic sump pumps for handling wastes such as chlorinated benzene compounds. Pumps are very corrosion-resistant. Vanton Pump and Equipment Corp. **153**

Lab apparatus. Catalog No. 7909 lists laboratory apparatus, such as hot plates, temperature controllers, many other items. Thermolyne Corp. **154**

PAH determination. Applications Note GC1 shows a new way to measure polynuclear aromatic hydrocarbons (PAH) in water, in a way that overcomes the difficulties normally involved. HNU Systems, Inc. **155**

Sludge handling. Reprint No. 269 tells why organic polymers are becoming more useful for municipal/industrial sludge treatment applications. Oil recovery is also featured. Nalco Chemical Co. **156**

Filter aids. Brochure FF-238A details advantages of cellulose-filter aids, such as longer cycles, stable cake formation, easy cleaning, and rapid pre-coat. Johns-Manville **157**

Filter media. Booklet FB-119 explains how "endless" filter media work more effectively to dewater sludge up to 100 gpm, or to filter up to 6000 gpm. Hoffman Air & Filtration Systems, Inc. **158**

Coal sulfur analysis. Bulletin No. AB-19 explains a time- and labor-saving way to determine sulfur in coal, in accordance with ASTM Methods D3177. Normally less than 3 min/sample. Fisher Scientific Co. **159**

CO detection. Application Bulletin 07-0135F details instruments and systems for detection and analysis of carbon monoxide (CO) in enclosed areas. Alarms are included. Devices can be programmed to activate ventilation equipment. Mine Safety Appliances Co. **160**

Mist eliminators. Bulletin KAL-1 is an aid to selecting mist eliminators, sludge dryers, items for cooling towers, and many other chemical engineering needs. Koch Engineering Co., Inc. **161**

Pesticide residues. Technical sheet describes co-distiller for rapid cleanup of pesticide-residue samples, fats, oils, and others. Samples of 2 g with residues as low as 0.025 ppm can be quickly cleaned. Specified in EPA-600/1-76-017. Kontes **162**

Spray nozzles. Catalog lists new line of solid and hollow spray nozzles for pollution control. Wm. Steinen Mfg. Co. **163**

Bacterial cultures. Brochure describes Type H-2 DBC Plus dried bacterial cultures for effective treatment of high-protein wastes in meat packing, dairy, and similar industries. Flow Laboratories **164**

O&M consulting. O&M means operations and maintenance. Paper tells how to select a wwt plant O&M consultant. It discusses "hands-on" experience, lab facilities, regulatory agencies, and many other pertinent topics. York Wastewater Consultants, Inc. **167**

Pump seals. Bulletin No. GL-01057 outlines seals, packings, and pump construction varieties in 300 combinations. The Gorman-Rupp Co. **168**

Coatings. "Water & Waste Portfolio" tells about protective coatings against corrosion and deterioration at water and wastewater-treatment (wwt) plants. Types/properties listed. Tnemec Co., Inc. **165**

Science supplies. "Fall Harvest of Values" lists temperature probes, balances, safety products, pH meters, and many other important items. Markson Science Inc. **166**

Heat recovery. Bulletin 104-32 lists heat exchangers for many purposes, including air cooling, heat recovery, steam condensing, and other applications. American Standard **169**

Chromatography. New 40-page issue of *Chromatography Newsletters* has 15 articles on advanced technology in liquid and gas chromatography. Ask for Order No. CHN-14. Perkin-Elmer **170**

Filtration. Brochure describes wide variety of filters and vessels used in industrial, aviation, and marine applications. Separators, media, other items described. Keene Corp. **171**

Plating recovery. Reprint explains how Rogate Industries (Mt. Vernon, OH) was able to clean wastewater and recover 98% of the chrome in its plating baths. Water is also conserved. Corning Glass Works **172**

Pollution lab equipment. Brochure features portable laboratory and control instruments for R&D pollution, quality, and test laboratories. Includes CO analyzers, oxygen indicators, others. Gas Technologies, Inc. **173**

Chromatography. Bulletin 34 lists special chromatography products and their applications. Organic vapor collection featured. Alltech Associates, Inc. **174**

***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*

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

ES&T
BOOKS

The Terrestrial Ecology of Aldabra. 263 pages. The Royal Society, 6 Carlton House Terrace, London SW1Y 5AG, England. 1979. $46.60.

Aldabra is an atoll in the western Indian Ocean, whose ecology is dominated by 150 000 giant tortoises. This is the only known ecology on earth dominated by a reptile. However, there are many other unique species, both animal and plant. The Royal Society maintains a research station on Aldabra which is, in some ways, perhaps analogous to the Galápagos Islands of the eastern Pacific Ocean.

1979 Users Guide to Waste Handling Equipment. Waste Equipment Manufacturers Institute (WEMI). Publications Dept., NSWMA, 1120 Connecticut Ave., N.W., Suite 930, Washington, DC 20036. 1979. $2, paper.

This guide lists 65 WEMI manufacturers' addresses and telephone numbers which are needed by anyone who makes decisions concerning waste handling equipment purchase. The **"Resource Recovery Decision-Makers Guide"** is available from the same address for $5.

Occupational Cancer—Prevention and Control. 36 pages. International Labour Office Publications, CH-1211 Geneva 22, Switzerland. 1979. $4.95.

This booklet is No. 39 of the Occupational Safety and Health Series. It is based on experience gained in the chemical industry, and deals with preventive measures, biological and environmental monitoring, medical surveillance, and administrative procedures. A list of suspected carcinogenic substances is also included.

Coal Liquefaction Processes. Perry Nowacki, xii + 339 pages. Noyes Data Corp., Mill Rd. at Grand Ave., Park Ridge, NJ 07656. 1979. $48, hard cover.

The aim here is to describe, in one book, all the coal-liquefaction technologies presently available. These include pyrolysis, solvent extraction, catalytic liquefaction, "H-Coal", Synthoil, and many others. Economic and environmental considerations, as well as equipment are also covered.

Water Management and Environment in Latin America. 360 pages. Pergamon Press, Fairview Park, Elmsford, NY 10523. 1979. $50, hard cover; $20, "flexicover".

This work covers patterns and trends, water management cases, biophysical factors, and recommendations for the future. Case studies are included. Environmental relationships and institutional factors are dealt with. The book is addressed to those concerned with international development, as well as students and research workers.

Evaluation of Ambient Air Quality by Personnel Monitoring. Adrian L. Linch. Volume I, 336 pages; Volume II, 288 pages. CRC Press, Inc., 2000 N.W. 24th St., Boca Raton, FL 33431. 1979. Volume I, $69.95; Volume II, $64.95 (add $10 to each for outside U.S.), hard cover.

Personnel monitoring (*ES&T*, April 1979, p 388) is a way of getting an idea of pollutant content in ambient air. NIOSH and OSHA have come out with recommended techniques for this type of monitoring, and these volumes update previous books on the subject, while adding much new information.

Biological Indicators of Water Quality. A. James, Lilian Evison, Eds. xvi + 640 pages. John Wiley & Sons, Inc., 605 Third Ave., New York, NY 10016. 1979. $37.50 hard cover.

Papers in this book relate to many physiological tests of living organisms for water quality, from bacteria to fish. Systems of classification are developed, effects of pollution on protozoa, algae, higher plants, fish, and other species are discussed. Advantages and disadvantages of biological methods are presented, as well as experience in Europe and North America.

Air Pollution Chemistry. J. D. Butler. viii + 408 pages. Academic Press, 111 Fifth Ave., New York, NY 10003. 1979. $52.50, hard cover.

What are sources, sinks, and removal mechanisms of air pollutants? This question is answered, as are many other questions concerning this chemistry. Meteorological influences are also taken into account quite thoroughly. Aerosols are studied, as are sampling/collection methods, health factors, analysis of pollutants, urban atmospheres, and other pertinent subjects.

Land Application of Wastes. Raymond C. Loehr, et al. Vol. 1, xxi + 308 pages; Vol. 2, xxi + 431 pages. Van Nostrand Reinhold, 135 W. 50th St., New York, NY 10020. 1979. Vol. 1, $19.95; Vol. 2, $22.50, hard cover.

Land application is being increasingly considered as a means to dispose of municipal/industrial/agricultural wastes. Volume 1 considers design procedures for land use, treatment systems, siting, cost, and legal matters. Vol. 2 looks at nitrogen, phosphorus, organic matter, toxics, pathogens, and crop selection. The authors are all with Cornell University.

At Work in Copper: Occupational Health and Safety in Copper Smelting. Manuel Gomez, et al. Vol. 1, xiii + 284 pages; Vol. 3, 484 pages. INFORM, 25 Broad St., New York, NY 10004. 1979. Vol. 1, $40; Vol. 3, $20, paper. Full 3-volume set, $70.

Vol. 1 looks at industry performance, hazard evaluation and controls, and copper company health/safety performance. Vol. 3 discusses particular companies and their smelter facilities, and addresses actual performance at those particular smelters. Vol. 2 was covered in *ES&T*, August 1979, p. 1006.

Soil 'Neath My Feet. Robert W. Terrell. xix + 68 pages. Vantage Press, 516 W. 34th St., New York, NY 10001. 1979. $5.50, hard cover.

The author explains how the various types of farming soils are composed, and how they work. He also presents arguments in favor of organic gardening/farming and against the use of inorganic fertilizers. Insect control, farm ponds, and animal husbandry are also discussed.

ES&T MEETINGS

January 7–10 San Diego, CA
The 14th IEEE Photovoltaic Specialists Conference

Write: Charles E. Backus, College of Engineering & Applied Sciences, Arizona State University, Tempe, AZ

January 8–10 Tampa, FL
Operation, Control & Management of Activated Sludge Plants Treating Industrial Wastewaters.

Write: Janet Vance, Vanderbilt University, Box 6222, Sta. B, Nashville, TN 37235

January 13–18 Sea Island, GA
Geotechnical and Environment Aspects of Geopressure Energy.

Write: Engineering Foundation Conferences, 345 East 47th St., New York, NY 10017

January 21–23 Houston, TX
1979 Annual Technical Meeting. The Cooling Tower Institute, Inc.

Write: Dorothy Garrison, executive secretary, 9030 North Freeway, #216, Houston, TX 77037

January 21–25 Orlando, FL
Energy from Biomass and Wastes. Institute of Gas Technology

Write: Kathy Fisher, Box 250, Institute of Gas Technology, IIT Center, 3424 South State St., Chicago, IL 60616

January 22–25 Austin, TX
The Second Conference on Air Quality Management in the Electric Power Industry. The Center for Energy Studies at the University of Texas

Write: Hal B. Cooper, program chairman, Center for Energy Studies, University of Texas at Austin, Austin, TX 78712

International

January 7–11 San Juan, PR
International Winter Conference 1980 on Developments in Atomic Plasma Spectrochemical Analyses. University of Massachusetts

Topics include energy production and energy-related materials, environmental monitoring and water-quality monitoring. *Write:* Winter Conference 1980, ICP Information Newsletter, Chemistry—GRC Tower 1, University of Massachusetts, Amherst, MA 01003

January 17–24 Bombay, India
Chem+Tech '80 Exhibition and Congress.

Write: S. K. Murti, executive vice-president, Journeyworld International, Ltd. 527 Madison Ave., New York, NY 10022

February 6–8 Stockholm, Sweden
Third International Congress on Industrial Waste Water and Wastes. International Union of Pure and Applied Chemistry

Write: Third International Congress on Industrial Waste Water and Wastes, Box 21060, S-100 31 Stockholm, Sweden

Call for papers

December 15 deadline
Second Annual Conference on Industrial Energy Conservation Technology and Exhibition. Texas Industrial Commission and the U.S. Department of Energy.

Conference will be held April 13–16, 1980 in Houston, TX *Write:* M. A. Williams, technical program director, 6203B Shadow Valley Dr., Austin, TX 78731

January 1 deadline
1980 Solar Jubilee. American Section of the International Solar Energy Society (AS/ISES)

Conference will be held June 2–6, 1980 in Phoenix, AZ *Write:* William Stephenson, Solar Energy Research Institute, 1536 Cole Blvd., Golden, CO 80401

January 1 deadline
IOPPEC '80 (International Oil Pollution Prevention Exhibition & Conference). IOPPEC.

Conference will be held September 23–27, 1980 in Hamburg, W. Germany. *Write:* Millard F. Smith, conference co-chairman, IOPPEC, 250 Pequot Ave., Southport, CT 06490

January 31 deadline
Eleventh Annual Pittsburgh Conference on Modeling and Simulation. University of Pittsburgh and others.

Conference will be held April 30–May 2, 1980 in Pittsburgh, PA *Write:* William G. Vogt, Modeling and Simulation Conference, 348 Benedum Engineering Hall, University of Pittsburgh, Pittsburgh, PA 15261

(continued on page 1549)

professional consulting services directory

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

CATALYTIC INC.

Consultants • Engineers • Constructors
Environmental Systems Division
Centre Square West, 1500 Market Street
Philadelphia, Pa. 19102, 215-864-8000
Charlotte, N.C. 28210, 704-542-4220
Baton Rouge, La. 70895, 504-293-6200

---

pms
permit management services

A personalized approach to air, water, and hazardous waste permits.

(703) 360-1400

8607 Camden Street
Alexandria, VA 22308

COMPLETE ENVIRONMENTAL SERVICES

- REGULATORY GUIDANCE
- 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
Marketing Manager

GCA CORPORATION
Technology Division
Burlington Road, Bedford, Mass. 01730
(617) 275-9000

Monsanto
Environmental Services

ENGINEERING CONSULTATION

- *SOURCE & AMBIENT AIR TESTING*
- *DIFFUSION MODELING*
- *GC/MS EPA PRIORITY POLLUTANTS*
- *BIOANALYTICAL LABORATORY*
- *TREATABILITY STUDIES*
- *INDUSTRIAL HYGIENE SURVEYS/ANALYSES*

MONSANTO RESEARCH CORPORATION
BOX 8 STATION B
DAYTON OHIO 45407
ATTN D.B. NELSON (513)-268-3411

LFE ENVIRONMENTAL
ANALYSIS LABORATORIES DIVISION

Air and Water Pollution • Radiochemistry
Geothermal Surveys • Industrial Hygiene
2030 Wright Avenue, Richmond, CA 94804
(415) 235-2633

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

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

---

enviroservice®
Programs

- Consulting engineering water • air • solid waste
- Air testing
- Analytical lab services

CHAGRIN FALLS, OHIO 44022
(216)247-5000
Arlington, TX • Charlotte, NC
Los Angeles, CA • Minneapolis, MN
Portland, OR • Windsor, CT

MOGUL
THE MOGUL CORPORATION

ENVIRONMENTAL ENGINEERING SERVICES

AEROVIRONMENT

- Air Quality
- Emissions Control Technology
- Low Level Nuclear Radiation

(213) 449-4392
145 Vista Ave
Pasadena, CA
91107

AIR & WATER
STACK & EXHAUST TESTS
CONSULTING • LABORATORY
Particulates • Aerosols • Odor • Smoke
Organics • Fumes • Acids • Foundries
G. C. Chemical Analyses/O.S.H.A.
"TEST IT FIRST SO YOU REALLY KNOW WHAT THE PROBLEM IS"

ROSSNAGEL & ASSOC.

Engineering & Testing Consultants
Medford, N.J. (609) 654-1441
Charlotte, N.C. (704) 333-8411
Atlanta, GA. (404) 377-4248
South Euclid, OH. (216) 777-5500

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

One Center Plaza
Boston, Massachusetts 02108

CDM
environmental engineers, scientists, planners, & management consultants

---

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

professional consulting services directory

THE CADRE CORPORATION
APC ENGINEERS & CONSTRUCTORS

- Cadre engineered CUSTOM Structural Baghouses for Hot Gas & Abrasive Applications
- Cadre Special-Design Fume & Fly Ash Collection Units - Shop Assembled
- Retrofit SPECIALIST of large existing Baghouse Systems
- Experts in correction of air flow or difficult duct design for reduction in pressure drop through laboratory & scale modeling
- Feasibility & cost trade-off studies with use of Cadre's Computing Center

PLEASE CONTACT: TERRY BARTLETT • THE CADRE CORPORATION
P.O. BOX 47837 • ATLANTA, GEORGIA 30362 • (404) 458-9521

TURNKEY AIR POLLUTION CONTROL SYSTEMS

Ambient Air Quality Studies
Diffusion Modeling
Source Sampling
Industrial Hygiene Services
Noise Surveys
Water & Wastewater Surveys
Laboratory Services
Engineering Services

Galson
Technical Services, Inc.

6601 Kirkville Road, East Syracuse, N.Y. 13057
(315) 437-7181

---

envirodyne engineers

222 West Adams St. • Chicago, Illinois 60606
(312)263-0114

A Professional Consulting Services Firm

Transportation • Environmental
Food Engineering • Energy • Civil/Sanitary
Systems Studies and Design

offices in principal U.S. cities

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

UNITED STATES TESTING CO. INC.

Complete Sampling & Analytical Services:

- Water & Wastewater Analyses
- Priority Pollutants
- Bench Scale Modeling
- Stack Sampling
- Industrial Hygiene
- Aquatic & Marine Bioassays

Home Office 1415 Park Avenue,
Hoboken, N.J. 07030
(201) 792-2400

ENVIRONMENTAL CONSULTANTS INC

ANALYTICAL TESTING AND SAMPLING SERVICES:

- EPA—Drinking water
- Certified bacteriological testing
- N.P.D.E.S. Permit
- EPA consent decree
- Workplace environments
- Stack emissions—particulates
- 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

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

Ground Water Associates, Inc.

Water Supply Geologists and Engineers

- **Hydrogeological Investigations**
- **Iron Removal by VYREDOX Process**
- **Hydrocarbon Bioreclamation**

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

Linden, New Jersey
Arlington, Massachusetts

MET

MET ELECTRICAL TESTING COMPANY, INC.

916 W. PATAPSCO AVE.
BALTO., MD. 21230
(301) 354-2200

984 GREENTREE RD.
PITTSBURGH, PA. 15220
(412) 922-9595

ELECTRICAL POWER SYSTEM ENGINEERING STUDIES
TESTING • SURVEYS • RECORDINGS
INSPECTIONS • EVALUATIONS

RECON SYSTEMS

INCINERATOR AND
HAZARDOUS WASTE
ENGINEERING & TESTING

Box 842
Somerville, N.J. 08876

(201)
685-0440

Consulting Engineers
Air Pollution Control
Drainage & Flood Control
Industrial Waste
Resource Recovery
Solid Waste
Water Supply
Water Pollution Control

Velzy ASSOCIATES

Charles R Velzy Associates, Inc., 355 Main St., Armonk, NY 10504
Mineola, NY / Babylon, NY

WATER
WASTEWATER
SOLID WASTES

- Chicago
- New York
- Philadelphia
- Richmond
- Tampa
- Atlanta

222 S Riverside Plaza Chicago 60606

GREELEY AND HANSEN
ENGINEERS
Since 1914

W I C

WATER INFORMATION CENTER, INC.

Publishers of reference books, texts,
and newsletters on the subject of water.
Send for catalog
The North Shore Atrium
6800 Jericho Tpke., Syosset, N.Y. 11791 (516) 921-7690

HAVENS AND EMERSON, INC.

Environmental Engineers

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

WALK, HAYDEL & ASSOCIATES, INC.

Complete Environmental Services

Refineries, Chemical Plants
Fertilizer Facilities, Pipelines, Docks,
Oil & Gas Offshore Facilities, Terminals
600 Carondelet St., New Orleans, La. 70130
504-586-8111

Baton Rouge, La
Mobile, Ala

USE THE CONSULTANTS' DIRECTORY

Executive Search Consultants

- **Environmental Engineering**
- **Industrial Toxicology**
- **Regulatory Compliance**

Blendow, Crowley & Oliver Inc
420 Lexington Ave New York, N.Y. 10017 (212) 986-0303

Courses

January 8–11 Birmingham, AL
Control of Particulate Emissions, Course #413. EPA Air Pollution Training Institute
Fee: $88. *Write:* Shelia Honeycutt, Air Pollution Training Institute, MD20, Environmental Research Center, Research Triangle Park, NC 27711

January 8–11 Puerto Rico
Air Pollution Control Technology, Course #431. EPA Air Pollution Training Institute
Fee: $88. *Write:* Shelia Honeycutt, Air Pollution Training Institute, MD20, Environmental Research Center, Research Triangle Park, NC 27711

January 9–11 Washington, DC
Advanced Environmental Assessment Techniques: Industrial Waste Water Discharges. The George Washington University
Fee: $455. *Write:* Director, Continuing Engineering Education Program, George Washington University, Washington, DC 20052

January 14–17 Madison, WI
Understanding microprocessors. University of Wisconsin
Fee: $430. *Write:* Engineering & Applied Science, University of Wisconsin, 432 North Lake Street, Madison, WI 53706

January 14–18 Atlanta, GA
Dispersion of Air Pollution—Theory and Model Application. EPA's Air Pollution Training Institute
Fee: $99. *Write:* Shelia Honeycutt, Air Pollution Training Institute, MD20, Environmental Research Center, Research Triangle Park, NC 27711

January 14–18 Las Vegas, NV
Water Quality Modeling. Desert Research Institute, University of Nevada
Fee: $425. *Write:* P. A. Krenkel, Water Resources Center, Desert Research Institute, P.O. Box 60220, Reno, NV 89506

January 16–18 East Brunswick, NJ
Industrial and Applied Microbiology and Acute Toxicity. The Center for Professional Advancement
Topics include quality control, regulatory affairs and AOAC methodology. Fee: $490. *Write:* Edith Webb, registrar, The Center for Professional Advancement, P.O. Box 964, East Brunswick, NJ 08816

January 16–18 Washington, DC
Operation and Management of Water Pollution Control Facilities. The George Washington University
Fee: $435. *Write:* Director, Continuing Engineering Education Program, George Washington University, Washington, DC 20052

professional consulting services directory

WATER AND AIR POLLUTION CONSULTANTS
Environmental Services - Water and Air Quality Testing - Emission & Ambient Air Testing - Microbiological and Chemical Analyses
(504) 889-0710
ANALYSIS LABORATORIES, INC.
2932 LIME STREET METAIRIE, LA. 70002

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

Dean Bixler—Toxicologist
Consultant for pre-market notification, product development, risk or hazard evaluation, regulatory compliance programs; projects basis or retainer.
4108 Redwine Dr.
Greensboro, N. C. 27410
919/299-9367

LAB SAFETY
Send for our 1980 Catalog
LAB SAFETY SUPPLY CO.
P.O. Box 1368 Janesville, WI 53545

ASBESTOS ANALYSIS
TEM (EPA Method), Optical Microscopy
X-ray Diffraction, SEM – EDX
EMS Laboratories
12517 Crenshaw Bl.
Hawthorne, CA 90250 (213) 973-6694

SpectroChem
LABORATORIES INC.
545 Commerce St. Franklin Lakes, N. J. 07417
201-337-4774 201-891-8787
• Atomic Absorption • Optical Emission
• Chemical • X-ray Spectrometry
Complete Analytical Services for Environmental Studies & Pollution Control

GIDLAB
CHEMICAL AND ENVIRONMENTAL TECHNOLOGY
FAIRHAVEN, MASS. U.S.A.

ENTROPY ENVIRONMENTALISTS, INC.
AIR POLLUTION MEASUREMENT IS OUR BUSINESS
P.O. Box 12291
Research Triangle Park, N.C. 27709
919-781-3550

Latest Techniques For Coal Gasification Process with Effects on Environment.
ECONOMICS IN THE MODERN IDIOM—APPLIED TO COAL GASIFICATION
Robert E. Ross, Engineer and Scientist for Thirty Years
RUNNYMEDE PRESS
Post Office Box 252
Ellicott City, MD 21043
815 pp with graphs, tables and solutions
$67.50 per copy (postpaid)
Discounts to Universities

ETI
SPECIALIZING IN SERVICE TO MINING AND ENERGY INDUSTRIES OF THE WESTERN UNITED STATES
Air, water, and land quality studies • Environmental analysis • Background and compliance monitoring • Meteorological monitoring • Site indexing & evaluation
ENVIROTECHNICS, INC.
ROOSEVELT, UTAH 84066
Postal Box 355 801 • 722 • 3827

SMALL PARTICLE ANALYSIS
BY ELECTRON MICROSCOPY
ERNEST F. FULLAM, INC.
P O BOX 444 • SCHENECTADY, N Y 12301
TELEPHONE 518-785-5533
SUPPLIER OF
ACCESSORIES FOR MICROSCOPY
WRITE OR PHONE FOR INFORMATION

IA INC BIOLOGICAL SUPPLY SECTION
Ecological and Experimental Research and Consulting
Marine and Estuarine Specimens for bioassay and experimental studies
ICHTHYOLOGICAL ASSOCIATES, INC.
BRIGANTINE EXPERIMENTAL LABORATORY
West Brook Lane
Absecon, New Jersey 08201
609-652-8375
(In Delaware 302-378-9626,9881)
Write or Call for Brochure

BC BROWN AND CALDWELL
CONSULTING ENGINEERS
1501 N Broadway
Walnut Creek, CA 94596
(415) 937 9010
ENVIRONMENTAL ENGINEERING
Source Control • Waste Treatment • Solids Handling
Reclamation • Energy and Resource Recovery
Operations Consultation and Training
Since 1947
Laboratory Analyses and Surveys
SEATTLE EUGENE PASADENA TUCSON ATLANTA

J.E. SIRRINE COMPANY
Engineers Since 1902 An Employee Owned Company
Complete Design of Environmental Facilities
USA Greenville SC 29606 • Houston TEX 77042
RTP NC 27709 Riyadh Saudi Arabia

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

● ● ●

INDEX TO THE ADVERTISERS IN THIS ISSUE

CIRCLE INQUIRY NO. **PAGE NO.**

1 ...... **Energetics Science** .... IFC
Langeler: Mason Inc.

2 ...... **ERT** 1439
Impact Advertising Inc.

11 ..... **Hamilton Company** 1450
Mealer & Emerson Adv.

31-36 .. **Matheson** 1446
Kenyon Hoag Associates

3 ...... **Martek** .... IBC
Tekmar Marketing Services

5 ...... **Rockwell International** 1442
Campbell-Eward Company

4 ...... **Rohm and Haas** .... OBC
Al Paul Lefton Co., Inc.

9 ...... **Tennessee Valley Authority** 1445
World Wide Agency Inc.

12 ..... **Pergamon Press** 1450
PCI Consultants, Inc.

10 ..... **Ventron** 1458
Impact Advertising Inc.

PAGE NO.

CLASSIFIED SECTION 1550
SERVICES DIRECTORY 1547-1549

Advertising Management for the American Chemical Society Publications

CENTCOM, LTD.

Thomas N. J. Koerwer, President; James A. Byrne, Vice President; Clay S. Holden, Vice President; Benjamin W. Jones, Vice President; Robert L. Voepel, Vice President; 25 Sylvan Rd. South, Westport, Connecticut 06880 (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 10017, (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. 06880, (Area Code 203) 226-7131
United Kingdom
Reading, England . . . Malcolm Thiele, Technomedia Ltd., Wood Cottage, Shurlock Row, Reading RG10 OQE. Telephone: 073-581-302
Manchester, England . . . Jill E. Loney, Technomedia Ltd., 216 Longhurst Lane, Mellor, Stockport SK6 5PW. Telephone: 061-427-5660
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

Environmental
Science & Technology

Volume 13, Number 12
December 1979

January	1–130	May	497–626	September	1017–1170
February	131–252	June	627–764	October	1171–1316
March	253–374	July	765–894	November	1317–1438
April	375–496	August	895–1016	December	1439–1568

Refer to the above listing to determine the issue in which an entry appears.

NAMES INDEX. This index contains the names of *ES&T* research and feature authors and of people mentioned in staff-written parts of *ES&T*. Authors are designated by boldface page numbers.

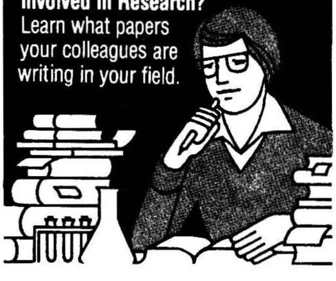
SUBJECT INDEX. Under the basic subject categories are listed the titles of papers and articles, arranged alphabetically.
All parts of *ES&T* have been indexed, with the exception of letters, currents, industry trends, products, literature, books and meeting guide.

NAMES INDEX

SUBJECT INDEX

Choosing your Graduate School?
Find out which schools are concentrating in your area.

Involved in Research?
Learn what papers your colleagues are writing in your field.



The Directory of Graduate Research 1979

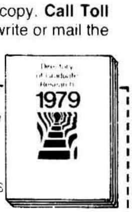
Comprehensive listing of U. S. and Canadian Universities offering doctoral programs in chemistry, chemical engineering, biochemistry and pharmaceutical/medicinal chemistry including detailed information on research professors and their publications.

Whether you are a recognized authority in your field, just about to start your graduate study, or concerned with research in chemical science, it is vital for you to know who is working in your area, what they are doing, and where they are doing it.

The Directory of Graduate Research lists complete information on universities—details on professors, the papers they have published, their areas of specialization. For added convenience, individual researchers are also listed alphabetically and individual telephone numbers are included in most cases.

Researcher or graduate student, you will find this comprehensive, 988 page, 8½ · 11 volume one of the best investments you can make. The cost is just $30.00.

To order your new 1979 copy, **Call Toll Free (I) (800) 424-6747**, write or mail the coupon below.



Dept. 102
American Chemical Society
1155 16th St., N.W.
Washington, D.C. 20036

Please send me copies of the Directory of Graduate Research, 1979 Edition @ $30.00 a copy
Name
Affiliation (if any)
Address Home Organization
City State
Zip Phone

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.

DIAL TOLL FREE
(1) 800-424-6747

From anywhere in the continental United States
D. C. Area Call 202-872-8065

TO ORDER AMERICAN CHEMICAL SOCIETY PRIMARY PUBLICATIONS

master charge
THE INTERBANK CARD

Call ACS Sales Office
Books and Journals Division
Kenneth Phillips, Sales Manager

VISA®

MICROFILM, MICROFICHE, and PRINTED EDITIONS

- Analytical Chemistry
- Chemical & Engineering News
- CHEMTECH
- Environmental Science and Technology
- SciQuest
- Accounts of Chemical Research
- Biochemistry
- Chemical Reviews
- I&EC Process Design and Development
- I&EC Product Research and Development
- I&EC Fundamentals
- Inorganic Chemistry
- Journal of Agricultural and Food Chemistry
- Journal of the American Chemical Society
- Journal of Chemical and Engineering Data
- Journal of Chemical Information and Computer Sciences
- Macromolecules
- Journal of Medicinal Chemistry
- The Journal of Organic Chemistry
- The Journal of Physical Chemistry

BOOKS and TAPE RECORDINGS

- Advances in Chemistry Series
- ACS Symposium Series
- ACS Monograph Series
- Data Reference Books
- Other Technical Books
- The Chemical Society's Specialist Periodical Reports

Cassette Tapes

- Science Symposia Series
- Lab Professionals Series

Office Hours are 8:30 A.M. to 5:00 P.M. Eastern Time
After 5:00 P.M., automatic answering and recording service

ES&T DECEMBER 1979 VALID THROUGH April 1980

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 DECEMBER 1979

VALID THROUGH
April 1980

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

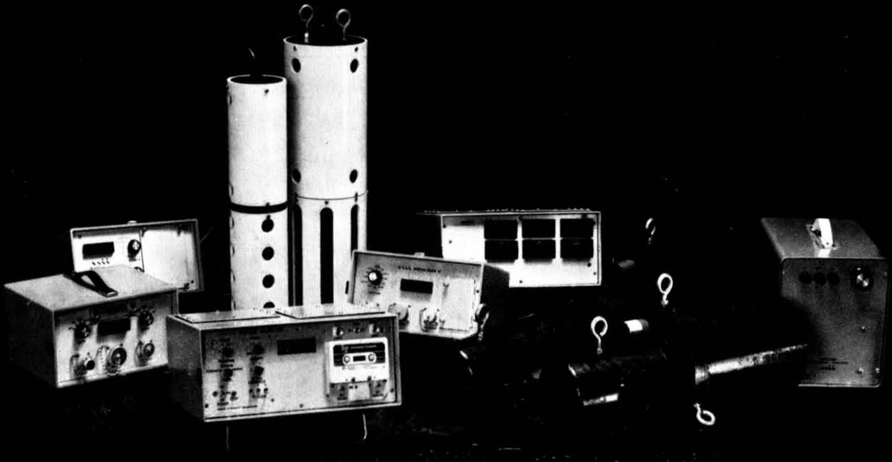
Areas of your responsibility:
☐ A. Air pollution only
☐ B. Water pollution only
☐ C. Waste treatment only
☐ D. Air & Water pollution
☐ E. Air & Waste treatment
☐ F. Water & Waste treat.
☐ G. Air/Water/Waste
☐ H. Other Environmental

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




CYANIDE