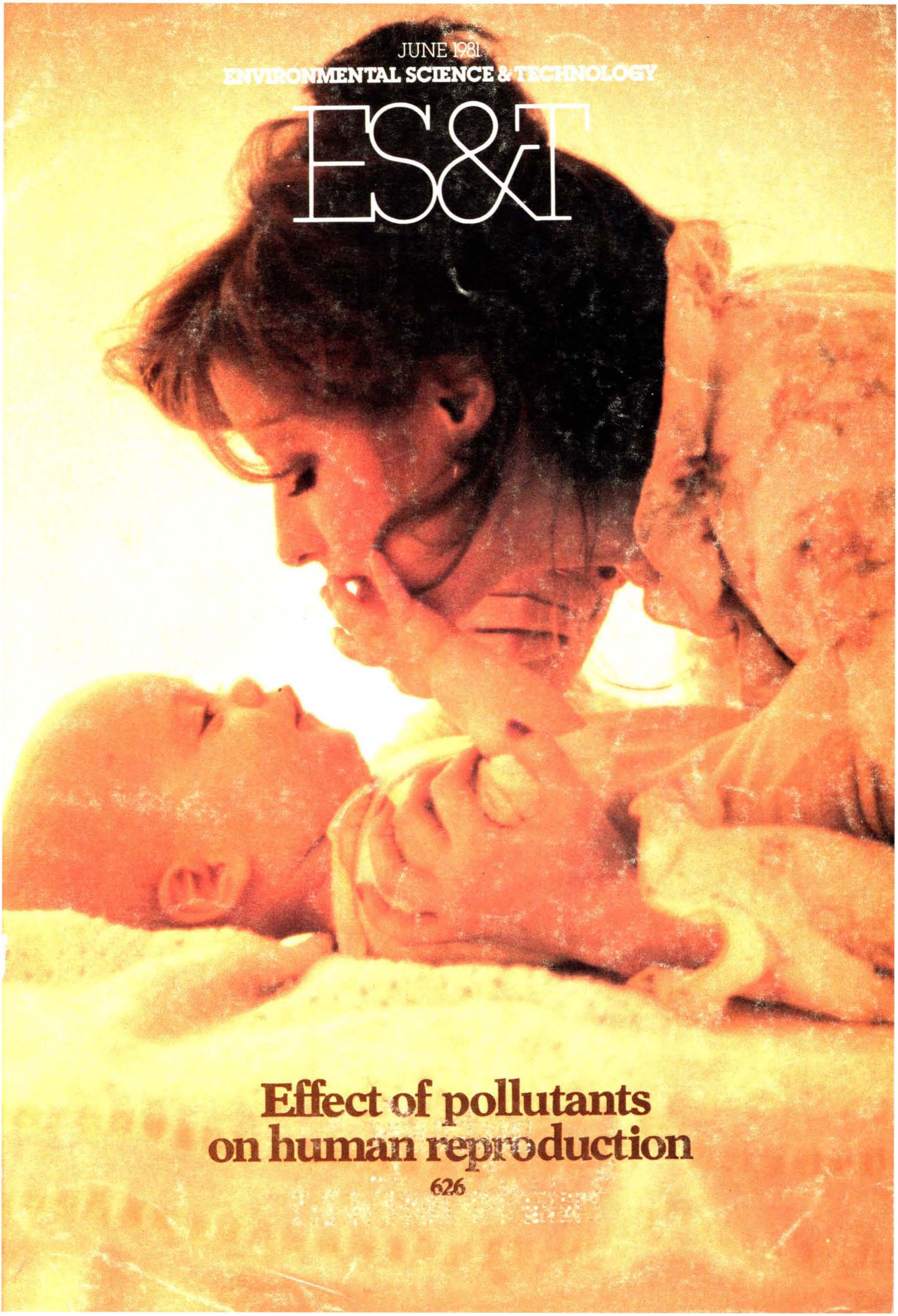
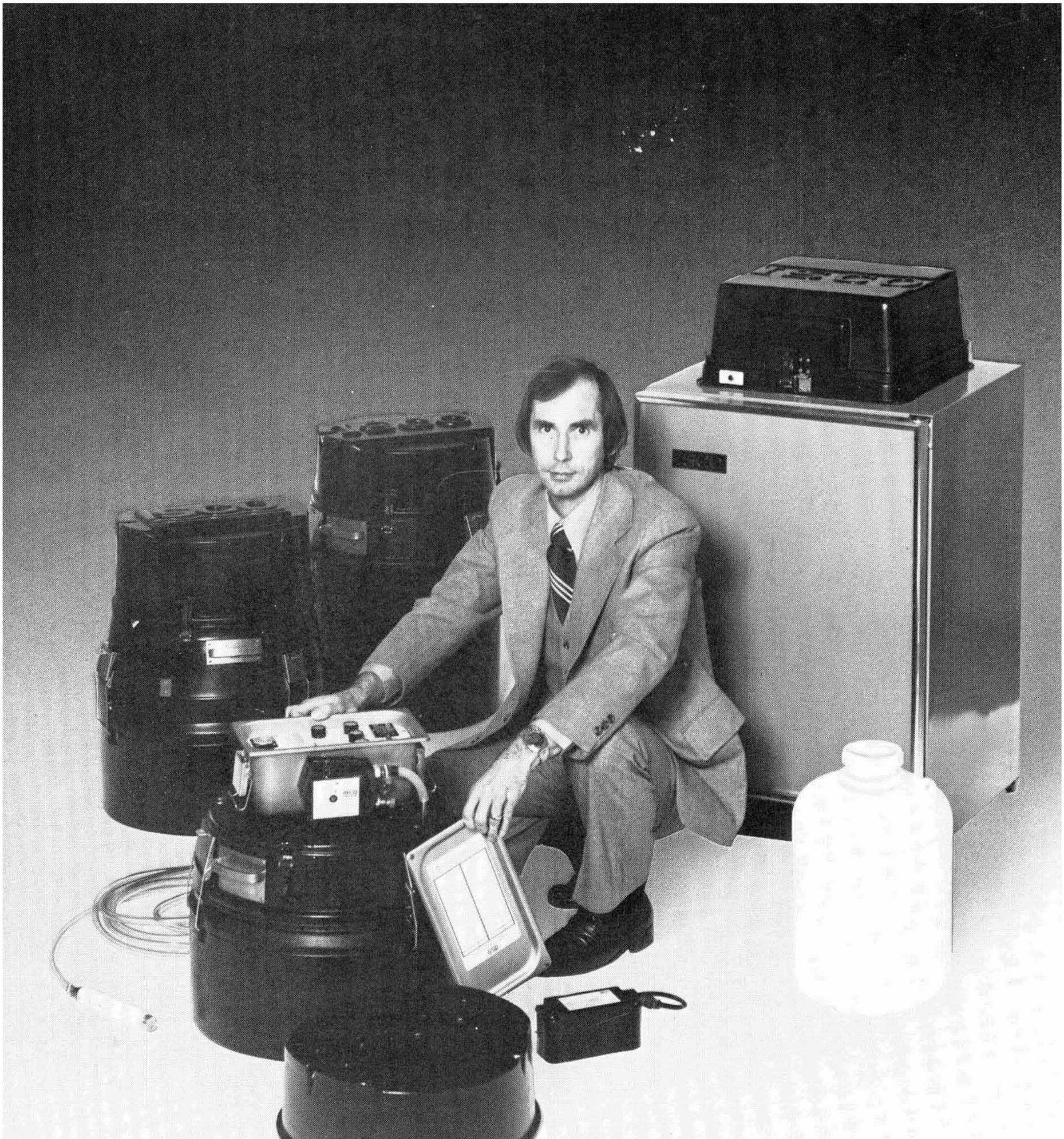
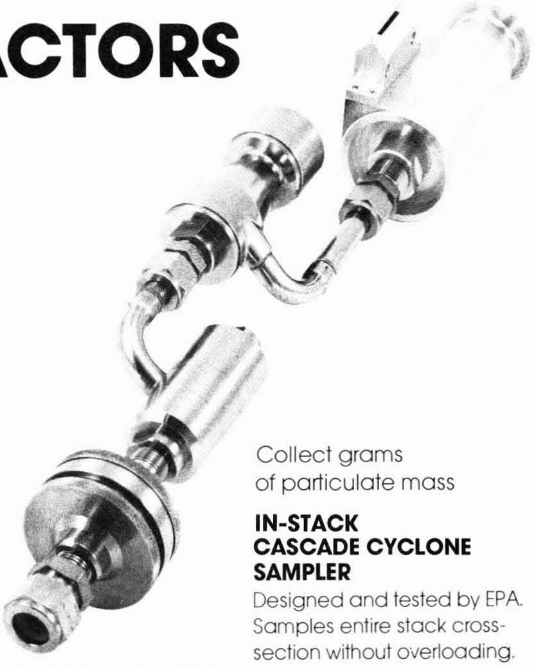
JUNE 1981
ENVIRONMENTAL SCIENCE & TECHNOLOGY
ES&T

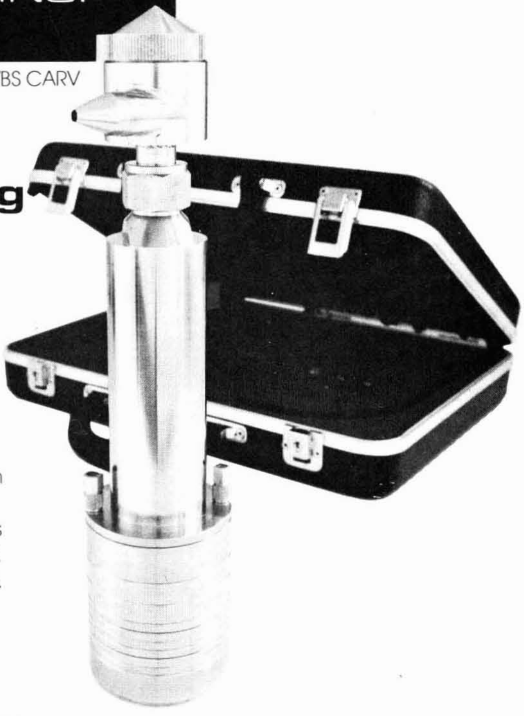


Effect of pollutants on human reproduction

626

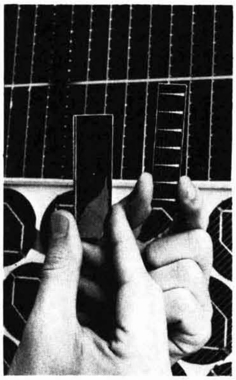




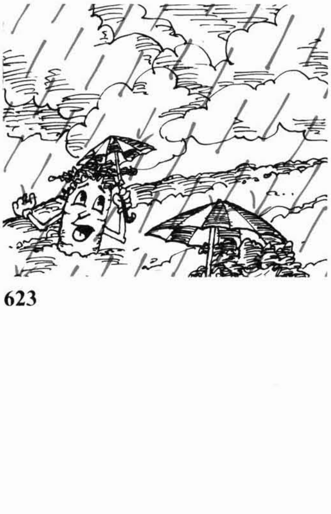


ES&T
CONTENTS

Volume 15, Number 6, June 1981



614



623

OUTLOOK

REGULATORY ALERT

CRITICAL REVIEW

RESEARCH

Environmental Science & Technology

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

SUBSCRIPTION PRICES 1981: Members, $18 per year; nonmembers (for personal use), $21 per year; institutions, $72 per year. Foreign postage, $7 additional per year. Air freight, air mail, and multiple-year rates available on request. Single issues $6.50 for current year; $7.50 for prior years. Back volumes $85.

SUBSCRIPTION SERVICE: Orders for new subscriptions, single issues, back volumes, and microfiche and microform editions should be sent with payment to Sales Office, ACS, 1155 16th St., N.W., Washington, D.C. 20036. Phone orders may be placed, using Visa or Master Card, by calling toll free (800) 424-6747 from anywhere in the continental U.S. Changes of address, subscription renewals, claims for missing issues, and inquiries concerning records and accounts should be directed to Manager, Membership and Subscription Services, ACS, P.O. Box 3337, Columbus, Ohio 43210. Changes of address should allow six weeks and be accompanied by old and new addresses and a recent mailing label. Claims for missing issues will not be allowed if loss was due to: insufficient notice of change of address, if claim is dated more than 90 days after the issue date for North American subscribers or more than one year for foreign subscribers, or if the reason given is "missing from files."

Credits: 616, 620, *ES&T* staff photo; 627, W. Eugene Smith

Cover: PHOTOFILE

ESTHAG 15(6) 603–716 (1981)
ISSN 0013-936X

671

Chemical mass accounting of urban aerosol. Arthur W. Stelson and John H. Seinfeld*

This analysis demonstrates several important points concerning mass accounting, the presence of electrolytic solutions, and aerosol pH.

680

A β-gauge method applied to aerosol samples. Joseph M. Jaklevic,* Ray C. Gatti, Fred S. Goulding, and Billy W. Loo

Results show that the β-gauge method for determining the mass of atmosphere aerosol samples is as accurate as gravimetric methods.

687

Automatic particulate sulfur measurements with a dichotomous sampler and on-line X-ray fluorescence analysis. Joseph M. Jaklevic,* Billy W. Loo, and Ted Y. Fujita

A rapid, sensitive, and accurate X-ray fluorescence method is reported for the analysis of elemental sulfur collected from ambient aerosol samples.

691

Use of lead isotopes in soils to identify the source of lead contamination near Adelaide, South Australia. Brian L. Gulson,* Kevin G. Tiller, Karen J. Mizon, and Richard H. Merry

Isotopes are used to trace lead contamination in surface soils to tetraethyllead from gasoline.

697

Alkylpyridines in surface waters, groundwaters, and subsoils of a drainage located adjacent to an oil shale facility. Robert G. Riley,* Thomas R. Garland, Kazumi Shiosaki, Dale C. Mann, and Raymond E. Wildung

Results indicate that alkylpyridines are useful in environmental studies as diagnostic indicators of water that has been in contact with shale oils.

701

Evaluation of Tenax-GC and XAD-2 as polymer adsorbents for sampling fossil fuel combustion products containing nitrogen oxides. Ray L. Hanson,* Charles R. Clark, Robert L. Carpenter, and Charles H. Hobbs

GC–MS analysis shows that Tenax-GC would be more suitable than XAD-2 for the sampling of stack effluents from fossil fuel combustion.

705

Modeling the flux of atmospheric polychlorinated biphenyls across the air/water interface. Paul V. Doskey and Anders W. Andren*

Problems involved in measuring and modeling PCB fluxes across the air/water interface are addressed, employing Lake Michigan as an example.

NOTES

711

Comparison of automated segmented-flow and discrete analyzers for the determination of nutrients in water. Vicenti C. Marti and David R. Hale*

The "discrete" analyzer provided a 50% increase in rate of analysis compared with the "segmented-flow" analyzer for the four determinations studied.

713

Automobile traffic and lung cancer. An update on Blumer's report. Lincoln Polissar* and Homer Warner, Jr.

In contrast with Blumer's results, this study found no significant associations between traffic volume and cancer risk.

715

Solubility behavior of three aromatic hydrocarbons in distilled water and natural seawater. Steven S. Rossi* and William H. Thomas

Except for toluene, data show that when the ionic strength of an aqueous solution is constant, maximal dissolution is strongly affected by temperature.

* To whom correspondence should be addressed.

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

DEPARTMENTS

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

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

For author's guide and editorial policy, see the January 1981 issue, page 62, or write Katherine I. Biggs, Manuscript Reviewing Office, *ES&T*. A sample copyright transfer form, which may be copied, appears on the inside back cover of the January 1981 issue.


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

ES&T
EDITORIAL

A significant risk

Buried in the muddy confusion of governmental statements about human health risks from environmental contaminants is a truly significant risk. I'm speaking of the loss of public confidence in the scientific community's ability to define risks in meaningful terms and, consequently, the loss of public support for continued research in this important area.

It has been said that the public's attention span can be measured in weeks for singular and newsworthy events. If this is true, the 10-year continuity of general interest in environmental protection has been nothing short of remarkable. Catastrophic events (Kepone, "Three Mile Island") are relatively easy to understand. Subtle, chronic effects from low levels of toxic materials in the environment rank much lower in the public's priorities for worry.

We began in the '60s with great public confidence in technology. Much was evidentiary of this trust: space frontier expansion, satellite weather descriptions, electronic wizardry, and so forth. Early reports of chemicals in the environment, such as *bis*-(2-chloroethyl) ether, chloroform, tetrachloroethylene in drinking water, nitrosamines in air, diethylstilbesterol in foods and contraceptives, chlorinated hydrocarbons everywhere, and the like, planted genuine seeds of worry. Subsequently, people learned of the dangers of charcoal broiling, potential carcinogenic effects of saccharin (yes it is, no it isn't), and coffee. The general perception is that the list grows as a result of every investigation and is in fact not based on substantial evidence. The fact that most scientists have been saying all along that the data are incomplete, the models poor, and the risk estimates unverifiable is not only discomforting to people, it is relevant to their decision not to place these concerns higher in their list of worries.

After all, there is a great deal for people to worry about, including political instability, warfare, and the state of the economy. Not surprisingly, people look to technologists for definitive statements regarding the severity of problems; but, at least in the case of toxic materials in the environment, definitive statements have not been forthcoming for reasons that make sense *only to scientists*.

Swept on the earlier tide of confidence, the '70s expressed an era of confidence in intervention through government regulation and professional stewardship. Consequently, the federal government has moved to *guarantee* the provision of public health, not simply to proclaim it as a goal. Many people have difficulty with this trend; nevertheless, we have moved in the last decade into a position in which individual enterprise can be held "guilty until proven innocent" with regard to public health impacts.

At this point, we are left with an environmental and legislative house of cards that, given the severity of social concern with general economic measures, is about to tumble. Perhaps it would not tumble if the risks could be more clearly stated to the public. Unfortunately, our legislative requirements are diverting too much of our time and energies away from arriving at definitive risk statements. Ironically, eroding public confidence may deprive us of the research support needed to justify any confidence.

But the need is even greater. We should have no patience with professionals who blame politicians, industry, and even the public for diminished support. More properly, the responsibility lies with the scientists and professionals who have failed to explain the basis, origin, and constraints surrounding present risk evaluations. In fact, the greatest problem we face is refusing to deal with what Lord Ashby has called the "fragile values, unquantified information, and the emotive elements which nourish the public conscience."

R F Christman

0013-936X/81/0915-0607$01.25/0

ES&T LETTERS

Mine waters

Dear Sir: The formation of the International Mine Water Association (IMWA) has been established with the following main objectives:

1. to improve exploitation of mineral deposits consistent with the desirable standards of safety against water hazards
2. to increase protection of the environment against the impact of mine drainage and related activities
3. to improve the utilization of mine waters
4. to improve technology and economy of mine drainage control operations
5. to create a forum for international exchange of information concerning the latest developments in the field of mine water problems.

The pressing needs of persons involved with mine water problems encouraged us to establish an international authoritative body, to provide individuals and institutions with a better opportunity to benefit from worldwide experiences in this field.

Dr. Rafael Fernández-Rubio
Professor of Hydrogeology and
International Mine Water Association
Secretary
Department of Hydrogeology
University of Granada
Apdo. de Correos 556 Granada, Spain

Activated carbon use

Dear Sir: I have read the article on activated carbon adsorption (*ES&T*, May 1981, p. 502) and appreciate the opportunity to make the following observations.

The need for "predictive generalizations" of the adsorption process may be needed to prove broad applicability in the legislative process, but this need is only superficial when applying adsorption to purification problems. Hundreds of adsorption facilities throughout the world have been installed as a result of rather simple technical evaluation techniques followed by a comparison of the results with *real* alternatives.

Until the advent of RCRA, the alternative of disposal of toxic wastes by landfill has been lawful and relatively cheap compared to destruction techniques. Processes such as adsorption and oxidation, which provide ultimate destruction, therefore have been clarified as costly and "in need of improvements." This change in regulatory posture will cause engineers to creatively solve such problems of toxic wastes by applying the teachings of Dr. Weber and other researchers who have studied these technologies and have provided us with a sound engineering base.

Many of the adsorption failures "of the '70s" have been traced to rather simple water chemistry phenomena and are not adsorption system problems per se. The failure to recognize and control bacterial slimes, unstable water in regard to hardness, and suspended solids concentrations have caused many adsorption process breakdowns. Application of *water* treatment chemistry to *waste*water adsorption treatment systems will avoid many of these bothersome problems.

In summary, the use of adsorption will experience rapid growth with existing technology when environmentally unacceptable alternatives to disposal of toxic wastes have been eliminated. Furthermore, adsorption system failures will be greatly reduced by more careful study and control of the water chemistry surrounding the adsorption process.

Donald G. Hager
President, Rubel and Hager, Inc.
Consulting Engineers
Tucson, Ariz. 85711

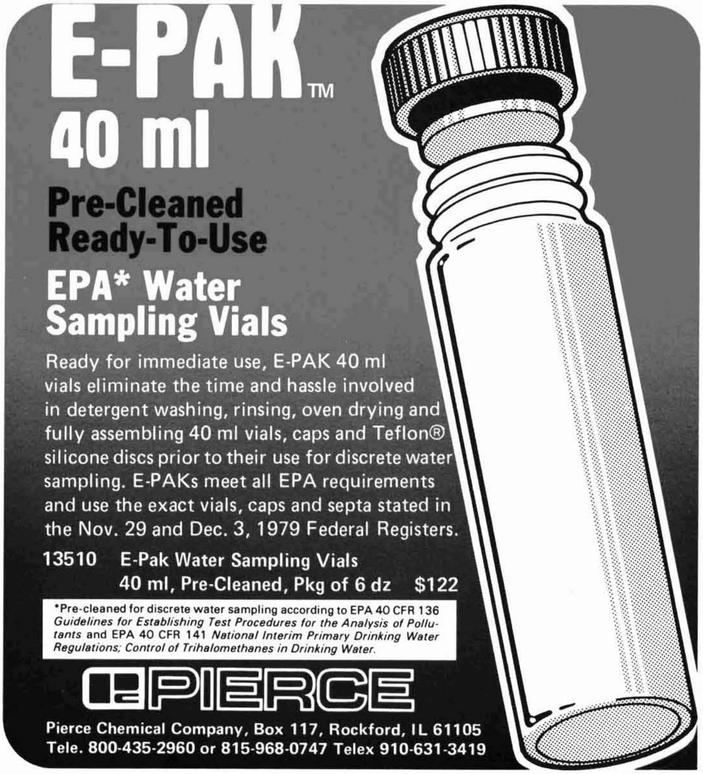
NRC associateships

Dear Sir: This letter is addressed to former National Research Council Research Associates and Visiting Scientists Research Associates.

The National Research Council Research Associateship Programs (tenable in federal laboratories) have been in existence over 25 years and now have about 3500 alumni in the sciences and engineering. The council is interested in locating former NRC Research Associates in order to verify certain information and to assess the value of the programs in their career development.

Would you help by sending us your correct mailing address, dates of tenure, and the name of the laboratory where you pursued the NRC Research Associateship? We are grateful for your assistance in this endeavor. Please contact:

F. A. Crump
Assistant to the Director of
Associateships
National Research Council
2101 Constitution Ave.
Washington, D.C. 20418



E-PAK™
40 ml
Pre-Cleaned
Ready-To-Use
EPA* Water
Sampling Vials

Ready for immediate use, E-PAK 40 ml vials eliminate the time and hassle involved in detergent washing, rinsing, oven drying and fully assembling 40 ml vials, caps and Teflon® silicone discs prior to their use for discrete water sampling. E-PAKs meet all EPA requirements and use the exact vials, caps and septa stated in the Nov. 29 and Dec. 3, 1979 Federal Registers.

13510 E-Pak Water Sampling Vials
40 ml, Pre-Cleaned, Pkg of 6 dz $122

*Pre-cleaned for discrete water sampling according to EPA 40 CFR 136 *Guidelines for Establishing Test Procedures for the Analysis of Pollutants* and EPA 40 CFR 141 *National Interim Primary Drinking Water Regulations; Control of Trihalomethanes in Drinking Water.*

PIERCE

Pierce Chemical Company, Box 117, Rockford, IL 61105
Tele. 800-435-2960 or 815-968-0747 Telex 910-631-3419

CIRCLE 8 ON READER SERVICE CARD

Genetic Engineering of Symbiotic Nitrogen Fixation and Conservation of Fixed Nitrogen
edited by **J.M. Lyons, R.C. Valentine, D.A. Phillips, D.W. Rains,** and **R.C. Huffaker**

Develops a basic understanding of the genetics, physiology, and biochemistry of symbiotic N_2 fixation and the effect of denitrification on this fixed nitrogen. *Basic Life Sciences, Volume 17.* approx. 675 pp., illus., 1981, $69.50

Mass Spectrometry of Priority Pollutants
by **Brian S. Middleditch, Stephen R. Missler,** and **Harry B. Hines**

Offers both the experienced mass spectroscopist and novice a convenient source of comprehensive information on 129 priority pollutants. 320 pp., illus., 1981, $29.50

Skeletal Growth of Aquatic Organisms
Biological Records of Environmental Change
edited by **Donald C. Rhoads** and **Richard A. Lutz**

Reflects the exciting new advances in bivalved mollusc and coral skeletal research in recent years. *Topics in Geobiology, Volume 1.* 764 pp., illus., 1980, $47.50

Risk Analysis
An International Journal
Official publication of the Society for Risk Analaysis
editor: **Robert B. Cumming**

Provides a focal point for new developments in this area for scientists from a wide range of disciplines.

Subscription: Volume 1, 1981 (4 issues) $60.00

Send for your free examination copy!

Plenum PUBLISHING CORPORATION 233 Spring Street, New York, N.Y. 10013

CIRCLE 9 ON READER SERVICE CARD

ES&T

CURRENTS

INTERNATIONAL

Cleaner air and less acid rain resulting from a 50% reduction in sulfur emissions by 1985 would cost an estimated $4.6 billion in annual investment in the 19 European member nations of the Organization for Economic Cooperation and Development. The investment figure, in 1980 dollars, comes from a new OECD study that develops a methodology for estimating the costs and benefits of controlling emissions of sulfur oxides from oil- and coal-fired power stations. The estimated investment is within the range of the estimated savings from improvements in lake quality, health, and crops, and reduced damage to buildings. The analysis is based on energy production and consumption forecasts from 1978 to 1985. However, OECD says the methodology can be applied to new energy forecasts.

WASHINGTON

Pinpointing the locations of the thousands of abandoned hazardous-waste sites in the U.S. is the goal of an EPA survey. The agency will obtain the information mainly from the companies and individuals that owned, operated, or used such sites. Submission of the reports is required by the superfund law; EPA is supplying notification forms and establishing receiving points in its regional offices. The only previous survey of this kind was published in 1979 by a subcommittee of the House Interstate and Foreign Commerce Committee. It identified 3300 sites. However, EPA believes that there may be 30 000–50 000 hazardous-waste dumps in the nation, many of them no longer in use.

Government spending on pollution control totaled $14 billion in fiscal 1979, up 17.5% from the previous year, according to the U.S. Bureau of the Census. Total governmental spending on pollution control averaged $64.27 per capita nationwide. Spending by environmental category was $9.7 billion for water, $3.3 billion for land, $449 million for air, and $475 million for other purposes. The federal government spent $5.7 billion, or 41% of the total—$4.4 billion of it in grants to local and state governments. State governments spent more than $800 million directly and gave another $600 million to local governments. Local governments spent almost $6.9 billion, nearly half the total. Local sewer fees totaled $3.3 billion, compared with $8.5 billion in direct spending; other sanitation revenue was $870 million, compared with $3 billion in direct spending.

Schmitt & Levitas: the legislative veto

Sen. Harrison Schmitt (R–N.M.) has introduced the Regulatory Reduction and Congressional Control Act (S. 890), which would permit Congress to overturn proposed regulations by legislative veto. The bill is cosponsored by Sen. Charles Grassley (R–Iowa) and 33 other senators. A very similar bill (H.R. 1776) has been introduced in the House by Rep. Elliott Levitas (D–Ga.) and 203 cosponsors. Both the Senate and House bills had been introduced in the previous Congress. Sen. Schmitt terms the legislative veto "an idea whose time has come." In the 36 states that require some form of legislative review of regulations, he notes, the mere presence of the procedure has been enough "to make regulators think twice" before acting. Schmitt would not expect the legislative veto to be used often during the Reagan administration, but believes it should be there to ensure that federal regulations are consistent with legislative intent.

Reconstruction of soil on strip-mined coal lands should be tailored to the individual site, says a committee of the National Research Council in a report to the U.S. Bureau of Mines. Federal law requires in general that the soil be restored so that it can support its premining use or an approved better use. The NRC committee concluded that strip-mined land should not necessarily be reclaimed to the original contour, but to the contour best suited to its final use. In the Midwest, for example, where mining disturbs agricultural land, return to original contours is reasonable only where more level grading would not improve soil productivity. The NRC group believes also that the legally mandated five- and 10-year restoration periods may often be too short to restore the diversity of vegetative species also required by law.

Plans for a nationwide survey of pesticide use in 1981 are being developed by the Economics and Statistics Service (ESS), U.S. Department of Agriculture. The survey will cover pesticide use and related data for major crops and livestock. The estimates of pesticide use will be valid at regional levels. Because of limitations on funding, however, ESS will be unable to develop estimates that are valid at the state level. As in the past, states will be given an opportunity to supply additional funds for the survey to obtain pesticide-use data that are valid at the state level. Estimated costs of obtaining such data will be developed by ESS on request. The agency plans to start collecting data in late fall of 1981.

STATES

An $18-million plant that can process 300 000 tons of industrial wastes per year will be built on a 250-acre site in Oakland County, Mich., for Stablex Corp. of Radnor, Pa. Engineering, procurement, and construction will be handled by Catalytic Enterprises, Ltd., Sarnia, Ont., Canada. The company is affiliated with Catalytic, Inc., of Philadelphia. Stablex will treat essentially inorganic hazardous and toxic wastes using its patented Sealosafe technology. The process reacts liquid and solid wastes with additives to form a material that hardens to a rocklike product that can be used for land reclamation. The plant is scheduled for completion by mid-1982.

Ships at anchor in Hampton Roads, Va., are required to contract for sewage and garbage removal services under a regulation adopted in May by the Virginia State Water Control Board. The regulation was brought on by the backlog of colliers in Hampton Roads. In mid-March, 143 colliers were lined up with at least a 70-day wait for port anchorages. The new regulation replaces an emergency regulation put into effect in March by the state's department of health. Hampton Roads is the largest coal port in the world. It has felt the strong impact of renewed domestic and foreign interest in coal.

Nine of the 20 solid-waste streams generated in converting coal to synthetic fuels will probably be classified as hazardous under the Resource Conservation and Recovery Act, according to a report prepared by Roy F. Weston Designers-Consultants for the Ohio River Basin Commission, Cincinnati. In addition, the environmental effects of six of the 20 streams are unknown. Weston estimates that a synthetic fuel plant processing 30 000 tons of coal daily, with zero wastewater discharge and 90% control of air emissions, would produce more than 7000 tons of residues per day. The main health concerns involve metals that can leach into groundwater, organics that can leach into groundwater or vaporize, and low-level radiation that can leach into groundwater or be transmitted as radon gas to nearby areas.

A toxicology option will be introduced this fall in the interdisciplinary master's program in environmental engineering/science at the New Jersey Institute of Technology, Newark. The program is for students with bachelor's degrees in engineering or science. Students will take courses both at the institute and at the College of Medicine and Dentistry of New Jersey, Newark. Program chairman Richard B. Trattner says the toxicology option will focus on the identification, management, treatment, and effects of hazardous and toxic materials.

Kempiners: health effects on a preventive basis

The Illinois Department of Public Health will expand its environmental toxicology program during the next two years with the help of a $475 000 federal grant, says department director William L. Kempiners. The grant was awarded by EPA. Kempiners says it will be used in part to establish a program for coping with the health effects of pollutants on a preventive basis. A statewise communications network will be set up to report unusual occurrences or outbreaks of disease. This information will be fed to a computerized data base designed to detect patterns of disease. The data base also will include factors such as occupation, socioeconomic status, and personal-health indicators.

AWARDS

An analyzer for toxic elements in groundwater prevents sample contamination with outside pollutants by pumping samples into airtight compartments. The analyzer won Mirko Riha the Australian Broadcasting Co.'s "Inventor of the Year Award" and a grant to exhibit the sampler at Geneva, Switzerland, where he won two gold medals in an international show.

SCIENCE

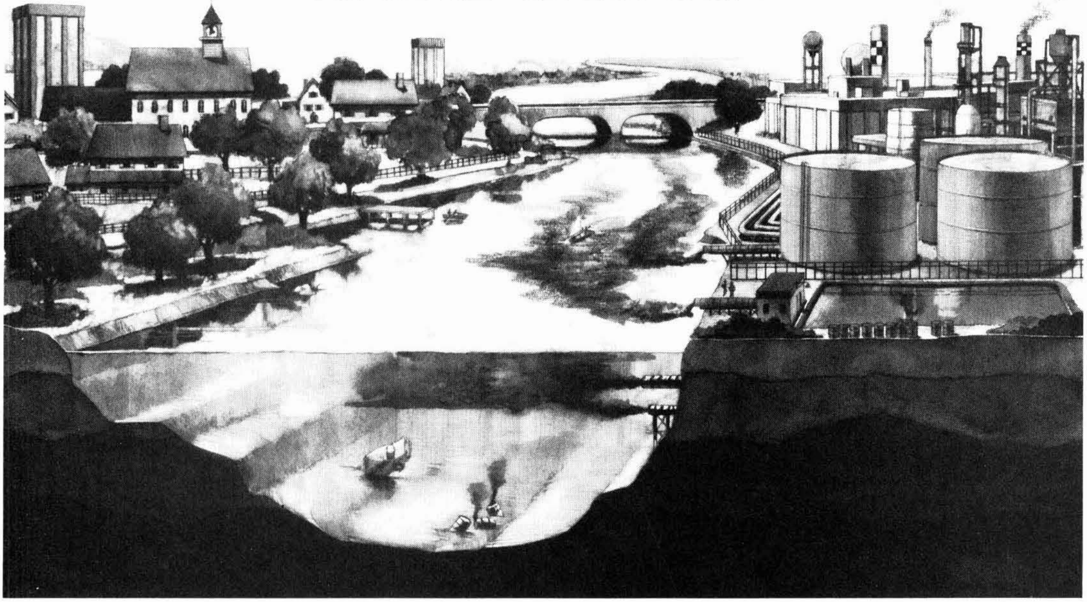
Mutagenic activity was not removed completely from wastewater by physicochemical, biological, or sand filtration processes in a study by EPA's Health Effects Research Laboratory in Cincinnati. The results indicated, moreover, that treatment steps may contribute mutagens to wastewater. The study was designed to assess the mutagenic potential of organic substances in renovated water. The waters examined were taken from four advanced wastewater treatment systems. Mutagenicity was determined with the Ames *Salmonella* test. EPA scientists say that further work is needed to determine the nature of the potentially hazardous compounds in renovated wastewater.

"There is no scientific evidence to justify a 2,4,5-T ban," said Elizabeth Whelan, executive director of the American Council on Science and Health (ACSH). She added that no convincing relationship between the herbicide and human illness has been shown. ACSH acknowledged a problem with dioxin, but said that it is rarely found in the environment after 2,4,5-T use; when found, there is not enough to present a health hazard. The council believes that stringent safeguards for manufacture and application of 2,4,5-T will "effectively reduce any risks" associated with the herbicide, while allowing for its continued use.

A way to pinpoint allergenic risk to certain chemical workers was announced by Meryl Karol of the University of Pittsburgh. As many as 10% of the workers who make polyurethanes may be allergic to a key ingredient, toluene diisocyanate (TDI). Karol said that a TDI allergy can now be detected through a unique antibody, "IgE," generated through tests with the monoisocyanate molecule. Most workers involved in accidents with TDI lose the antibodies after several weeks, but in those who are allergic, the IgE can remain for years.

Wastewater ozonation at a treatment plant at Estes Park, Colo., disinfected the effluent, but seemed to leave more of some aldehydes, alkanes, fatty acids, and aromatic hydrocarbons than before the water was treated. Other aromatic hydro-

Water pollution. You could be accused of a lot more than bad taste.



No responsible company can risk non-compliance with environmental regulations. The risks are too great.

Higher insurance premiums. Fines. Lawsuits. Even jail sentences.

But today, however, compliance is not enough; you have to *prove* it. If you can't, the risks and penalties can be the same.

Sun Information Services, a subsidiary of Sun Company — America's 20th largest industrial — has solved this complex problem.

A combination of Sun's vast industrial experience and Sun Information's highly advanced data processing technology provided the solution: Suneco™ Environmental Information Management Services.

Suneco is both an information management system and a compliance system. It maintains the necessary balance between your process, its effects on the environment, and the regulations applied to both. Now and in the future. And Suneco controls water, air and hazardous waste management with equal skill. All you do is select the modules you require.

A data management system stores, processes and reports data pertaining to NPDES discharge streams, accidental spills, air emissions and hazardous wastes. A team of engineers and systems analysts constantly reviews government regulations and advises accordingly.

With the Suneco system, compliance becomes the norm — a norm that may result in reduced insurance costs.

The future depends on thriving industry. And a thriving environment.

Let us make sure that both maintain a clear bill of health. Call us in the East at 215-293-0660, or in the West at 214-739-9800. Or write to Suneco, Sun Information Services Company, 280 King of Prussia Road, Radnor, PA. 19087 to request our fully descriptive brochure.

A Sun Company Subsidiary

Sun INFORMATION SERVICES COMPANY

Copyright 1981, Sun Information Services Company.

CIRCLE 15 ON READER SERVICE CARD

carbons, alkanes, fatty acids, and chlorinated hydrocarbons were unchanged, according to results of tests run under auspices of EPA (Cincinnati, Ohio). EPA noted that there may have been insufficient ozone to meet total chemical ozone demand. However, no determination was made as to whether it is necessary or desirable to treat with more ozone than is needed to bring about disinfection.

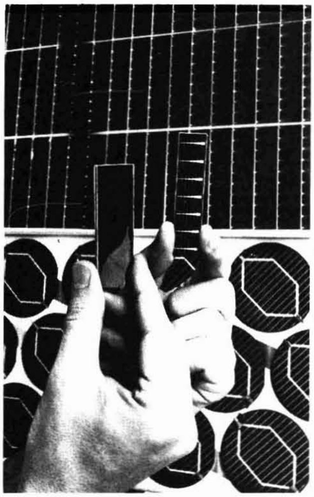
A comprehensive field study of acid rain focuses on April storms in the Midwest. Sponsored by EPA and the Department of Energy, and conducted by Battelle (Richland, Wash.), it is known as Oxidation and Scavenging Characteristics of April Rain (OSCAR). The study will involve 100 researchers, a network of precipitation samplers in about 30 states, and three fully instrumented aircraft. The idea is to find sources of depositing pollutants, spatial/temporal variabilities of deposition, and the scavenging behavior of different substances. OSCAR field headquarters are in Fort Wayne, Ind.

TECHNOLOGY

Air pollution compliance costs may be sharply cut with the help of minicomputers equipped with EPA's air quality monitoring "software." This software, as well as pertinent "hardware," is offered by Form & Substance, Inc. (Westlake Village, Calif.). The computer, a low-cost "stand-alone" system, can work out air pollution/control models that indicate the most rational ways to achieve compliance. It can also model comparisons between alternative approaches. The company says that with this system, engineers can bypass expensive consultants and large computer systems and do their own calculations.

About a dozen plants' genetic systems can be used to monitor or screen chemical and physical mutagens, Shahbeg Sandhu of EPA says. Plants such as *Tradescantia*, *Arabidopsis*, and waxy maize are in the process of being validated for use in environmental monitoring. Among advantages of plant use are that their tissues are very complex, as are human tissues; plants can often be used on site; they are normally easy and inexpensive to culture; and they can show many genetic and chromosomal changes.

Phenoxyacid herbicides, PCBs, and trihalomethanes can be determined by gas chromatography with electron-capture detection. A single, packed column, isothermally operated, provides adequate resolution for these compounds. Environmental samples are now routinely analyzed this way, according to Oak Ridge National Laboratory.



Photovoltaics: dendritic-web ribbons

Photovoltaics may be advanced with dendritic-web ribbons, developed by Westinghouse with joint funding from Southern California Edison Co. (SCE). A typical panel is 45 in. × 16 in., and contains 228 laser-etched cells made from dendritic-web ribbon. In good sunlight, each panel would produce almost 50 W, enough to light a small room. The rectangular shape conserves space wasted by the conventional round cells, SCE says. If plans work out, efficiencies of 14–16% are expected, perhaps by 1987, according to Westinghouse. A commercial production line to produce a number of panels totaling 25 MW is expected by 1987, SCE says.

INDUSTRY

Nuclear power plant insurance risks have been reduced since the Three Mile Island mishap because of safety improvements implemented since then, said LeRoy Simon, chairman of American Nuclear Insurers. Simon mentioned across-the-board changes leading to upgraded capabilities to prevent a wide class of reactor accidents. If an accident still happens, earlier recognition is now possible, and a normal situation can be restored more quickly, Simon said. He noted that there is no situation for which the insurance risk is absolutely zero, but that pathways for reactor system failure have been substantially reduced because of "TMI modifications."

To overcome deficiencies in the Clean Air Act, the Chemical Manufacturers Association (CMA) proposes that credible air quality standard setting be backed by independent peer group review. Also, CMA calls for abolishing Classes II and III, since, it claims, use of best available control technology (BACT) and standard compliance are adequate to protect air quality. The association also advocates eliminating requirements for lowest achievable emission rate (LAER) because, although BACT and LAER control differences are "minimal," LAER is far more energy-consumptive and costly. (LAER is required for nonattainment areas.) CMA adds that the "unreasonable risk" concept should be written into the law's language.

Miller: suggested some rule changes

An approach to ensure that cars meet emission standards and stay "clean" for their useful lives was proposed by Duane Miller, vice-president–engineering, of Volkswagen of America. Miller called for elimination of government preproduction approval of vehicle design, and compliance with government-defined assembly-line testing. He said that compliance should be evaluated from samples of vehicles in actual, normal use, and should be defined in terms of *average* emissions from each manufacturer's total light-duty vehicle and truck production. For vehicles that fail to comply, Miller proposed emission fees related to the seriousness of violations and the numbers and retail values of vehicles sold in a model year.

ES&T
OUTLOOK

Is cancer environmentally caused?

It depends on the definition of "environment"

"For 30 years, oncologists have tried to prove a link between cancer and air pollution, and in every case it's been negligible." That was what John Higginson, director of the International Agency for Research on Cancer (Lyon, France), told a symposium held at the ACS Atlanta meeting under the auspices of the ACS Committee on Environmental Improvement, and it was the message that other physicians and risk experts also brought. Despite public perceptions to the contrary, industrial chemicals at large in the environment account for only a few percent of all cancers.

The growing support for that conclusion has come hand in hand with a growing recognition that the development of cancer is a complex, multistep process that can be modulated by many factors—especially diet and general "life-style." "The subject of cancer became very simplified in the '60s and '70s," said Higginson, and many believed that single chemicals, in small quantities and by themselves, could simply and diversely cause cancer. "We realize now that we oversimplified the problem."

Some factors, of course, have clearly been shown to cause cancer in man by themselves; these include cigarette smoking, alcohol consumption, and occupational exposure to vinyl chloride and asbestos. But, according to R. K. Boutwell of the McArdle Laboratory for Cancer Research at the University of Wisconsin (Madison), most of the agents in the environment that are considered to be carcinogenic need metabolic activation or promotion by another chemical to make their effects felt. A chemical that is only an initiator may have no effect without subsequent promotion. "Small doses of an initiator do not add up," he said.

Because carcinogenesis is a multistep process, it is difficult—except in such extreme cases as cigarette smoke—to point to a direct "cause." "If I hit somebody on the head with a hammer and a lump appears, everyone knows what it means," said Higginson. "Unfortunately, a great many cancers appear to be associated with what we call 'risk factors' "—which cannot be called carcinogens themselves. Examples include absence of dietary fiber, age at first marriage, and obesity.

A study by Higginson of cancer statistics from communities at different stages of development in southern Africa suggested that 70–80% of cancers can be attributed to environmental factors—where "environmental" refers not only to industrial chemicals but also to diet and behavior. This study and others suggest that over three-quarters of these environmental factors are derived from life-style.

The most persuasive argument for this view is in data on cancer incidence among Mormons, who have strict dietary laws. Mormons, who do not smoke or drink alcohol or anything containing caffeine, have a rate of cancer incidence half that of the average U.S. white population. What is more, no significant differences in cancer incidence are seen between urban and rural Mormons. "These data and others suggest that only a small part of the total cancer burden can be directly related to industrialization in a general sense or to diffuse exposures in the general population," said Higginson.

As for the possibility that hereditary factors might be involved, data on Japanese immigrants to the U.S. show that by the third generation, incidence of colon, rectum, breast, and prostate cancer—all very rare in Japan—have risen to average U.S. levels; stomach cancer—common in Japan—has dropped to the low U.S. level.

According to Richard Wilson, a Harvard nuclear physicist turned risk assessor, less than 1% of cancers are due to general exposure to industrial chemicals; 3–5% are due to occupational exposures. (Higginson added the observation that "most epidemiologists are falling all over themselves to push up the estimate so they won't be accused of selling out to industry"; both he and Wilson apparently feel that these numbers are upper limits.) And Wilson points out that given such a small total risk when all industrial chemicals are combined, the risk of any given chemical to the general population becomes very small and very hard to estimate. "The uncertainty is colossal," he said.

Wilson also said that the issue of a carcinogenic chemical's having a threshold, or "safe" level, is a red herring: "It's really an irrelevant question. It's very hard to find out, and once you do find out, so what?" For example, he said, there is no threshold level in accidents between automobiles and pedestrians—one person and one car in the street implies some finite risk of an accident; yet it is a risk that people are willing to take. "The issue is really whether the risk of a chemical is big or small, and it can be small because exposure is low, or small because its potency is low," he said.

What does all this say about protecting the public from environmentally caused cancers? Higginson puts it this way: "It is a common fallacy when considering multifactorial origin of disease to imply that all factors must be controlled to prevent it. In fact, all stepwise processes have their weak link and all that may be necessary is to break the chain." Both he and Wilson said there was a need to make sure that future chemicals do not add to the problem, but they both had strong words for the current approach. "There's a problem these days," Higginson said. "When you do a study on organic chemical X, the whole focus is on chemical X, ignoring the 100 other parameters."

—Stephen Budiansky

0013-936X/81/0915-0615$01.25/0 © 1981 American Chemical Society

Protection for chemical workers

Technology for reducing workplace and laboratory hazards is evolving rapidly; one task is to ensure that this technology is properly used

Chemical industry employees in many plant areas, especially in laboratories, come in contact with a wide variety of hazardous substances. "If 'zero hazard' or 'zero risk' to the employee cannot be achieved, because of the inability to substitute a nonhazardous substance for a hazardous one, or to contain it totally, then exposure must be minimized," said Walter Haag of the National Institute for Occupational Safety and Health (NIOSH). "This can be done through a workplace design that creates a system of engineering controls, monitoring mechanisms, work practices, and personal protective equipment. The key ingredient to the system's functioning effectively is the attitude exhibited by management and employees," Haag added.

Haag: *steps for minimizing exposure*

Work area risks

In the laboratory, risks can be increased because of the diversity and sometimes highly toxic nature of the chemicals in use, Robert Hill, Jr., of the Center for Disease Control (CDC, Atlanta, Ga.) pointed out to a recent Chemical Manufacturers Association/NIOSH-sponsored Symposium on Control of Workplace Hazards in the Chemical Manufacturing Industry. Risks are high in analytical, medical, quality control, and research laboratories, he observed.

Hill listed several sources of exposure to chemicals, including the opening of closed vessels, transfer and mixing/blending operations, preparation of analytical standards, spillages, and even removal of syringes from gas chromatographs. The gases, fumes, and aerosols are the main vehicles by which lab workers may be exposed; skin absorption is another prime contamination route.

But a major cause of exposure may be someone's attitude. For example, Hill and Haag told *ES&T* that a large percentage of laboratory chemists and technicians fail to follow health and safety procedures or to use personal protective devices. Deleterious exposure can take the form of allergic reactions, liver or lung afflictions, chronic poisoning, or other adverse physiological events.

Hill said that much of the exposure risk can be avoided through proper design of laboratory equipment, and materials-handling procedures. Before the particular laboratory work is about to begin, plans should be made for spillage cleanup and other decontamination steps necessary in the event of an accident. If highly toxic substances have to be used, their procurement should be restricted in quantity to immediate needs. Users should be fully familiarized with risks; the material should be introduced into the process with as little outside exposure as possible; and waste disposal must be done with extreme care, Hill said.

Defining risks

Before engineering countermeasures and employee rules and procedures are instituted in the workplace or laboratory, exposure risks must be defined. What contaminants may be present, and in what forms and amounts, must be determined, as should their threshold limit values (TLVs), or permissible exposure limits (PELs). An American Conference of Governmental and Industrial Hygienists measurement, a TLV is the maximum concentration of a substance, in air, that can be breathed in by an employee eight hours a day, five days a week with no known adverse effects.

Michael Wallace, senior environmental engineer at Sandoz, Inc. (East Hanover, N.J.), reminded the symposium that TLVs are guidelines and should not be construed as distinguishing hazardous from safe concentrations of a substance. By themselves, they do not have legal or regulatory force. On the other hand, PELs, promulgated by OSHA, have full force. Zack Mansdorf, an industrial hygiene expert at Midwest Research Institute (MRI, Kansas City, Mo.) told *ES&T* that quite often TLVs are more stringent than PELs. For example, for nuisance particulates, the PEL is 15 $\mu g/m^3$, but the TLV is 10 $\mu g/m^3$.

Instrument types

The detection and reduction of chemical hazards in the workplace and laboratory calls for many different types of equipment and procedures.

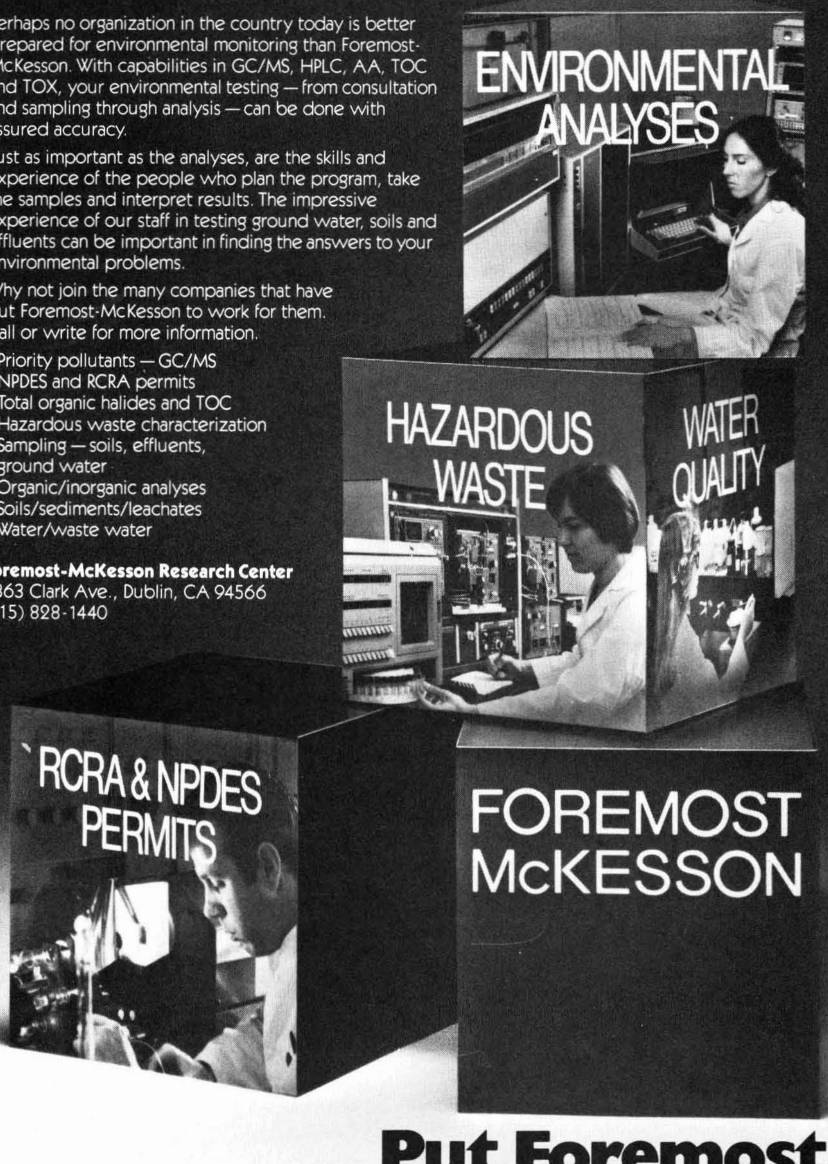
Monitoring instruments to detect chemical hazards principally use electromagnetic, electrochemical, chromatographic, mass spectrometric (MS), or automated wet-chemical methods. Microprocessor-based equipment and solid-state sensors make it possible for many of these instruments, especially the newer ones, to monitor on a continuous rather than

OSHA rules for laboratories?

In the later days of the Carter administration, signals came from OSHA concerning exposure limits in industrial and other research laboratories, including those of universities. These signals raised concern that the cost of meeting any such exposure limits could take a heavy toll on funds normally devoted to research work.

However, no proposal has yet been made, nor have any hearings been held. Given the feelings of the present administration concerning regulations, it is probably safe to say that rulemaking for laboratories is "on hold" for the time being.

0013-936X/81/0915-0616$01.25/0 © 1981 American Chemical Society


ENVIRONMENTAL ANALYSES
HAZARDOUS WASTE
WATER QUALITY
RCRA & NPDES PERMITS
FOREMOST McKESSON

batch basis. And computers allow these instruments to provide reliable results closer to real time.

A recent advance in electromagnetic detection is the single-wavelength infrared (SWIR) analyzer, said Marvin Weiss of Bechtel, Inc. SWIR permits the use of a narrow-wavelength band for monitoring organic vapors and gases in the workplace. Improvements in the tunable filter and solid-state-detector technology made this approach feasible. Substances typically appropriate for SWIR monitoring include *n*-hexane, methane, ethylene, CO_2, CO, NO, and water vapor. Another electromagnetic detector, a solid-state, nondispersive ultraviolet (UV) analyzer, determines a wide range of organic vapors or liquids.

Weiss noted that chromatography is a "work horse" for contaminant analysis. It can determine several components at once and is quite dependable. However, chromatography is discontinuous and some analysis cycles need as much as 30 minutes to complete. On the other hand, IR and UV are continuous, but can handle only one component at a time.

When chromatography must be used, but rapid results are needed, the system can bypass the chromatography column and go to a flame-ionization detector (FID). If a contaminant level exceeds tolerance, the FID can sound an alarm and, at the same time, forward the sample through the column for further analysis. The contaminant source can then be found through the study of recorded data obtained from the FID/chromatograph system.

Among other weapons in the detection arsenal are toxic-vapor monitors, which use solid-state electrochemical detectors and are useful for toxic halogenated hydrocarbons and halogens; solid-state electrochemical analyzers, for CO and vinyl chloride; reactive photometers, for SO_2; and magnetic-field, time-of-flight, and quadrupole MS devices.

Personal monitoring

Dosimeters, personal sampling devices, monitor and assess the dose of a contaminant the employee may be exposed to. If the TLV, or PEL, is exceeded, the device sounds an audible alarm. Some samplers may also be plugged into a unit that reads out the accumulated exposure and even prints a hard copy of the data, which can be useful for record keeping.

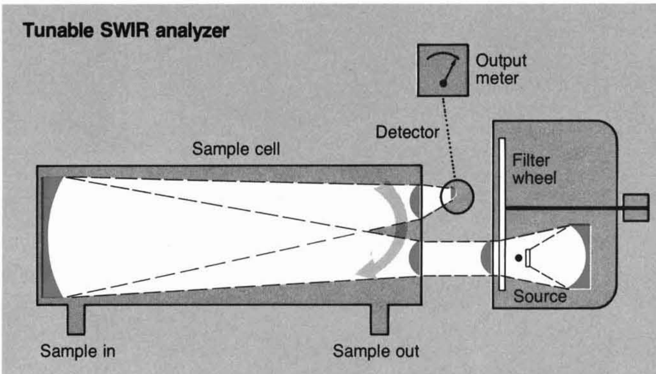
Personal monitors are contaminant-specific for toxic gases, such as CO, ammonia, chlorine, phosgene, hydrogen sulfide, hydrogen cyanide, and NO_2. However, they cannot yet handle several gases at once. That function must still be performed by area samplers. To date, the same holds true for workplace dust and particulate matter samplers.

Lines of defense

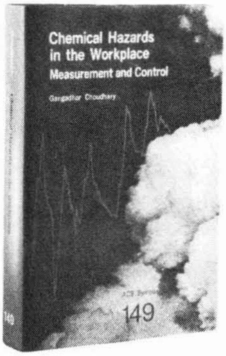
One engineering line of defense against exposure to toxic chemicals is the fume hood. Its design should allow air to flow along its bottom in order to block heavy vapors. Flow inside the hood should be laminar, and the structure must contain no L-shaped corners that could cause turbulence. The surface should be provided with recesses so that spillages may be trapped. For some procedures, CDC's Hill suggested the use of an auxiliary air hood to furnish a protective "curtain" of outside air between the worker and the material in the fume hood.

Other defenses run the gamut from special surface coverings, to disposable laboratory coats and gloves, to impermeable air-supplied suits equipped with respirators. Such health and safety precautions are being addressed by ongoing work at MRI. Alfred Meiners, senior advisor for toxic

Tunable SWIR analyzer



Source: Symposium presentation by Bechtel's Weiss



chemical assessments, and his colleagues there have looked into the requirements of laboratories that handle carcinogens. They urge that negative air pressure be maintained in the laboratory and that air vented out not be allowed to circulate to any other room. Safety cabinets must be thoroughly ventilated and their exhaust air should be filtered or otherwise treated before discharge to the atmosphere. All wall, floor, and ceiling surface finishes in the laboratory must be impervious to liquids and readily cleanable, according to the MRI team.

Disposal of laboratory wastes into even the most secure landfills should be phased out, Meiners believes. He calls for incineration and estimates that all but the most refractory organic compounds ($>99.99\%$ of the active component) would be effectively destroyed at 1000 °C or more with a two-second retention time.

To study incineration, MRI has set up a bench-scale incinerator that can handle gram quantities of solid and liquid wastes, either as single compounds or in mixtures. An MRI spokesperson told *ES&T* that most, if not all, experimental incinerators for hazardous chemicals can handle only single compounds, and in much smaller quantities.

Technology is available

Technologies and systems to monitor workplaces, laboratories, and employee exposure to hazardous substances are rapidly evolving—some at considerable cost—as are protection systems for employees. But the immediate task at hand may be a more administrative one: to make certain that employees are indoctrinated with a proper appreciation of the risks involved in handling dangerous chemicals. They may then become more conscientious about using protective equipment and taking other measures to ensure maximum safety in the workplace and laboratory, without the need for draconian measures on the part of management.

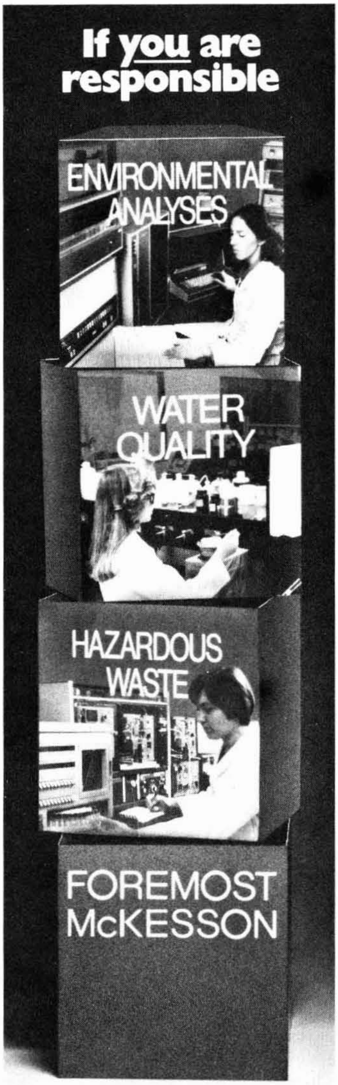
—Julian Josephson

Additional reading

"Safe Handling of Chemical Carcinogens, Mutagens, Teratogens, and Highly Toxic Substances," Volume 2; Douglas B. Walters, Ed.; Ann Arbor Science Publishers: Ann Arbor, Mich.

Mansdorf, Zack. "Industrial Hygiene Manual"; Midwest Research Institute: Kansas City, Mo.

NIOSH Certified Equipment List; Division of Technical Services, National Institute for Occupational Safety and Health, Robert A. Taft Laboratories: Cincinnati, Ohio. Single copies available.



Water regulations

Some proposed Clean Water Act revisions call for a stronger scientific base and more flexibility for criteria determination and standards setting

Next year, Congress must reauthorize most of the Clean Water Act, which has already become the object of many calls for major revisions, as is currently happening to the Clean Air Act.

The principal goals of the revisions are greater flexibility and enhanced cost-effectiveness of water pollution criteria and standards, which would ultimately be reflected by improved receiving water quality. These goals were advocated by a Water Pollution Control Federation (WPCF) task group chaired by Paul Eastman, executive director of the Interstate Commission on the Potomac River Basin (ICPRB, Rockville, Md.). The group maintains that this approach would go much further toward achieving socially and economically optimum water quality goals for the nation than the past approach would have. The act now applies uniform criteria and standards to all water bodies, while ignoring regional socioeconomic factors and variations in physical, chemical, and biological properties of stream segments and other water bodies, according to the task group.

Criteria critiques

Water quality criteria and standards are under fire. Critics have suggested that the scientific base upon which some of them were constructed is not very firm.

An example given by John Doyle, minority professional staff member of the House Public Works and Transportation Subcommittee on Water Resources, addressed priority pollutants covered by the *NRDC* vs. *Train* consent decree. He said that in a recent Heritage Foundation report, EPA's own Science Advisory Board (SAB) criticized the inadequacy of data bases to support the establishment of criteria for such pollutants. The report, submitted by the Investigation and Oversight Subcommittee, stated that water quality criteria and standards are viewed by many scientists as being neither valid nor useful, and as lacking adequate input by peer review groups.

On the other hand, Eastman believes that because of the SAB criticisms and many other comments received, final criteria documents—such as those for priority pollutants, which EPA published last November—"were greatly changed for the better."

Since 1972, many clean water regulations have been technology-based and aimed at effluents, with little or no account taken of the nature and uses of the receiving water, Doyle noted. Often they have been "based more on legal, judicial, and administrative decisions than on defensible conclusions drawn from scientific investigations," he observed. Doyle pointed out the great difficulty of relating water quality only to effluent limits, while leaving out the many other factors which affect water bodies and which vary greatly among different water bodies.

Some corrective steps

Mauzy: *suggested corrective steps*

Some corrective steps to develop defensible criteria and standards were enumerated by Michael Mauzy, director of the Illinois Environmental Protection Agency, at a recent WPCF government affairs seminar. One suggestion was that all standards development, and documentation related thereto, reflect peer review on a par with that accorded a formal research paper. Another was the substitution of uniform effluent standards with water quality standards that consider each waterway and its ability to handle pollutants according to its own biological, chemical, and physical characteristics. The regulatory thrust, then, might be more cost-effectively directed toward those pollutants and contaminants that present dangers receiving waters cannot mitigate. (Mauzy's own state of Illinois requires cost–benefit analyses as part of the environmental regulatory process.)

State priorities

Since receiving waters vary so widely, it has been suggested that priority pollutant lists, criteria, and standards be established by individual states; EPA, however, would reserve the right to overrule the states for scientific, technical, or socioeconomic reasons. Limits for a given pollutant would be flexible and tailored to a specific receiving water use. This recommendation was made by Eastman's WPCF task group and was subsequently adopted by the federation.

Under this proposal, a pollutant's presence would be determined through local knowledge, literature surveys, and, as appropriate, water sampling and monitoring programs. Next, a compilation of chemical and biological fate and transport data, analytical methodology, and toxicological information would be prepared. Simultaneously, studies of the physical and chemical nature of the receiving water would be conducted to ascertain its natural ability to control, neutralize, or immobilize pollutants. Where practicable, cost–benefit relationships between pollutant load reduction and the water use and quality expected from given degrees of control would be determined.

Will suggestions concerning criteria and standards, and others aimed at streamlining the Clean Water Act, be put into effect when the law is reauthorized? Perhaps not all will be, but one can expect that the present administration will certainly put pressure on Congress to enact regulatory changes, especially from the standpoint of costs and benefits.

—Julian Josephson

0013-936X/81/0915-0620$01.25/0

Whether you have one – a few – or a few hundred gases to analyze, Foxboro has the right ambient air analyzer for you!

MIRAN portable Ambient Air Analyzers offer significant advantages for laboratory, plant and field applications.

Samples can be collected as far away as 100 feet. Measurements are accurate, response time is a few seconds, and monitoring is continuous. The instruments are lightweight for use anywhere required; they're simple to use: no routine recalibration is required, as is true of NDIR analyzers. MIRAN analyzers are rugged: there are no columns to change – or break – as with GC portables, and no gas supplies are needed.

There's a MIRAN Portable Ambient Air Analyzer just right for you. Let us prove it. Send for our new brochure.

Fast help for toxic gas problems!
CALL THE FOXBORO TOXIC GAS ACTION CENTER at (203) 853-1616.

If you have a toxic gas problem requiring immediate attention, call us. You'll get the advice you need fast. We'll help you select the right measuring instrument, give you applications information and, when required, send a specialist to your facility for immediate direct assistance. Foxboro Analytical, A Division of The Foxboro Company, P.O. Box 5449, South Norwalk, CT 06856, (203) 853-1616.

Another dimension in analytical measurement and control

FOXBORO

MIRAN-1A: The ultimate instrument for measurement of trace (less than 1 ppm) to percentage concentrations of more than 300 OSHA-defined gases and vapors, as well as hundreds of others. Fast, accurate, portable, rugged, easy to operate.

MIRAN-104: Slightly less sensitive but also lighter in weight and less expensive than the MIRAN-1A. Designed for rugged field use.

MIRAN-80: Built-in microprocessor automatically computes concentration of each component in a mixture of vapors, prints out concentrations on a permanent paper tape. Accuracy to 1% relative.

MIRAN-103: "Modular" concept of quickly-changeable filter/scale sets permits measuring any of more than 300 OSHA-defined gases and vapors without recalibration. Excellent choice for plant engineers, OSHA or insurance inspectors.

MIRAN-101: Calibrated at factory to measure *one* specific gas or vapor. MIRAN-101 measures lower concentrations; MIRAN-101S measures higher concentrations. Economical price permits the purchase of several to cover all your air monitoring requirements.

CIRCLE 5 ON READER SERVICE CARD

Much more than measurement.

The full measure of Martek Instruments, Inc., is not only its complete line of water quality measurement systems, but also its expertise in the fields of environmental analysis and data acquisition. Since the late 1960's, the company has designed and manufactured its own sensors for use in one of the broadest lines of water quality systems available from a single source.

Martek-developed systems provide *in situ* measurement of conductivity, salinity, dissolved oxygen, pH, specific ions, turbidity, flow rate, depth/pressure, or temperature. There are sophisticated fully automated monitoring and control systems, such as the Mark IX System. For remote, unattended field measurements, there is the Mark VIII Water Quality Data Logger. For turbidity measurement, there is the Model XMS Transmissometer. For versatility in profiling applications, there are the Mark VI and Mark VII variable parameter analyzers. And for the accumulation and processing of data, there is the self-contained Model DMP Data Microprocessor. These are but a few of the numerous products available from Martek.

Martek systems run the gamut from hand-held portable systems to unattended buoy systems, from ultrapure water in nuclear power plants to brine solution in boreholes. They make measurement easier in such diverse fields as process control, ecology, agriculture, and oceanography.

The quality of Martek products is matched only by the quality of its service and post-sale technical support. You save time **and** money when you deal with one source for all your system needs.

More than likely, Martek has the solution to your water quality problem.

MARTEK INSTRUMENTS, INC.

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

CIRCLE 6 ON READER SERVICE CARD

Understanding acid rain

The complexity of the phenomenon is now becoming clear. Many factors, from weather to biology, determine deposition and effects of acid precipitation

"As a rule, rain is not acid far from towns," wrote one R. A. Smith in 1872. "If it is acid, artificial circumstances must be suspected." Recognition of acid rain, and its link to man's activities, is thus nothing new. But only in the last few years have we begun to understand the phenomenon; with this beginning has come an appreciation of its utter complexity. Meteorology, geology, chemistry, and biology all play parts; varying weather, varying soils, the presence of other pollutants, and species differences all act to blur the connections between industrial emissions, acid rain, and environmental damage.

"The acid rain phenomenon involves almost every component of the biosphere," said Richard A. Linthurst of North Carolina State University (Raleigh, N.C.) at a session on acid rain at the ACS Atlanta meeting. "It's almost the ecologist's dream."

Which way the wind blows

Gilbert S. Raynor of the Department of Energy and Environment at Brookhaven National Laboratory (Upton, N.Y.) reported some striking effects of meteorological condition on amounts of chemical wet deposition. "If one is interested in short-term effects, one must be aware of the variations that can occur," he said. Wind direction, wind speed, temperature, type of precipitation, rate of precipitation, and synoptic condition were recorded while hourly samples of precipitation were taken; a number of systematic relationships appeared between weather and the amounts of chemicals deposited.

The highest concentrations of H^+ ions and sulfates were seen in precipitation associated with cold fronts and squall lines; the lowest, in warm fronts. Thunderstorms show a disproportionately large amount of deposition in relation to amount of precipitation. Raynor showed, too, that concentrations increase in the summer to the point that the greatest total deposition of H^+ and sulfate occurs in the summer—when total rainfall is the least.

Raynor's data covers four years and over 2500 samples. He has shown definitely that weather conditions can affect the concentrations of chemicals of interest—that amount of precipitation is by no means the only meteorological factor affecting amount of deposition. Beyond that is guesswork, he is careful to say.

But he is willing to offer some speculation. The correlation between rate of precipitation and deposition—chemical concentrations are higher at slower precipitation rates—may, for example, be due to the smaller droplet size, associated with slower rain, that is more effective in scavenging material from the air.

Thunderstorms may produce higher concentrations because they are "tapping parts of the atmosphere that aren't being tapped by warm-front clouds."

Raynor suggests that behind most of his data may be two fundamental competing effects. One is a dilution effect. If you get a heavy rain, it would tend to dilute the material. Then, you get a washout effect of the material below the cloud base. So one thing we often see when looking at these short-term samples is that you see a high concentration and lower pH at the early stages of the rain."

A hole in the bucket

Raynor and others at Brookhaven are also addressing a variable that has confounded much of the data on acid precipitation to date: sampling. Although they are now operating a continuous and systematic sampling network, much of the data elsewhere—and all of the historical data—are in bits and pieces.

Florida, which has a sampling network from the panhandle to the Keys, is fortunate, too, to have some of the better historical data. But even that data does not include direct measurements of pH. According to Charles D. Hendry of the University of Florida (Gainesville), calculations from the available historical data (recorded concentrations of various ionic species) suggest a pH near geochemical neutrality (pH 5.6) in 1956 for four sites around the state. Recent sampling shows a range of pH from 5.6 in the south to 4.6 in the panhandle, with the lowest sample at 3.7.

But it is not just with the historical data that fault can be found. Jack L. Durham of EPA (Research Triangle Park, N.C.) reported some serious flaws with methods used to sample dry deposition. "Wet deposition monitoring and measurement techniques are in much better shape than are dry deposition methods," he said. The most commonly used collector, a plastic bucket, "is not a very good surrogate for a plant or a tree," said Gary E. Glass, coordinator of the session, from EPA's Environmental Research Laboratory (Duluth, Minn.). Durham reported that a workshop held on the subject at Argonne National Laboratory a year and a half ago found that "surrogate surfaces and collection vessels are not sufficiently accurate for

0013-936X/81/0915-0623$01.25/0 © 1981 American Chemical Society

use in networks." They are unable to measure dry gaseous deposition, for example, and they cannot possibly simulate the complex processes by which particles and gases are trapped and absorbed by natural surfaces such as leaves. Nonetheless, the bucket is still widely used, and a large body of data is being accumulated that may turn out to be of little or no value.

Durham also noted that wet samples can continue to react after collection, another confounding factor.

One's man meat . . .

Variations within ecosystems that have been drenched by acid rain add to the confusion of identifying the effects of acid rain. "An ecosystem is very, very complex," said John M. Skelly of Virginia Polytechnic Institute and State University (Blacksburg, Va.), who has been studying the effects of air pollution on plants in the Shenandoah Forest and elsewhere. "When you consider the total number of species in the Shenandoah Forest, we know very little about the ecosystem effect. We know about one plant at a time," he said.

The real question is how the entire forest responds when perturbed by pollution. An example where this is of immediate practical importance is the San Bernadino Mountains; air pollution there, Skelly believes, has altered the mix of plants and the ecosystem in such a way as to make it more susceptible to forest fires, which have claimed hundreds of homes.

If one side of the coin is understanding the effects of a pollutant on more than one plant, the other side is understanding the effects of more than one pollutant on one plant. Plants, as Skelly put it, "see everything," after all. To test the effects of "everything," Skelly compared growth in open plots in the Shenandoah Forest with growth in adjacent plots exposed only to filtered air. (The enclosed plots had openings at the top; air was pumped in at the bottom. Controls that had unfiltered air pumped in were also run.) Total biomass was 50% lower in the open plots in one summer's study.

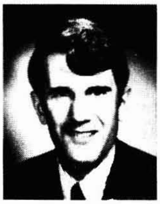
Skelly's experiment demonstrated the effects of "everything"; it also demonstrated the difficulty of separating the effects of one pollutant from another in the real world. But he believes that the "major problem facing vegetation in the Northeast is not acid precipitation, not sulfur dioxide, but ozone." Thus a question remains: How much of the plant damage ascribed to acid rain by other studies is actually due to ozone?

A second confounding effect is seen a step further down the chain of events of an ecosystem perturbed by acid rain. Glass of EPA noted that the greatest pH shock to lakes occurs when snow melts and runs off in the spring. "You have to consider the fact that snowmelt takes not only what's in the snow but what's under the snow," he said. Soil type, the hardness of the winter's freeze, and the amount of dry deposition all determine the amount of acidic material that has accumulated and been absorbed into the soil. Thus another variable is added to the equation that relates the pollution to the ultimate effects.

The amount of work that needs to be done was perhaps best summed up by Skelly. We've been studying ozone's effects for over 20 years and still don't have answers there, he said; we've only been studying acid rain's effects for about four years.

—Stephen Budiansky

Reagan's regulatory reform



Michael R. Deland
ERT, Concord, MA

In less than six months, the Reagan administration has set in motion a process of "regulatory reform" that has subtly, yet dramatically, altered the way in which decisions affecting the environment are made.

During the 1970s, essentially all of the country's major environmental laws were enacted. The legislative initiative began with the passage of the National Environmental Policy Act and was followed by the evolution of the Clean Air and Clean Water Acts and statutes regulating pesticides, noise, surface mining, and the disposal of hazardous and toxic wastes. "Superfund"—the only major missing piece of a total environmental package—finally passed just before Congress adjourned in 1980, leaving a long-overdue bill to govern the disposal of nuclear waste.

While few can quarrel with the basic intent of these statutes, compelling argument can be made that most, if not all, are far too cumbersome and detailed. The regulatory agencies, such as EPA and the Interior, have compounded the problem by promulgating regulations that are among the most complex issued by the federal government. This complexity inevitably has led to law suits which have prolonged progress toward a cleaner and safer environment and which have not yet cleared the climate of uncertainty in which industry must operate.

Against this backdrop, the administration moved with dispatch and precision. Within a week of his inauguration, the President placed a 60-day freeze on pending regulations and appointed the Vice President to chair a Task Force on Regulatory Relief. The task force, working with the Office of Management and Budget (OMB), is to ensure that forthcoming regulations will be "less burdensome and more rational." The task force quickly required EPA to reevaluate numerous regulations including those for "best conventional control technology" and "pretreatment" under the Clean Water Act and those governing the handling, transportation, treatment, and storage of hazardous wastes under RCRA.

In another key move, the President, on Feb. 17, 1981, signed Executive Order 12291, which requires that all "major" regulations be subject to a "regulatory impact analysis," which includes a cost-benefit study and an examination of alternatives. The OMB director has broad new oversight power, including authority to determine whether the potential benefits of a proposed regulation in fact exceed its potential costs and whether the agency chose the least costly and burdensome approach to any regulatory objective. By these steps, the President not only clearly specified that regulations be streamlined, but through the task force and OMB created a clearinghouse to monitor that process.

Agency response

While the task force unquestionably is masterminding the movement, the agencies appear to have gotten the message and are active participants. For example, EPA endorsed and is busily drafting proposed changes to 18 air pollution regulations that Vice President Bush announced would save the automobile industry an estimated $800 million in capital expenditures over five years. EPA recently responded to industry's longstanding petitions and modified its definition of "source" under the Clean Air Act, thereby lessening the confusion between attainment and nonattainment areas.

Again, pressured by the task force, the agency approved New Jersey's generic guidelines for the "bubble policy." This move significantly increased state discretion and rendered moot a year-old suit brought by the Chemical Manufacturers Association against EPA for its failure to approve New Jersey's request.

Congressional initiatives

The momentum built by the President seems also to have rubbed off on Congress. "Regulatory reform" has long been debated but thus far has been without the consensus to lead to legislation. However, it now appears likely that legislation will pass this session. Rep. Danielson (D–Calif.) has introduced a bill in the House that is similar in many important respects to Sen. Laxalt's (R–Nev.) Senate version. Both require economic analysis of major federal rules, emphasize expanded public participation in the rule-making process, and formalize "sunset" requirements by which agencies must review existing rules.

The President, by aggressively pursuing regulatory reform, is leading the movement toward meaningful change. The reforms of the first six months appear real. However, between now and the end of the summer, EPA must issue nearly 100 new regulations, many of them substantial and complicated. The format that these regulations take will serve notice as to the success of the administration's drive toward simplicity and clarity.

0013-936X/81/0915-0625$01.25/0

ES&T
CRITICAL REVIEW

The effect of environmental pollutants on human reproduction, including birth defects

Richard B. Kurzel
Curtis L. Cetrulo
Tufts University School of Medicine
Boston, Mass. 02125

Nothing can cause greater fear in an expectant mother than the prospect of her unborn child being defective. And nothing touches on a man or woman more closely or personally than their reproductive capacity. In recent years, the public has become alarmed that inadvertent or careless exposure to chemicals in the environment might predispose birth defects or reproductive failure. This fear and awareness is reflected by the titles of articles in the popular press, such as "The Poisoning of America" (*1*), and the admission into our household vocabulary of a whole new set of names that reflect this problem: toxic wastes, Love Canal, Agent Orange, dioxin, PCBs. Chemicals from a range of environmental sources have been implicated in birth defects and reproductive failure. We will concern ourselves here with chemicals in the workplace, chemicals in the environment (from air pollution and from carelessly disposed materials that contaminate the land, water supply, or food chain), and food additives or contaminants. Chemicals knowingly ingested for therapeutic (pharmaceuticals) or other reasons (alcohol, cigarettes, drugs) are covered in other reviews (*2*).

Concepts in teratology

The study of the induction of birth defects by exogenous agents constitutes the discipline of teratology. *Terat* derives from the French meaning "monster." In terms of environmental factors, there are four classes of known teratogens: radiation, viruses, drugs, and chemicals. We will concern ourselves only with this last class.

Birth defects are known to occur in 2–3% of all births (*2*). Of these, 25% have underlying genetic causes, while 5–10% result from the influence of the above classes of teratogens (*3*). The remaining 60–65% arise from unknown causes, but may follow from an interplay of multiple environmental agents with genetic factors. Of those birth defects caused by environmental agents, an estimated 4–6% are due to chemicals (*3*); yet of all the sources of birth defects, this is potentially the most preventable. To date, only about 25 chemicals are known to be teratogenic in humans, compared to over 800 in laboratory animals (*4*). It is unknown if this discrepancy rests with a greater resistance of humans to these agents or a failure in our ability to determine sources of teratogenicity in humans. The potential danger is great and growing, however, because of the estimated 2000 new chemicals synthesized each year and introduced into the environment.

In terms of the development of a newborn, there are three periods of development during which the fetus is at risk for injury (*5*): fertilization and implantation, the embryonic period, and the fetal period. The period of fertilization and implantation spans from conception to 17 days, through the blastocyst and early gastrula stages. An injury during this stage results in cell death, from which the aggregate of still totipotential cells can recover and multiply, or if a lethal dose is given, abortion or resorption of the developing organism results. If recovery follows, no structural deformity in the embryo is seen. The embryonic period (18–55 days) is when organogenesis takes place; therefore, this period is one of extreme sensitivity to teratogens (*6*). Within this time, each organ system or morphologic trait has its own critical period of development (Figure 1). In later stages, the fetus is

---

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/81/0915-0626$01.25/0

Chisso–Minamata disease: *the effect of mercury poisoning in a small Japanese fishing village*

less sensitive, but not immune to environmental influences. During the fetal period (56 days to term), toxicity is mainly manifested as a reduction in cell size and number. Growth retardation or functional deficits (e.g., central nervous system injury or retarded development) usually result from injury during this stage of development, since growth in size is the primary process active at this time. The developing brain is still prone to injury, since its development (e.g., myelination) is incomplete even at birth.

Over the years, a number of factors have been determined to play a role in the susceptibility of a fetus to the teratogenic effects of an agent (*7*, *8*). These include:

1. the *time of administration* of the agent during gestation, with the most sensitive period being that of organ differentiation
2. the *route of administration* and *dose*, which involve the chemistry of the compound, its toxicity, metabolism, and toxicology of its degradation products. As in other types of toxic responses, the teratogenic effects of most compounds follow a dose response. However, the dose thresholds for teratogenic effects are generally not known. Safe thresholds are currently determined by both epidemiologic and laboratory studies. Manson (*5*) has proposed that in teratology, unlike mutagenic and carcinogenic effects, safe threshold levels of a chemical may exist; much work is being expended in determining these levels of exposure.

   The unborn fetus is exposed to chemical agents by hematogenous transplacental transfer. The routes of administration to the mother, on the other hand, are by the usual routes, including inhalation, absorption by contact with the skin and mucous membranes, and, most importantly, ingestion.
3. the *number of doses*, with a single dose being most effective in producing defects. It is assumed with the single high dose that the mother is not given the chance to adjust to the agent and to mobilize her detoxification mechanisms. These mechanisms may be protective in chronic low level exposures.
4. *species variation*, most strikingly demonstrated by the thalidomide incident, in which exposure produced limb defects in man, monkeys, and rabbits, but not in mice and rats, on which the drug was tested (*7*). Therefore, the susceptibility to a chemical depends on the genotype of the conceptus, with different effects being seen in different species and different strains of the same species. The difficulty this poses in the animal testing of compounds and in the interpretation and extrapolation of the results to humans is obvious. In humans, racial and familial differences may even play a role in susceptibility.
5. *other factors*, including the extrinsic effects of maternal metabolic diseases, maternal age (the young are more likely to have defects), and stresses such as nutritional deficiencies (protein or vitamin A, E, and B_2 deficiencies). Lastly, an embryo may be more susceptible than the mother to the effects of interaction between multiple agents to which they have been concurrently exposed (*5*). Experiments in animal systems have demonstrated the possibility of producing additive, synergistic, or antagonistic effects between multiple agents.

Manifestations of damage to the developing organism caused by a chemical agent follows the injury or death of certain cells; this interferes with the orderly sequence of development, giving rise to morphologic aberrations. A description of various histologic and physiologic processes whose alteration may give rise to aberration can be found elsewhere (*2*). Depending on the dose and stage of embryonic development, the effect may be teratogenic or fetotoxic. Fetotoxicity is usually seen at doses higher than those expected for teratogenicity; at high doses, fetotoxicity may culminate in fetal death. Although teratogenic agents are usually also fetotoxic, as we shall see, not all fetotoxic agents are teratogenic (*9*).

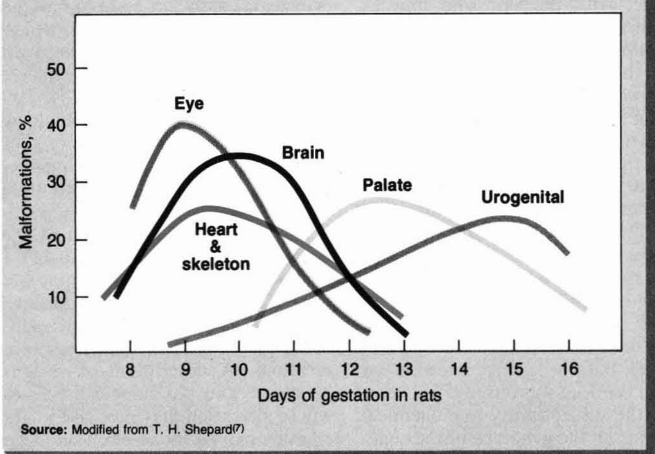
The mechanisms by which chemicals induce teratogenic actions are in general unknown. Unlike mutagenic chemicals, which usually belong to the alkylating class, teratogens may belong to many classes of chemicals; their mechanisms of action are therefore different. Malformations and mutations thus cannot be equated (*10*), nor can carcinogens and teratogens (*11*). Chemicals may act directly on the embryo, fetus, or neonate, or indirectly via interference with maternal, placental, or fetal membrane functions (*12*). Through laboratory animal studies it has been shown that, as a rule, chemicals lack specificity and may affect many structures depending on the time of administration (*9*). For example, trypan blue in rats affects 15 structures, resulting in nine defects. Conversely, different teratogens may produce the same malformations.

It has been proposed that a fetus may be more susceptible to damage by chemical exposure than an adult, depending in part on the development of its liver enzyme conjugating systems and on its greater blood-brain permeability (*13*). Indeed, for a given exposure, there may be no maternal signs of toxicity and the fetus may be the only victim of the toxicant. This has been verified in animal studies as well as in human accidents, for example, chronic low level exposure to methylmercury. Since all substances cross the placenta to some extent, susceptibility to fetal damage may be related to the effective dose reaching the fetus. Some chemicals, such as methylmercury, are preferentially concentrated in the fetus, resulting in injury to the central nervous system. In most other instances, however, the fetus is separated from maternal circulation by the placenta, which permits only a fraction of the concentration of chemical to reach the developing offspring. The placenta therefore serves a protective role in reducing the dose to the fetus. Transfer of a compound across the placenta decreases with increasing molecular weight, increasing electrical charge, and decreasing lipid solubility. Transfer is by simple diffusion for unbound chemicals or for those with high dissociation constants; in other cases, the mechanisms of transfer include active transport and pinocytosis. In some cases, the placenta may also be involved in biotransformation of the compound.

The fetus may also be protected by maternal homeostatic mechanisms that lower the dose reaching the fetus via detoxification by the liver (although some metabolites may be more toxic), excretion by the kidneys or in the bile, or removal of the chemical via binding to plasma proteins which are less likely to cross the placenta. Peak concentrations in maternal circulation may also be decreased by deposition into maternal storage depots. DDT and other lipid-soluble compounds, for example, are deposited in the adipose tissue, while some heavy metals are deposited in bone. It has been suggested that variation in the dose of chemical that reaches the fetus, controlled by the factors outlined above, may underlie the variability in observed species' susceptibility.

Much of what we know about teratology in humans comes from clinical observations and epidemiologic studies (*8*). The bulk of information, however, derives from animal studies. In the discussion to follow, we will not limit ourselves to evidence linking chemicals with birth defects alone, but also will consider general aspects of fetal damage, fetal loss, and reproductive impairment in both the female and male. Fetal damage may be in the form of birth defects or neonatal sequelae of fetal toxicity. This toxicity may be compounded by continued exposure during the neonatal period (postpartum) to residues present in breast milk. Fetal loss may be postimplantation ("early"), manifested by spontaneous abortion, or by a late fetal loss, called a stillbirth. Death may also follow in the postpartum period due to either severe life-threatening malformations or to cumulative toxicity to vital organs. Reproductive impairment is the most difficult entity to document. In females, this may take the form of preimplantation loss (damage to the blastocyst, or even damage to the zygote) or menstrual irregularities. In males, impaired fertility may take the form of decreased sperm counts, decreased motility, or abnormal morphology. In addition, reproductive failure may be manifested as an increased frequency of spontaneous abortions in unexposed females due to mutations in male gametes (*5*).

FIGURE 1
The critical periods for teratogenicity



Source: Modified from T. H. Shepard(*7*)

Air pollutants

Air pollutants commonly include those compounds produced by combustion of fossil fuels, such as the oxides of nitrogen and sulfur and incompletely oxidized hydrocarbons such as carbon monoxide. The most serious source of air pollution to a pregnant woman is cigarette smoke because it exposes the unborn baby to high levels of CO, HCN, cadmium, nicotine, and polycyclic aromatic compounds such as benzo[*a*]pyrene, which can cross the placenta (*14*). Exposure to harmful gases may also follow from occupational exposures, such as to ozone, anesthetic gases, or solvent vapors.

Ozone. A constituent of the earth's upper atmosphere, ozone is considered hazardous in exposures to concentrations over 1 ppm. In areas prone to smog, such as Los Angeles, levels may reach 0.1 ppm, at which point an alert

"The most serious source of air pollution to a pregnant woman is cigarette smoke because it exposes the unborn baby to high levels of CO, HCN, cadmium, nicotine, and polycyclic aromatic compounds such as benzo[*a*]pyrene, which can cross the placenta."

may be called. Ozone concentrations in high-altitude aircraft have been measured at 1.2 ppm, four times the permissible occupational exposure level set by OSHA. Some flight attendants have claimed that they suffer higher rates of spontaneous abortions and birth defects due to ozone exposure (*14*), but no confirmation of these claims is available. However, Fetner (*15*) has shown that ozone is mutagenic to human cell lines in culture, producing chromosomal breaks (at 8 ppm) equivalent to that produced by 200-roentgen x-rays.

Carbon monoxide. More information exists on the effects of carbon monoxide (CO) on the fetus than any other air pollutant. Industrial combustion, automobile exhaust, and cigarettes are the major sources of exposure to CO. Although "mean" urban CO concentrations are 3–10 ppm, near factories or at busy street intersections levels may be 50–100 ppm. With these high CO concentrations, the blood concentration of carboxyhemoglobin can be 4–6% (the equivalent of smoking a pack of cigarettes per day), and smoking may raise these levels an additional 4–5% per pack per day (*14*).

Carbon monoxide diffuses across the placenta and has a half-life of 1.5–2 hours. Under steady-state conditions, the carboxyhemoglobin concentration in the fetus exceeds that in the mother by 10–15%; the fetal arterial oxygen tension, which is much less than that in the adult, is decreased further. The decreased oxygen tension is associated with a redistribution of fetal blood to the brain, heart, and adrenals. Experiments with CO on rats and rabbits have shown a decrease in fetal weight and increase in perinatal mortality (*14*). Brain damage with decreased brain concentrations of protein, nucleic acids, and neurotransmitters has been demonstrated and is assumed to follow from cellular hypoxia. Studies in rats show that reproductive failure via reabsorption of the embryo and early spontaneous abortions (*16*) is concentration-dependent. Teratogenic limb deformities were produced in chicks (*17*) and rabbits (*16*) exposed to high concentrations (180–250 ppm). Brain damage occurred in Long–Evans rats (*16*). In animal studies in which the concentration of carboxyhemoglobin exceeded 15% for 30 minutes, the incidence of fetal death was 57%. In a survey on human carbon monoxide poisonings, Longo (*16*) reported an increased rate of stillbirths when the concentration of carboxyhemoglobin was 20–49%. Some of the surviving infants from these poisonings had neurologic sequelae including mental retardation, seizures, spasticity, and retarded psychomotor development. Autopsies on the stillborns confirmed brain damage (cerebral atrophy).

The 1970 amendment to the Clean Air Act recommended a maximum allowable concentration of CO of 9 ppm for eight hours; however, a pregnant woman may be more susceptible to the effects of CO since in pregnancy oxygen consumption is increased 15–25%, and the blood oxygen capacity is decreased. Safe levels for pregnant females therefore are expected to be lower than this.

Other air pollutants. Hydrogen cyanide may be significant in its effects on the fetus and is primarily found in cigarette smoke. Its mechanism of action is expected to be similar to that of CO, and it may inhibit the development of the fetal central nervous system. No data is available on the effects in the pregnant woman.

Certain heavy metals may be found in polluted air and may act as teratogens. Primarily these include lead and cadmium and are discussed below.

Vapors from occupational exposure. Many vapors one may be occupationally exposed to are toxic, but few are known to be associated with teratogenic or fetotoxic effects in humans. The only two implicated so far are tetrachloroethylene and, with less certainty, nitrous oxide.

It has been known for many years that female anesthesiologists and anesthetists, as well as the unexposed wives of male anesthetists, have a significantly higher risk of spontaneous abortions, infertility, and birth defects. A review by Smithells (*18*) noted that the rate of spontaneous abortions was elevated twofold (29.7–37.8%); a study by the American Society of Anesthesiologists found a higher malformation rate (60% increased) in those exposed, as well as in the wives of exposed males. The identity of the anesthetic gas has not been established, but the effects may be due to nitrous oxide (N_2O). In animal studies, Fink (*19*) found N_2O to be lethal to chick embryos, and both fetotoxic and teratogenic to Sprague–Dawley rats. These results were confirmed by Lane et al. (*20*), who noted a fourfold increase in fetal resorption as well as ocular, central nervous system (CNS), and skeletal defects in rats. It has been hypothesized that N_2O or its metabolites may interfere with organogenesis by inhibiting vitamin B_{12}-dependent reactions, with inactivation via oxidation of cobalamine taking place. Apparently in addition to acting as a teratogen, the offending gas also is a mutagen, causing abortions in the unexposed female via mutations in the male gametes. In animal studies on other anesthetics, isoflurane (*21*) has not been shown to have fetotoxic or teratogenic effects.

Exposure to various solvent vapors (such as benzene and vinyl chloride) are considered hazardous to the pregnant woman, but no data on teratogenic effects in humans are available. Benzene and its methyl derivatives were found to be fetotoxic in rats (*22*), mice, and rabbits (*23*) at high doses, but Watanabe has described teratogenic effects (cleft palate and micrognathia at 3 cm^3/kg subcutaneous) in mice (*24*). Vinyl chloride was found to cause CNS defects in rats (*25*), and trichloroethylene is toxic and teratogenic in rats (*26*).

Tetrachloroethylene, a solvent present in dry-cleaning fluid, has been reported to cause cholestatic jaundice in a breast-fed infant (*27*). The mother was exposed to the vapors chronically, which accumulated in her breast milk. This chlorinated hydrocarbon is therefore fetotoxic, but its teratogenic capability is undetermined. An extensive list of solvents shown to be fetotoxic in various animal systems was tabulated by Wilson (*13*); a few others include DMSO, carbon tetrachloride, chloroform, and methylene chloride.

Food additives

Food additives are compounds knowingly added to food products to color, preserve, or enhance the taste of the product. In a broader context, they may also include some natural constituents of food that have teratogenic potential, as well as inadvertent additives or contaminants. These may be natural products, contaminants of processing, or residues, either on grains or stored in animal tissues. Examples of these are pesticides, PCBs, and heavy metals; these will be discussed later.

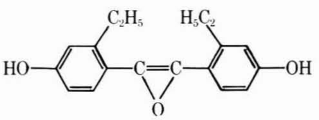
Although the Delaney Clause of the Food, Drug, and Cosmetics Act protects the public from additives that may be carcinogenic based on animal studies, no such clause exists with respect to teratogens. Cognizant of the difficulties involved in performing teratogenic testing and in interpreting the sometimes contradictory results, the Teratology Society has felt it inadvisable to enact such regulations (*28*).

Food dyes. No food coloring has come under closer scrutiny or criticism than Red Dye #2, or Amaranth, a dye used since the turn of the century without reported hazards to humans. The dye was used in soft drinks, gelatins, cereals, candy, lipsticks, pill coatings, etc. One study on Osborne–Mendel rats reported a dose-related embryotoxicity with both early and late deaths (*29*). No teratogenic effects were seen, but it was also carcinogenic in rats. Subsequent studies in the same and other mammalian species revealed a mild tendency for preimplantation loss and increased embryo resorption (*30–36*). The variability of the results among investigating groups brought the significance of these results under question. Again, no teratogenic effects were seen. The dye was removed from the market because of its potential carcinogenicity. However, subsequent work has not verified this azo compound's carcinogenicity (*37*).

Artificial sweeteners. Calcium cyclamate is an artificial sweetener first introduced in 1950 and widely used without ill effects. In 1969, one case report (*38*) appeared describing two infants born with a rather rare combination of cleft lip, cleft palate, and a lobster claw deformity. Allegedly, the only positive factor in the history of both mothers was the use of artificial sweeteners (cyclamates) in low-calorie foods. No other information of teratogenic effects of artificial sweeteners in humans is available. Studies on cyclamate, saccharin, and sucrose have failed to show teratogenic or embryotoxic effects in rats, mice, rabbits (*39*), or zebra fish (*40*). Studies with ^{35}S-cyclamate (*39*) show that it does cross the placenta and that its metabolite, cyclohexylamine, causes preimplantation loss, early fetal death, and growth retardation in Swiss mice (*41*). Because cyclamate caused bladder tumors in rats, its use was limited in 1969.

DES. Few people today are unaware of DES (diethylstilbestrol), a drug prescribed between 1940 and 1970 to prevent miscarriages. Herbst (*42*) showed that the infants exposed in-utero suffered carcinogenic and teratogenic effects in the females, and teratogenic effects in the males. The birth defects centered around the genitalia, with the females having cervical and vaginal adenosis and possible hypoplastic cervixes and uterine anomalies (*43*). These females later in life have a higher incidence of premature deliveries due to these defects. The exposed males have a higher incidence of sperm abnormalities (and therefore possible infertility), undescended testes, hypospadias, and epididymal cysts. DES also has the distinction of being the only known transplacental carcinogen in humans, giving rise to vaginal clear-cell adenocarcinoma in select females. About 350 recorded cases of this cancer in young women are known, 80% with documented exposure to DES. Significantly, Herbst pointed out that the effects of DES seem to be independent of dose, unlike most teratogens. Besides exposure to the pharmaceutical, the population at large may have been exposed to DES as a contaminant in food because of its use to fatten beef and poultry. Before its use for this purpose was discontinued, an estimated 50 million people were exposed to this compound in trace amounts. The effects, if any, of such an exposure have not been determined. Birth defects similar to those found in humans have been reproduced in mice (*44*).

The mechanism of action of DES proposed by Vorherr et al. (*44*) involves the unstable cis form, which attracts electrons to form an epoxide at the double bond that can then attach to DNA. A DES metabolite, hydroxydienestrol:



may also form an epoxide that is highly reactive. This may explain the carcinogenic action.

Preservatives. Sodium nitrite, a food preservative with antibacterial properties, has come under fire because of its tendency to be converted by bacteria in the gut to nitrosamines. By itself, $NaNO_2$ has mutagenic action in bacteria, fungi, and phages. Studies in mice (*46*), as well as our long-term experience in humans, have failed to show reproductive or teratogenic effects. The only demonstrable effect of $NaNO_2$ on the mammalian fetus (CD-1 mice) is its involvement in the oxidation of ferrous iron in hemoglobin to produce methemoglobin, with a resultant decreased blood oxygen carrying capacity. This oxygen deprivation in the fetus is manifested by an increased liver production of

"Studies with radiolabeled cyclamate (an artificial sweetener used as a food additive) show that it does cross the placenta and that its metabolite, cyclohexylamine, causes preimplantation loss, early fetal death, and growth retardation in Swiss mice. . . . its use was limited in 1969."

fetal red blood cells. The effect is dose-dependent (*46*) and is probably insignificant in humans at usual doses of exposure.

Nitrosamines are of concern because of their mutagenic and carcinogenic action in lower animals. Several nitrosamines are also known to be transplacental carcinogens in animals. In humans, they are formed in the colon by bacterial conversion of $NaNO_2$ and enzymatic reduction of nitrates. Independent of their carcinogenic effect, the ethyl and methyl derivatives are embryotoxic in rats, chicks, and hamsters (*47*); malformations have been demonstrated in BD-rats (*48*) only at near-lethal doses (ocular, brain, skeletal, and limb defects). Effects on humans are unknown. In addition to the above, *N*-nitrosodimethylamine may be found outright in six out of seven Scotch whiskeys and in 18 brands of beer (*14*). Beer may be the major dietary source of this compound to some pregnant women. FDA has estimated the levels of nitrosamines in beer to be at or below 1 ppb (*49*).

Another bactericidal food preservative, ethyl-*p*-hydroxy benzoate, was found to be without reproductive effect in studies on rats (*50*).

Chemicals naturally occurring in foods and inadvertent food additives. That natural products may be embryotoxic in lower animals is well known. For example, to the unlucky and unwary swine, wild black cherry, poison hemlock, jimsonweed, and tobacco stalks all are embryotoxic (*13*). Little is known of the teratogenic potential of natural products in humans. For centuries, Mexican women have terminated unwanted early pregnancies by drinking tea brewed from the zoapatle leaf; the active components, zoapatanol and montanol, have oxepane diterpene structures (*51*). Labor can also be induced and early pregnancies terminated by ingestion of ergot alkaloids produced by the fungus *Claviceps purpurea* (*52*), which may be a contaminant of grain, especially rye. Epidemics of ergot poisoning still occur. But in both of these cases, the action of the natural products is probably to induce abortion by eliciting labor, rather than by being embryotoxic. Mycotoxins may also be embryotoxic and teratogenic in lower animals, the most notorious of these being aflatoxin B_1 and G_1, ochratoxin A, rubratoxin B, and T-2 toxin (*53*). There has been speculation that a toxic product of the fungus *Phytophthera infestans* on blighted potatoes (*52*) may cause the higher incidence of neural tube defects (anencephaly and spina bifida) in humans seen in Ireland and the British Isles. This theory remains unproven.

Indirect additives may also take the form of trace chemicals migrating from food packaging, such as vinylidine chloride from plastic wrapping. Studies of this compound in rats and rabbits have shown embryotoxicity (at 80 ppm and 160 ppm), but no birth defects (*54*). One of the more studied possible food contaminants is nitrilotriacetate (NTA)—a compound used in detergents to replace sodiumtripolyphosphate, and which can enter food by adhering to eating utensils. The compound is a weak chelating agent able to sequester divalent cations, e.g., Ca^{2+}. The compound was voluntarily discontinued by its manufacturers in 1970 due to preliminary data suggesting teratogenic capacity by its ability to mobilize heavy metals, perhaps inactivating enzymes (e.g., containing Zn^{2+}), and its ability to concentrate these heavy metals in the fetus. It was speculated that it could perhaps enhance the teratogenic effects of cadmium and mercury (*55*). Studies by Nolan (*56, 57*) on rats and rabbits failed to substantiate fears of embryotoxicity or teratogenicity. In addition, Scharpf (*58*) showed that NTA had no effect on accumulation of cadmium in the fetus and that, in fact, this chelator offered some protection against the toxicity of cadmium (*59*) by inhibiting the deposition of this metal in maternal and fetal tissues in rats (*58*). In humans, however, chelating agents are useful in the treatment of acute inorganic lead and mercury poisoning, but not in the treatment of chronic mercury or cadmium toxicity (*60*). Likewise, chelating agents have not been effective in protecting the unborn human fetus in select cases of heavy-metal poisoning (Pb, Hg).

Caffeine is an additive to soft drinks, chocolate, and analgesics, but a natural constituent of coffee and tea. In September 1980, FDA issued a warning to pregnant women to stop or limit their use of caffeine (*61*), based on its observations of teratogenic effects. Some rats given the equivalent of 12–24 cups of coffee per day had missing digits, delayed skeletal development, and growth retardation. Concern was raised because these defects were seen at doses corresponding to the higher levels of human caffeine consumption. About 100 000 pregnant women are estimated to consume eight or more cups of coffee per day, and the intake from all sources is about 193 mg/day. More severe defects (limb reduction, cleft palate) were seen in higher doses in three strains of mice and two strains of rats (*62*). However, other studies (*63*) at low caffeine doses failed to duplicate these findings in rats.

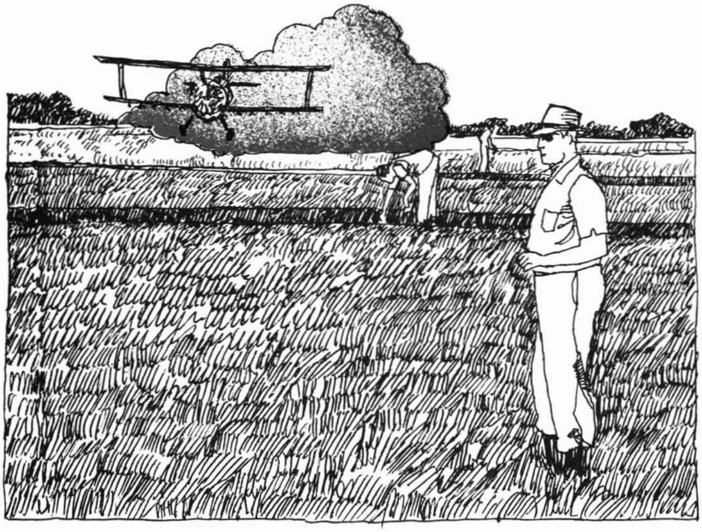
Caffeine is structurally a purine and is mutagenic in bacteria. It crosses the human placenta and is distributed to all fetal tissues. Uptake by the blastocyst has been demonstrated.

No effects of caffeine on humans are proven. However Lechat (*64*) studied 202 cases of birth defects in humans and found a statistically significant difference in the coffee consumption in the group with defective babies. An increase in the frequency of birth defects was seen in those who tended to be heavy drinkers (over seven cups per day). The study was controlled for age and for cigarette and drug consumption.

Caffeine (as well as calcium cyclamate and dimethylnitrosamine), although a mutagen, has also been demonstrated to be without effect in inducing sperm abnormalities in male mice (*65*).

Polyhalogenated biphenyls

PCBs. Polychlorinated biphenyls are a family of compounds largely used as heat exchangers (for example, in



transformers). Over the years, careless disposal of PCBs has contaminated the surface soil and aquatic system of this country. Its deleterious effects on health and reproduction were not fully appreciated until this last decade. Gradually, a picture of embryotoxicity and teratogenicity in many species evolved. In fish, spinal defects and decreasing numbers of striped bass in the Hudson River (*66*) and East Coast waters was seen, and the commercial salmon industry in the Great Lakes was virtually destroyed (*67*). Accidental poisoning of chickens (*68*) with fish meal resulted in decreased hatchability, and CNS and ocular defects. Growth retardation, liver damage, and neonatal deaths were observed (*69*). In mammals, an increase in premature deliveries with neonatal deaths were observed in California sea lions (*70*) which had a two- to eightfold increase in concentration of PCBs and organochlorine pesticides in the mothers and pups. Reproductive failure in ranch minks (*70*) and embryotoxicity in rabbits (*47*) have also been recorded. In 1968, teratogenicity in humans was established.

PCBs tend to persist and accumulate in the environment because of its slow or nonexistent biodegradation. The compound is readily passed through the marine food chain and accumulates in fish tissues. This accumulation is related to the compound's relative insolubility in water and high lipid solubility, which causes tissue levels to be elevated by conceivably a factor of a million or more. This is called bioconcentration. PCBs are usually sequestered in fatty tissues such as adipose and in the breast. Long-term, low-level exposures to PCB therefore give rise to high concentrations in breast milk, especially in fish eaters, since human milk is 1–4% fat and exists in equilibrium with the body's other fat stores in terms of chemicals present. PCBs have been detected in human breast milk at mean concentrations of about 87 ppb (*71*).

Human experience with PCBs stemmed from a large-scale poisoning from ingestion of contaminated rice (cooking) oil in southern Japan in 1968 (*72*). Leakage of the heat exchanger from a pinhole in the heating coils contaminated the rice oil to levels of 2000–3000 ppm. The poisoning dose in this incident amounted to 0.5–2 g/day. One thousand fifty-seven recorded victims had symptoms which included an acnelike rash, headache, nausea, and diarrhea. Thirteen infants were born to exposed women—two were stillborn and the others showed growth retardation; dark cola-colored pigmentation of the skin, gingiva, and nails; conjunctivitis; and neonatal jaundice at birth. Infants who were breast-fed had higher serum PCB levels, and a nine-year follow-up revealed some neurologic and developmental impairment. A 13-year follow-up found PCBs in the tissues of children who had been breast-fed, the level varying with the duration of breast feeding (*71*).

In studies with rats, transfer of PCBs by breast milk exceeded transplacental transfer by a factor of 10 (2% vs. 0.28%) (*73*). Therefore, for women with high exposures to PCBs, the American Academy of Pediatrics has recommended assaying the breast milk before suckling the infant. Also, eating sports fish is discouraged during pregnancy since this is the major dietary source of PCBs. Dieting during pregnancy is discouraged since this may encourage mobilization of chemicals from the fat stores.

This clinical entity related to PCB ingestion has been variously named "Yusho" (oil disease), "cola-colored baby syndrome," and "PCB-induced fetopathy." The mechanism of action is unknown. PCBs are a family (*68*) of 210 possible chlorinated compounds, and some indication exists that the less-chlorinated species may be more toxic (*69*). Although the original heat exchanger in the Japanese poisoning was known to contain contaminants such as polychlorinated dibenzofurans, which are embryotoxic and more potent than PCBs (*68*), the full spectrum of the disease was still produced in rhesus monkeys with purified PCBs (*74*).

PBBs: Little is known of the teratogenic potential of polybrominated biphenyls, used as fire retardants. Only one accident with this compound is recorded. In 1973–1974, PBB was accidentally mixed with cattle feed in Michigan (*14*) and an increase in the incidence of stillbirths in the fed cattle was noted. Subsequently 30 000 cattle, sheep, swine, and poultry were slaughtered. Unfortunately, the cattle carcasses were used as pig food and the manure was used for fertilizer throughout the state. PBBs at 68 ppb have since been detected in the breast milk of women in Michigan (*71*). No harmful effects on human pregnancies or infants have been reported, however.

Pesticides

Organic pesticides become pollutants when they enter our food supplies as inadvertent additives; they are present in trace amounts on grains, in our surface and ground drinking water, and even in the tissues of lower animal forms. Pesticides by definition include insecticides, herbicides, and fungicides. These in turn can be variously subclassified by chemical groups, such as the methyl carbamates, organophosphates, organochlorides, ureas, and phenoxyacetic acids. The teratogenic capability of pesticides is not limited to any particular grouping, but rather transcends all groups; the same is true of pesticides and their mutagenic action.

That pesticides were associated with reproductive failure in lower animals became apparent in the 1960s with decreased hatchability of avian species ("The Silent Spring"). Since then, the teratogenic action of pesticides has been confirmed, and extensive listings

"In 1969, scientists reported that DDT, DDE, lindane, dieldrin, and heptachlorepoxide were present in cord blood (fetal) and tissues of 10 stillborn infants, in levels equal to that of adults. This confirms the transplacental transfer of these compounds, which we now know can also reach the newborn via breast milk."

of pesticides and their embryotoxic and teratogenic effects on various lower species have been published; see, for example, Wilson (*13*). Good studies and well-documented cases of teratogenic effects of pesticides in humans, on the other hand, are lacking. Only the organomercurials are conclusively known to be teratogenic in humans (*13*).

Because of their lipid solubility and resistance to degradation, the presence of organochlorine pesticides have also been well documented in human adult tissues (*75*). In 1969, Curley et al. (*76*) reported that DDT, DDE, lindane, dieldrin, and heptachlorepoxide were present in the cord blood (fetal) and tissues of 10 stillborn infants, in levels equal to that of adults. This confirms the transplacental transfer of these compounds, which we know can also reach the newborn via breast milk. Whether these compounds reaching the fetus exert toxic or teratogenic effects is speculative. One Japanese report (*12*) notes increased fetal deaths and malformations following acute high-level spraying of organophosphorus insecticides on field workers. Another contention of birth defects in humans from such sprayings was raised by Nora (*77*), who reported two infants with limb defects (talipes equinovarus) from 50 mothers with first trimester exposure, and 125 with later exposures. However, in this poor study, the pesticides were not identified, nor was the history of concurrent drug exposure explored.

An interesting observation by O'Leary et al. (*78*), noting elevated pesticide levels in premature infants, may have some implications with respect to human fetal toxicity. Measuring DDE levels in fetal whole blood, they found that premature infants had levels elevated three- to fourfold relative to control, term infants. Although these elevations could be explained by the absence of body fat to store the compound, which is common in preterm infants, a causative role of chlorinated pesticides in inducing premature deliveries cannot be ruled out. Other supporting data comes from animal studies. DeLong (*70*) reported that California sea lions which delivered their pups prematurely had an eightfold increase in fat levels of chlorinated pesticides (DDT, DDD, DDE, and PCB) relative to those which delivered pups at term. The premature pups themselves had a twofold elevation in fat levels of these compounds. Similarly, in New Zealand, in white rabbits fed DDT (50 mg/kg), a premature delivery rate of 57% was noted, with a 25% early fetal loss (*79*).

Two classes of compounds of particular interest are phenoxyacetic acids (2,4-D and 2,4,5-T) and dioxins (2,4,7,8-TCDD). The question of their teratogenic potential arose following their use in Vietnam, where an increase in birth defects was reported (*80*) with the initiation of the defoliation program. "Agent Orange" is a mixture of 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) and 2,4-dichlorophenoxyacetic acid (2,4-D), herbicides that also contain the contaminant 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD), formed from chlorophenols in the synthesis of the herbicides (*9*). Questions have been raised about the effects of these chemicals on the fertility of 3000 exposed veterans and about possible mutagenic effects on their gametes. Evidence linking 2,4,5-T with defects in mice was first provided by a Bionetics study (*80*). Subsequent work by Courtney (*81*) showing increased incidences of cleft palate and cystic kidneys in mice and rats was later shown to be primarily due to the contaminant TCDD (*82*, *83*). TCDD is an extremely potent fetotoxicant and teratogen, and can induce cleft palate in mice with doses as low as 1 μg/kg · d (*84*). Purified 2,4,5-T in high doses has been found to be teratogenic also (*85*); data on 2,4-D is as yet inconclusive. Of all the isomers of dioxin, only the 2,3,7,8-tetrachloro- form has a high embryotoxic effect; an important aspect of TCDD's effect may be to potentiate the teratogenic effect of other compounds (*86*).

The National Toxicology Program's latest study on male mice fed 2,4-D, 2,4,5-T, and TCDD has been unable to show an effect on male fertility, reproduction, germ cell toxicology, or survival or development of offspring (*87*). However, the results of the teratologic studies in animals with 2,4,5-T and TCDD are clearly positive. In humans, on the other hand, a relationship between exposure to these compounds and teratogenic or fetotoxic effects as listed below are suggestive but largely circumstantial:

1. An inordinate number of abortions were noted in women in Alsea, Ore., in 1978 after the area had been sprayed with 2,4,5-T containing TCDD (*88*).
2. A similar spraying in New Zealand resulted in two children with meningomyeloceles from mothers who drank rainwater collected from the roofs (*89*). The rainwater was not assayed for TCDD, however, and so this association was implied but unproven.
3. An elevated incidence of cleft palate was noted in Australia in areas following sprayings with 2,4,5-T (*90*).
4. An elevated rate of spontaneous abortions was noted in the Love Canal district. Dioxin, along with many other chemicals, was present in the toxic wastes at the dump site, but direct cause and effect has not been shown.

Another pesticide that gives evidence of human neonatal toxicity is hexachlorobenzene, a fungicide. Although human fetotoxicity or teratogenicity has not been established, the compound's presence in breast milk is known, and incidents of newborn poisonings following breast-feeding have been documented in Turkey. Skin pigmentation and a syndrome of toxicity resembling porphyria cutania tarda was described (*91*).

The class of pesticides called the phthalimides is of interest because of their structural similarity to thalidomide, a known teratogen. Captan, folpet, and difolatan, fungicides in wide usage, are mutagenic in bacteria, and captan has alkylating capability. Adducts of $SCCl_3$ with guanine have been isolated and usually result in base pair substitutions (*92*). Although birth defects are seen in chicks, none have been documented in mammals. Likewise, no adverse effects have been seen in humans. As described below, the mechanism of action of teratogenicity of thalidomide in terms of structure–function relationships is unsolved (*93*).

Metals and inorganic compounds

Of all classes of chemical compounds, the metals are said to have the greatest potential for embryotoxicity and teratogenicity. Wilson summarized the experience of animal testing with metals (*13*) and found that of 25 metals, 20 were associated with increased fetal death and 17 were teratogenic. Some of what we know of the teratogenic potential of metals in animals is given in Table 1. Metals which are definitely embryotoxic or teratogenic in humans include mercury and lead. Those for which a high index of suspicion exists include lithium, selenium, arsenic, and copper. These compounds as well as tellurium, cadmium, zinc, and chelates will be discussed below.

Alkyl mercury. Of all human teratogens, no other compound has been involved in more poisoning incidents or claimed more victims than mercury. Its organic form is used as an antifungal grain seed dressing, and multiple accidental poisonings have occurred when contaminated grain was mistakenly consumed. The first such incident occurred in Sweden in 1952 when methylmercury dicyandiamide (panogen) was ingested, resulting in intrauterine toxic effects (*94*). The infant born had brain damage manifested by mental retardation, incoordination, and inability to move. Poisonings with the same antifungal compound occurred in Guatemala in 1963–1965 (*95*). In 1963 in Pakistan, 100 cases of poisoning were recorded following ingestion of seed treated with Agrosan-GN, a mixture of phenylmercury acetate and ethylmercury chloride (*96*). Large-scale poisonings occurred in Iraq (*95*) in 1956 and 1960, with 6530 victims and 459 documented hospital deaths. In this case, flour was prepared from wheat seed treated with the antifungal seed dressing ethylmercury *p*-toluene sulfonanilide. Thirty-one pregnant women were victims and 45% died. Infants born with blood mercury concentrations of 2500 ng/mL suffered severe brain damage.

Also, infants born before the epidemic were exposed to organic mercury in breast milk, where its concentration was 3% of that in the mother's blood. One poisoning in the U.S. was noted when a pregnant woman in New Mexico ate pigs that had been fed contaminated grain (*97*). Her infant was born with tremors and convul-

TABLE 1

Teratogenic metals

Element	Species	Effect on fetus	Reference
Arsenic	Mice	Increase in males born	*117*
	Hamsters	Eye defects, exencephaly, renal agenesis	*115*
Cadmium	Mice	Abortions, many defects	*125*
	Rats	Abortions, many defects	*126, 127*
	Hamsters	Brain, eye, limb, craniofacial defects	*128*
Calcium	Hens	Increased anomalies	*47*
Cobalt	Chicks	Eyes, lower limb defects	*156*
Copper	Mice	Abortions	*13*
Gallium	Hamsters	Spina bifida, limb defects, exencephaly	*155*
Germanium	Hamsters	Spina bifida, limb defects, exencephaly	*155*
Indium	Hamsters	Digital defects	*155*
Lead	Rats	Early & late deaths	*152*
	Mice	Abortions, many defects	*152*
	Chicks	Growth retardation, eye and neck defects, micromelia	*153*
	Hamsters	Sacral vertebral defects, spina bifida, eye defects, exencephaly	*113, 151*
Lithium	Primates	Cardiac anomalies	*13*
Mercury	Birds	Fetotoxic	*47*
	Mice	High fetal deaths, cleft palate, retardation in growth and brain development	*102*
	Rats	Abortions, brain damage	*100*
	Hamsters	Poor head ossification	*9*
Molybdenum	Mice	Slight toxicity	*125*
Nickel	Chicks	Abortions, growth retardation, eye and limb defects, exencephaly	*149*
	Rats	Abortions, growth retardation, eye defects	*150*
	Hamsters	Abortions	*149*
Selenium	Chicks	Abortions, many defects	*118*
	Mice	Abortions, growth retardation	*46*
	Sheep	Limb, eye defects	*119*
Strontium	Rats	Abortions, growth retardation, increase in anomalies	*47*
Thallium	Chicks	Abortions, growth retardation, achondroplasia	*154*
	Rats	Growth retardation hydronephrosis, ossification defects	
Titanium	Rats	Abortions, growth retardation	*125*
Zinc	Hamsters	Abortions, exencephaly	*47*

ENJOY YOUR OWN MONTHLY COPY OF

ENVIRONMENTAL SCIENCE & TECHNOLOGY

ES&T

Toll Free: New Orders: (800) 424-6747 **1981**

	U.S.	Foreign**
ACS Members*	☐ $18.00	☐ $25.00
Nonmembers-Personal	☐ $21.00	☐ $28.00
Nonmembers-Institutional	☐ $72.00	☐ $79.00

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

Charge my ☐ Master Card ☐ VISA

Card # ______________ Interbank # ______________
(Master Card Only)

Exp. Date ______________ Signature ______________

Name ______________

Job Title ______________

Your Employer ______________

Address ☐ Home ☐ Business ______________

City ______________ State ______________ Zip ______________

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

If manufacturing, type of products produced ______________

____

*Subscription at ACS member rates are for personal use only.

**Payment must be made in U.S. Currency, by international money order, UNESCO coupons, U.S. bank draft, or through your book dealer.

Allow 60 days for your first copy to be put in the mail 1109A

Mail This Postage-Free Card Today

ENJOY YOUR OWN MONTHLY COPY OF

ENVIRONMENTAL SCIENCE & TECHNOLOGY

ES&T

Toll Free: New Orders: (800) 424-6747 **1981**

	U.S.	Foreign**
ACS Members*	☐ $18.00	☐ $25.00
Nonmembers-Personal	☐ $21.00	☐ $28.00
Nonmembers-Institutional	☐ $72.00	☐ $79.00

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

Charge my ☐ Master Card ☐ VISA

Card # ______________ Interbank # ______________
(Master Card Only)

Exp. Date ______________ Signature ______________

Name ______________

Job Title ______________

Your Employer ______________

Address ☐ Home ☐ Business ______________

City ______________ State ______________ Zip ______________

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

If manufacturing, type of products produced ______________

____

*Subscription at ACS member rates are for personal use only.

**Payment must be made in U.S. Currency, by international money order, UNESCO coupons, U.S. bank draft, or through your book dealer.

Allow 60 days for your first copy to be put in the mail 1109A

Mail This Postage-Free Card Today

NO POSTAGE
NECESSARY
IF MAILED
IN THE
UNITED STATES

BUSINESS REPLY CARD

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

POSTAGE WILL BE PAID BY ADDRESSEE

AMERICAN CHEMICAL SOCIETY
Circulation Dept.
1155 Sixteenth Street, N.W.
Washington, D.C. 20036

NO POSTAGE
NECESSARY
IF MAILED
IN THE
UNITED STATES

BUSINESS REPLY CARD

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

POSTAGE WILL BE PAID BY ADDRESSEE

AMERICAN CHEMICAL SOCIETY
Circulation Dept.
1155 Sixteenth Street, N.W.
Washington, D.C. 20036

"No other compound has been involved in more poisoning incidents or claimed more victims than mercury. At Minamata, Japan, 700 cases of human poisonings were recorded with a 38% mortality rate. . . . The lack of maternal symptoms attests to the ease with which methylmercury crosses the human placenta."

sions, and at the age of one year was blind and could not sit up.

Other mercury poisonings have followed from discharge of this element into natural bodies of water. For example, the wood pulp industry has been guilty of discharging phenyl mercury compounds into fresh water bodies, and chlorine-alkali plants have discharged metallic and inorganic mercury compounds (*95*). Discharge into our salt waters has essentially destroyed the swordfish industry, because of the high flesh alkyl mercury content. Currently, FDA limits for methylmercury in fish for consumption is 0.5–1.0 ppm. Large-scale poisonings of humans who ate fish contaminated with methylmercury were recorded in Japan at Minimata Bay (1953) and at Niigata (1964) (*95, 98*). The fetal encephalopathy or neurological damage that resulted from exposure during intrauterine development has since been named Minimata disease.

At Minimata Bay, inorganic mercury compounds used as catalysts at a plastics plant were dumped into the bay. The metallic and inorganic mercury salts were converted to alkyl compounds by anaerobic bacteria. The compounds were then taken up into the aquatic chain and by bioconcentration attained high levels in fish flesh. About 700 cases of human poisonings, and a 38% mortality rate, were recorded. In one area, the excess of newborn victims (17.3% of victims) relative to pregnant victims underscored the greater susceptibility of the newborn to mercury poisoning (*47*). In fact, in 17 of these infant victims with cerebral palsy, the mother had no symptoms to warn her of danger, and only a few had numbness of their fingers or fatigue (*99*). The lack of maternal symptoms attests to the ease with which methylmercury crosses the human placenta. The sequelae in these infants has been brain damage, manifested as mental retardation, spasticity, chronic seizures, and blindness. A follow-up study of surviving infants in one area from 1955–1959 showed that 6% of the children developed cerebral palsy (*14*).

Minimata disease has been reproduced in animals (*100*); the resulting brain damage involves diffuse neuronal degeneration in all regions of the brain, although the cerebellum and calcarine cortex appear most sensitive to methylmercury (*101*). Segmental atrophy of the axons, thinning of the myelin sheaths, and abnormal synaptic complexes also are seen. Methylmercury is able to produce such toxicity because of several factors: It has an affinity for the CNS (*47*); the dose is cumulative over time (*102*); and there is the phenomenon of fetal mercury "trapping" (*101*)—mercury crosses the placenta by facilitated transfer, at which point it is "trapped" by the fetus. The mercury is bound tightly to receptors forming a concentration gradient. The concentration of mercury in the fetal brain is four times that of the maternal brain, and the level in the fetal blood is 28% higher than in the maternal blood (*101*), indicating preferential accumulation in the fetus. The ease in crossing the placenta is greatest for alkyl compounds, aryl, and then inorganic compounds with lower transfer rates (*47*). With alkyl mercury, chronic exposures are more effective in causing deformities than single doses, since accumulation of the metal results in larger effective doses (*102*).

The chemical mechanism of alkyl mercury toxicity is unknown, but it may rest with its affinity for ligands, e.g., sulfhydryl groups. In this way it may affect a cell's permeability by action on the enzymes on the cell surface. Mercury is known to interrupt the normal function of mitochondria and lysosomes (*103*).

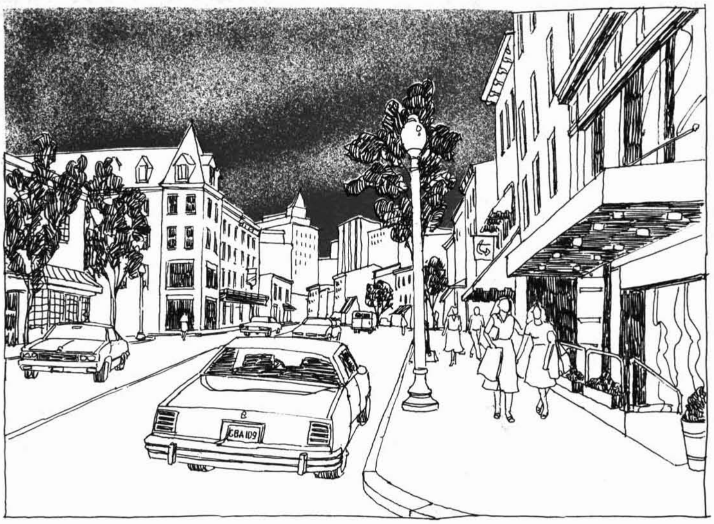
An effect of mercury and methylmercury in decreasing male fertility is well known (*37*). Whether a mutagenic effect on human gametes also can occur is not established. The frequency of chromosomal breaks in lymphocytes of 18 men and women in Sweden who chronically ate fish contaminated with methylmercury (*104*), was proportional to the mercury concentration in their erythrocytes. Concurrent studies of effects on human spermatocytes by such exposure and the outcome of the pregnancy have not been conducted.

Lead. Lead, like methylmercury, is embryotoxic and teratogenic in humans. Its milder effects may be due to a lower transplacental transfer or to differential potency. In pregnant women, its main effect is to increase the rate of spontaneous abortions. Its effect on the fetus may cause low birth weight or brain damage with convulsions and other CNS disorders (*105*). If poisoning takes place in the third trimester, fetal toxicity is below 25% and living infants are underweight, anemic, and develop slowly (*106*). Decreased reproductive ability in men occupationally exposed to lead has been documented via toxicity to sperm (*5, 107*) (decreased counts), which has also been confirmed by animal studies.

The association of high occupational lead exposure with sterility, abortions, and high fetal neonatal loss is well documented. Angle and McIntire (*105*), summarizing data from the turn of the century, cited a 60% stillborn and abortion rate among female lead factory workers and a 70% newborn mortality by the age of three. Industrial exposure data from Japan also cites a doubling of the spontaneous abortion rate, with blood lead levels of 0.11–0.317 mg% (*106, 108*).

At the turn of the century, the ability of lead to induce abortions was well recognized and was used illegally to terminate unwanted pregnancies. Hall (*109*) described 30 cases of maternal ingestion of a lead-containing compound (Diachylon) to induce abortions in England. The abortion rate was high, but so was maternal toxicity, including brain damage and blindness. In the same era in Denmark (*105*), lead oxide poisoning was reported in 25 cases of self-inflicted abortions. In this series, the abortion rate was 60% in the first trimester, with four abortions beyond 20 weeks. Three live births resulted from unsuccessful abortion attempts and one of these children died at the age of two months, possibly from toxic effects.

More recently, lead contamination of acidic drinking water from lead pipes has been implicated in Scotland (*110*), where there was a late fetal



death (lead was found in the fetal kidneys and the maternal urinary lead concentration was 86 mg/24°), one mother with frequent miscarriages and bleeding disorders of pregnancy, and two infants with anomalies (congenital nystagmus and hemangiomata). Transplacental lead intoxication has also been reported from maternal inhalation of fumes from the burning of battery cases and consumption of moonshine whiskeys (*111*). In fact, Palmisano (*111*) reported that 53% of these whiskeys contain lead concentrations over 1 mg/L and may be a common cause of lead intoxication in the southeastern U.S.

Lead crosses the placenta only if given in high concentrations; it tends to concentrate in the fetal bone and liver (*105*). Lead accumulates in the placenta and may induce abortions. Catz and Jaffee (*106*) reported a tendency for abortion associated with placental hemorrhage.

The chemical mechanism of lead teratogenesis and embryotoxicity is assumed to be related to its effects on the metalloenzymes involved in embryonic differentiation. Cole (*112*) suggested an inhibitory effect similar to that which it exerts on the enzymes of the heme synthetic pathway, e.g., delta amino levulinic acid. Lead interacts with other metals in teratogenesis in animal studies. The frequency and severity of lead-induced malformations in hamsters is potentiated by the presence of cadmium, which, when acting in concert, introduces new malformations (sympodia) (*113*).

Arsenic. Arsenic (Na_3AsO_4) is the only teratogenic member of the Group V elements. In rats, ewes, and hamsters, it causes cleft palate, exencephaly, anophthalmia, microphthalmia, and renal agenesis (*114*). In humans, however, organic arsenicals do not cross the placenta, but rather accumulate there. These compounds were used in the past in the treatment of syphilis without report of fetotoxicity (*115*). In the anionic form, however, arsenic does cross the mammalian placenta to some extent. One case (*116*) reports a human fetal death resulting from a mother's suicide attempt. She ingested a toxic dose of rat poison (As_2O_3) and subsequently delivered a live (30 week) infant. The infant soon died of severe intraalveolar pulmonary hemorrhages and had high arsenic levels in its liver, kidneys, and brain. No birth defects were noted. Arsenic therefore has the potential to be fetotoxic in humans.

The effect of arsenic can be reduced by administering selenium (*117*). Presumably, selenium acts by competitive inhibition at the sites where arsenic exerts its activity.

Copper. Copper ($CuCl_2$) is known to be lethal to mice embryos in the blastocyst and late preimplantation stage (*13*). Considering the effective use of metallic copper in intrauterine contraceptive devices in preventing pregnancy in humans, it is interesting to speculate whether embryolethal effects of copper may hold true in humans also. Prevention of implantation by endometrial inflammation from the device has also been proposed.

Selenium. Selenium (Na_2SeO_3) is embryotoxic and teratogenic in hens, sheep, and calves; among other defects, shortened limbs are produced (*118*, *47*). One case describes reputed effects of selenium in humans whereby five pregnancies in women employed in handling selenium gave rise to four abortions and to one live birth of a child with clubbed feet (*119*).

A contention that the high content of selenium in Ireland's soil is causally related to the high incidence of neural tube birth defects in that country is also unproven.

In hamsters, selenium blocks the teratogenic effects of cadmium and arsenic (*120*). It has been suggested that this may be due to its chelation to cadmium that is bound to the sulfur on sulfhydryl groups.

Tellurium. There is no evidence that tellurium (Na_2TeO_3) is embryotoxic or teratogenic in humans. In fact, at one time it also was used to treat syphilis. Overdoses of tellurium in men were detected by the classical sign of a garlic odor on the breath, due to dimethyltelluride, a metabolic product (*121*). No effect on human pregnancies was ever recorded, probably due to low transplacental transfer. Tellurium does cross the placenta and the blood–brain barrier in other mammals, however; this is of interest because it causes a very specific defect: nonobstructive hydrocephalus (*122*). Elemental tellurium is crystallized as a black precipitate in the brains of rats, and toxic changes are seen in the ependymal cells of the lateral ventricles, which perhaps breaks down the blood–brain barrier. Neurologic damage has similarly been seen in rabbits (ataxia). Since tellurium belongs to the same group as sulfur and selenium, its effect may be mediated by interaction with sulfur-metabolizing mechanisms (*123*).

Cadmium. Although cadmium poisoning is known to occur in humans, (the Japanese named it "Itai, Itai," meaning "agony"), embryotoxic or teratogenic effects in humans have never been documented. We do know, however, that cadmium crosses the human placenta and is retained in the fetus, mainly in the liver and kidneys, where it accumulates (*124*). Cadmium is embryotoxic in mice (*125*), and teratogenic in the rats (*126*, *127*), in which it causes growth retardation, hypoplastic lungs, clubbed feet, and cleft palate. In hamsters (*128*), it causes craniofacial, brain, eye, and limb defects.

The mechanism of cadmium teratogenicity is believed to involve competition with zinc for divalent cationic sites in metalloenzymes (*129*, *130*). It has been observed that Zn^{2+} antagonized the action of Cd^{2+} (*131*), and a high Cd^{2+}/Zn^{2+} ratio is needed for toxicity (*124*). Barr (*127*) has made the observation that the limb-reduction anomalies associated with cadmium

> **"Previously, industry sought to protect the unborn fetus by removing it and the mother from the toxic source. But for effects produced through the male partner, it is clear that this policy is inadequate; reduction of occupational exposures for both sexes is the key."**

exposure bore a resemblance to those seen with acetazolamide exposure. Since acetazolamide inhibits carbonic anhydrase, a zinc-containing metalloenzyme, Barr proposed that cadmium may exert its teratogenic effect in animals by competing with zinc and affecting the activity of carbonic anhydrase in the developing fetus. Zinc (*127*) and selenium (*120*), therefore, are antagonists of cadmium; lead and mercury (*132*) potentiate the action of cadmium (in hamsters).

In a study of pregnant rats, Parizek (*133*) noted that as they approached term they became increasingly sensitive to the toxic effects of cadmium. He described the effects observed as resembling "toxemia," or hypertensive disease of pregnancy in the human. Pathological changes in the animals included renal cortical necrosis, venous congestions, adrenal hemorrhage, and convulsions. An association of hypertension with high renal cadmium levels may follow from the nephrotoxicity of cadmium (*124*). Parizek observed that cadmium chloride or acetate causes destruction of the fetal part of the placenta in rats (0.04 mmol/kg · d subcutaneous), with necrosis of the placenta and decidua, and intrauterine or external hemorrhage (*134*, *135*). In humans, heavy cigarette smoking is associated with an increased incidence of bleeding due to placental separation (abruption), with underlying placental and decidual necrosis (*136*). Whether this results from the cadmium present in cigarette smoke (*124*) or from the vasospastic action of nicotine (*136*) or some other factor is yet undetermined.

Zinc and chelates. Zinc deficiency in rats is associated with gross malformations (*137*). Therefore, any situation simulating zinc deficiency, whether by antagonism of other divalent cations as described above or by binding by chelating agents, is expected to produce teratogenic effects. Strong chelators such as ethylene diamine tetraacetic acid (EDTA), as expected, produce such defects in rats as cleft palate, malformed digits, clubbed feet, and brain defects, as well as increased abortions (*137*, *138*). Weak chelators such as trisodium nitrilotriacetate (*56*) and trisodium citrate (*59*) are without teratogenic effects. On the other hand, one might expect chelates to be useful tools to counter the effects of teratogenic divalent cations (e.g., Hg, Pb, Cd). Although in animals this has been confirmed with nitrilotriacetate (*58*) and trisodium citrate (*59*) (which are weakly efficacious in preventing fetal accumulation of cadmium and mercury, respectively), chelating compounds have not been found to be efficacious in humans to protect the fetus. Such experience is limited, however.

Other concerns

A relatively new concern that was unrecognized until recently is the adverse effects on human reproduction secondary to male exposure in the workplace. Previously, industry sought to protect the unborn fetus by removing it and the mother from the toxic source. But for effects produced through the male partner, it is clear that this policy is inadequate; reduction of occupational exposures for both sexes is the key.

Male sterility, fetal loss, and birth defects in their offspring was first recognized in the 1970s with exposure to Kepone and DBCP (1,2 dibromo-3-chloropropane) (*139*). Kepone, a chlorinated insecticide used to control fire ants, was implicated in 1975 when exposed workers suffered CNS changes, liver damage, and testicular damage (*3*). Sperm counts decreased and infertility resulted. Although production of Kepone was subsequently halted by the EPA, sources of exposure still exist in the environment (such as the contaminated James River (*140*)) and it is still produced by breakdown of other pesticides, such as Mirex. Similarly, DBCP, a soil fumigant used to control nematodes, decreases sperm counts in exposed workers and results in infertility (*5*). Production of DBCP was discontinued in 1977.

To date, compounds that decrease male fertility by toxic action on the testes and sperm include lead (*107*), DBCP (*5*), Kepone (*3*), and chloroprene (*5*). In addition, chloroprene exerts mutagenic effects on male gametes, manifested by a threefold increase in spontaneous abortions in the unexposed female. Possible mutagenic effects of vinyl chloride (*5*) are an increase in late fetal deaths, miscarriages, and stillborns. In addition to its effect on male sterility, DBCP may also induce birth defects; one case of penile abnormalities in an offspring has been noted.

The effect of male exposure to hydrocarbons remains controversial. A report of an increased cancer mortality rate in the children of exposed males has not been verified by further studies (*139*). Also, the contention that male exposure to the herbicide Oryzalin (*141*) results in an increased abortion rate and congenital cardiac defects has not been substantiated to date.

Another recently recognized problem in toxicology is poisoning of the newborn via chemicals present in breast milk. It is an avenue for neonatal toxicity for those compounds that cannot cross the placenta and for continued exposure and toxicity extending into the postpartum period and later stages of development. Pollutants in breast milk are generally characterized by high lipid solubility, resistance to degradation, and slow excretion rates. Long-term low-level exposure results in accumulation; lactation is the only way in which large amounts of the chemicals can be excreted.

Only three known compounds exerting such toxicity have been documented and these have already been discussed: hexachlorobenzene, PCB, and tetrachloroethylene. In addition to these, Rogan et al. (*71*) have recently confirmed and quantitated the levels of DDT (50–2000 ppb) and its primary metabolite DDE (2130 ppb) in whole milk, as well as the less-common pesticides dieldrin, heptachlor and its epoxide, chlordane, and oxychlordane. Concentrations of these chemicals in whole milk were 91–164 ppb. Human toxicity of these compounds is low, especially at these levels, but the possibility of increased susceptibility of newborns has not been studied. No reports of illness in the newborn due to transmission of these chemicals has been reported.

The job ahead

Teratology had its birth as a science with the thalidomide disaster. It then became more than just an academic curiosity. It is unfortunate that much of what we know of chemical teratology in humans stems from disasters, rather than from testing. The toxicologic testing of chemicals is a reality, in spite of its critics who quote Karnofsky's law (*142*): Any compound can be teratogenic if given to the right species, at the right dose, at the right time. To be certain, the task is monumental, but the moral responsibility cannot be shaken.

Currently, teratologic screening as recommended by FDA consists of three segments (*142*), each to be applied to two or more species and at several concentrations:

1. Fertility and general reproductive performance is studied for both sexes over three generations from premating on.
2. Embryotoxicity and teratogenicity is studied in pregnant females (Somer's Test) during the period of organogenesis.
3. Peri- and postnatal studies in females are carried out to assess late injuries through the period of lactation.

This present mode of screening is expensive, time-consuming, and, according to some, low in predictive value. The future in teratologic screening will be in more rapid, inexpensive mass screening of chemicals. These methods, some still experimental, include:

1. in-vitro embryo cultures (*143*)—in rats to the early limb bud stage (48 hours)
2. post-abortive investigations on human embryos (*8*)—correlating malformations in the abortus with events during the pregnancy or in the maternal history
3. developmental enzyme patterns (*144*)—to assess late (i.e., other than first trimester) toxicity giving rise to functional deficits
4. epidemiologic (population) studies (*145*)
5. behavioral teratology—to study neurotoxicity from late exposures.

As chemists, we would think that structure-function relationships would hold great promise to predict teratologic potential. Unfortunately, no great insights have followed from such studies on two promising classes of teratogens: trypan blue and the diazo group of teratogens (trypan blue, niagara blue 2B and 4B, afridol blue, and azovan blue) (*146*), and the phthalimide family of compounds. Although thalidomide is a potent teratogen, none of the other *N*-substituted phthalimides (Figure 2), all containing the *o*-dicarboximido structure (captan, folpet, difolatan, etc.), have shown such a tendency (*147*). The active site or responsible functional group is still unknown. Only in terms of predicting a compound's alkylating ability have theoretical studies borne fruit; but, as already mentioned, this is more true in predicting a compound's mutagenic rather than teratogenic capability.

Through toxicologic testing of chemicals, our goal is to prevent future mishaps. But an important lesson must be learned from incidents like the ban on spray adhesives in 1973 (*148*). The ban, following one study implicating industrial exposure of women with increased chromosomal breaks and birth defects, prompted nine women to have abortions, only to see the ban lifted six months later when the associations could not be confirmed by further experiments. Testing and reporting must be accurate and responsible or else the end result will be the hysteria and human anguish that we sought to prevent.

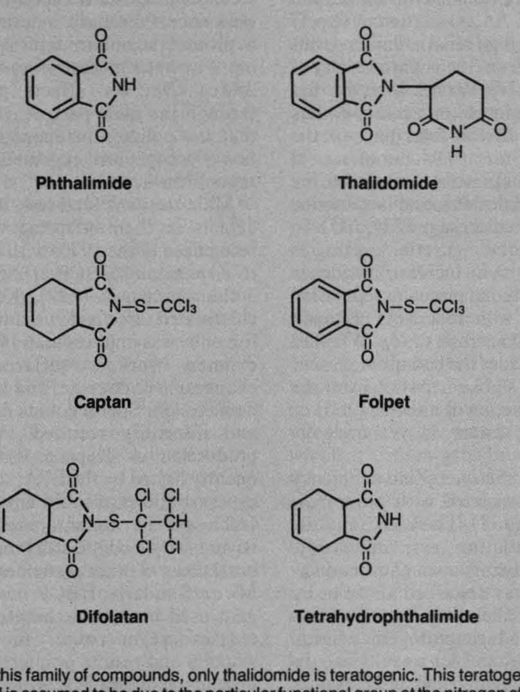
Acknowledgment

This article was read and commented on for appropriateness and suitability as an *ES&T* Critical Review by Dr. Robert Tardiff, National Academy of Sciences, Washington, D.C.

References

(1) Magnuson, E. *Time* **1980,** *116*, 58–69.
(2) Howard, F. M.; Hill, J. M. *Obstet. Gynecol. Survey* **1979,** *34*, 643–653.
(3) Sternberg, S. S. *Pharmacol Ther.* **1979,** *6*, 147–166.
(4) Staples, R. E. *Environ. Health Perspect.* **1976,** *18*, 95–96.
(5) Manson, J. M. *Prev. Med.* **1978,** *7*, 322–331.
(6) Monie, I. W. *Calif. Med.* **1963** *99*, 323–327.
(7) Shepard, T. H. *Curr. Prob. in Ped.* **1973,** *10*, 1–43.
(8) Goodwin, J.; Godden, J.; Chance, G. "Perinatal Medicine"; Williams & Wilkins: Baltimore, Md., 1976, Ch. 5.
(9) Durham, W. F.; Williams, C. H. *Ann. Rev. Entomol.* **1972,** *17*, 123–148.
(10) Kalter, H. *Mutation Res.* **1975,** *33*, 29–36.
(11) Miller, R. W. *J. Nat. Cancer Inst.* **1977,** *58*, 471–474.
(12) Khera, K. S.; Clegg, D. J. *Can. Med. Assoc. J.* **1969,** *100*, 167–172.
(13) Wilson, J. G. *Fed. Proc.* **1977,** *36*,

FIGURE 2
The phthalimide family



Among this family of compounds, only thalidomide is teratogenic. This teratogenic potential is assumed to be due to the particular functional group at the nitrogen of the phthalimide moiety.

1698–1703.

(14) Longo, L. D. *Am. J. Obstet. Gynecol.* **1980,** *137*, 162–173.

(15) Fetner, R. H. *Nature* **1962,** *194*, 793–794.

(16) Longo, L. D. *Am. J. Obstet. Gynecol.* **1977,** *129*, 69–103.

(17) Baker, F. D.; Tumasonis, C. F. *Arch. Environ. Health* **1972,** *24*, 53–61.

(18) Smithells, R. W. *Br. Med. Bull.* **1976,** *32*, 27–33.

(19) Fink, B. R.; Shepard, T. H.; Blandau, R. J. *Nature* **1967,** *214*, 146–148.

(20) Lane, G.; Nahrwold, M.; Tait, A.; Taylor-Busch, M.; Cohen, P.; Beaudoin, A. *Science* **1980,** *210*, 899–901.

(21) Kennedy, G. L., Jr.; Smith, S. H.; Keplinger, M. L.; Calandra, J.C. *Drug Chem. Toxicol.* **1978,** *1*, 75–88.

(22) Hudak, A.; Ungvary, G. *Toxicology* **1978,** *11*, 55–63.

(23) Murray, F. J.; John, J. A.; Rampy, L. W.; Kuna, R. A.; Schwetz, B. A. *Am. Ind. Hyg. Assoc. J.* **1979,** *40*, 993–998.

(24) Watanabe, G.; Yoshida, S. *Acta Medica et Biologica* **1970,** *17*, 285–291.

(25) Ungvary, G.; Hudak, A.; Tatrai, E.; Lorincz, M.; Folly, G. *Toxicology* **1978,** *11*, 45–54.

(26) Dorfmueller, M.; Henne, S.; York, R.; Bornschein, R.; Manson, J. *Toxicology* **1979,** *14*, 153–166.

(27) Bagnell, P. C.; Ellenberger, H. A. *Can. Med. Assoc. J.* **1977,** *117*, 1047.

(28) *Teratology* **1974,** *10*, 1.

(29) Collins, T. F. X.; McLaughlin, J. *Food Cosmet. Toxicol.* **1972,** *10*, 619–624.

(30) Keplinger, M. L.; Wright, P. L.; Plank, J.B.; Calandra, J. C. *Toxicol. Appl. Pharmacol.* **1974,** *28*, 209–215.

(31) Larsson, K. S. *Toxicology* **1975,** *4*, 75–82.

(32) Collins, T. F. X.; Ruggles, D. I.; Holson, J. F., Jr.; Schumacher, H.; Gaylor, D. W.; Kennedy, G. L., Jr. *J. Toxicol. Environ. Health* **1976,** *1*, 851–856.

(33) Collins, T. F. X.; Black, T. N.; Ruggles, D. I.; Gray, G. C. *J. Toxicol. Environ. Health* **1976,** *1*, 857–862.

(34) Keplinger, M. L.; Kinoshita, F. K.; Smith, S. H.; Kennedy, G. L., Jr. *J. Toxicol. Environ. Health* **1976,** *1*, 863–866.

(35) Holson, J. F., Jr.; Schumacher, H. J.; Gaylor, D. W.; Gaines, T. B. *J. Toxicol. Environ. Health* **1976,** *1*, 867–874.

(36) Collins, T. F. X.; Ruggles, D. I.; Holson, J. F., Jr.; Schumacher, H.; Gaylor, D. W.; Kennedy, G. L., Jr. *J. Toxicol. Environ. Health* **1976,** *1*, 875–885.

(37) Doull, J.; Klaassen, C.; Amdur, M. "Toxicology"; 2nd ed.; MacMillan Publishing Co. Inc.: New York, 1980, p. 96.

(38) Hillman, S. A.; Fraser, F. C. *Ped.* **1969,** *44*, 299–300.

(39) Fritz, H.; Hess, R. *Experientia* **1968,** *24*, 1140–1141.

(40) Farkas, G.; Ropp, M. *Ped.* **1971,** *48*, 337.

(41) Kroes, R.; Peters, P. W. J.; Berkvens, J.; Verschuuren, H.; DeVries, T.; Van Esch, G. J. *Toxicology* **1977,** *8*, 285–300.

(42) Herbst, A.; Cole, P.; Colton, T.; Robboy, S.; Scully, R. *Am. J. Obstet. Gynecol.* **1977,** *128*, 43–50.

(43) Kaufman, R. H.; Binder, G.; Gray, P.; Adams, E. *Am. J. Obstet. Gynecol.* **1977,** *128*, 51–59.

(44) Vorherr, H.; Messer, R.; Vorherr, U.; Jordan, S.; Kornfeld, M. *Biochem. Pharmacol.* **1979,** *28*, 1865–1877.

(45) Invi, N.; Nishi, Y.; Taketomi, M.; Mori, M. *Mut. Res.* **1979,** *66*, 149–158.

(46) Globus, M.; Samuel, D. *Teratology* **1978,** *18*, 367–373.

(47) Clegg, D. J. *Food. Cosmet. Toxicol.* **1971,** *9*, 195–205.

(48) Montesano, R.; Bartsch, H. *Mut. Res.* **1976,** *32*, 179–228.

(49) *Chem. Eng. News* **1980,** *June 30*, 14.

(50) Moriyama, I.; Hiraoka, K.; Yamaguchi, R. *Acta Obstet. Gynecol. Japan* **1975,** *22*, 94–106.

(51) Levine, S., et al. *J. Am. Chem. Soc.*, **1979,** *101*, 3404–3405.

(52) Rice, J. M. In "Prevention of Embryonic, Fetal, and Perinatal Disease"; R. L. Brest, M. I. Harris, Eds.; Fogarty Int. Center Series on Preventive Medicine, NIH: Bethesda, Md., Vol. 3, Ch. 8, p. 163–177.

(53) Hayes, A. W. *Mycopathologia* **1978,** *65*, 29–41.

(54) Murray, F. J.; Nitschke, K. D.; Rampy, L. W.; Schwetz, B. A. *Toxicol. Appl. Pharmacol.* **1979,** *49*, 189–202.

(55) Shepard, T. H. *Teratology* **1972,** *6*, 127–128.

(56) Nolen, G. A.; Klusman, L. W.; Back, D. L.; Buehler, E. V. *Food Cosmet. Toxicol.* **1971,** *9*, 509–518.

(57) Nolen, G. A.; Buehler, E. V.; Geil, R. G.; Goldenthal, E. I. *Toxicol. Appl. Pharmacol.* **1972,** *23*, 222–237.

(58) Scharpf, L. G.; Hill, I. D.; Wright, P. L.; Plank, J. B.; Keplinger, M. L.; Calandra, J. C. *Nature* **1972,** *239*, 231–234.

(59) Nolen, G. A.; Bohne, R. L.; Buehler, E. V. *Toxicol. Appl. Pharmacol.* **1972,** *23*, 238–250.

(60) Chisolm, J. J., Jr. *Ped. Annals* **1980,** *9*, 28–42.

(61) *Forum* (National Family Planning & Reproductive Health Assoc. Inc.) **1980,** *7*(3), 1, 4.

(62) Mulvihill, J. J. *Teratology* **1973,** *8*, 69–72.

(63) Palm, P. E.; Arnold, E. P.; Rachwall, P. C.; Leyczek, J. C.; Teague, K. L.; Kensler, C. J. *Toxicol. Appl. Pharmacol.* **1978,** *44*, 1–16.

(64) Lechat, M. F.; Borlee, I.; Bouckaert, A.; Misson, C. *Science* **1980,** *207*, 1296–1297.

(65) Wyrobek, A. J.; Bruce, W. R. *Proc. Nat. Acad. Sci. USA* **1975,** *72*, 4425–4429.

(66) *Chem. Eng. News* **1980,** *July 21*, 24.

(67) *Chem. Eng. News* **1980,** *June 30*, 14.

(68) Cecil, H.; Bitman, J.; Lillie, R. J.; Fries, G.; Verrett, J. *Bull. Environ. Contam. Toxicol.* **1974,** *11*, 489–495.

(69) Carlson, R. W.; Duboy, R. T. *Bull. Environ. Contam. Toxicol.* **1973,** *9*, 261–266.

(70) DeLong, R.; Gilmartin, W.; Simpson, J. *Science* **1973,** *181*, 1168–1170.

(71) Rogan, W.; Bagniewska, A.; Damstra, T. *N. Eng. J. Med.* **1980,** *302*, 1450–1453.

(72) Kuratsune, M.; Yoshimura, T.; Matsuzaka, J.; Yamaguchi, A. *Environ. Health Perspec.* **1972,** *1*, 119–128.

(73) Takagi, Y.; Otake, T.; Kataoka, M.; Murata, Y.; Aburada, S.; Akasaka, S.; Hashimoto, K.; Uda, H.; Kitaura, T. *Toxicol. Appl. Pharmacol.* **1976,** *38*, 549–558.

(74) Bowman, R. E.; Heironimus, M.; Allen, J. R. *Pharmacol. Biochem. Behav.* **1978,** *9*, 49–56.

(75) Krauthacker, B.; Alebic-Kolbah, T.; Buntic, A.; Tkalcevic, B.; Reiner, E. *Int. Arch. Occup. Environ. Health* **1980,** *46*, 267–273.

(76) Curley, A.; Copeland, M. F.; Kimbrough, R. D. *Arch. Environ. Health* **1969,** *19*, 628–632.

(77) Nora, J. J.; Nora, A. H.; Sommerville, R. J.; Hill, R.; McNamara, D. *J. Am. Med. Assoc.* **1967,** *202*, 1065–1069.

(78) O'Leary, J. A.; Davies, J.; Edmundson, W.; Feldman, M. *Am. J. Obstet. Gynecol.* **1970,** *106*, 939.

(79) Hart, M.; Adamson, R.; Fabro, S. *Arch. Intern. Pharmacodyn. Therapy* **1971,** *192*, 286–290.

(80) Nelson, B. *Science* **1969,** *166*, 977–979.

(81) Courtney, K. D.; Gaylor, D. W.; Hogan, M.; Falk, H.; Bates, R.; Mitchell, I. *Science* **1970,** *168*, 864–866.

(82) Emerson, J. L.; Thompson, D. J.; Streing, R. J.; Gerbig, C. G.; Robinson, V. B. *Food Cosmet. Toxicol.* **1971,** *9*, 395–404.

(83) Sparschu, G. L.; Dunn, F. L.; Rowe, V. K. *Food Cosmet. Toxicol.* **1971,** *9*, 405–412.

(84) Smith, F. A.; Schwetz, B. A.; Nitschke, K. D. *Toxicol. Appl. Pharmacol.* **1976,** *38*, 517–523.

(85) Bage, G.; Clekanova, E.; Larsson, K. S. *Acta Pharmacol. Toxicol.* **1973,** *32*, 408–416.

(86) Neubert, D.; Zens, P.; Rotheneallner, A.; Merker, H. J. *Environ. Health Perspec.* **1973,** *5*, 67–79.

(87) *Chem. Eng. News* **1980,** *Aug. 11*, 4.

(88) *Fed. Register* **1979,** *44*(15), 874.

(89) Sare, W. M.; Forbes, P. I. *N.Z. Med. J.* **1972,** *75*, 37–38.

(90) Brogan, W. F.; Brogan, C. E.; Dodd, J. T. *Lancet II* **1980,** p. 597.

(91) Cam, C.; Nigogosyan, G. *J. Am. Med. Assoc.* **1963,** *183*, 88–91.

(92) Bridges, B. A. *Mut. Res.* **1975,** *32*, 3–34.

(93) Fabro, S.; Smith, R. L.; Williams, R. T. *Food Cosmet. Toxicol.* **1965,** *3*, 587–590.

(94) Engleson, G.; Herner, T. *Acta Paediatrica* **1952,** *41*, 289–294.

(95) Bakir, F., et al. *Science* **1973,** *181*, 230–241.

(96) Haq, I. U. *Br. Med. J.* **1963,** *1*, 1579–1582.

(97) Pierce, P. E.; Thompson, J. F.; Likosky, W.; Nickey, L.; Barthel, W.; Hinman, A. *J. Am. Med. Assoc.* **1972,** *220*, 1429–1442.

(98) Durham, W. F.; Williams, C. H. *Ann. Rev. Entomol.* **1972,** *17*, 123–148.

(99) Matsumoto, H.; Koya, G.; Takeuchi, T. *J. Neuropath. Exp. Neurol.* **1965,** *24*, 563–574.

(100) Nanaka, I. *Kumamoto Med. J.* **1969,** *22*, 27–33.

(101) Chang, L.; Reuhl, K.; Spyker, J. *Environ. Res.* **1977,** *13*, 171–185.

(102) Su, M.; Okita, G. T. *Toxicol. Appl. Pharmacol.* **1976,** *38*, 207–216.

(103) Gale, T.; Ferm, V. H. *Life Sci.* (*II*) **1971,** *10*, 1341–1347.

(104) Skerfing, S.; Hansson, K.; Lindsten, J. *Arch. Environ. Health* **1970,** *21*, 133–139.

(105) Angle, C. R.; McIntire, M. S. *Am. J. Dis. Child.* **1964,** *108*, 436–439.

(106) Catz, C. S.; Jaffee, S. J. In "Prevention of Embryonic, Fetal, and Perinatal Disease"; R. L. Brent, M. I. Harris, Eds.; NIH: Bethesda, Md., Vol. 3, pp. 119–145.

(107) Lancranjan, I.; Popesca, H. I.; Gavenescu, O.; Klepsch, I.; Serbanescu, M. *Arch. Environ. Health* **1975,** *30*, 396.

(108) Nogaki, K. *Excerpta Med.* **1958,** *18*, 2176.

(109) Hall, A. *Br. Med. J.* **1905,** *1*, 584–587.

(110) Wilson, A. T. *Scott. Med. J.* **1966,** *11*, 73–82.

(111) Palmisano, P.; Sneed, R.; Cassady, G. *J. Peds.* **1969,** *75*, 869–872.

(112) Cole, R.; Cole, J. *Lancet* **1976,** *2*, 640.

(113) Ferm, V. H. *Experientia* **1969,** *25*, 56–57.

(114) Leonard, A.; Lauwerys, R. R. *Mut. Res.* **1980,** *75*, 49–62.

(115) Ferm, V. H.; Carpenter, S. J. *J. Reprod. Fert.* **1968,** *17*, 199–201.

(116) Lugo, G.; Cassady, G.; Palmisano, P. *Am. J. Dis. Child.* **1969,** *117*, 328–330.

(117) Beaudoin, A. R. *Teratology* **1974,** *10*, 153–157.

(118) Wright, P. L.; Mraz, F. R. *Proc. Soc. Exp. Biol. Med.* **1965,** *118*, 534–539.

(119) Robertson, D. S. F. *Lancet* **1970,** *1*, 518–519.

(120) Holmberg, R., Jr.; Ferm, V. H. *Arch Environ. Health* **1969,** *18*, 873–877.

(121) Duckett, S. *Experientia* **1970,** *26*, 1239–1241.

(122) Garro, F.; Pentschew, A. *Arch. Psychiat. Neurol.* **1964,** *206*, 272–280.

(123) Duckett, S. *Ann. N.Y. Acad. Sci.* **1972,** *19*, 220–226.

(124) Flick, D. F.; Kraybill, H. F.; Dimitroff, J. M. *Environ. Res.* **1971,** *4*, 71–85.

(125) Schroeder, H. A.; Mitchener, M. *Arch. Environ. Health* **1971,** *23*, 102–106.

(126) Chernoff, N. *Teratology* **1973,** *8*, 29–32.

(127) Barr, M., Jr. *Teratology* **1973,** *7*, 237–242.

(128) Gale, T. F.; Ferm, V. H. *Biol. Neonate* **1973,** *23*, 149–160.
(129) Ferm, V. H.; Carpenter, S. J. *Nature* **1967,** *216*, 1123.
(130) Ferm, V. H.; Carpenter, S. J. *Lab. Invest.* **1968,** *18*, 429–432.
(131) Chiquoine, A. D. *J. Reprod. Fert.* **1965,** *10*, 263–265.
(132) Gale, T. F. *Environ. Res.* **1973,** *6*, 95–105.
(133) Parizek, J. *J. Reprod. Fert.* **1965,** *9*, 111–112.
(134) Parizek, J. *J. Reprod. Fert.* **1964,** *7*, 263–265.
(135) Ferm, V. H. *Biol. Neonate* **1971,** *19*, 101–107.
(136) Naeye, R. *Obstet. Gynecol.* **1980,** *55*, 701–704.
(137) Swenerton, H.; Hurley, L. S. *Science* **1971,** *173*, 62–64.
(138) Chang, C.; Mann, D. E., Jr.; Gautieri, R. F. *J. Pharm. Sci.* **1977,** *66*, 1755–1758.
(139) Hakulinen, T.; Salonen, T.; Teppo, L. *Br. J. Prev. Soc. Med.* **1976,** *30*, 138–140.
(140) Huggett, R. J.; Bender, M. E. *Environ. Sci. Technol.* **1980,** *14*, 918–923.
(141) Rawls, R. *Chem. Eng. News* **1980,** *58*(6), 28–31.
(142) Palmer, A. K. *Environ. Health Perspect.* **1976,** *18*, 97–104.
(143) New, D. A. T. *Environ. Health Perspect.* **1976,** *18*, 105–110.
(144) Andrews, F. D. *Environ. Health Perspect.* **1976,** *18*, 111–116.
(145) Flint, V. W., Jr. *Environ. Health Perspect.* **1976,** *18*, 117–123.
(146) Lloyd, J. B.; Beck, F.; Griffiths, A. *J. Pharm. Pharmacol.* **1965,** *17*, 126–128.
(147) Kennedy, G.; Fancher, O.; Calandra, J. C. *Toxicol. Appl. Pharmacol.* **1968,** *13*, 420–430.
(148) Hook, E. B.; Healy, K. M. *Science* **1976,** *191*, 566–567.
(149) Gilani, S. H.; Marano, M. *Arch. Environ. Contam. Toxicol.* **1980,** *9*, 17–22.
(150) Warner, J. S. *Science* **1979,** *203*, 1194–1195.
(151) Ferm, V. H.; Carpenter, S. J. *Exp. Molec. Pathol.* **1967,** *7*, 208–213.
(152) Kennedy, G. L.; Arnold, D. W.; Calandra, J. C. *Food Cosmet. Toxicol.* **1975,** *13*, 629–632.
(153) Gilani, S. *Obstet. Gynecol.* **1973,** *41*, 265–269.
(154) Gibson, J. E.; Becker, B. A. *Toxicol. Appl. Pharmacol.* **1970,** *6*, 120–132.
(155) Ferm, V. H.; Carpenter, S. V. *Toxicol. Appl. Pharmacol.* **1970,** *16*, 166–170.
(156) Kury, G.; Crosby, R. J. *Toxicol. Appl. Pharmacol.* **1968,** *13*, 199–206.

Richard B. Kurzel (*l.*), *Ph.D. (chemistry), M.D., is assistant professor of obstetrics and gynecology at the Tuft University School of Medicine, where he is also a Fellow in Perinatal Medicine. His research involves toxicology and high-risk pregnancies.*

Curtis L. Cetrulo (*r.*), *M.D., is associate professor of obstetrics and gynecology at the Tufts University School of Medicine, and director of the Division of Maternal–Fetal Medicine.*

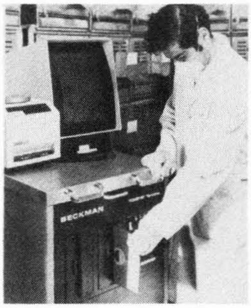
ES&T PRODUCTS

Particulate monitoring
New multipoint measuring system can monitor dust, fumes, and other airborne particulate levels at 128 locations. Real-time Aerosol Monitor-Sensor has data acquisition/logging station and individual sensor modules that can be placed throughout the monitoring environment. Continuous unattended operation for several months. GCA/Technology Division **101**

Radon daughter dosimetry
Personal monitoring device is worn by miners to sample air for radon and thoron daughter content. Solid-state detector and electronics with constant-flow pump and filter system. Can be interfaced to digital computer processing and printout. alphaNUCLEAR **102**

Post column reaction system
A self-contained universal post column reaction system, the URS 100 can be applied to high-performance liquid chromatography. Post column derivatization increases detectability of many biochemicals, especially those with little or no ultraviolet absorbance or fluorescence characteristics. Kratos/Schoeffel Instrument Division **103**

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



Toxicology system with software
TOXYS™ system collects, stores, analyzes, and reports toxicological laboratory test data in keeping with Good Laboratory Practices regulations. The system features Gross Pathology Data System software to record important observations and expedite subsequent microscopic analysis. Beckman Instruments **104**

Impinger system
Impinger system analyzes volatile organic compounds in fish. Samples can be directly weighed into the system, then immediately connected to the purge-and-trap apparatus. Sample handling is minimized. Foaming is not a problem. Wheaton Scientific **105**

Liquid chromatography aids
A line of products and accessories extends chromatographers' problem-solving capabilities through increased accuracy/efficiency in HPLC technology. Many analytes can be precisely determined. Waters Associates **106**

Digital thermometer
Model 5100 portable digital thermometer has continuous range from −200 °F to +200 °F. Can run 10 continuous hours after a single four-hour battery charge, or work out of the electric current directly. High LED display. IMC Instruments **107**

Scanner/recorder for LANDSAT
A large format scanner/laser recorder, Optronics X4040 records images on black-and-white film for remote sensing. Resolution is 25 μ, with up to 64 gray levels; writing is up to 1300 lines/minute of data for mapping. Optronics International **108**

Atomic absorption
Zeeman/500 Atomic Absorption Spectrophotometer determines trace elements in difficult samples such as oils, biological matrices, and steels. Corrects for background absorption, even at 1.5 Å or higher. Amenable to computer aid. Perkin-Elmer **109**

Mobile air cleaner
Mobile industrial electronic air cleaner removes airborne contaminants at source. F65A can help an industry meet local and industry codes for indoor air quality. Wheel-mounted. Honeywell **110**

Oxygen/gas monitoring
Dual-sensor instruments continually monitor oxygen levels and combustible gas concentrations in air. Models MX 240 and MX 241 are battery-operated, solid-state, and give readouts in percentages of lower explosive limits. National Mine Service **111**

Portable pH meters
Designed to be read in sunlight, these meters have 1-cm-high LCD displays. Resolution is 0.01 pH. Slope adjustment and recorder output are provided. A foam-lined carrying case holds the meter, gel-filled electrode, rinse water, buffer containers, and a line adapter. Orion Research **112**

***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*

Drinking water monitor
Specific chemicals, including cadmium, calcium, chloride, copper, cyanide, lead, fluoride, as well as water pH, hardness, and oxygenation, can be monitored using ion-sensitive electrodes. Kentucky Water Treatment **115**

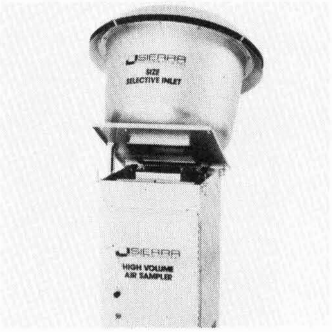
Particulate calibration
Calibration standards for x-ray fluorescence analysis of trace elements in air particulate samples are now available. At least 38 single elements are available (3–50 $\mu g/cm^2$), as well as two multielement standards (1–50 $\mu g/cm^2$ concentration). Mineral standards also available. Columbia Scientific Industries **116**

Radioactivity detection
Laboratory Monitor/Ratemeter 450 detects radioactivity and x-rays over wide activity and energy ranges. Count ranges can be 0–100 cpm to 0–3 million cpm in 10 selectable ranges. Useful for nuclear plants, university reactors, x-ray facilities. Baird **117**

Reversed-phase TLC
New Linear-K (preadsorbent) reversed-phase thin-layer chromatography plate eliminates difficulty in spotting aqueous samples on the hydrophobic surface of hydrocarbonaceous plates. Higher sample loadings are possible. Whatman Chemical Separation **118**

Size distribution measurement
The 210K Cascade Impactor is used for versatile measurement of size distribution and respirable mass of ambient airborne suspended particles. Cyclone preseparator, built-in backup filter, and six, eight, or 10 impactor stages available. Sierra Instruments **119**

pH transmitter
GLI Model 690 two-wire pH transmitter is useful in both hazardous *and* remote locations. Reads pH 0–14 mA and 4–20 mA. Temperature compensation automatic 0–95 °C. Great Lakes Instruments **120**



Air sampling
Model 302-2000 high-volume air samplers. Rugged, easy to use, many options available. Digital timer–programmer, selective inlet, other accessories can be fitted to the sampler. Sierra Instruments **121**

Water polishers
Units have application to point-of-use production of ultrahigh-purity water on a small scale. Uses demineralizing principles. Options are 130 or 90 psig, and 100, 200, or 300 gph flow. Penfield **122**

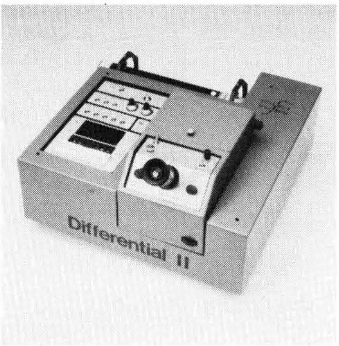
H_2S monitoring
Hydrogen sulfide analyzer monitors dissolved H_2S, pH, and total soluble sulfides in aqueous solutions. Soluble sulfide concentrations are detectable to less than one part per billion. Digital display; data collected by electrodes. Can interface with control equipment. Applications include municipal/industrial wastewater. Delphian **123**

Laboratory hood
Lab workers can be protected from noxious or toxic materials with Fiberglass-47 Laboratory Hood, which provides full-service work station. Easy to clean; chemical/corrosion-resistant. Add-Air or By-Pass models available. Can be made explosionproof. No joints, cracks, or crevices to collect undesirable residue. Labconco **124**

pH electrode
Submersible, continuous-monitoring pH electrode is usable at pressures as high as 100 psig. Model S650C is compatible with almost all pH meters and is easy to mount without tools. Flat surface minimizes fouling and breakage. Sensorex **125**

Water monitoring systems
A wide range of instruments for water quality monitoring is offered for field and industrial applications. The digital, portable instruments can provide in-situ measurements of temperature, pH, selective ions, dissolved oxygen, turbidity, and depth. Each provides a recorder output for a chart recorder or data logger. Martek Instruments **113**

English/metric chart recorder
A switch selects between English and metric chart speeds of 0.05–20 in./min or /h and 1–50 cm/min or /h. Features include a crystal-controlled oscillator that provides 0.01% accuracy, 15 calibrated input ranges from 1 mV to 50 V full scale, polarity reversal switches, automatic shutdown for over-range signals, and remote on/off and pen lift. Both single- and double-pen models are available. Pedersen Instruments **114**



Microparticle analysis
Redesigned *Differential II* light-scattering photometer measures light-scattering properties of fly ash, natural aerosols, smog, combustion products, other single microparticles. Can handle 100–5000 nm particles. Easy operation. Science Spectrum **126**

Temperature probe
Platinum probe can monitor temperatures of −30 °C to +100 °C continuously in hostile atmospheres. Sensors of 0.00385 or 0.00392 ohms/ohm · °C with resistances of 100, 200, or 500 ohms at 0 °C are available. Model 4119 applies to thermal pollution monitoring, ocean and lake temperature studies, other uses. Yellow Springs Instrument **127**

Air sampler filter holder
Model SH810 uses 8-x-10-in. filter papers for sampling suspended dusts in monitoring procedures. Large intake surface area allows high air flow rates for sampling. Staplex **128**

ES&T LITERATURE

Spectrometer. Booklet describes the IL Plasma-100 ICP emission spectrometer. Can determine up to 70 elements in many sample types, and is microcomputer-controlled. Instrumentaiton Laboratory **151**

Respirators. Data Sheet 10-00-05 describes belt-mounted respirators to protect against certain gases, vapors, dusts, mists, and fumes. Has 28-in. breathing tube, plenum assembly, facepiece. Mine Safety Appliances **152**

Carbon service. Air/Water Report for March 1981 describes company's developments and activities in air and water treatment, especially with activated carbon. Calgon **153**

SO_2 in malt. Application Note 27 tells how ion chromatography analyzes SO_2 in malt. SO_2 inhibits NO_x–amine reactions and reduces levels of potentially carcinogenic nitrosamines. Analysis time is less than 18 minutes; no known interferences. Dionex **154**

Dissolved oxygen. "Procedure 516" explains step-by-step procedures for measuring 10–14 ppm of dissolved oxygen in water, wastewater, BOD samples. Direct reading on any pH meter. Orion Research **155**

Filter collector. Brochure describes pulse-jet fabric-filter collector, the JAMAC. One application is emission control for hot-mix asphalt plant. Very little downtime. JAMAC Industries **156**

Air pollution models. Literature describes dispersion models for hazardous chemical spills, photochemical oxidants, and other applications. Applied Modeling **157**

Data logger. Brochure describes what company says may be only data logger with completely self-contained data acquisition/replay capabilities. Model M1600L is especially for science/engineering field use. Up to 100 analog or digital channels. Crodata **158**

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

Titrator systems. Brochure BR 416 highlights company's line of Metrohm titrator systems. Can accommodate multiple endpoints. Titration curve, endpoint volume, other data displayable on printed sheet. Sybron/Brinkmann **159**

Emissions monitoring. Brochure describes KVB Continuous Emissions Monitoring System. Stack and flue-gas desulfurization monitoring. Automatic calibration and other features. KVB Equipment Systems Division of Research-Cottrell **160**

pH meter/tester. Seven-ounce "Mini-Test" provides signal source to test and calibrate pH meters and much ancillary equipment. pH 0–14; 0–700 mV; 0–100 °C. L.G. Nester **161**

Hazardous waste labels. Catalog lists *mandatory* hazardous waste labels, manifest forms, and placarding pursuant to Dept. of Transportation regulations. LABELMASTER **162**

X-ray spectrometer. News release describes Dataplus+ and wavelength-dispersive x-ray spectrometer systems for analysis. Can "interface" with APPLE II Plus computer in BASIC language. DAPPLE SYSTEMS **163**

Oil/water separator. News release and brochure describe KC716 cleaner–oil/water separator, which can break existing emulsions and recover the oil. Effluent separation below 1 ppm of oil. Kensington Products **164**

Ozone treatment. "Ozone Treatment of Potable Water" explains the latest use of ozone to treat drinking water in depth. Decolorization, turbidity, other parameters discussed. PCI Ozone **165**

Controllers. Bulletin 9601 announces compact design controllers for a variety of metal-finishing waste-treatment applications. ERC/Lancy **166**

Liquid-level gauging. Form No. 114-2-81 describes level gauges for continuous monitoring/control of liquid level and weight within a tank. Hartel **167**

Environmental information. Bulletin describes overnight data retrieval, literature searching, current awareness, document retrieval, and information acquisition services. Environmental Resource Center **168**

Ozone analyzer. Brochure describes portable chemiluminescent ozone analyzer. Ranges 0.1–1.0 ppm; 4 ppb minimum detectable sensitivity. Has batteries and gas source for up to 10 hours of operation. EPA-designated reference method. Columbia Scientific Industries **169**

Conductivity. Brochure describes conductivity and salinity measuring instruments for water/wastewater testing, manufacturing, and general laboratory applications. Yellow Springs Instrument **170**

Baghouse/scrubber selector. Selector chart enables one to choose a baghouse or gas scrubber for specific air pollution control applications. W.W. Sly Manufacturing **171**

Waste-oil screening. Bulletin describes efficient removal of suspended, floating, and settleable solids from waste oil. SWECO **172**

Safe chemical storage. Wall chart explains how to organize chemical storage in accordance with recognized safety procedures. Covers carcinogens, teratogens, many other dangerous substances. Lab Safety Supply **173**

Hazardous materials detection. Vol. 5, No. 1 of *News and Notes for the Analyst* features portable items for hazardous materials detection labs. Hach Chemical **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*

Pollution standards. Mini-catalog 5A features extensive list of important standards, including dioxins, PCBs, pesticides, furans, other. ULTRA Scientific **175**

Leachates. Brochure announces a RCRA guidance manual entitled, "Management of Hazardous Waste Leachate." Prepared for EPA, manual covers many areas of leachates. Touhill, Shuckrow, and Associates **176**

Smelter pollution control. News release tells how automatic air controls "significantly" cut air pollution and improved overall efficiency of a lead furnace. Bunker Hill **177**

Stack monitoring. Brochure describes the 8900 Series Stack Monitoring System. It meets EPA requirements for cost-effective monitoring and has up-to-date microcomputer control. Bendix **178**

Natural gas calibration. Form No. 6680 describes calibration standard for precise/accurate comparison for analyzing natural gas composition. Ultra-sensitive. Liquid Carbonic **179**

pH papers. Brochure describes pH papers for fast measurement. Various ranges available. Airtight, lightproof packaging. Fil-Chem **180**

Extraction columns. Release describes VAC-ELUT vacuum manifold which can process up to 10 BOND ELUT columns simultaneously. Can be used to analyze organic pollutants in water, for example. Analytichem International **181**

Water improvement. Catalog lists 20 ways to improve surface water and wastewater. Many use enzyme formulas. Applied Biochemists **182**

Analytical services. Brochures list total chemical analytical services in areas of water/wastewater, hazardous materials, and related chemical disciplines. GM/MS, HPLC, other up-to-date instrumentation at hand. Hauser Laboratories **183**

Phenols. LC Note No. 96 explains how to determine trace levels of phenols in water by liquid chromatography. EPA-required method. Varian **184**

Alternative energy. Release announces *Alternative Energy Data Summary*, which compiles market penetration, sales revenues, price trends, other information for solar, biomass, and the like. Resource & Technology Management **185**

Solar hot water. SUN-PRIDE brochure describes line of solar domestic hot-water heating systems, components, and how to assess how much equipment is needed for hot-water requirements. Revere Solar and Architectural Products **186**

pH monitor. Brochure 4215 describes latest-technology pH monitor for wastewater and industrial effluent monitoring. Beckman Instruments **187**

Reactor analysis. Release discusses new computer-aided method of analyzing nuclear reactor systems for safety and reliability. Potential system weaknesses can be pinpointed. EG&G Idaho **188**

Reagents. 1981 buying guide lists a broad line of reagents and lab accessories. MCB Manufacturing Chemists **189**

Stack sampler. Brochure describes Model 797 diluting stack-sampling system; uses ambient air monitors for source measurement. Kipp Analytica B.V., Box 620, 7800 AP Emmen, The Netherlands (write direct)

Wood energy. *Human Environment*, February 1981, No. 18, "Wood Energy in Sweden," by Anne S. Fage. Swedish Information Service, Swedish Consulate General, 825 Third Ave., New York, N.Y. 10022 (write direct)

Engineering index. Technical abstract service. Catalog available. Engineering Index, Inc., 345 East 47th St., New York, N.Y. 10017 (write direct)

EPA R&D publications announcements. Research summaries, decision series, other. ORD Publications, Box 14249B, Cincinnati, Ohio 45214 (write direct)

Permit directory. "CJRP Permit Directory" and "CJRP Manual of Colorado Joint Review Process," for mineral and energy development, with small charge to cover postage/handling. Dept. of Natural Resources, Rm. 718, 1313 Sherman St., Denver, Colo. 80203 (write direct)

ES&T BOOKS

Alternative Energy Sources II. Vols. 1–9. T. Nejat Veziroğlu, Ed. xxi + 4171 pages. Hemisphere Publishing, 1025 Vermont Ave., N.W., Washington, D.C. 20005. 1981. $595/set.

This set of books covers many aspects of direct and indirect solar energy, geothermal, nuclear, hydrocarbon conversion, hydrogen, conservation, economics, and policy. Papers are from contributors worldwide. Of the nine volumes, four are devoted to solar energy.

Pollution and Water Resources: Columbia University Seminar Series. Vol. XIII, Parts 1–3. George J. Halasi-Kun, Ed. vii + 203, 187, 205 pages, respectively. Pergamon Press, Maxwell House, Fairview Park, Elmsford, N.Y. 10523. 1981. $60/set.

These volumes cover a range of topics, including New York Metropolitan area studies, agricultural runoff effects, stream ecology and aquatic biology, hydrology of dry and wet areas, water laws, and pollution studies of surface and groundwater. A portion of the papers are from the American Academy of Ocean Sciences.

Environmental Pollution. H. M. Dix. x + 286 pages. John Wiley & Sons, 605 Third Ave., New York, N.Y. 10016. 1981. $44.50, hard cover.

This work discusses general aspects, atmosphere, land, water, noise, and legislation. It offers comprehensive coverage with an objective and nonextreme treatment of the topics of pollution. It is aimed at "filling a niche" between the popular and the academic.

Clean Coal/Dirty Air. Bruce A. Ackerman, William T. Hassler. x + 193 pages. Yale University Press, 92A Yale Station, New Haven, Conn. 06520. 1981. $5.95, paper.

The authors point up what they believe to be major flaws in the Clean Air Act and pursuant regulations, and call for a virtually complete overhaul of the law. They advocate specifying clean air targets and leaving implementation up to technical experts. One approach they felt was questionable was requiring stack scrubbers for coal-burning power plants (for new plants only), rather than cleaning coal or using low-sulfur coal.

The Handbook of Environmental Chemistry, Vol. 3, Part A, Anthropogenic Compounds. O. Huntzinger, Ed. Springer-Verlag New York, 175 Fifth Ave., New York, N.Y. 10010. 1980. $70.80, hard cover.

Many, and sometimes hazardous, are the environmental chemicals of human origin. This book considers chemistry, analysis, fate/transport, and other aspects of mercury, cadmium, organic and inorganic dyes and pigments, polynuclear aromatic and heteroaromatic hydrocarbons, chlorinated compounds, radionuclides, and many other anthropogenic materials that escape into the environment.

Biochemical Indicators of Subsurface Pollution. Otis C. Dermer et al. xii + 203 pages. Ann Arbor Science, Box 1425, Ann Arbor, Mich. 48106. 1980. $24, hard cover.

This book discusses the uses of biochemistry and biochemical analysis techniques to assess soil and groundwater pollution. Among topics covered are "specific" enzymes, macromolecules, analytical biochemical principles, and metabolic products usable for detection of pollutants in low concentrations.

Principles of Desalination, Parts A and B. 2nd ed. K. S. Spiegler, A. D. K. Laird, Eds. xiii + 821 pages. Academic Press, 111 Fifth Ave., New York, N.Y. 10003. 1980. Part A, $41; Part B, $52, hard cover.

Desalination may become a significant water supply source for the future, given the proper technical and economic picture. These books examine that field with respect to thermoeconomics, distillation, electrodialysis, freezing methods, hyperfiltration (reverse osmosis), and solar techniques. Scale countermeasures, costs, and seawater properties are also considered.

Guide to Chemical Education in the U.S. for Foreign Students. xi + 106 pages. Special Issue Sales, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. 1981. $7.50, paper.

This guide was prepared by the ACS Committee on International Activities. Generally, it discusses the U.S. education system, course content that students should complete before coming to the U.S. or that they can take in the U.S., and other pertinent topics. Representative chemical texts are listed in bibliographies, as appropriate, and sample examination questions are offered.

The Self-Managing Environment. Alan Roberts. 189 pages. Rowman and Littlefield, 81 Adams Dr., Totowa, N.J. 07512. 1980. $15, hard cover.

This work assesses environmental dilemmas in their social context. Technical and financial problems of nuclear power are examined, as are the "falsely posed" oppositions between the "consumer society" and technological retrogression. The author proposes that neither the randomness of the free market nor Soviet-type planning can keep up with the constantly increasing complexity and scale of environmental tasks. He also explains how a fully "self-managed society" might be able to do so.

Trace substances wall chart. 22 in. × 34 in. Environmental Sciences Associates, 45 Wiggins Ave., Bedford, Mass. 01730. 1981. First copy free; $3.50 each in quantities from two to 49. Includes editorial on toxic and trace metals.

The chart and accompanying publication cover routes of entry, preventive measures, and toxic metals. OSHA, EPA, and threshold limit values and standards are included.

Environmental Policies in New Zealand. OECD report. 82 pages. OECD Publications and Information Center, Ste. 1207, 1750 Pennsylvania Ave., N.W., Washington, D.C. 20006. 1981. Inquire as to price.

New Zealand is one of the least polluted and congested countries of OECD's 24 member nations; this report explains why. Many environmental areas, as well as expected present and future developmental impacts are discussed.

Infrared Spectra Handbook of Priority Pollutants and Toxic Chemicals. Sadtler Research Laboratories, 3316 Spring Garden St., Philadelphia, Pa. 19104. 1981. $210 (10% discount until July 15).

This work contains more than 500 condensed- and vapor-phase spectra of pollutants and other chemicals of concern. Many are included in the "EPA Priority Pollutants List," or in the "OSHA Category I List of Carcinogenic Substances." There is also a list of hazardous compounds common in industry and subject to interstate transportation regulations.

The *Ignis Fatuus* of Biogas. Small-Scale Anaerobic Digesters. J. van Brakel. viii + 141 pages. Delft University Press, Mijnbouwplein 11, 2628 RT Delft, The Netherlands. 1980. About $16, paper.

This book critically reviews the pre-1970 literature; newer developments are discussed elsewhere or, according to the author, what is seemingly new is actually a "reinvention." Anaerobic systems worldwide are covered, as are the inner workings of systems and the applications of their products.

Fundamental and Applied Toxicology. Periodical, bimonthly. Society of Toxicology, 475 Wolf Ledges Pkwy., Akron, Ohio 44311. Inquire as to subscription price; free to Society of Toxicology members.

This journal is directed to the practicing toxicologist. It covers aquatic/environmental toxicology, risk assessment, regulatory controls, safety evaluation for specific purposes, and other germane topics.

Climate Change and Society: Consequences of Increasing Atmospheric Carbon Dioxide. William W. Kellogg, Robert Schware. Westview Press, 5500 Central Ave., Boulder, Colo. 80301. 1981. Inquire as to price.

Will nations take action to avert increasing CO_2 quantities in the air? Probably not, say the authors. The idea, then, is to adopt long-term strategies that will increase human societies' resiliency if climate changes occur. The authors list several such strategies that would be beneficial, even if the worst does not come about.

Interim Performance Criteria for Photovoltaic Energy Systems. 225 pages. National Technical Information Service, 5285 Port Royal Rd., Springfield, Va. 22161. 1981. $9.50.

This document establishes a technical base for qualification/evaluation of photovoltaic systems and items. It also offers guidance for designers, producers, marketers, and operators of PV systems, as well as a basis for developing consensus standards in the private sector.

Chromatographic Methods in Inorganic Analysis. 226 pages. Dr. Alfred Hüthig Verlag GmbH, Postfach 10 28 69, 6900 Heidelberg 1, West Germany. 1981. $38.

This book gives an overview of various chromatographic methods to separate inorganics, organometallics, and metal chelates. Detection and trace analysis are also featured. Environmental and toxicological applications are among subjects addressed.

Trace-Element Geochemistry of Coal Resource Development Related to Environmental Quality and Health. xi + 153 pages. National Academy Press, 2101 Constitution Ave., N.W., Washington, D.C. 20418. 1980. $11, paper.

Coal may contain many trace elements, such as uranium, iron, cadmium, and numerous others. They can enter the environment through mining, coal cleaning, storage, and combustion, and synfuel processes. This book examines that problem in detail.

Small is Possible. George McRobie. xv + 311 pages. Harper & Row, 10 East 53rd St., New York, N.Y. 10022. 1981. $14.95, cloth; $5.95, paper.

This book gives an overview of a "countereconomy" in the U.S., U.K., and Canada, including small-scale aquaculture, waste metal and sewage recycling, alternative energy systems, and biological pest control. Numerous concrete examples of this countereconomy in practice are listed and described in detail.

Biomonitoring Air Pollutants With Plants. William J. Manning, William A. Feder. x + 142 pages. Applied Science Publishers, 22 Rippleside Commercial Estate, Ripple Road, Barking, Essex IG11 OSA, U.K. 1980. $26, hard cover.

Numerous annual and perennial plants make quite reliable monitors for air pollutants. For example, they can confirm results otherwise obtained, and extend monitoring networks. This book tells how various plants can monitor ozone, peroxyacetyl nitrate (PAN), NO_x, SO_x, heavy metals, dusts, and ethylene. Problems and progress in this field are discussed.

ES&T

MEETINGS

June 21–25 Nashville, Tenn.
ASTM Committee D-34 on Waste Disposal Meeting. ASTM Committee D-34 on Waste Disposal
Write: D. A. Tobias, ASTM, 1916 Race St., Philadelphia, Pa. 19103; (215) 299-5546

June 22–25 Atlanta, Ga.
Hazardous Waste Management. Technical Seminars, Inc.
Fee: $685. *Write:* Technical Seminars, Inc., 125 Wolf Rd., Albany, N.Y. 12205; (518) 458-1767

June 22–26 Philadelphia, Pa.
74th Annual Meeting & Exhibition. Air Pollution Control Association.
Write: Public Relations Dept., Air Pollution Control Association, Box 2861, Pittsburgh, Pa. 15230; (412) 621-1090

June 22–26 Nashville, Tenn.
International Symposium on Health Impact of Different Sources of Energy. The World Health Organization, The United Nations Environment Program, and others
Write: John H. Kane, Conference Manager, Office of International Affairs MS:AI-5216, U.S. DOE, Washington, D.C. 20585; (301) 353-3378. If outside U.S.: Robert Najar, Chief, Conference Service Section, Division of External Relations, International Atomic Energy Agency, Karnter Ring 11, Box 590, A-1011 Vienna, Austria

June 24–25 Arlington, Va.
Principles of Industrial Toxicology. American Industrial Hygiene Association
Fee: $150. *Write:* John R. Conti, American Industrial Hygiene Association, 475 Wolf Ledges Pkwy., Akron, Ohio 44311

June 24–25 Seattle, Wash.
Fundamentals of Groundwater Management. Resource Seminars
Fee: $320. *Write:* Jannie Dresser, Resource Seminars, 2914 Domingo Ave., Berkeley, Calif. 94705; (415) 841-2091

June 29–30 Newark, Del.
13th Mid-Atlantic Industrial Waste Conference. University of Delaware
Write: Dr. C. P. Huang, Department of Civil Engineering, University of Delaware, Newark, Del. 19711

June 29–July 1 Chicago, Ill.
Water Pollution Control Technology. The Center for Professional Advancement
Fee: $590. *Write:* Edith Webb, Registrar, Box 964, The Center for Professional Advancement, East Brunswick, N.J. 08816; (201) 249-1400

July 6–10 Ann Arbor, Mich.
Combustion Engine Performance Economy and Emissions. University of Michigan College of Engineering
Fee: $550. *Write:* Engineering Summer Conferences, 200 Chrysler Center, North Campus, University of Michigan, Ann Arbor, Mich. 48109; (313) 764-8490

July 6–17 Ann Arbor, Mich.
Chemical Engineering for Engineers, Scientists, and Managers. University of Michigan College of Engineering
Fee: $1900. *Write:* Engineering Summer Conferences, 200 Chrysler Center, North Campus, University of Michigan, Ann Arbor, Mich. 48109; (313) 764-8490

July 13–17 Alexandria, Va.
Radioactive Waste Management for Nuclear Power Reactors and Other Facilities. The American Society of Mechanical Engineers
Write: ASME, Professional Development, 345 East 47th St., New York, N.Y. 10017; (212) 644-7743

July 14–15 Tampa, Fla.
Seminar on Waste Incineration. Engineering School, Continuing Engineering Education Program, Vanderbilt University
Write: Janet Vance, Continuing Engineering Education, Vanderbilt University, Box 1525, State B, Nashville, Tenn. 37235; (615) 322-2924

Courses

June 22–23 Atlantic City, N.J.
Plant Energy Seminar. Association of Energy Engineers
Fee: AEE members, $370; nonmembers, $425. *Write:* Registrar, Association of Energy Engineers, 4025 Pleasantdale Rd., Ste. 340, Atlanta, Ga. 30340; (404) 447-6424

June 22–25 Houston, Tex.
Industrial Hygiene Technology. The Center for Professional Advancement
Fee: $760. *Write:* Edith Webb, Registrar, Box 964, The Center for Professional Advancement, East Brunswick, N.J. 08816; (201) 249-1400

July 6–10 Washington, D.C.
Solar Heating and Cooling: Residential and Commercial Applications. George Washington University
Fee: $715. *Write:* Director, Continuing Engineering Education Program, George Washington University, Washington, D.C. 20052; (800) 424-9773

July 7–8 Chicago, Ill.
Management Impact of the Coal Energy Option. Institute of Gas Technology
Fee: $330, IGT members; $390, all others. *Write:* Industrial Education, Institute of Gas Technology, 3424 South State St., Chicago, Ill. 60616

July 13–17 Cincinnati, Ohio
Gas Chromatography. Finnigan Institute
Fee: $675. *Write:* Nancy Kranpitz, Registrar, Finnigan Institute, 11 Triangle Park Dr., Cincinnati, Ohio 45246; (513) 772-5500

July 14–16 Madison, Wis.
Wastewater Sludge Management Facilities. University of Wisconsin–Madison

(continued on page 654)

professional consulting services directory

Clayton Environmental Consultants, Inc.

Comprehensive Industrial Hygiene Surveys
Ambient Air and Emission Measurement Services
Hazardous Waste Management

Engineering Design
Complete, Accredited Environmental Laboratories
(GC/MS, HPLC, SEM/EDS, X-Ray Diffraction, AA, Ion Chromatography)

25711 Southfield Road
Southfield, MI 48075
(313) 424-8860

Branch offices in
Marietta, Georgia
and Houston, Texas

NORTHWESTERN AQUATIC SCIENCES, INC.

MARINE AND FRESHWATER TOXICOLOGY
Acute, Chronic, Life Cycle Bioassays
Bioaccumulation and Biomagnification Studies
Analytical Support Capabilities

P. O. Box 1437
Newport, Oregon 97365 (503) 265-7225

J.E. SIRRINE COMPANY

Engineers Since 1902 **An Employee Owned Company**

Complete Design of Environmental Facilities

USA Greenville, SC 29606 • Houston, TEX 77042
Research Triangle Park, NC 27709
Sao Paulo, Brazil

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

DAVID KEITH TODD

CONSULTING ENGINEERS, INC.

Groundwater Planning, Development, Management, and Protection

2914 Domingo Avenue
Berkeley, California 94705 415/841-2091

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

One Center Plaza
Boston, Massachusetts 02108

CDM

environmental engineers, scientists, planners, & management consultants

---

ENVIRONMENTAL SERVICES

AeroVironment Inc.

Tel. (213) 449-4392
145 Vista Ave
Pasadena, CA
91107
&
Casper, WY

- Air Quality Monitoring
- Dispersion Modeling
- Low Level Nuclear Radiation

AeroVironment Inc.

ENVIRONMENTAL PLANNING and PROBLEM SOLVING for INDUSTRY and GOVERNMENT

• AIR • WATER • SOLIDS • NOISE • ODOR

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

TRC Environmental Consultants, Inc.

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

8775 East Orchard Rd.
Suite 816
Englewood, CO 80111
(303) 779-4940

Complete Analytical Services

SINCE 1919

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

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

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

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

POLLUTION CONTROL PROFESSIONALS

We're specialists in placing environmental personnel exclusively. All disciplines, all levels. National/International affiliations. No fees.

"PIONEERS IN POLLUTION CONTROL PLACEMENT"

PROFESSIONNEL at Rossmoor
Rossmoor Bank Building
Jamesburg, N.J. 08831 **201-521-2210**

THE CONSULTANTS' DIRECTORY

EFFECTIVE JANUARY 1981

UNIT	Six Issues	Twelve Issues
1″ × 1 col.	$43	$41
1″ × 2 col.	85	80
1″ × 3 col.	125	112
2″ × 1 col.	85	80
2″ × 2 col.	160	145
4″ × 1 col.	160	145

Patricia E. Hauge
ENVIRONMENTAL SCIENCE & TECHNOLOGY
25 Sylvan Road South
Westport, CT 06881
Or call her at (203) 226-7131

professional consulting services directory

wcts inc.

17605 Fabrica Way
Cerritos, California 90701
213/921-9831
714/523-9200

SERVING INDUSTRY NATIONWIDE

Your Only FULL SERVICE Independent Laboratory

FOR: Priority Pollutant, Pesticide, PCB, THM, PNA, and Metals Analyses. Also GC, MS, GC-MS, LC, IR, AA, DTA, TGA, and DSC. We are EPA approved, AIHA accredited, and a Calif. licensed water lab.

Brochure and/or fee schedule available on request

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

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

ENVIRO-MED LABORATORIES, INC.

414 W. California—Ruston, LA 71270 (318) 255-0060
1874 Dallas Drive—Baton Rouge, LA 70806 (504) 928-0232
13201 Northwest Freeway, Suite 202, Houston, Texas 77040 (713) 462-1631

- Wastewater
- Drinking Water
- Bacteriology
- OSHA-NIOSH
- Priority Pollutants
- Hazardous Waste
- Toxicology
- Bioassays
- Resource Recovery
- Leachate Studies
- PCB's
- Pesticides
- R & D
- GC, GC/MS, AA
- Permits

ENVIRONMENTAL CONSULTANTS INC

ANALYTICAL TESTING AND SAMPLING SERVICES:

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

USING:

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

CONSULTATION—PLANNING

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

HAVENS AND EMERSON, INC.

Environmental Engineers

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

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

FERGUSON TECHNICAL

P.O. BOX 400916 DALLAS, TEXAS 75240 (214) 690-8859

ENVIRONMENTAL CONSULTING

HAZARDOUS WASTE ASSESSMENT
REGULATION TRAINING & UPDATING
RCRA NPDES

SpectroChem LABORATORIES INC.

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

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

Complete Analytical Services for Environmental Studies & Pollution Control

---

eis Environmental Instrument Systems, Inc.

Environmental Engineers & Chemists

AIR • WATER • HAZARDOUS WASTES
ENGINEERING • LABORATORY • FIELD SURVEYS

116 N. Hill St., South Bend, IN 46617 • 219/287-7151

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

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

CATALYTIC, INC.

Consultants • Engineers • Constructors
Environmental Systems Division
Centre Square West
1500 Market St.,
Philadelphia, PA 19102 • 215-864-8000
Charlotte, NC 704-542-4220
Baton Rouge, LA 504-293-6200

Environmental Testing Services

- EPA priority pollutants —GC/MS
- Hazardous waste characterization
- Work environment analyses
- Organic/inorganic analyses
- TOC and Total Organic Halides

WATER • EFFLUENTS
SOILS • SLUDGES

Put Foremost-McKesson to work for you.

Foremost-McKesson Research Center
6363 Clark Ave., Dublin, CA 94566
(415) 828-1440

BIOASSAY & BIOLOGICAL SUPPLY DIVISION
ICHTHYOLOGICAL ASSOCIATES, inc.

Freshwater & Marine Bioassays
Specimens for Bioassays

Middletown, Del.
302-378-9626

Absecon, NJ
609-652-8375

Complete Environmental Research & Consulting—Other Offices Throughout the Northeast

professional consulting services directory

Flaherty·Giavara Associates, P.C.

ONE COLUMBUS PLAZA,
NEW HAVEN, CT. 06510
203·789·1260

THE COMPLETE RESOURCE
ENGINEERS·PLANNERS
ENVIRONMENTAL SCIENTISTS

Dames & Moore

Engineering and Environmental Consultants

- Environmental Impact Assessment
- Geotechnical and Environmental Engineering
- Meteorology and Air Quality Monitoring
- Water Pollution Control Engineering
- Modelling and Numerical Analyses
- Permitting and Licensing Consultation
- Solid and Hazardous Waste Management

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

WATER INFORMATION CENTER, INC.
PUBLISHERS
THE GROUND WATER NEWSLETTER
Reference Books, Texts, Newsletters
The North Shore Atrium, 6800 Jericho Tpke.,
Syosset, N.Y. 11791 (516-921-7690)

A.F. Meyer and Associates, Inc.

Environmental, Systems Safety, and Occupational Health Consultants

Alvin F. Meyer, Jr., P.E.
President

1317 Vincent Place, McLean, Virginia 22101 (703) 734-9093

Ground Water Associates, Inc.

Water Supply Geologists and Engineers

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

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

Cranford, New Jersey
Arlington, Massachusetts

Jones & Henry Engineers, Limited

2000 WEST CENTRAL AVENUE, TOLEDO, OHIO 43606 · TEL. 419/473-9611

ENVIRONMENTAL ENGINEERS / PLANNERS

- ENERGY & RESOURCE RECOVERY
- ENVIRONMENTAL ASSESSMENTS
- GROUND WATER MONITORING
- HAZARDOUS WASTE MANAGEMENT
- LABORATORY SERVICES
- POLLUTION CONTROL ECONOMICS
- PRE-TREATMENT SYSTEMS
- RESIDUAL WASTE MANAGEMENT
- SPILL PREVENTION SYSTEMS
- WASTE TREATMENT SYSTEMS
- WATER CONSERVATION/REUSE
- WATER SUPPLY TREATMENT

ENTROPY ENVIRONMENTALISTS, INC.

AIR POLLUTION MEASUREMENT IS OUR BUSINESS

P.O. Box 12291
Research Triangle Park, N.C. 27709
919-781-3550

CLASSIFIED SECTION ■ POSITIONS OPEN

Environmental Marketing Opportunities

• UTILITIES INDUSTRY MANAGER
• GOVERNMENT INDUSTRY MANAGER

TRC, a nationally recognized leader in environmental consulting services, is seeking two qualified marketing professionals to join our Marketing team.

These Industry Managers will be responsible for directing marketing activities to the Utilities Industry and Federal Government. Both positions involve the identification of potential clients, regular contacts with existing clients and industry associations, and participation in related professional activities. Other responsibilities include market research, budget control of marketing related expenditures, and development of an annual industry marketing plan.

The successful candidates will have a minimum of 5 years experience in the specific industry and 2 years experience with environmental affairs. A minimum of 2 years sales/marketing experience and proven ability to communicate and identify problems are required. Active participation with an industry association or a regulating agency is desirable.

We offer excellent compensation and an excellent relocation and benefits package. Send resume to:

Theresa F. Giblo, Personnel Administrator

TRC
ENVIRONMENTAL CONSULTANTS, INC.
"From compliance to innovative state of the art technology"
125 Silas Deane Highway,
Wethersfield, Ct. 06109
An Equal Opportunity Employer M/F/H/V

RESEARCH ASSISTANT PROFESSOR

Water Resources Research Center and the School of Natural Resources at the University of Vermont. This non-tenure track 12 month position will be a member of a research team to provide guidance to a long-term research program investigating relationships between agricultural land management practices, surface runoff quality and impact on lakes and wetlands. The individual will supervise graduate students, develop future research opportunities and participate in selected teaching activities.

Ph.D. degree is required in a field related to job responsibilities. Individual should be well-educated in water quality, mathematical and computer modeling and surface water hydrology. Knowledge of soil systems is desirable. Interest and some experience in carrying out field research activities is required.

Send resume *and* names of three references to: Dr. E. Alan Cassell, Director, Vermont Water Resources Research Center, University of Vermont, 601 Main Street, Burlington, VT 05405. Telephone: (802) 656-4057. Closing is July 15, 1981. The University of Vermont is an equal opportunity, affirmative action employer.

IMPORTANT NOTICE

Various state laws against discrimination and the Federal Civil Rights Act of 1964 prohibit discrimination in employment because of race, color, religion, national origin, age, and sex (unless based on a bona fide occupational qualification). Help wanted and situations wanted advertisements on these pages are for readers convenience and are not to be construed as instruments leading to unlawful discrimination.

The University of Pennsylvania is seeking applications for a tenure-track faculty position at the level of Assistant Professor in the area of Environmental and Resources Engineering. The candidate should have a Ph.D. and professional experience is desirable. Duties will include: Teaching undergraduate and graduate courses in environmental systems engineering; participation in team research (e.g., hazardous waste management, life cycle studies of resources, environmental management); development of independent research activities. Reply with credentials to: **Dr. John D. Keenan, Chairman of Search Committee, Department of Civil and Urban Engineering, Towne Building D/3, University of Pennsylvania, Philadelphia, Pennsylvania 19104.** The University of Pennsylvania is an equal opportunity/affirmative action employer.

The air pollution program at The University of Toledo announces the availability of several graduate assistantships commencing in September (1981) or January and July (1982). Current on-going research projects include application and development of air quality models (physical models and trend models), study of boundary layer, development of historical air quality data banks, design of air quality prediction systems, air quality monitoring, long-range transport problems and impact of new energy projects. Persons with background in engineering, atmospheric sciences, physics or applied mathematics are encouraged to apply. For more information, contact: **Dr. Ashok Kumar, Department of Civil Engineering, The University of Toledo, Toledo, Ohio 43606, Telephone No. (419) 537-2312 or (419) 537-2640.**

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

It's computer processed

for fast

response

to your inquiries.

AND, IT'S

FREE

ES&T JUNE 1981

VALID THROUGH
Oct 1981

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

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

NAME:

TITLE:

FIRM:

STREET:

CITY:

STATE: ZIP:

PHONE: ( ) -

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

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

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

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

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

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

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

Circle 94 for subscription form to ES&T

NEED MORE INFORMATION?

CIRCLE a key number. . .

SEND IN the postage paid reply card. . .

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

NO POSTAGE
NECESSARY
IF MAILED
IN THE
UNITED STATES

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

POSTAGE WILL BE PAID BY ADDRESSEE

Environmental
Science & Technology

P.O. BOX #7826
PHILADELPHIA, PA 19101

NO POSTAGE
NECESSARY
IF MAILED
IN THE
UNITED STATES

BUSINESS REPLY CARD

FIRST CLASS Permit #27346 Philadelphia, Pa.

POSTAGE WILL BE PAID BY ADDRESSEE

Environmental
Science & Technology

P.O. BOX #7826
PHILADELPHIA, PA 19101

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

It's computer processed for fast response to your inquiries.

AND, IT'S FREE

NEED MORE INFORMATION?

CIRCLE a key number. . .

SEND IN the postage paid reply card. . .

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

ES&T JUNE 1981

VALID THROUGH
Oct 1981

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

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

NAME: ____________________

TITLE: ____________________

FIRM: ____________________

STREET: ____________________

CITY: ____________________

STATE: ______________ ZIP: __________

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

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

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

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

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

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

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

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

Circle 94 for subscription form to ES&T

CLASSIFIED SECTION ■ POSITIONS OPEN

INDOOR AIR QUALITY SCIENTIST

The Lawrence Berkeley Laboratory, a major multipurpose laboratory operated by the University of California for the U.S. Department of Energy, is seeking an individual to direct research projects including laboratory experiments and field monitoring of indoor pollutants and the development of contaminant control strategies and techniques. Assist in the technical management of a large number of professionals working in indoor air quality. Responsible for the design and coordination of experiments and development of proposals.

The position requires significant research experience applicable to indoor air pollution, and the successful candidate must have substantial background in technical management and supervising professionals. Prefer a Ph.D. in Science or Engineering with a strong background in chemistry or physical measurements.

To apply, send TWO resumes, including salary history, to: **Employment Office, LAWRENCE BERKELEY LABORATORY, One Cyclotron Road, Berkeley, CA 94720.** An equal opportunity employer, M/F/H.

LAWRENCE
BERKELEY
LABORATORY

M.S. in Water Resources Management, with experience in ground water modeling and knowledge of ground water and soil sampling and measuring devices. Provide consulting service on geology and ground water as they relate to solid and hazardous waste disposal. Conduct research on ground water pollution, and plan and conduct field investigations of disposal sites including borings and wells. Sample and monitor soils and water, and interpret data. Prepare disposal site selection studies and environmental reports. Direct the office and field project work of technicians and interface with engineers on facility design. Provide liaison with clients and regulatory agencies. Develop familiarity with engineering design concepts for land disposal. 40-hour week. Initial salary $1300/month plus eligibility for bonus and profit-sharing plan. Submit application by June 30, 1981, to: **Thomas P. Kunes, Residuals Management Technology, Inc., 1406 E. Washington Avenue, Suite 124, Madison, WI 53703.**

MANAGER ENVIRONMENTAL HEALTH & SAFETY

Top Specialty Chemical Operation

A major division of a Fortune 50 corporation is seeking a manager who can shoulder broad responsibilities in a sensitive, highly visible, influential position.

You will manage and implement programs that will assure over 1500 employees a safe working environment; and will be our prime liaison with regulatory agencies. Moreover, you will contribute to our division's planning process by providing responsible alternatives and strategies to meet current and long term environmental compliance objectives.

Your credentials must inspire confidence. Specifically, your technically oriented background should be supported by an environmental-related engineering degree, and direct or related management experience preferably in the chemicals business. Salary to mid-$50K. Attractive northeast New York location.

All responses will be forwarded unopened to our client. Write in confidence to Box 328, Deutsch, Shea & Evans, Inc., 49 E. 53rd St., New York, N.Y. 10022. Client is an equal opportunity employer.

DS&E
DEUTSCH, SHEA & EVANS, INC.
ADVERTISING

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

STAFF EXPANSION

International environmental consulting firm offers challenging opportunities to those candidates qualified in the following career areas to be part of our rapidly expanding suburban headquarters.

Expansion in our modeling group provides the need for a **Mathematical Modeling Specialist** experienced in various aspects of simulation, numerical analysis, fluid/thermodynamics as well as water and air quality modeling; a **Fluid Dynamicist** experienced in formulating mathematical models for pollutant and thermal dispersion as well as for behavior of vessels during maneuver operations; and an **Air Quality Scientist** possessing solid background in ambient air monitoring and pollutant dispersion.

Advanced technical degrees in pertinent fields are required. Interested candidates should send resume and salary expectations to Theresa Slimko at:

ecology and environment, inc.
International Specialists in the Environmental Sciences
P.O. BOX D,
BUFFALO, NEW YORK 14225
An Equal Opportunity Employer

ENVIRONMENTAL ENGINEERS

We are a leading national environmental engineering and consulting firm engaged in challenging air pollution programs for both government and industry. We are seeking highly motivated professionals with strong technical backgrounds.

Individuals will have complete project responsibility. Must have a technical degree (preferably engineering, chemical, or environmental science), program/project management experience and background in air pollution.

Our continuing growth has created outstanding opportunities for qualified professionals. Excellent working conditions and benefits. Willing to relocate to Southern California. Send resume and salary requirements to:

SCOTT
ENVIRONMENTAL TECHNOLOGY, INC.
2600 Cajon Boulevard
San Bernardino, California 92411
EOM/MF

ENGINEERING/ARCHITECTURE/ENVIRONMENTAL STUDIES FACULTY. Full-time, tenure track position in community college. Inter-departmental assignment in two of the following three areas: 1) engineering including graphics, 2) environmental studies including some combination of wastewater, air pollution, industrial hygiene, and/or basic environmental science, or 3) architecture including some combination of courses such as structural analysis, surveying, or mechanical systems. MSCE preferred; appropriate Bachelor's degree with experience considered. Position starts August 20. Deadline for receipt or postmark of completed applications is June 30, 1981. Contact **Personnel Office, Northampton County Area Community College, 3835 Green Pond Road, Bethlehem, PA 18017, or call (215) 865-5351, ext. 342** for application.

MEETINGS *(continued)*

Fee: $300. *Write:* Philip R. O'Leary, Program Director, Department of Engineering & Applied Science, University of Wisconsin-Extension, 432 North Lake St., Madison, Wis. 53706; (608) 262-0493

July 27–31 Bloomington, Ind.
Environmental Applications of Gas Chromatographic Mass Spectrometry. Indiana University

Fee: $650. *Write:* The Executive Education Program, School of Public and Environmental Affairs, 323 Poplars and 400 E. Seventh St., Bloomington, Ind. 47405; (812) 337-5922

Call for Papers

June deadline
17th American Water Resources Conference on Waste Impact on Water. American Water Resources Association

The conference will be Oct. 4–7, 1981, in Atlanta, Ga. *Write:* AWRA-1981 Conference, St. Anthony Falls Hydraulic Laboratory, Mississippi River at Third Ave. S.E., Minneapolis, Minn. 55414; (612) 376-5050

July 1 deadline
3rd Annual Northeast Conference on Hazardous Waste. Environmental Hazards Management Institute and the Northeast Hazardous Waste Advisory Board

The conference will be Oct. 25–28, 1981, in Portsmouth, N.H. *Write:* Alan J. Borner, Adams Point Rd., Durham, N.H. 03824; (603) 868-7250

August 14 deadline
9th Annual Energy Technology Conference and Exposition. American Gas Association and others

The conference will be Feb. 15–17, 1982, in Washington, D.C. *Write:* ET'82 Program Chairman, c/o Government Institutes, Inc., Box 1096, Rockville, Md. 20850; (301) 251-9250

August 25 deadline
3rd International Symposium on Environmental Pollution. Chromatography/Spectroscopy Research Institute and Alena Enterprises of Canada

The symposium will be June 17–19, 1982, in Nice, France, and Nov. 15–19, 1982, in Montreal, Canada. *Write:* Dr. V. M. Bhatnagar, Alena Enterprises of Canada, Box 1779, Cornwall, Ontario K6H 5V7, Canada

International

June 20–25 Munich, West Germany
June 25–26 Rome, Italy
Requirements, Application, and Practical Experience of Control and Automation in Water Quality Monitoring. The International Association of Water Pollution Research

Write: Prof. W. Bischofsberger, Technische Universitat Munchen, Arcisstrasse 21, 8000 Munchen 2, West Germany

June 23–27 Munich, West Germany
6th International Trade Fair for Waste Treatment & Disposal Systems. IFAT '81

Write: Munchener Messeund, Ausstellungsgesellschaft, mbH, Messegelande, Postfach 12 10 09, D-8000 Munchen 12

July 6–18 Istanbul, Turkey
Energy Production and Conservation from Wastes. Bogazici University

Write: Dr. Kriton Curi, School of Engineering, Bogazici University, P.K.2, Bebek, Istanbul, Turkey

INDEX TO THE ADVERTISERS IN THIS ISSUE

Advertising Management for the
American Chemical Society Publications

CENTCOM, LTD.

Thomas N. J. Koerwer, President; James A. Byrne, Vice President; Alfred L. Gregory, Vice President; Clay S. Holden, Vice President; Benjamin W. Jones, Vice President; Robert L. Voepel, Vice President; 25 Sylvan Rd. South, Westport, Connecticut 06881 (Area Code 203) 226-7131

ADVERTISING SALES MANAGER
James A. Byrne

SALES REPRESENTATIVES

Atlanta, Ga. . . . Donald B. Davis, CENTCOM, LTD., Phone (Area Code 203) 226-7131

Boston, Ma. . . . Thomas Carey, CENTCOM, LTD., (Area Code 212) 972-9660

Chicago, Ill. . . . Bruce Poorman, CENTCOM, LTD., 540 Frontage Rd., Northfield, Ill 60093 (Area Code 312) 441-6383

Cleveland, Oh. . . . Bruce Poorman, CENTCOM, LTD., 17 Church St., Berea, OH 44017 (Area Code 216) 234-1333

Denver, Co. . . . Clay S. Holden, CENTCOM, LTD., (Area Code 213) 325-1903

Houston, Tx. . . . Robert E. LaPointe, CENTCOM, LTD., (Area Code 415) 781-3430

Los Angeles, Ca. . . . Clay S. Holden, Robert E. LaPointe, CENTCOM, 3142 Pacific Coast Highway, Suite 200, Torrance, CA 90505, (Area Code 213) 325-1903

New York, N.Y. . . . Thomas Carey, CENTCOM, LTD., 60 E. 42nd Street, New York 10165 (Area Code 212) 972-9660

Philadelphia, Pa. . . . Thomas Carey, CENTCOM, LTD., GSB Building, Suite 425, 1 Belmont Ave., Bala Cynwyd, Pa 19004 (Area Code 215) 667-9666

San Francisco, Ca. . . . Robert E. LaPointe, CENTCOM, LTD., Suite 303, 211 Sutter Street, San Francisco, CA 94108. Telephone: 415-781-3430

Westport, Ct. . . . Thomas Carey, CENTCOM, LTD., 25 Sylvan Rd. South, Westport, Ct. 06881, (Area Code 203) 226-7131

United Kingdom:
Lancashire, England—Technomedia, Ltd. . . . c/o Meconomics Ltd., Meconomics House, 31 Old Street, Ashton Under Lyne, Lancashire, England
Reading, England—Technomedia, Ltd. . . . Wood Cottage, Shurlock Row, Reading RG10 OQE, Berkshire, England

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
Patricia E. Hauge

ES&T
RESEARCH

Characterization of Soluble and Colloidal-Phase Metal Complexes in River Water by Ultrafiltration. A Mass-Balance Approach

Michael R. Hoffmann,*[†] Eric C. Yost, Steven J. Eisenreich, and Walter J. Maier

Environmental Engineering Program, Department of Civil and Mineral Engineering, University of Minnesota,
Minneapolis, Minnesota 55455

■ Ultrafiltration, anodic stripping voltammetry, and atomic absorption spectrophotometry have been used to determine the distribution and degree of association of major trace metals with discrete size fractions of dissolved organic matter which passes initially through a 0.4-μm membrane filter. A novel mass-balance approach has been developed for fractionation of operationally defined, dissolved organic matter and organometallic complexes into well-defined molecular-size ranges. The highest concentrations of trace metals were found in intermediate molecular weight fractions (10^3–10^4) with no detectable free or labile metal as determined by anodic stripping voltammetry. Calcium and magnesium which were found predominantly in the lower molecular size ranges appear to have minimal impact on the extent of interaction of copper with dissolved organic matter. A residual complexation capacity for copper of 1.0 ± 0.1 μM and relatively high pseudostability constant ($\log K = 10.4$) for copper complexation was observed.

Introduction

Water-quality studies have been focused primarily on the measurement of potentially toxic trace metals and anthropogenically derived organic substances and, in some cases, on their interactions in river water. However, naturally occurring organic matter has been implicated as an important factor governing the fate of trace metals (*1–8*). Adsorption, chelation, or entrapment of trace metals by dissolved or colloidal organic matter may affect biological availability, toxicity to microorganisms, and transport mechanisms in rivers. Some investigators (*9–13*) have suggested that complexation of micronutrients by soluble organic chelates can increase the physiological availability of trace metals to aquatic organisms when the ratio of organic matter to trace metal is reasonably high, while others (*14–21*) have shown inverse relationships between the complexation capacity of natural waters and relative toxicity of Cu and Cd to planktonic algae. These studies indicate that, in addition to total metal concentrations in soluble and particulate phases, it is necessary to know the form or species of the metal to reliably predict biological availability and ultimate fate in aquatic systems. Size fractionation by ultrafiltration (UF) followed by atomic absorption spectrophotometry (AAS) and anodic stripping voltammetry (ASV) measurements of metal concentrations can be utilized to provide more detailed experimental information about trace-metal speciation in aquatic systems (*5, 6, 16, 22*).

Size fractionation by ultrafiltration has been employed previously to characterize naturally occurring organic matter (*6, 23–29*) and organometallic complexes (*5, 16, 22, 30–41*).

Advantages of the ultrafiltration method over gel permeation (*24, 42*), dialysis (*37*), ion exchange (*6*), and vapor pressure osmometry have been discussed adequately by other investigators. Disadvantages involved with the ultrafiltration method (*22, 25–28, 30, 35, 37, 43*) have been enumerated and discussed carefully.

With both the advantages and the disadvantages of UF clearly in mind, a new approach to UF size fractionation using a cascade procedure (*35*) and a system of mass-balance equations, which obviates the need for repeated washings (*16*) or excessive concentration (*31*), has been developed and applied to the problem of trace-metal speciation in the Mississippi and Minnesota Rivers.

Experimental Section

Apparatus. Millipore 90-mm High-Flux ultrafiltration cells and UMO5 (Amicon), PSAC, PTGC, PSED, and PTHK (Millipore Corp.) membranes were employed for ultrafiltration experiments. Atomic absorption measurements were made on a Perkin-Elmer Model 360 AAS equipped with a Heated Graphite Atomizer (HGA 2100) and a deuterium background corrector. A Princeton Applied Research polarographic analyzer Model 174A equipped with a Metrohm E410 HMD electrode and a Scientific Products Magnestir were used for anodic stripping voltammetry. An HP-7040A X–Y recorder was used to record scans. Dissolved organic carbon (DOC), total organic carbon (TOC), and total inorganic carbon (TIC) measurements were made with a Beckman 915-A carbon analyzer.

Sampling Procedure. Mississippi and Minnesota River water samples were obtained from locations designated as Bemidji (BEM, 1), Royalton (ROY, 2), St. Anthony Falls (SAF, 3), Inver Grove Heights IGH, 4), and Mendota Heights (MEN, 5). The Bemidji site was located near the headwaters of the Mississippi River, the Royalton site was located near prime agricultural land, and the St. Anthony Falls and Invergrove Heights sites were located near industrial/urban

---

[†] Present address: W. M. Keck Laboratories, California Institute of Technology, Pasadena, CA 91125.

0013-936X/81/0915-0655$01.25/0

stretches of the river. Water samples were collected at midstream ~1 m from the surface by using a polyethylene (PE) bucket suspended from a bridge. Samples were stored in acid-cleaned polyethylene carboys and 2-l LPE bottles. Duplicate 100-mL samples were filtered through 0.40-μm Nuclepore membranes using a Millipore polycarbonate filtration cell. Filtrates were acidified to pH 1.5 with ultrapure HNO_3 (Baker). Unfiltered water samples were collected in carbon-free glass bottles with Al-lined caps. All containers were rinsed 3 times with river water to preclude contamination. Temperature and pH were measured on site.

Laboratory Procedure. All water samples were stored at 4.0 °C before analysis. Bulk water samples were centrifuged continuously at 11 000 rpm by using a DuPont-Sorvall centrifuge with a KSB continuous-flow attachment. The resulting centrifugate was filtered through a 0.40-μm membrane immediately before ultrafiltration. After pretreatment, a sample of known volume ($0.4 \leq v \leq 1.4$ L) was introduced into a well-cleaned UF cell, and the sytem was pressurized with nitrogen to 25 or 40 psig depending on the membrane to be used. The ultrafiltrate was collected in an acid-washed polyethylene bottle. When the retentate volume had been reduced to ~50% of the initial volume, the system was depressurized and the retentate was transferred to three different acid-washed bottles and stored for AAS, ASV, and DOC analysis. The AAS portion was acidified immediately. Volumes were determined with graduated cylinders. The ultrafiltrate from the above step was sequentially fractionated by using membranes with the next lower pore size until the smallest pore size was used. Volumes of both the retentate and the ultrafiltrate were recorded at each stage. Membranes were cleaned by soaking in purified water (Milli-Q/Milli RO 4 System, Millipore Corp.) at pH 2.4 for 24 h before use. Both membranes and cells were rinsed with 2 L of Milli-Q water (four cell volumes). The final 60 mL was collected for blank determinations.

Free and labile Cu, Cd, and Pb and complexation-capacity measurements for Cu were made by ASV in the direct-current mode with a plating potential of 0.8 V vs. SCE, a plating time of 150 s, a 30-s quiescent period, a scan rate of 20 mV/s, a current range of 0.2 μA and a low pass filter time constant of 0.3 s. A CO_2/N_2 gas stream was used to maintain a $H_2CO_3^*/HCO_3^-$ buffering system. Carbon dioxide and N_2 (Matheson) was mixed by using Matheson rotometers No. 610 for CO_2 and No. 602 for N_2. After mixing, the mixture was deoxygenated with an acidic vanadate solution containing 2.3 g of V_2O_5, amalgamated Zn, and 12 M HCl in 250 mL of water. Standard Cu solutions (10^{-4}–10^{-5} M) were made from AR copper wire dissolved in a small amount of concentrated HNO_3. $NaClO_4$ (G. F. Smith) was recrystallized and used as the inert electrolyte at a concentration of 30 mM.

Results

Specific analytical procedures for ultrafiltration were established expressly to maintain the integrity of the in situ metal–organic interactions. According to Buffle et al. (*35*), use of sequential ultrafiltration procedures minimizes the problems of inconsistent organic fractionations (*25, 43*), sorption (*22, 37*), and leakage of organic material when the retentate concentration factor is large (*26, 27*). To avoid a large concentration gradient, we have employed either partial separation or repetitive washing of the retentate with distilled water of fixed ionic strength. However, the latter procedure may result in irreversible alteration of the original metal–organic associations. In order to minimize the effect of solute enhancement by UF on metal–organic interactions and to resolve completely the distribution of organic matter, organometallic colloidal complexes, and microparticulate material according to molecular size, we developed a material-balance formalism.

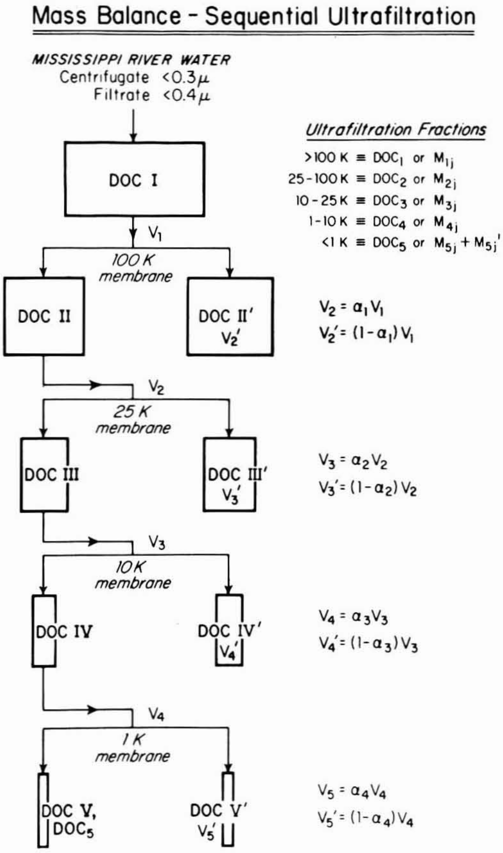


Figure 1. Flow diagram for sequential ultrafiltration procedure that illustrates the mass-balance approach and the successive volume reduction principle.

In sequential ultrafiltration successive volume reductions occur. This sequence is schematically illustrated in Figure 1. Since volume is reduced by 50% at each stage, both the filtrates and the retentates contain components of other molecular size fractions; consequently, those components contributing to each measured fraction must be taken into account in a mass balance.

The material-balance problem can be readily solved for organic carbon. The filtrates of each fraction filtered sequentially are missing organic matter of a size larger than the membrane cutoff. By measuring either the retentate or filtrate DOC in mg/L, one can determine the mass of DOC in each successive filtrate fraction if it is assumed that DOC of molecular weight less than the membrane cutoff passes in proportion to the volume, that the membrane behaves ideally as a molecular sieve at each cutoff, and that the volume is known. Given these conditions, a system of equations (Table I) for either retentate or filtrate fractions can be written which account for the total mass of organic carbon in the original (<0.40 μm) sample. This system of five simultaneous equations has five unknowns for which an exact solution can be obtained. For DOC in mass units, the solution to the mass-balance problem is given in eq 1–5, where α_1, α_2, α_3, and α_4 are successive volume reduction factors.

$$\mathrm{DOC}_5 = (\mathrm{DOC\ V})/(\alpha_1\alpha_2\alpha_3\alpha_4) \qquad (1)$$

$$\mathrm{DOC}_4 = (\mathrm{DOC\ IV})/(\alpha_1\alpha_2\alpha_3) - \mathrm{DOC}_5 \qquad (2)$$

$$\mathrm{DOC}_3 = (\mathrm{DOC\ III})/(\alpha_1\alpha_2) - \mathrm{DOC}_4 - \mathrm{DOC}_5 \qquad (3)$$

$$\mathrm{DOC}_2 = (\mathrm{DOC\ II})/\alpha_1 - \mathrm{DOC}_3 - \mathrm{DOC}_4 - \mathrm{DOC}_5 \qquad (4)$$

$$\mathrm{DOC}_1 = (\mathrm{DOC\ I}) - \mathrm{DOC}_2 - \mathrm{DOC}_3 - \mathrm{DOC}_4 - \mathrm{DOC}_4 \qquad (5)$$

Values for DOC I to DOC V in mass units are determined analytically by measurement of DOC (mg/L) in retentate or filtrate fractions and by knowing the total volume in each fraction. Alternatively the measured retentate masses may be used directly to solve the same problem. The solution presented in eq 1–5 can be expressed conveniently in the following series of equations for the filtrate fractions:

$$\mathrm{DOC}_1 = (\mathrm{DOC\ I}) - (\mathrm{DOC\ II})/\alpha_1 \qquad (6)$$

$$\mathrm{DOC}_2 = (\mathrm{DOC\ II})/\alpha_1 - (\mathrm{DOC\ III})/(\alpha_1\alpha_2) \qquad (7)$$

$$\mathrm{DOC}_3\ (\mathrm{DOC\ III})/(\alpha_1\alpha_2) - (\mathrm{DOC\ IV})/(\alpha_1\alpha_2\alpha_3) \qquad (8)$$

$$\mathrm{DOC}_4 = (\mathrm{DOC\ IV})/(\alpha_1\alpha_2\alpha_3) - (\mathrm{DOC\ V})/(\alpha_1\alpha_2\alpha_3\alpha_4) \qquad (9)$$

$$\mathrm{DOC}_5 = (\mathrm{DOC\ V})/(\alpha_1\alpha_2\alpha_3\alpha_4) \qquad (10)$$

where DOC_1 = >100K fraction, DOC_2 = 25–100K fraction, DOC_3 = 10–25K fraction, DOC_4 = 1–10K fraction, and DOC_5 = <1K fraction (K refers to molecular weight in multiples of 1000). A similar set of simultaneous equations (Table II) can be written for metal ions associated with the five different molecular-weight fractions, although in each case the summation of free aquated metal and low molecular weight inorganic complexes must be taken into account. Unfortunately, this results in five equations and six unknowns. For example, solution to the metal–retentate distribution is given in the following equations:

$$M_{1j} = \{M(\mathrm{I})\} - M(\mathrm{II})/\alpha_1 \qquad (11)$$

Table I. Two Systems of Simultaneous Equations Used To Solve Sequential Ultrafiltration Mass Balance for Dissolved Organic Carbon in Mass Units

DOC I = $\mathrm{DOC}_1 + \mathrm{DOC}_2 + \mathrm{DOC}_3 + \mathrm{DOC}_4 + \mathrm{DOC}_5$

DOC II′ (retentate) = $\mathrm{DOC}_1 + (1 - \alpha_1)[\mathrm{DOC}_2 + \mathrm{DOC}_3 + \mathrm{DOC}_4 + \mathrm{DOC}_5]$

DOC II (filtrate) = $\alpha_1[\mathrm{DOC}_2 + \mathrm{DOC}_3 + \mathrm{DOC}_4 + \mathrm{DOC}_5]$

DOC III′ (retentate) = $\alpha_1\mathrm{DOC}_2 + (1 - \alpha_2)\alpha_1[\mathrm{DOC}_3 + \mathrm{DOC}_4 + \mathrm{DOC}_5]$

DOC III (filtrate) = $\alpha_1\alpha_2[\mathrm{DOC}_3 + \mathrm{DOC}_4 + \mathrm{DOC}_5]$

DOC IV′ (retentate) = $\alpha_1\alpha_2\mathrm{DOC}_3 + (1 - \alpha_3)\alpha_1\alpha_2[\mathrm{DOC}_4 + \mathrm{DOC}_5]$

DOC IV (filtrate) = $\alpha_1\alpha_2\alpha_3[\mathrm{DOC}_4 + \mathrm{DOC}_5]$

DOC V′ (retentate) = $\alpha_1\alpha_2\alpha_3\mathrm{DOC}_4 + (1 - \alpha_4)\alpha_1\alpha_2\alpha_3\mathrm{DOC}_5$

DOC V (filtrate) = $\alpha_1\alpha_2\alpha_3\alpha_4\mathrm{DOC}_5$

Table II. System of Simultaneous Equations Used To Solve Sequential Ultrafiltration Mass Balance for Total <0.4 Metal

$$M(\mathrm{I}) = \sum_{i=1}^{5} M_{ij} + M_{5j}'$$

$$M(II) = \sum_{i=2}^{5} \alpha_1(M_{ij} + M_{5j}')$$

$$M(III) = \sum_{i=3}^{5} \alpha_1\alpha_2(M_{ij} + M_{5j}')$$

$$M(IV) = \sum_{i=4}^{5} \alpha_1\alpha_2\alpha_3(M_{ij} + M_{5j}')$$

$$M(V) = \alpha_1\alpha_2\alpha_3\alpha_4(M_{ij} + M_{5j}')$$

$$M_{2j} = \{M(\mathrm{II})/\alpha_1\} - M(\mathrm{III})/(\alpha_1\alpha_2) \qquad (12)$$

$$M_{3j} = \{M(\mathrm{III})/(\alpha_1\alpha_2)\} - M(\mathrm{IV})/(\alpha_1\alpha_2\alpha_3) \qquad (13)$$

$$M_{4j} = \{M(\mathrm{IV})/(\alpha_1\alpha_2\alpha_3)\} - M(\mathrm{V})/(\alpha_1\alpha_2\alpha_3\alpha_4) \qquad (14)$$

$$M_{5j} = \{M(\mathrm{V})/(\alpha_1\alpha_2\alpha_3\alpha_4)\} - M_{5j}' \qquad (15)$$

where M_{ij} is the mass of metal M_j in the ith molecular-weight fraction which is nominally associated with dissolved organic carbon or colloidal materal, and M_{5j}' is the summation of free aquated metal and monomeric or polymeric inorganic complexes which because of their size should appear in the

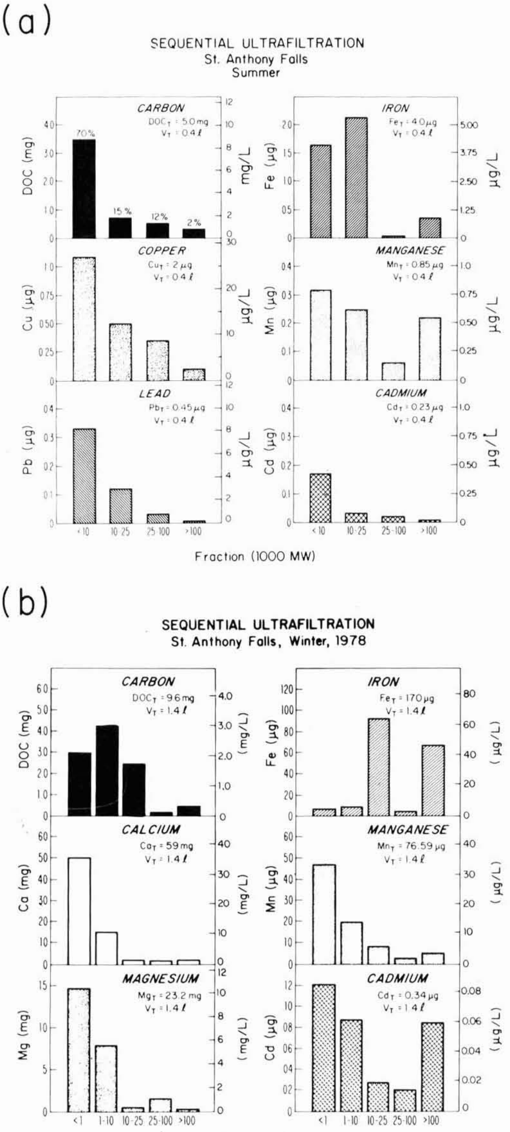


Figure 2. Results of sequential ultrafiltration separations for site 3 during summer 1977 (a) and for site 3 during winter 1978 (b). Concentrations for each fraction are given by M_{ij}/V_T with units of mg/L or μg/L. Additional water-quality data for site 3 averaged over 42 sampling dates are presented in ref *64*.

smallest-size fraction. M_{5j}' can be estimated with ASV measurements for the special cases involving Cu, Zn, Pb, and Cd.

This general UF procedure assumes that, in the absence of metal associations in successive molecular fractions, as the total volume is reduced the mass of metal found in each successive fraction will be reduced proportionately. The reduction in mass of each metal in successive retentate fractions can be predicted by knowing the volume fraction factors and assuming a negligible adsorptive or desorptive interaction with the membrane or support surface. This simple hypothesis was tested with standard solutions of the appropriate metal salts in water at pH 2.5 and was shown to be valid.

Representative results of sequential ultrafiltration separations for SAF, summer and winter, are presented in bar graph fashion in Figure 2. Although flow and temperature conditions were typical of late summer for SAF, the terrestrial ecosystem conditions were autumnal. From these distributions some general observations can be made. The majority of organic carbon is found in less than 10K nominal molecular weight fractions. Trace metals such as Cu, Cd, Pb, and Mn are found most frequently in size fractions which are less than 10K in molecular weight. However, a significant fraction of Fe, Mn, and Cd is found in higher molecular weight fractions. Sharp (*44*) has defined colloidal material to be in the size range of 2.8–12.0 nm and microparticulate material to be in the size range of 12.0–400 nm. Within the limits of these definitions, some of the Fe, Mn, and Cd in the higher molecular weight fractions may be colloidal or microparticulate in nature, suggesting that the oxides, oxyhydroxides, or surface-adsorbed species may be important factors controlling the speciation of these metals under certain conditions.

Calcium and magnesium were found to appear largely in the lowest molecular weight fractions, as shown in Figure 2b. When the 0.5K membrane was used, most of the Ca and Mg was found in the fraction which was less than 0.5K in nominal molecular weight.

Results of a spring 1978 sampling during a period of peak flow are presented in Figure 3a–d for sites 1, 2, 4, and 5. Analytical procedures for trace metals were complicated by the fact that concentrations of Cu, Pb, and Cd were extremely low. However, metal levels were consistent with an overall lower

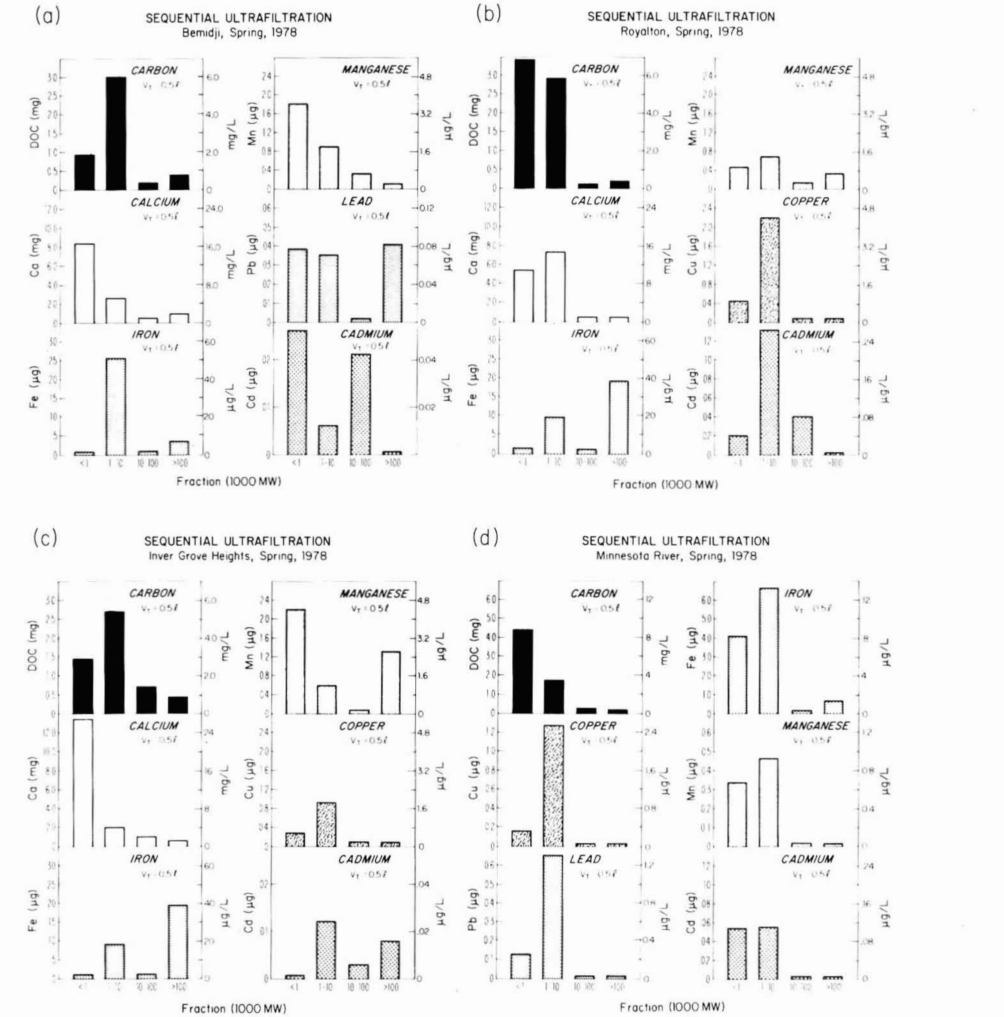


Figure 3. Results of sequential ultrafiltration separations for sites 1–5 during spring 1978. Concentrations for each fraction are given by M_{ij}/V_T with units of mg/L or μg/L. Additional water-quality data for sites 1–5 are presented in ref *64*.

DOC level during spring runoff. Trends in metal distribution tended to approximate the distribution of organic carbon at each site with the major fraction of Cu and Cd found most frequently in the 1–10K fraction with the exception of Cd (<1K fraction) in the spring sample at Bemidji. With the exception of Fe at ROY and IGH, the majority of metals are found in the two lower molecular weight fractions. Anodic stripping voltammetry measurements for Cu, Cd, and Pb showed no detectable free or labile metal at the five study sites. These combined results suggest that organometallic complexes play an important role in trace-metal speciation in the upper Mississippi River.

Further evidence for possible organometallic interactions was provided by complexation-capacity measurements and pseudostability constant determinations. Complexation capacity or the residual complexing ability of a natural water sample was determined by complexometric titration of the <0.4 μm filtrate with soluble Cu(II) (*39, 46–50*) followed by ASV measurement of free and labile copper. Plots of ASV peak current vs. the cumulative Cu concentration were made, and the intersection of lines drawn from the initial and final linear response regions was defined as the residual complexation capacity (*49–51*). Complexation-capacity measurements for fall 1978 are listed in Table III. The average values for sites 1–4 were 0.88, 0.99, 0.90, and 1.08 μM, respectively.

Stability-constant determinations were based on the methods of Shuman and Woodward (*49, 50*) using ASV complexometric titration data. The conditional formation constant for the formation of a metal–ligand complex with an assumed stoichiometry of 1:1 can be determined from eq 16

$$K_{\mathrm{ML}}' = \frac{C_{\mathrm{M}} - (i_{\mathrm{a}}/k)}{(i_{\mathrm{a}}/k)(C_{\mathrm{L}} - C_{\mathrm{M}} + i_{\mathrm{a}}/k)} \qquad (16)$$

where C_{M} is the total analytical metal concentration, C_{L} is the total ligand concentration determined graphically, i_{a} is the anodic stripping peak current, and k is the slope of the upper portion of the titration curve. The numerator in eq 16 corresponds to the total complex concentration, and the denominator is the product of the ASV free-metal concentration, i_{a}/k, and the equilibrium ligand concentration, $(C_{\mathrm{L}} - C_{\mathrm{M}} + i_{\mathrm{a}}/k)$. During the initial stages of titration when $C_{\mathrm{L}} \gg C_{\mathrm{M}}$, eq 16 can be reduced to

$$K_{\mathrm{ML}}' = C_{\mathrm{M}}/[(i_{\mathrm{a}}/k)(C_{\mathrm{L}} - C_{\mathrm{M}})] \qquad (17)$$

Since samples were buffered by a continuous flow of CO_2 gas during titrations and because the samples had a high alkalinity, a slight correction for competitive complexation of Cu^{2+} by carbonato and hydroxy complexes was made according to the method proposed by Allen (*52*). This correction is based on the ASV current response when $C_{\mathrm{M}} > C_{\mathrm{L}}$ or, in the case of copper complexation, when $[Cu^{2+}]_{\mathrm{T}} > [\mathrm{L}]$. Essentially, this procedure provides a method of correcting for the impact of labile copper–inorganic complexes on the apparent equilibrium constant. In the absence of competitive ligands, electrochemically active copper is given by $[Cu^{2+}]_{\mathrm{T}} = [Cu^{2+}] + [Cu(OH)_n{}^{(2-n)+}]$. However, because of the constant level of $[H_2CO_3{}^*]$ and the high initial alkalinity of the river water samples, the ASV response in the upper region of the titration curve will be affected also by the formation of carbonato complexes. In order to account for known labile copper–inorganic complexes and to determine a K that more closely represents the nonlabile complexes in equilibrium with the free metal, Allen (*52*) proposed that the free hexaaquo copper ion was proportional to the total labile metal as follows:

$$[Cu^{2+}] \simeq \alpha_0[Cu^{2+}]_{\mathrm{T}} \qquad (18)$$

where

$$\alpha_0 = (1 + \beta_1[OH^-] + \beta_2[CO_3{}^{2-}] + \beta_3[CO_3{}^{2-}]^2)^{-1} \qquad (19)$$

and β_1, β_2, and β_3 are the formation constants for the monohydroxy, monocarbonato, and dicarbonato complexes, respectively. An essential assumption in this development is that CuL complexes are not ASV active. However, some metal–organic complexes may be electrochemically labile because of relatively rapid dissociation rates. Consequently, ASV measurements may underestimate the total extent of residual organic complexation.

Table III. Complexation-Capacity and Stability-Constant Data Fall 1978

site	TOC, mg/L	pH	$pC_T{}^a$	CC, μM	log K_{ML}
1	18.4	8.05	2.39	0.88	10.4
2	13.2	8.23	2.60	0.99	9.9
3	24.3	8.29	2.52	0.90	10.7
4	17.6	8.16	2.43	1.08	10.0

[a] C_{T} = total carbonate concentration.

From the pH, alkalinity, and pK_{a} values for $H_2CO_3{}^*$, a value for α_0 can be readily obtained, when values for β_1, β_2, and β_3 of $10^{6.3}$, $10^{6.75}$, and $10^{9.92}$, respectively, are used (*53*). Substitution of eq 18 for $[Cu^{2+}]$ in eq 17 followed by rearrangement will give the following expression:

$$i_{\mathrm{a}} = \frac{k}{\alpha_0 K_{\mathrm{ML}}'}\left(\frac{C_{\mathrm{M}}}{C_{\mathrm{L}} - C_{\mathrm{M}}}\right) \qquad (20)$$

A linear regression fit of eq 20 was used to determine K_{ML}' for Cu where C_{L} was given by the complexation-capacity measurement assuming the formation of a 1:1 complex. Average pseudostability constants for copper are given in Table III. log K_{M}' ranged from 9.7 to 10.7 for sites 1–4. In all determinations of K_{ML}', the effect of α_0 on the magnitude of the constant was slight.

Discussion

Ultrafiltration procedures and methods for data reduction by mass-balance techniques developed as a part of this study have been shown to be useful for characterization of metal complexes by size fractionation. When ultrafiltration is coupled with ASV measurements for Cu, Cd, and Pb, the degree of metal association in discrete molecular-size fractions can be determined. Common UF problems such as membrane clogging, leakage, concentration polarization, ionic-strength changes, and excessive concentration, which may lead to an alteration of the actual distribution of complexes, are minimized with these procedures when the concentration factor is ≤ 2. Flushing procedures with artificial waters of similar composition and ionic strength may effect changes in the degree of metal complexation by dilution or introduction of trace-metal contaminants. However, it should be pointed out that size fractionation by UF with these procedures is not problem free. Nominal molecular weight cutoffs are imprecise since the shape and degree of ionization of the molecule is an important factor in retention by or passage through a particular membrane. Ogura (*26*) has shown that cytochrome *c* (M_{r} = 12.6K) was 95% retained by a 100K membrane and that cobalamin (M_{r} = 1.357K) was 76% retained by a 0.5K membrane, although urea (M_{r} = 0.06K) was not retained by either membrane. Macko et al. (*43*) have shown that the degree of ionization of low molecular weight organic acids is critical to the degree of retention by membranes with higher molecular weight cutoffs. They have shown also that retention is partially a function of flow rate and ionic strength when Ca^{2+}, Mg^{2+}, and $SO_4{}^{2-}$ are primary solution components. Charged sulfonated membranes, which were developed to avoid fouling problems, are known to retain relatively high concentrations of Ca^{2+} and Mg^{2+} (*54*). Flow-rate problems can be overcome by passing sufficient water through new membranes until a constant flux has been obtained or alternatively by using scrupulously cleaned and washed used membranes which tend to have relatively constant fluxes (*43*). When metal distributions are of primary concern, results of the present study show that new well-washed membranes with constant fluxes are preferable to clean but used membranes.

Storage procedures are also important in UF experiments. Unacidified field samples should be filtered as soon as possible to avoid sorptive losses to LPE bottle walls (*55*), especially when low levels of Cd, Pb, and Cu are present initially.

Size fractionation of the dissolved components of Mississippi River water at five different sites has shown that in most cases Cu, Cd, and Pb mass distributions are similar to those of dissolved organic carbon and that these metals are most often found in the 1–10K nominal molecular weight fraction. On the other hand, Fe and Mn are frequently found in higher molecular weight fractions and their dominant mass peaks do not correlate well with the mass distribution of organic carbon. ASV measurements as summarized in Table III show, firstly, that there is no detectable free or labile Cu, Cd, or Pb at any of the five sampling sites, secondly, that the residual complexation capacity for Cu is high, and, thirdly, that the pseudostability constants for Cu complexation are moderately high (i.e., 10^{10}). Stability constants in the range of $10^{9.9}$–$10^{10.7}$ are indicative of metal complexes with multidentate organic ligands (*56–58*) containing a mixture of amino, sulfhydryl, carboxylate, or hydroxy functional groups.

Results of this study agree in general with the observations of other investigators who have studied molecular size distributions and Cu stability constants in freshwaters. Bacinni and Sutter (*59*) found most Cu in a number of Swiss lakes to lie in the 1–10K nominal molecular weight fraction as determined by ultrafiltration and gel filtration methods. They concluded that copper was complexed primarily by organic ligands and that the conditional stability constant at pH 8.8 was $\log K = 11.0 \pm 0.2$ as determined by ion-exchange. Complexation capacities or the total ligand concentration, C_L, was determined to be 2.4 ± 0.5 μM. Tuschall and Brezonik (*60*) studied the size distribution of isolated proteinaceous matter from two freshwater lakes and determined that the organic nitrogen had an apparent molecular weight between 1K and 50K. The complexation capacity and conditional stability constants for copper were determined to be in the range of $0.8 \le C_L \le 1.6$ μm and $6.2 \le \log K_{CuL} \le 7.1$, respectively. They concluded that soluble organic nitrogen of proteinaceous origin may be important in the complexation of heavy metals in natural waters.

Buffle and co-workers (*35, 61*) found roughly similar molecular size distributions with the bulk of DOC in the 1–10K size range and conditional stability constants of 10.8–11.6 for Cu in Zaire river water. van den Berg and Kramer (*62*) used a MnO_2 adsorption technique to determine pseudostability constants for some Canadian rivers and lakes that were found in the range $7.2 \le \log_{CuL} \le 9.5$. Similarly large stability constants ($\log_{CuL} = 10.0$) were reported by Sunda and Hanson (*21*) for Cu in the Neuse River.

Results of this study and those reported above suggest that Cu complexation in many waters is dominated by aquatic organics and that in many waters formation of carbonato complexes is of secondary importance. The magnitude of the observed stability constants for apparent 1:1 complexes indicates that the ligands involved are multidentate. Conditional stability constants for Cu complexes with bidentate ligands such as glycine are on the order of $10^{6.5}$ at pH 8. Stronger multidentate ligands containing a mixture of amino, sulfhydryl, and carboxylate groups more closely approximate the observed Cu complexation characteristics in natural waters. Macrocyclic ligands such as porphyrins and phthalocyanines in which bonding takes place through pyrrole nitrogens may also play an important role in metal chelation in natural waters. The work of Tuschall and Brezonik (*60*) is particularly relevant in terms of relating apparent Cu complex stabilities directly to nitrogen-containing proteinaceous material. Similarly, Baccini and Sutter (*59*) conclude that Cu may be preferentially bound to natural molecules containing peptide chains in which the N-terminal end can form a tridendate ligand for copper in the pH region of natural waters. Alternatively they (*59*) have suggested that Cu may be bound in a folded molecule such as a chromophore.

The potential role of multiple organic nitrogen and sulfur functionalities is strengthened by the experimental observation made by Perdue (*63*) that aquatic fulvic material isolated from Oregon river water contained aromatic carboxylic acids with two-thirds of the phenolic hydroxyl groups in meta and para positions. Only phenolic acids with *orthro*-hydroxyl groups could participate in chelation via salicylate-like functional groups. The apparent strength of Cu complexes in natural waters cannot be ascribed to carboxylate ligands alone.

Conclusion

Ultrafiltration, anodic stripping voltammetry, and atomic absorption spectrophotometry have been used to determine the distribution and the degree of association of major trace metals with discrete size fractions of organic matter which pass initially through a 0.4-μm membrane filter. A novel mass-balance approach has been developed for fractionation of operationally defined, dissolved organic matter and trace-metal species into well-defined molecular size ranges. In order to minimize adverse interactions with membrane surfaces and to ensure the integrity of metal complexes, we maintained volume reduction in the retentate fractions near 50% for a sequential ultrafiltration procedure. With known volume reduction factors and measured concentrations in either retentate or filtrate fractions, a system of simultaneous equations has been developed where the number of independent variables is equal to the number of independent equations. Application of this procedure to Mississippi and Minnesota River water shows that the highest concentrations of trace metals are often found in intermediate molecular weight (1 000–10 000) ranges with no detectable free or labile metal as determined by ASV. Calcium and magnesium are found predominantly in lower molecular size ranges. They appear to have minimal impact on the apparent extent of interaction of other metals with dissolved organic matter. The Mississippi River water shows a moderate residual complexation capacity for copper of 1.0 ± 0.1 μM and a relative high pseudostability constant of 10^{10} M^{-1}. These results suggest that complexation of trace metals such as Cu, Cd, and Pb may be dominated by aquatic organics and that formation of carbonato complexes is of secondary importance.

Acknowledgment

We are grateful to many colleagues who were helpful during this study. Special thanks go to Drs. W. Combs, N. Carriker, and H. Allen for stimulating discussions and assistance.

Literature Cited

(1) Siegel, A. In "Organic Compounds in Aquatic Environment"; Faust, S. D., Hunter, J. V., Eds.; Marcel Dekker: New York, 1971.

(2) Andelman, J. B. In "Trace Metals and Metal–Organic Interactions in Natural Waters"; Singer, P. C., Ed.; Ann Arbor Science Publishers: Ann Arbor, MI, 1974.

(3) Stumm, W.; Brauner, P. In "Chemical Oceanography"; Riley, J. P., Skirrow, G. D., Eds.; Academic Press: London, 1971; Vol. 1.

(4) Jackson, T. A. *Soil Sci.* **1975,** *119,* 56.

(5) Guy, R. D.; Chakrabarti, C. L.; *Can. J. Chem.* **1976,** *54,* 2600.

(6) Florence, T. M.; Batley, G. E. *Talanta* **1977,** *24,* 151.

(7) Reuter, J. H.; Perdue, E. M. *Geochim. Cosmochim. Acta* **1977,** *41*, 325.
(8) Steelink, C. *J. Chem. Educ.* **1977,** *54*, 599.
(9) Barber, R. T. In "Trace Metals and Metal–Organic Interactions in Natural Waters"; Singer, P. C., Ed.; Ann Arbor Science Publishers: Ann Arbor, MI, 1974.
(10) Johnston, R. *J. Mar. Biol. Assoc. U.K.* **1964,** *44*, 87.
(11) Barber, R. T.; Ryther, J. H. *J. Exp. Mar. Biol. Ecol.* **1969,** *3*, 191.
(12) Barber, R. T.; Dugdale, R. C.; MacIsaac, J. J.; Smith, R. L. *Invest. Pesq.* **1971,** *35*, 171.
(13) (a) Reuter, J. G. Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, MA, 1980. (b) Reuter, J. G.; Morel, F. M., in preparation.
(14) Jackson, G. A.; Morgan, J. J. *Limnol. Oceanogr.* **1978,** *23*, 268.
(15) Davey, E. W.; Morgan, M. J.; Erickson, S. J. *Limnol. Oceanogr.* **1973,** *18*, 993.
(16) Giesy, J. P., Jr.; Lawrence, G. J.; Williams, D. R. *Water Res.* **1977,** *11*, 1013.
(17) Gachter, R.; Lum-Shue-Chan, K.; Chau, Y. K. *Schweiz. Z. Hydrol.* **1973,** *35*, 252.
(18) Lewis, A. G.; Whitfield, P. H.; Ramnarine, A. *Mar. Biol. (Berlin)* **1972,** *17*, 215.
(19) Steeman Nielsen, E.; Wium-Anderson, S. *Mar. Biol. (Berlin)* **1970,** *6*, 93.
(20) Sunda, W. G.; Lewis, J. A. M. *Limmol. Oceanogr.* **1978,** *23*, 870.
(21) Sunda, W. G.; Hanson, P. J. *ACS Symp. Ser.* **1979,** *93*.
(22) Guy, R. D.; Chakrabarti, O. L. *Int. Conf. Heavy Met. Environ. [Symp. Proc.], 1st, 1975* **1977,** 275.
(23) Gjessing, E. T. *Environ. Sci. Technol.* **1970,** *4*, 437.
(24) Gjessing, E. T. *Schweiz. Z. Hydrol.* **1975,** *35*, 286.
(25) Wilander, A. *Schweiz. Z. Hydrol.* **1972,** *34*, 190.
(26) Ogura, N. *Mar. Biol. (Berlin)* **1974,** *24*, 305.
(27) Wheeler, J. R. *Limmol. Oceanogr.* **1976,** *21*, 846.
(28) Kwak, J. C.; Nelson, R. W.; Gamble, D. S. *Geochim. Cosmochim. Acta* **1977,** *41*, 993.
(29) Allen, H. E. *Oikos* **1976,** *27*, 64.
(30) Schindler, J. E.; Alberts, J. J. *Arch. Hydrobiol.* **1974,** *74*, 429.
(31) Smith, R. G., Jr. *Anal. Chem.* **1976,** *48*, 76.
(32) Alberts, J. J.; Schindler, J. E.; Nutter, D. E., Jr.; Davis, E. *Geochim. Cosmochim. Acta* **1976,** *40*, 369.
(33) Gnassia-Barelli, M.; Romeo, M.; Laumond; Pesando, D. *Mar. Biol. (Berlin)* **1978,** *47*, 15.
(34) Giesy, J. P., Jr.; Briese, L. A. *Chem. Geol.* **1977,** *20*, 109.
(35) Buffle, J.; Deladoey, P.; Haerdi, W. *Anal. Chim. Acta* **1978,** *101*, 339.
(36) Schindler, J. E.; Alberts, J. J.; Honick, K. R. *Limmol. Oceanogr.* **1972,** *17*, 952.
(37) Benes, P.; Steinnes, E. *Water Res.* **1974,** *8*, 947.
(38) Ramamoorthy, S.; Kishner, D. J. *J. Fish. Res. Board Can.* **1975,** *32*, 1755.
(39) Chau, Y. K. *J. Chromatogr. Sci.* **1973,** *11*, 579.
(40) Gillespie, P. A.; Vaccaro, R. F. *Limmol. Oceanogr.* **1978,** *23*, 543.
(41) Benes, P.; Gjessing, E. T.; Steinnes *Water Res.* **1976,** *10*, 711.
(42) Mantoura, R. F. C.; Riley, J. P. *Anal. Chem.* **1975,** *78*, 193.
(43) Macko, C. A.; Maier, W. J.; Hoffmann, M. R.; Eisenreich, S. J. *AIChE Symp. Ser.* **1979,** *75*, 162–9.
(44) Sharp, J. H. *Limmol. Oceanogr.* **1973** *18*, 441.
(45) Stumm, W.; Morgan, J. J. "Aquatic Chemistry"; Wiley-Interscience: New York, 1970.
(46) Chau, Y. K.; Lum-Shue-Chan, K. *J. Fish Res. Board Can.* **1974,** *31*, 1515.
(47) Gachter, R.; Lum-Shue-Chan, K.; Chau, Y. K. *Schweiz. Z. Hydrol.* **1973,** *35*, 252.
(48) Chau, Y. K.; Lum-Shue-Chan, K. *Water Res.* **1974,** *8*, 383.
(49) Shuman, M. S.; Woodward, G. P., Jr. *Anal. Chem.* **1973,** *45*, 2032.
(50) Shuman, M. S.; Woodward, G. P., Jr. *Environ. Sci. Technol.* **1977,** *11*, 809.
(51) Rosenthal, D.; Jones, G. L., Jr. *Anal. Chim. Acta* **1971,** *53*, 141.
(52) Allen, H. L. "Biological Consequences of Chemical Speciation of Heavy Metals in Natural Waters"; Final Report; U.S. Department of Energy: Washington, DC, 1978.
(53) Smith, R. M.; Martell, A. E. "Critical Stability Constants"; Plenum Press: New York, 1976; Vol. 4.
(54) Kesting, R. E. "Polymeric Membranes"; McGraw-Hill: New York, 1971.
(55) Batley, G. E.; Gardner, D. *Water Res.* **1977,** *11*, 745.
(56) Martell, A. E.; Smith, R. M. "Critical Stability Constants", Plenum Press: New York, 1974; Vol. 1.
(57) Smith, R. M.; Martell, A. E. "Critical Stability Constants", Plenum Press: New York, 1975; Vol. 2.
(58) Smith, R. M.; Martell, A. E. "Critical Stability Constants"; Plenum Press: New York, 1977; Vol. 3.
(59) Baccini, P.; Sutter, U. *Schweiz. Z. Hydrol.* **1979,** *41*, 291.
(60) Tuschall, J. R., Jr.; Brezonik, P. L. *Limmol. Oceanogr.* **1980,** *25*, 495.
(61) Buffle, J.; Greter, F. L.; Haerdi, W. *Anal. Chem.* **1977** *49*, 216.
(62) van den Berg, C. M. G.; Kramer, J. R. *Anal. Chim. Acta* **1979,** *106*, 113.
(63) Perdue, E. M. *Geochim. Cosmochim. Acta* **1978,** *42*, 1351.
(64) Eisenreich, S. J.; Hoffmann, M. R.; Rastetter, D.; Yost, E.; Maier, W. J. *Adv. Chem. Ser.* **1980,** *No. 189*, 136–76.

Received for review December 20, 1979. Accepted February 2, 1981. This research was supported by a grant from the National Science Foundation (ENV77-04496) to M.R.H., S.J.E., and W.J.M.

Photochemical Ozone Formation in the Irradiation of Ambient Air Samples by Using a Mobile Smog Chamber

Katsuo Shibuya and Tsunekazu Nagashima

Japan Environmental Sanitation Center, Yotsuya-Kamicho 10-6, Kawasaki-ku, Kawasaki-shi, Kanagawa 210, Japan

Senro Imai

Planning Division, Air Quality Bureau, Japan Environment Agency, Kasumigaseki, Chiyoda-ku, Tokyo 100, Japan

Hajime Akimoto*

Division of Atmospheric Environment, The National Institute for Environmental Studies,
P.O. Tsukuba-gakuen, Ibaraki, 305, Japan

Although many studies have been carried out on the irradiation of synthetic hydrocarbon–nitrogen oxide mixtures and of auto exhaust in regard to photochemical air pollution, few studies (*1–5*) have reported on the irradiation of samples of ambient polluted air. All previous studies (*1–5*) on the irradiation of atmospheric samples were essentially concerned with the photochemical decay of individual hydrocarbons and with trying to characterize the relative hydrocarbon reactivity. Although the formation of products, oxidant, formaldehyde, and peroxyacetyl nitrate was also reported (*3–5*), no systematic characterization of ozone (oxidant) formation has been reported.

Previous studies (*6–8*) at the National Institute for Environmental Studies (NIES) have revealed that, in the hydrocarbon-excess region, the maximum ozone formed ultimately ($[O_3]_{max}$) from 1-olefin–nitrogen oxide mixtures is, in general, proportional to the square root of both the initial concentration of NO_x and the primary photodissociation rate of NO_2,

■ Photochemical ozone formation in the irradiation of the sampled ambient polluted air was studied by using a mobile smog chamber. As a control, experiments were also performed for a propylene–NO_x–humidified air system (30 °C, relative humidity = 65 ± 5%). The proportional relationship between $[O_3]_{max}$, the maximum concentration of ozone reached ultimately, and $[O_3]_{ps}$, the photostationary-state concentration parameter, was obtained for both systems. The ozone formation potential defined by the ratio of $[O_3]_{max}$ to $[O_3]_{ps}$ for the ambient air was 81 ± 14% of that of propylene. The sampled ambient air was found to be in the hydrocarbon-excess region at $[NMHC]_0/[NO_x]_0 \gtrsim 7$ ppmC/ppm, where $[O_3]_{max}$ does not depend strongly on the initial concentration of hydrocarbon.

k_1, and thus is proportional to the photostationary-state parameter, $[O_3]_{ps}$. It has also been proposed that the ozone formation potential which is defined by the ratio of $[O_3]_{max}$ to $[O_3]_{ps}$ may be a useful parameter to characterize the maximum concentration of ozone expected from a specific hydrocarbon–NO_x mixture.

It is very interesting to see whether such a general relationship still holds not only for selected synthetic mixtures of hydrocarbons and nitrogen oxides but also for samples of ambient polluted air. If this is the case, determining the ozone formation potential of ambient air would be of great significance from the viewpoint of ozone control strategy.

This study reports the photochemical ozone formation in the irradiation of sampled ambient air studied by using a mobile smog chamber. As a control, photochemical runs of a propylene–NO_x–air system were also studied by using the same smog chamber, and the results are compared with the data obtained at NIES by using a smog chamber which could be evacuated and baked.

Experimental Section

Experiments were carried out by using a mobile smog chamber system constructed and operated under contract with the Japan Environment Agency. The system consists of two vehicles, a smog-chamber vehicle, which carries the reaction chamber and the irradiation source, and a mobile laboratory, which carries instruments for gas analysis. The two vehicles are set side by side, and the smog chamber and the analytical instruments are connected by Teflon tubing of ca. 6-m length and 6-mm i.d.

The reaction chamber is 1.5 m high, 1.0 m wide, 2.8 m long, and 4.28 m^3 in volume. Two sides of the chamber wall (1.5 × 2.8 m) are made of aluminum-framed FEP (fluoroethylene–propylene copolymer) film (0.127 mm in thickness) through which the sample air is irradiated. Other sides of the chamber wall are made of aluminum panels covered with the FEP film of the same thickness. The irradiation source is external to the chamber and consists of 120 40-W fluorescent lamps (Toshiba, FLP 40 SBL-A, 60 on each side), which emit light in the wavelength region of 310–420 nm with the intensity maximum at ~360 nm. The chamber wall can be temperature controlled between 0 and 45 °C within ±1 °C by allowing thermostated air to flow through channels on the outside wall. In order to compensate for the pressure drop caused by the sampling of the reaction mixture, the chamber is equipped with three Tedlar bags (250 L each) inside. During the experiment the Tedlar bags are inflated gradually with pure N_2 gas to a size large enough to compensate for the pressure drop, thus always keeping the chamber pressure at 5 mmH_2O above the atmospheric pressure.

The air sampling was done by flushing the chamber with the ambient air by using a blower (maximum capacity, 0.5 m^3 min^{-1}). The ambient air is sampled through a Teflon-coated sampling tube whose inlet is located ~15 m above the ground. When the experiment with synthetic polluted air was performed, ambient air was first passed through an air purifier and then introduced into the chamber in the same manner as above. The premeasured amounts of hydrocarbon and NO_x were then injected into the chamber by using the purified air as a carrier gas. The air purifier is composed of an NO-oxidizing filter, NO_2- and SO_2-removing filters, soda lime for CO_2 removal, and a molecular sieve for hydrocarbon ($\geq C_4$) removal. The purified air typically contained less than 10 ppb of NO, NO_2, and SO_2 and less than 200 ppbC of nonmethane hydrocarbon (NMHC). A humidifier can add heated water vapor to the sampled air in the chamber. The reaction mixture was stirred by a fan during the experiment. All experiments were carried out at 30 ± 1 °C and at a relative humidity of 65 ± 5%. For the ambient air sample, water vapor was added only when the humidity was lower than this range.

The chamber wall was preconditioned before every run. The chamber temperature was first kept at 45 °C for 14 h while the chamber was continuously flushed with the purified air. After the blower was stopped and the temperature was set at 30 °C, the chamber was exposed to ~10 ppm of O_3 for 30 min. Then the chamber was flushed by the sample air (ambient or purified air) until the ozone disappeared completely. After these procedures, the decay of 0.1 ppm O_3 in humidified air (65 ± 5% at 30 °C) was typically 0.081 h^{-1}.

Measurements of NO_x and NO were made by a chemiluminescent analyzer (Kyoto Denshi, Model NX-17S) which was calibrated with a capillary flow calibrator (Standard Technology Inc., Model SGGC-14) using NO/NO_2 standard gas (Takachiho Shoji Co., 1000 ppm). An automatic Saltzman analyzer (Denki Kagaku Keiki Co., Model GPH-74S) was also used for several of the runs to monitor NO and NO_2. Ozone was monitored by a UV analyzer (DASIBI Co., Model 1003AH), which was calibrated against a secondary standard DASIBI analyzer at NIES (*6*, *9*). A nonmethane hydrocarbon monitor with GC–FID (Shimadzu, Model HCM-3S) was used to measure NMHC concentration. Calibration was made with CH_4/air standard gas (Takachiho Shoji, Co., 4 ppm). Analysis of each hydrocarbon component was made by using FID–GC with three different columns: 1% squalane on activated alumina (2 m × 3 mm o.d.) for C_2H_4 and C_2H_6, 25% DMS on Chromosorb W (3 m × 3 mm o.d.) + sebaconitrile on Chromosorb W (6 m × mm o.d.) for C_2–C_5, and 10% squalane (90 m × 0.25 mm i.d.) for C_6–C_9.

The effective UV light intensity inside the chamber was measured by photolyzing 0.5~0.9 ppm of NO_2 in pure N_2 in a Tedlar bag which was hung inside the chamber and by continuously monitoring NO and NO_x concentration with the chemiluminescent analyzer for a few minutes. The primary photolysis rate constants, k_1, were calculated by using the equation proposed by Wu and Niki (*10*) (eq N in their paper). The correction for the wavelength-averaged transmittance of the Tedlar bag was made by using a correction factor calculated from the absorption spectrum of the bag film and spectral distribution of the light source (*11*).

Irradiation of the purified air which contained 0.1~0.15 ppmC of NMHC, 1.7 ppm of CH_4, and 4–8 ppb of NO_x formed 40–65 ppb of ozone after 5 h (k_1 = 0.30 min^{-1}). Since the sample air used in the present study contained a much higher concentration of NMHC, the conclusions are thought to be unaffected by the background reactivity.

Results and Discussion

Irradiation of the C_3H_6–NO_x–Air Mixture. In order to characterize the photochemical ozone formation in the mobile smog chamber, we studied the dependence of the maximum concentration of ozone formed ultimately, $[O_3]_{max}$, on the initial concentration of $[NO_x]_0$ and k_1. In the first series of experiments, $[NO_x]_0$ was varied from 0.035 to 0.166 ppm under the condition of constant $[C_3H_6]$ ($\sim$0.5 ppm) and of constant k_1 (0.29 min^{-1}). In the second series of experiments, the k_1 value was varied from 0.066 to 0.29 min^{-1} while $[C_3H_6]_0$ and $[NO_x]_0$ were kept constant at $\sim$0.5 and $\sim$0.09 ppm, respectively. These concentrations of $[C_3H_6]_0$ and $[NO_x]_0$ were selected so as to keep the $[C_3H_6]_0/[NO_x]_0$ ratio in the propylene excess region ($[C_3H_6]_0/[NO_x]_0 \gtrsim 3$) (*6*). Table I gives the experimental results of ozone formation together with data on the initial conditions. Figure 1 illustrates the plot of the observed $[O_3]_{max}$ vs. $[O_3]_{ps}$ (*6, 12*) which is calculated from

$$[O_3]_{ps} = \frac{-k_1 + (k_1^2 + 4k_1k_2[NO_x]_0)^{1/2}}{2k_2} \qquad (I)$$

where k_2 is the NO–O_3 reaction rate constant, 27.5 ppm^{-1} min^{-1} (*10*). The meaning of $[O_3]_{ps}$ has been discussed before (*6, 7*). As shown in Figure 1, $[O_3]_{max}$ is found to be proportional to $[O_3]_{ps}$ as in the case of the data from the evacuable smog chamber at NIES (*6–8*). This fact also implies that $[O_3]_{max}$ is approximately proportional to $[NO]_0^{1/2}$ and $k_1^{1/2}$, as shown in the previous study (*6*). The proportionality constant between $[O_3]_{max}$ and $[O_3]_{ps}$, or the ozone formation potential of C_3H_6, is determined to be 6.9 ± 0.8 from Figure 1, which can be compared with the corresponding value of 9.2 obtained from the evacuable smog chamber (*7*). The error given above is the standard deviation of the scatter of data. Since the wall decay rate of O_3 is even lower for the mobile chamber than for the evacuable chamber, the lower ozone formation potential in the present study might be due to the difference in the spectral distribution of the light sources.

These results would imply that the proportionality between $[O_3]_{max}$ and $[O_3]_{ps}$ is established generally for 1-olefins regardless of the type of smog chambers. The proportionality constant between $[O_3]_{max}$ and $[O_3]_{ps}$, e.g., for C_3H_6, can be taken as a characteristic constant of a specific smog chamber and can be used as a normalization factor when a comparison of data on $[O_3]_{max}$ obtained either from different smog chambers or for different hydrocarbon systems such as ambient air is to be made.

Irradiation of the Ambient Polluted Air. Sampling of the ambient air was made at two different sites. One sampling site was at Kitanomaru Park, near downtown Tokyo, and the other was at the Japan Environmental Sanitation Center in Kawasaki City. Both sampling sites are located near main highways, and the contribution of auto exhaust to the sampled polluted air is supposed to be predominant. Table II summarizes the initial concentration data and the experimental results on the photochemical ozone formation. The typical compositions of NMHC for the runs with $[NMHC]_0/[NO_x]_0 < 15$ are as follows: paraffins, 35–55%; olefins, 5–10%; aromatics, 35–55%. Most of the polluted air with $[NMHC]_0/[NO_x]_0 > 20$ contained aromatic hydrocarbons predominantly: paraffins, 5–25%; olefins, 1–5%; aromatics, 70–90%. Irradiation continued until the ozone maximum was reached. Under the experimental condition of $k_1 = 0.30$ min^{-1}, however, the ozone maximum was not reached within the 8-h irradiation for three of the runs, and those cases were discarded from Table II. Thus, the $[O_3]_{max}$ in the present study is the maximum concentration of ozone reached ultimately after irradiation time prolonged enough to bring the true maximum.

Table II shows that the initial concentrations of NO_x and NMHC in the sampled air varied in the range of 0.029$\sim$0.189 ppm and 0.63$\sim$4.05 ppmC, respectively, and the ratio of $[NMHC]_0/[NO_x]_0$ ranged fairly widely from 6.6 to 35.6 ppmC/ppm. Figure 2 shows the plot of the observed $[O_3]_{max}$ against $[O_3]_{ps}$. In order to see whether the quantitative relationship between $[O_3]_{max}$ and $[O_3]_{ps}$ depends on the $[NMHC]_0/[NO_x]_0$ ratio, we have distinguished between the data points with ratios higher and lower than 12.0 ppmC/ppm. The data obtained at the two different sampling sites in Tokyo and Kawasaki are also differentiated.

As shown in Figure 2, a proportional relationship between $[O_3]_{max}$ and $[O_3]_{ps}$ seems to hold for the irradiation of ambient air as in the case of the synthetic mixture of 1-olefin–NO_x–air

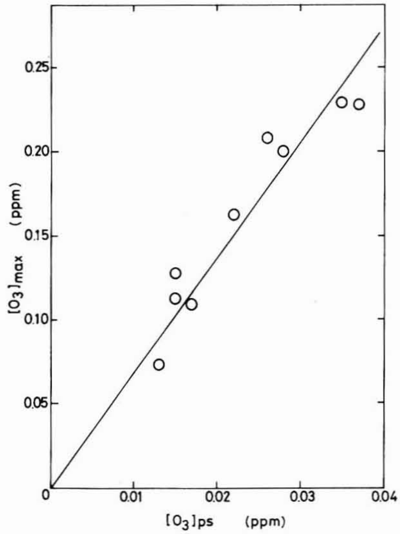


Figure 1. Plot of $[O_3]_{max}$ vs. $[O_3]_{ps}$ in the propylene–NO_x–air system. $[C_3H_6]_0$ = 0.5 ppm; relative humidity = 65 ± 5%; 30 °C.

Table I. Irradiation of the C_3H_6–NO_x–Air System [a]

Run	$[C_3H_6]_0$, ppm	$[NO_x]_0$,[b] ppm	k_1, min^{-1}	$[O_3]_{ps}$, ppm	$[O_3]_{max}$, ppm	t_{max}, min
1	0.59	0.035	0.29	0.015	0.114	90
2	0.42	0.035	0.29	0.015	0.127	90
3	0.52	0.099	0.29	0.028	0.201	120
4	0.53	0.089	0.29	0.026	0.207	120
5	0.55	0.152	0.29	0.035	0.228	150
6	0.61	0.166	0.29	0.037	0.227	150
7	0.54	0.086	0.066	0.013	0.073	180
8	0.57	0.094	0.10	0.017	0.109	150
9	0.51	0.084	0.22	0.022	0.165	120

[a] Experimental data of the dependence of $[O_3]_{max}$ on $[NO_x]_0$ and k_1. 30 °C; relative humidity = 65 ± 5%. [b] $[NO]_0/[NO_x]_0$ = 0.74$\sim$0.99.

Table II. Experimental Data of the Irradiation of the Sampled Ambient Air [a]

run	date in 1979 [b]	$[\mathrm{NMHC}]_0$, ppmC	$[\mathrm{NO}_x]_0$, [c] ppm	$[\mathrm{NMHC}]_0/[\mathrm{NO}_x]_0$, ppmC/ppm	$[\mathrm{O}_3]_{\mathrm{ps}}$, ppm	$[\mathrm{O}_3]_{\mathrm{max}}$, ppm	t_{max}, min
			Kitanomaru Park, Tokyo				
1	Aug 24	0.63	0.029	21.7	0.013	0.111	450
2	25	0.65	0.074	8.8	0.023	0.130	330
3	29	0.64	0.063	10.2	0.021	0.130	420
4	30	0.57	0.086	6.6	0.026	0.133	420
			Japan Environmental Sanitation Center, Kawasaki				
5	Sept 17	2.03	0.057	35.6	0.020	0.098	90
6	18	1.47	0.109	13.5	0.029	0.133	240
7	19	3.50	0.158	22.2	0.036	0.187	300
8	20	1.80	0.057	31.6	0.020	0.120	420
9	21	0.85	0.085	10.0	0.025	0.145	360
10	26	1.05	0.132	8.0	0.033	0.174	390
11	27	4.05	0.189	21.4	0.040	0.226	210
12	Oct. 1	0.75	0.080	9.4	0.025	0.141	420
13	2	0.55	0.080	6.9	0.025	0.111	300
14	4	1.37	0.117	11.7	0.031	0.172	360
15	6	3.50	0.118	29.7	0.031	0.210	180
16	8	0.75	0.114	6.6	0.030	0.185	420
17	9	2.27	0.071	32.0	0.023	0.135	210
18	10	0.76	0.084	9.0	0.025	0.158	390

[a] 30 °C; relative humidity = 65 ± 5%; $k_1 = 0.30\ \mathrm{min}^{-1}$. [b] Sampling time is ~30 min during 7:40~9:40 a.m. [c] $[\mathrm{NO}]_0/[\mathrm{NO}_x]_0 = 0.35{\sim}0.83$.

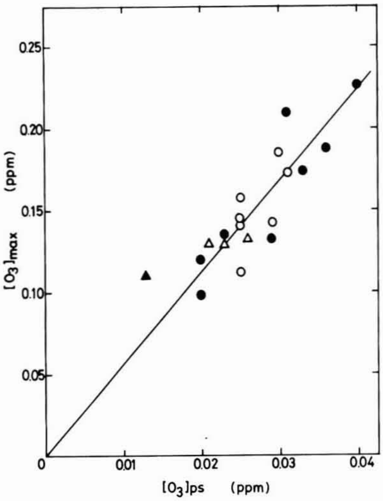


Figure 2. Plot of $[\mathrm{O}_3]_{\mathrm{max}}$ vs. $[\mathrm{O}_3]_{\mathrm{ps}}$ in the irradiation of ambient air sample. Sampling sites: (△, ▲) Tokyo and (○, ●) Kawasaki. $[\mathrm{NMHC}]_0/[\mathrm{NO}_x]_0$: (▲, ●) ≥ 12 and (△, ○) < 12 ppmC/ppm. $k_1 = 0.30\ \mathrm{min}^{-1}$; relative humidity = 65 ± 5%; 30 °C.

(*6–8*). The proportionality factor was determined to be 5.6 ± 0.7 from Figure 2. Figure 2 suggests that $[\mathrm{O}_3]_{\mathrm{max}}$ obtained for the sampled air in this study depends on neither the $[\mathrm{NMHC}]_0/[\mathrm{NO}_x]_0$ ratio nor the sampling site within the scatter of the experimental data. The insensitivity of $[\mathrm{O}_3]_{\mathrm{max}}$ to the initial concentration of NMHC means that the sampled air is in the hydrocarbon-excess region, where $[\mathrm{O}_3]_{\mathrm{max}}$ is nearly independent of the initial concentration of hydrocarbon as defined in the previous study (*6*). Therefore, the proportionality constant, 5.6 ± 0.7, between $[\mathrm{O}_3]_{\mathrm{max}}$ and $[\mathrm{O}_3]_{\mathrm{ps}}$ can be thought to represent the ozone formation potential of the sampled ambient polluted air. Thus, the ozone formation potential of the ambient air is 81 ± 14% of that of propylene.

It is rather surprising to see that the ambient air with $[\mathrm{NMHC}]_0/[\mathrm{NO}_x]_0 \simeq 7$ ppmC/ppm (Table II) is already in the hydrocarbon-excess region. If we take the average carbon number of the nonmethane hydrocarbon of the sampled ambient air to be ~5, the above ratio of $[\mathrm{NMHC}]_0/[\mathrm{NO}_x]_0$ is reduced to ~1.4 on a molar concentration basis. This value is much smaller than the ratio for propylene, $[\mathrm{C}_3\mathrm{H}_6]_0/[\mathrm{NO}_x]_0 \simeq 3$, which the hydrocarbon-excess condition yielded (*6*). There are no previous studies to allow a direct comparison with the present data. However, it is very interesting to note that the ozone isopleths composed from a 10-h irradiation of a synthetic surrogate hydrocarbon and NO_x mixture simulating auto exhaust obtained at the Statewide Air Pollution Research Center, University of California, and cited by Holmes and Bonnamassa (*13*) suggests a hydrocarbon-excess region of $[\mathrm{NMHC}]_0/[\mathrm{NO}_x]_0 \gtrsim 7{\sim}8$, which is quite consistent with the data obtained in the present study.

The "apparent" ozone maximum observed in the ambient atmosphere under the diurnal variation of sunlight intensity should be determined by the combination of the ozone formation rate and the ultimate ozone formation potential. The initial ozone formation rate which can be represented by the NO oxidation rate has been known (*14*) to be strongly dependent on the $[\mathrm{NMHC}]_0/[\mathrm{NO}_x]_0$ ratio. Therefore, the result of the present study indicating that the sampled ambient air mostly falls into the hydrocarbon-excess region where the ultimate ozone formation potential is solely affected by $[\mathrm{NO}_x]_0$ rather than $[\mathrm{NMHC}]_0$ does not mean at all that $[\mathrm{NMHC}]_0$ does not affect the "apparent" ozone maximum expected in the real atmosphere within a diurnal irradiation time. We believe that, in order to construct a meaningful ozone control strategy, one should introduce these two factors obtained in the smog-chamber studies into a computer model together with the emission source date and meteorological data. Our data for the sampled ambient air presented in this work would be significant in the sense that it offers a reliable basis for such a computer model, but the smog-chamber data alone do not indicate directly the best control strategy in an urban area.

Conclusions

(1) The proportionality between $[O_3]_{max}$ and $[O_3]_{ps}$ was determined for the propylene–NO_x–air system to be valid in any type of smog chamber.

(2) The proportionality constant between $[O_3]_{max}$ and $[O_3]_{ps}$ for propylene can be taken as a characteristic constant of a specific smog chamber and can be used as a normalization factor when comparison of the data of $[O_3]_{max}$ obtained either from different smog chambers or for different hydrocarbon systems is to be made.

(3) The ozone formation potential of the ambient polluted air sampled in Tokyo and Kawasaki is 81 ± 14% of that of air polluted synthetically with propylene and NO_x.

(4) The ambient air sampled in the present study ($[NMHC]_0/[NO_x]_0 \gtrsim 7$ ppmC/ppm) was in the hydrocarbon-excess region where $[O_3]_{max}$ (maximum ozone concentration reached ultimately after prolonged irradiation) does not depend strongly on the initial concentration of hydrocarbon.

Literature Cited

(1) Stephens, E. R.; Scott, W. E. *Proc., Am. Pet. Inst., Sect. 3* **1962,** *42*, 665.

(2) Stephens, E. R.; Burleson, R. F. *J. Air Pollut. Control Assoc.* **1967,** *17*, 147.

(3) Altshuller, A. P.; Kopczynski, S. L.; Lonneman, W. A.; Sutterfield, F. D. *Environ. Sci. Technol.* **1970,** *4*, 503.

(4) Kopczynski, S. L.; Lonneman, W. A.; Sutterfield, F. D.; Darley, P. E. *Environ. Sci. Technol.* **1972,** *6*, 342.

(5) Bufalini, J. J.; Lonneman, W. A. *Environ. Lett.* **1973,** *4*, 95.

(6) Akimoto, H.; Sakamaki, F.; Hoshino, M.; Inoue, G.; Okuda, M. *Environ. Sci. Technol.* **1979,** *13*, 53.

(7) Sakamaki, F.; Akimoto, H.; Okuda, M. *Environ. Sci. Technol.* **1980,** *14*, 985.

(8) Sakamaki, F.; Akimoto, H.; Okuda, M., *Environ. Sci. Technol.*, in press.

(9) Akimoto, H.; Inoue, G.; Sakamaki, F.; Hoshino, M.; Okuda, M. *J. Jpn. Soc. Air Pollut.* **1978,** *13*, 266.

(10) Wu, C. H.; Niki, H. *Environ. Sci. Technol.* **1975,** *9*, 46.

(11) Japan Environmental Sanitation Center "Survey in Urban Air by Utilization of a Mobile Photochemical Smog Chamber, 1977" (in Japanese); Japan Environment Agency, Air Quality Bureau, Planning Division, March 1978.

(12) Stephens, E. R., *J. Air Pollut. Control Assoc.* **1969,** *19*, 181.

(13) Dimitriades, B., Ed. "Smog Chamber Conference Proceedings"; EPA-600/3-76-029; April 1976, p 102.

(14) Futsuhara, N.; Masuda, K.; Suzuki, M.; Yamaki, N., *Proc. Int. Clean Air Congr. 14th*, **1977,** 478.

Received for review June 2, 1980. Accepted January 26, 1981.

Photochemical Reactivity and Ozone Formation in 1-Olefin–Nitrogen Oxide–Air Systems

Fumio Sakamaki, Hajime Akimoto,* and Michio Okuda

The National Institute for Environmental Studies, P.O. Tsukuba-gakuen, Ibaraki, 305, Japan

■ The photooxidation of a series of 1-olefins, C_2H_4, C_3H_6, 1-C_4H_8, and 1-C_5H_{10} in the presence of sub-ppm levels of nitrogen oxides was studied by using an evacuable and bakable photochemical smog chamber. The proportionality between $[O_3]_{max}$ and $[O_3]_{ps}$ was established in general in the hydrocarbon-excess region, where $[O_3]_{ps}$ is the generalized parameter related to the photostationary-state concentration of ozone in the absence of hydrocarbon. The ozone formation potentials defined by the proportionality factor were 9.9, 9.2, 8.5, and 8.2 for C_2H_4, C_3H_6, 1-C_4H_8, and 1-C_5H_{10}, respectively. The ratio of the ozone formation rates for this series of 1-olefins was 0.27:1.00:0.77:0.57 and does not agree with the ratio of the OH–olefin reaction rate constant. The average concentration of OH radical was estimated from the decay rate of each hydrocarbon, and a new concept of OH radical formation potential of hydrocarbon was introduced. The relative OH radical formation potentials were 0.68, 1.00, 0.77, and 0.56 for C_2H_4, C_3H_6, 1-C_4H_8, and 1-C_5H_{10}, respectively.

Introduction

In photochemical smog phenomena, it is well-known that ozone, or photochemical oxidant, is produced by the action of sunlight on mixtures of hydrocarbons and nitrogen oxides (*1*). Many laboratory investigations (*2–13*) using "smog chambers" or "environmental chambers" have been conducted on the hydrocarbon–nitrogen oxide–air system in order to study photochemical ozone formation under simulated atmospheric conditions. Although they have made fairly clear that the amount of ozone formed depends on several parameters, e.g., the initial concentrations of hydrocarbon and nitrogen oxides, light intensity, humidity, and temperature, attempts to establish general relationships between these parameters are scarce. In our previous studies on the propylene–nitrogen oxide–air system (*14, 15*), we showed that the maximum concentration of ozone ultimately formed ($[O_3]_{max}$) depends on the square root of light intensity and the initial concentration of nitrogen oxides in the propylene-excess region. From this evidence, we proposed to represent the ozone formation potential of each hydrocarbon by the ratio of $[O_3]_{max}$ to $[O_3]_{ps}$. Here $[O_3]_{ps}$ is the photostationary-state concentration of ozone when air containing the same concentration of nitrogen dioxide is irradiated in the absence of hydrocarbon.

In addition to the ozone formation potential, the photochemical reactivity of individual hydrocarbons in terms of reaction rate is of great importance. In previous investigations, hydrocarbon reactivity has been discussed and classified by various indexes, for example, the photooxidation rate of nitric oxide (*16–18*), maximum ozone concentration within a fixed irradiation time (*19*) obtained directly from smog-chamber experiments, or the elementary reaction rate constant with the hydroxyl radical (*13, 20*). Since recent evidence of ozone formation in rural areas by long-term transport of polluted air (*21–23*) suggests that even a hydrocarbon classified as having low reactivity has a substantial ozone formation potential, the reactivity and the ozone formation potential should be determined independently.

The objective of this investigation is to establish the ozone formation potential and photochemical reactivity of 1-olefins based on the photochemical runs using the evacuable and bakable smog chamber at NIES. Four species of 1-olefins, C_2H_4, C_3H_6, 1-C_4H_8, and 1-C_5H_{10}, were used, and the maximum concentrations of ozone were obtained under the experimental condition of hydrocarbon excess (HC, 0.5 ppm; NO_x, 0.01∼0.3 ppm). The hydrocarbon reactivity of the four 1-olefins was also discussed from the viewpoint of rate parameters, such as the ozone formation rate, and the hydrocarbon consumption rate, and a new concept of OH radical formation potential was introduced.

Experimental Section

Since the details of the evacuable and bakable photochemical smog chamber and the experimental procedure at NIES have been described previously (*14, 24*), only a brief description will be given here. Irradiation of the hydrocarbon–NO_x–air mixture was carried out in the cylindrical reaction chamber which is 6065 L in volume and can be evacuated to ~1×10^{-6} torr. The chamber wall temperature was maintained at 30 ± 1 °C during the experiments. The purified air used in the experiments contained less than 30 ppbC of total hydrocarbon (THC) and 1 ppm of CO_2. The relative humidity of the air was kept constant (50 ± 10% at 30 °C) by a humidifier. The light intensity was measured by photolyzing NO_2 in purified air, and the values of the NO_2 photolysis rate (k_1) for each hydrocarbon runs are shown in Table I.

Before each run, the humidified air was introduced into the chamber at ~770 torr. The premeasured amounts of hydrocarbon and NO_x were then injected into the chamber by using the purified air as carrier gas. The reaction mixture was stirred by fans during the experiment. For each run, irradiation continued until the maximum of ozone concentration was reached.

The concentrations of O_3, NO, and NO_x were monitored continuously by using commercial chemiluminescent analyzers (Monitor Labs, Models 8410 and 8440L). Hydrocarbons were monitored by gas chromatography with a flame ionization detector (FID) using a 2-m stainless-steel column of Porapak Q at 80~140 °C. Ethylene (99.9% purity), propylene (99.7% purity), and 1-butene (99.0% purity), were purchased from Takachiho Shoji Co., and 1-pentene (research grade) was obtained from Wako Pure Chemical Co. These olefins were used in experiments without further purification except for degassing. Impurity hydrocarbons were less than 1% from their purity check by GC analysis.

Results and Discussion

Ozone Formation Potential. The initial conditions and the results of the olefin–nitrogen oxide–air systems are summarized in Table I. The initial concentration of hydrocarbon ($[HC]_0$) was kept constant at 0.5 ppm, and the initial concentrations of nitrogen oxides ($[NO_x]_0$) were varied from 0.01 to 0.3 ppm, thus keeping the $[HC]_0/[NO_x]_0$ ratio in the hydrocarbon-excess region (*14*). The maximum concentrations of ozone ($[O_3]_{max}$) shown in Table I are not the values obtained within a certain fixed reaction time but are the ones reached

Table I. Experimental Conditions and the Maximum Yield of Ozone in 1-Olefin–NO_x–Air Systems

run	$[HC]_0$, ppm	$[NO_x]_0$, ppm	$[NO]_0$, ppm	$[NO_2]_0$, ppm	$[HC]_0/[NO_x]_0$	$[O_3]_{max}$, ppm	t_{max}, min
			(A) C_2H_4, $k_1 = 0.21\ min^{-1}$				
1	0.487	0.0116	0.0030	0.0086	42.0	0.0636	300
2	0.501	0.0252	0.0038	0.0214	19.9	0.1054	235
3	0.498	0.0306	0.0033	0.0273	16.3	0.127	275
4	0.490	0.0422	0.0041	0.0381	11.6	0.173	290
5	0.486	0.0637	0.0029	0.0608	7.6	0.210	355
6	0.491	0.0798	0.0035	0.0763	6.2	0.237	370
7	0.493	0.1030	0.0047	0.0983	4.8	0.250	450
8	0.493	0.135	0.0044	0.131	3.7	0.277	460
9	0.491	0.186	0.0431	0.143	2.6	0.271	570
			(B) C_3H_6, $k_1 = 0.24\ min^{-1}$				
10	0.498	0.0461	0.0022	0.0439	10.8	0.165	110
11	0.497	0.0842	0.0025	0.0817	5.9	0.215	110
12	0.508	0.0867	0.0031	0.0836	5.9	0.246	90
13	0.500	0.1007	0.0108	0.0899	5.0	0.241	110
14	0.497	0.144	0.0037	0.140	3.5	0.322	140
15	0.500	0.200	0.0062	0.194	2.5	0.339	110
16	0.504	0.284	0.0059	0.278	1.8	0.410	225
			(C) 1-C_4H_8, $k_1 = 0.21\ min^{-1}$				
17	0.500	0.0225	0.0032	0.0193	22.2	0.0770	115
18	0.498	0.0399	0.0034	0.0365	12.5	0.130	120
19	0.490	0.0766	0.0039	0.0727	6.4	0.200	140
20	0.495	0.0792	0.0035	0.0757	6.3	0.201	140
21	0.490	0.151	0.0044	0.146	3.2	0.266	180
22	0.494	0.194	0.0039	0.190	2.5	0.293	200
23	0.501	0.252	0.0041	0.248	2.0	0.321	240
24	0.502	0.315	0.0041	0.311	1.6	0.331	320
			(D) 1-C_5H_8, $k_1 = 0.20\ min^{-1}$				
25	0.502	0.0231	0.0025	0.0206	21.7	0.0684	123
26	0.495	0.0434	0.0032	0.0402	11.4	0.124	125
27	0.495	0.0834	0.0035	0.0799	5.9	0.191	153
28	0.497	0.156	0.0038	0.152	3.2	0.257	195
29	0.502	0.206	0.0036	0.202	2.4	0.283	245
30	0.499	0.258	0.0050	0.253	1.9	0.325	270

ultimately. The propylene runs cited in Table I are the same as those in our previous investigation (*15*).

In our previous studies (*14, 15*) of the propylene–NO_x–air system, we showed that the maximum concentration of ozone is approximately proportional to the square root of the initial concentration of nitrogen oxides in the hydrocarbon-excess region. $[O_3]_{max}$ was plotted against $[NO_x]_0^{1/2}$ for each olefin as shown in Figure 1. Figure 1 shows that such an approximate linear relationship between $[O_3]_{max}$ and the square root of $[NO_x]_0$ generally holds for all olefins studied. Departure of some of the points at higher $[NO_x]_0$ (run 9 for C_2H_4 and runs 23 and 24 for 1-C_4H_8) from the linear relationship is due to the fact that the condition of the hydrocarbon excess was not satisfied. Though the reason that $[O_3]_{max}$ is approximately proportional to $[NO_x]_0^{1/2}$ cannot be explained from photochemical smog reaction mechanisms at this stage, it is interesting to note that such a relationship in the hydrocarbon-excess region is suggested from the ozone isopleths obtained in a recent computer modeling study by Whitten et al. (*25*).

In our previous studies (*14, 15*), we proposed that the ozone formation potential of each hydrocarbon may be defined as a proportionality factor between $[O_3]_{max}$ and a generalized parameter, $[O_3]_{ps}$, in the hydrocarbon-excess region. Here, $[O_3]_{ps}$ is the ozone concentration expected in the photostationary state when the NO_2–air mixture is irradiated and is defined as

$$[O_3]_{ps} = \frac{-k_1 + (k_1{}^2 + 4k_1k_2[NO_x]_0)^{1/2}}{2k_2} \qquad \text{(I)}$$

$$[O_3]_{ps} \simeq \{(k_1/k_2)[NO_x]_0\}^{1/2} \qquad \text{(II)}$$

In the equations, k_1 is the primary photodecomposition rate constant of NO_2 and k_2 is the bimolecular rate constant of the NO–O_3 reaction (k_2 = 27.5 $ppm^{-1}\ min^{-1}$ (*26*)). Since $[O_3]_{max}$ was found to be proportional to the square root of $[NO_x]_0$, as shown in Figure 1, and the square root dependence on the light intensity has been established in the previous studies (*14, 15*), it should be worthwhile to discuss $[O_3]_{max}$ by using the parameter $[O_3]_{ps}$ in this study, too.

Figure 2 shows the plots of $[O_3]_{max}$ vs. $[O_3]_{ps}$ calculated from eq I for the data shown in Figure 1. Runs 9, 23, and 24 were not plotted because they do not seem to satisfy the condition of hydrocarbon excess. For each olefin, the data in Figure 2 show linear relationships between $[O_3]_{max}$ and $[O_3]_{ps}$ approximately. The least-squares fits give

$$[O_3]_{max} = 0.01 + 9.93[O_3]_{ps} \qquad \text{for } C_2H_4 \qquad \text{(III)}$$

$$[O_3]_{max} = 0.00 + 9.21[O_3]_{ps} \qquad \text{for } C_3H_6 \qquad \text{(IV)}$$

$$[O_3]_{max} = 0.01 + 8.45[O_3]_{ps} \qquad \text{for 1-}C_4H_8 \qquad \text{(V)}$$

$$[O_3]_{max} = 0.00 + 8.24[O_3]_{ps} \qquad \text{for 1-}C_5H_{10} \qquad \text{(VI)}$$

Here, eq IV for C_3H_6 was obtained not only from the results of seven runs in Table I but also from the results of other C_3H_6 runs in our previous study (*15*). Thus, neglecting small intercepts, one may say that the approximate proportional relationship between $[O_3]_{max}$ and $[O_3]_{ps}$ has been established for the 1-olefins. Therefore, the proportionality constant, or the ratio $[O_3]_{max}/[O_3]_{ps}$, may be referred to as the ultimate ozone formation potential for each olefin as in the case of C_3H_6 (*14, 15*). The ozone formation potentials determined above are cited in Table II together with the ozone formation rate and the OH radical formation potential discussed below and the OH–olefin reaction rate constants. The ozone formation potentials determined above were not corrected for the decomposition of ozone on the chamber wall. In the case of C_2H_4, especially, since the time to reach the ozone maximum is much longer than for other olefins, as shown in Table I, its real ozone formation potential would be appreciably larger than 9.9 if the correction is to be made. However, since the qualitative conclusions discussed below are not affected, such a correction was not made in the present study.

It should be noted in Table II that the ozone formation potential of 1-olefins are all in the range of 8~10 regardless of the difference in the ozone formation rate by a factor of more than 4. It is also interesting to note that C_2H_4, which has the lowest reaction rate among the 1-olefins studied, has the highest ozone formation potential, and the larger the number of carbon atoms in the 1-olefin, the lower the ozone formation potential. These results imply that the ozone formation potential and a rate factor, such as the ozone formation rate, are independent parameters and that one cannot be determined by knowing the other.

In the past decade extensive effort has been devoted (*16–20*) to the classification of the atmospheric hydrocarbons according to their "photochemical reactivity," and it is generally agreed that the most suitable criterion with respect to photochemical ozone control strategies is maximum ozone concentration. This criterion is sometimes quoted (*19*) as the "ozone-forming potential" and defined as a maximum ozone

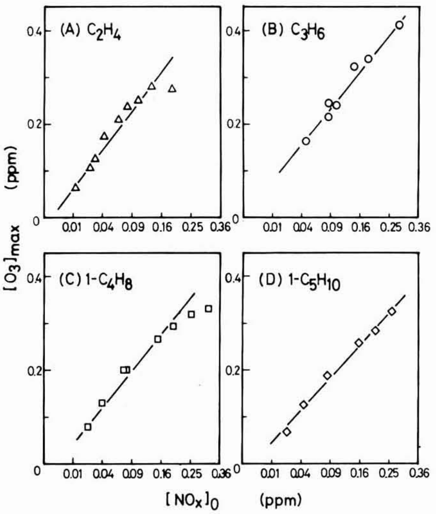


Figure 1. Plots of $[O_3]_{max}$ vs. $[NO_x]_0$ for each olefin. $[olefin]_0$ = 0.5 ppm.

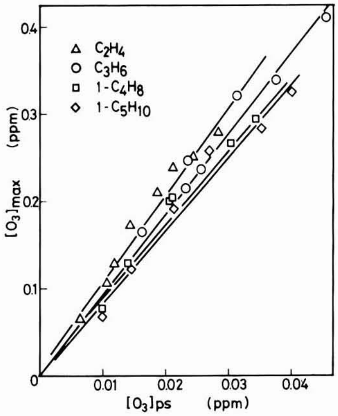


Figure 2. Plots of $[O_3]_{max}$ vs. $[O_3]_{ps}$ for each olefin. $[olefin]_0$ = 0.5 ppm.

Table II. Summary of the Ozone Formation Potentials, Ozone Formation Rates, Hydrocarbon Decay Rates, OH Radical Formation Potentials and Selected OH Rate Constants for 1-Olefins

1-olefin	10^{-4} (OH-olefin rate constant), $ppm^{-1}\ min^{-1}$	ozone formation potential ($[O_3]_{max}/[O_3]_{ps}$)	ozone formation rate,[a] ppb min^{-1}	10^3 (hydrocarbon decay rate due to OH),[a] min^{-1}	10^7 (OH radical formation potential),[a] ppm
C_2H_4	1.45 ± 0.25[c] (0.40)[b] 1.14 ± 0.11[d]	9.9	0.81 (0.27)[b]	1.5 (0.27)[b]	1.03 (0.68)[b]
C_3H_6	3.57 ± 0.41[e] (1.00) 3.64 ± 0.36[f]	9.2	3.0 (1.00)	5.4 (1.00)	1.51 (1.00)
1-C_4H_8	4.84 ± 0.48[e] (1.36) 5.12 ± 0.52[f]	8.5	2.3 (0.77)	5.7 (1.06)	1.17 (0.77)
1-C_5H_{10}	5.76 ± 0.55[e] (1.61)	8.2	1.7 (0.57)	4.9 (0.91)	0.85 (0.56)

[a] Absolute rates are normalized to $k_1 = 0.20\ min^{-1}$. [b] Figures in parentheses are relative values with respect to C_3H_6. [c] Reference *33*, 296 K. [d] Reference *34*, 297 K. [e] Reference *35*, 299 K. [f] Reference *36*, 298 K.

yield within a fixed irradiation time (e.g., 6 h) which is arbitrarily thought to correspond to one solar day's irradiation. However, it is apparent that the criterion is not a well-defined combination of the ultimate ozone formation potential as defined in the present study and the ozone formation rate which will be discussed below and that it should be very susceptible to the light intensity and an arbitrarily chosen hydrocarbon/NO_x ratio. According to the results of the present study, it is concluded that the reactivity scaling of hydrocarbons based on the maximum ozone concentration should be more carefully made with the aid of computer simulation for "one solar day's" or "many solar days' " irradiation.

The reason that C_2H_4 gives the highest ozone formation potential will not be clear without obtaining a greater understanding of the detailed reaction pathways. It is only speculated at this stage that a slower ozone destruction rate by C_2H_4 itself and the absence of the NO_x sink as a PAN-type compound may cause the higher ultimate ozone level for C_2H_4.

Ozone Formation Rate. In addition to the ozone formation potential, the ozone formation rate is thought to be the most straightforward index of photochemical reactivity of hydrocarbons with respect to ozone control strategy, if the ozone formation rate can be defined properly. In the present study, the ozone formation rate was defined as the maximum slope of the plot of ozone concentration vs. irradiation time for the photochemical run starting with a high initial NO_2/NO ratio. In this case, the NO_2/NO ratio just after the start of irradiation adjusts itself to the photostationary-state ratio, and the ozone formation rate, $(d[O_3]/dt)_{max}$, which is independent of the precise initial ratio of NO_2/NO can be determined. In order to check the validity of the ozone formation rate defined above as a proper rate parameter, we first studied its dependence on the light intensity and on the initial hydrocarbon concentration. Figure 3 shows the plot of $(d[O_3]/dt)_{max}$ vs. k_1 for the C_3H_6–NO_x system of fixed initial concentrations ($[C_3H_6]_0$ = 0.50 ppm, $[NO_x]_0$ = 0.09 ppm). Thus, the ozone formation rate is found to be proportional to the light intensity as in the case of the NO oxidation rate, studied by Glasson and Tuesday (*27*), and the hydrocarbon decay rate due to OH radical, studied in our previous work (*28*). Similarly, in the C_3H_6–NO_x system, $(d[O_3]/dt)_{max}$ was found to be proportional to the initial C_3H_6 concentration under the condition of constant light intensity and initial NO_x concentration ($[NO_x]_0$ = 0.09 ppm). Therefore, the ozone formation rate can be recognized as a very well-behaved rate parameter of the photochemical smog reaction system.

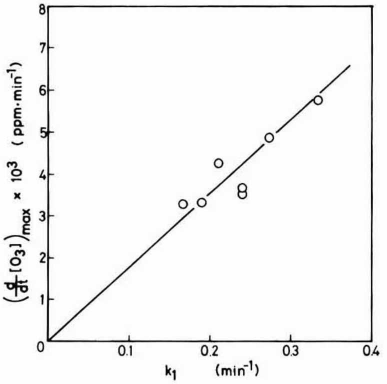


Figure 3. Plots of $(d[O_3]/dt)_{max}$ vs. k_1 for the C_3H_6–NO_x–air system. $[C_3H_6]_0$ = 0.5 ppm, $[NO_x]_0$ = 0.085 ppm.

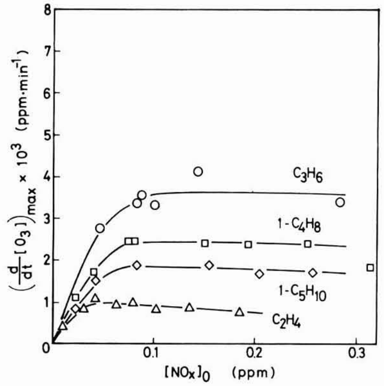


Figure 4. Plots of $(d[O_3]/dt)_{max}$ vs. $[NO_x]_0$ for each olefin. $[\text{olefin}]_0$ = 0.5 ppm. The k_1 values for C_2H_4, C_3H_6, 1-C_4H_8, and 1-C_5H_{10} are 0.21, 0.24, 0.21, and 0.20, respectively.

Figure 4 shows the dependence of $(d[O_3]/dt)_{max}$ on $[NO_x]_0$ for constant initial concentrations of 1-olefins (0.5 ppm). As shown in Figure 4, the ozone formation rate first increased with the increase of $[NO_x]_0$ and then leveled off. The leveling off occurs at $[NO_x]_0/[\text{olefin}]_0$ ratios higher than 0.06, 0.20, 0.16, and 0.16 for C_2H_4, C_3H_6, 1-C_4H_8, and 1-C_5H_{10}, respectively. The ratio at which the leveling off starts to occur is higher for olefins with higher reactivity. The relative ozone formation rate for each olefin can easily be obtained from the relative plateau value of $(d[O_3]/dt)_{max}$ normalized to the light intensity and can be used as a new reactivity scale. Further, the absolute value of the ozone formation rate in the plateau region should also be useful both for a comparison of the data obtained from different laboratories and for an evaluation of reactivity of hydrocarbon mixtures. As a measure of photochemical reaction rate, the ozone formation rate proposed here should be superior to the traditionally used rate parameters, such as NO oxidation rate or the times for NO_2 or O_3 to reach their maximum concentration, because the new index is not dependent on the initial NO_x concentration above a certain level and can be easily normalized by both the light intensity and the initial hydrocarbon concentration.

The absolute and relative ozone formation rates for each olefin normalized by k_1 are shown in Table II. If one considers the scatter of the data points and the slight decreasing tendency of the ozone formation rate with the increase of $[NO_x]_0$, which is most apparent for C_2H_4, the associated error to the ratio cited in Table II is ca. ±10%.

It is very interesting to compare the relative ozone formation rate determined above with the relative rate constant of the OH–olefin reactions, since the latter has been proposed by Darnall et al. (*20*) as a photochemical reactivity scale of hydrocarbons in the atmosphere. As shown in Table II, the reactivity scales do not agree in general, and even the qualitative trends are reversed among C_3H_6, 1-C_4H_8, and 1-C_5H_{10}. Thus, the ozone formation rate decreases whereas the OH reaction rate constant increases as the carbon number increases from C_3H_6 to 1-C_5H_{10}. In other words, the reactivity scale based on the OH rate constant differs from that based on the ozone formation rate by a factor of more than 2. On the other hand, the relative reactivity based on both criteria agrees within 20% for C_2H_4 and C_3H_6. These results would imply that, although the concept of the reactivity based on the OH reaction rate should be important as an intrinsic rather than phenomenological parameter to govern the photochemical smog reaction, it is not necessarily representative of the ozone formation rate of practical importance, if the difference by a factor of 2 is to be of concern.

Glasson and Tuesday (*6*) discussed the effect of initial NO concentration on the rate of ozone formation and reported the inhibition effect of NO even when the delay effect of NO on ozone formation was eliminated. However, the present study revealed that such an inhibition by NO_x is negligible, at least when the irradiation is started with a high NO_2/NO ratio. This would also be the case for the runs starting with a low NO_2/NO ratio, since the difference in the NO_2/NO ratio in the initial reaction mixture is expected only to shift the time scale without affecting the concentration–time profile as a first approximation (*14*). Since their "modified ozone formation rate" defined as $[O_3]_{max}/2(t_{1/2} - t_0)$, where $t_{1/2}$ and t_0 are the times required for formation of one-half the maximum ozone concentration and the time at which ozone first appeared, respectively, is not so well characterized as our $(d[O_3]/dt)_{max}$, the apparent inhibition effect might reflect the inappropriateness of their index.

The photooxidation rate of NO has sometimes been used as a measure of ozone formation rate. In their extensive study of hydrocarbon reactivity scaling based on the NO photooxidation, Glasson and Tuesday (*16*) reported the relative ratio of the photooxidation rates to be 0.49:1.0:0.83:0.60 for C_2H_4, C_3H_6, 1-C_4H_8, and 1-C_5H_{10}. The ratio among C_3H_6, 1-C_4H_8, and 1-C_5H_{10} agrees well with that of the ozone formation rate shown in Table II, and the decreasing trend of reactivity with increasing chain length has clearly been noted. The reactivity ratio of C_2H_4 to C_3H_6 in the present study, however, is nearly half of that reported by them and shows better agreement with the ratio reported by Altshuller and Cohen (*17*). We conclude that the reactivity of C_2H_4 is overestimated in the study of Glasson and Tuesday (*16*).

OH Radical Formation Potential. In order to get more insight into the photochemical reactivity, we next analyzed the consumption rate of hydrocarbon. The apparent decay rate of hydrocarbon can be obtained from the plots of ln [HC] vs. time since each olefin decreased exponentially after some induction period (*28*). The apparent rates of each olefin obtained are shown in Figure 5 by open symbols. As shown in Figure 5, the apparent hydrocarbon decay rate increased with the initial concentration of nitrogen oxides. In our previous study (*28*) of the C_3H_6 system, the apparent hydrocarbon decay rate increased linearly with the square root of the $[NO_x]_0$ as did the maximum ozone concentration. The linear dependence of the hydrocarbon decay rate on $[NO_x]_0^{1/2}$ was confirmed for each of the olefins studied. In fact, the plots of the maximum ozone concentration vs. hydrocarbon decay rate show good linear relationships, as shown in Figure 6. It is interesting to note that the slope for C_2H_4 is much different from those for the other three olefins. The lack of an NO_x sink as

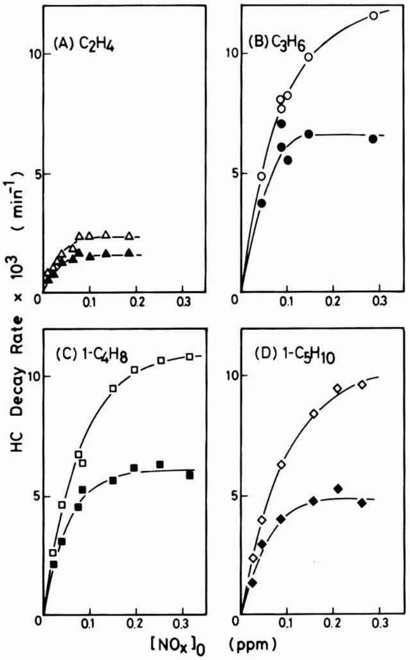


Figure 5. Variation of total hydrocarbon decay rate (open symbols) and hydrocarbon decay rate due to OH (solid symbols) as a function of $[NO_x]_0$. The k_1 values for C_2H_4, C_3H_6, 1-C_4H_8, and 1-C_5H_{10} are the same as those in Figure 4. $[\text{olefin}]_0 = 0.50$ ppm.

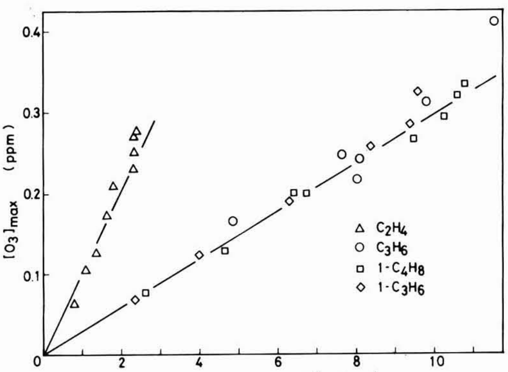


Figure 6. Plots of $[O_3]_{max}$ vs. total hydrocarbon decay rate for each olefin. The k_1 values are the same as those in Figure 4.

a PAN-type compound might cause a larger slope in the case of C_2H_4.

The apparent decay rates obtained can be described (*28*) by eq VII because olefins react mainly with the OH radical and ozone in the photochemical system

$$-\frac{1}{[\text{olefin}]}\frac{\mathrm{d}}{\mathrm{d}t}[\text{olefin}] = k_3[\text{OH}] + k_4[\text{O}_3] \tag{VII}$$

where k_3 and k_4 are the rate constants of the reaction of olefin with OH radical and ozone. In order to estimate the olefin decay rate due to the OH radical only, by integrating and rearranging eq VII one can derive the following equation (*28*):

$$\ln([\text{olefin}]_t/[\text{olefin}]_0) + k_4 \int_0^t [\text{O}_3]\,\mathrm{d}t = -k_3[\text{OH}]_{\text{av}}t \tag{VIII}$$

The slope of the plot of the left-hand side vs. time should be equal to the decay rate due to the OH radical. The values of k_4 used for the calculation were 0.28×10^{-2} (*29*), 1.68×10^{-2} (*29*), 1.62×10^{-2} (*30*), and 1.58×10^{-2} (*31*) ppm^{-1} min^{-1} for C_2H_4, C_3H_6, 1-C_4H_8, and 1-C_5H_{10}, respectively. The hydrocarbon decay rates due to the OH radical obtained by such a method are also shown in Figure 5 by solid symbols. The decay rate due to the OH radical first increased with the increase of the initial NO_x concentration and then leveled off, whereas the total decay rate kept increasing.

The average concentration of the OH radical in the system, $[\text{OH}]_{\text{av}}$, can be estimated by dividing the decay rate due to the OH radical by the rate constant of each olefin with OH radical shown in Table II. The values of Overand et al. (*33*) and Nip et al. (*35*) were used to calculate the OH concentration. The estimated concentrations of OH radical are shown in Figure 7. The leveling off is observed at a concentration of NO_x higher than 0.1 ppm for C_2H_4 and 0.15 ppm for C_3H_6, 1-C_4H_8, and 1-C_5H_{10} for the constant initial olefin concentration of 0.5 ppm. $[\text{OH}]_{\text{av}}$ may decrease again for values of $[NO_x]_0$ still higher than those studied in the present work, but a region of such high NO_x-to-hydrocarbon ratios would not be important in the practical photochemical smog problem.

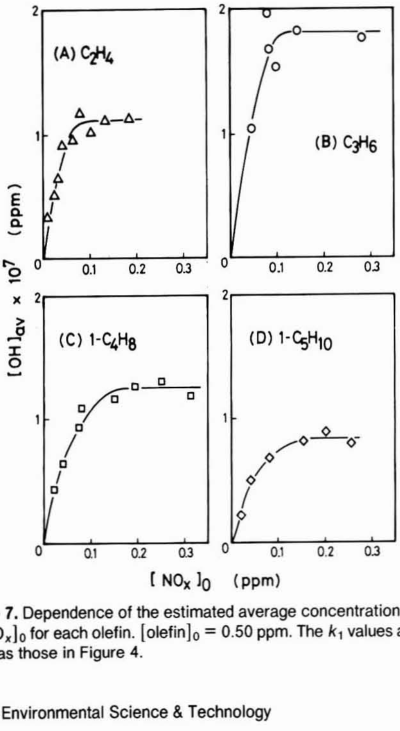


Figure 7. Dependence of the estimated average concentration of OH on $[NO_x]_0$ for each olefin. $[\text{olefin}]_0 = 0.50$ ppm. The k_1 values are the same as those in Figure 4.

Here we introduce the concept of the OH radical formation potential of each hydrocarbon as defined by the plateau level of $[\text{OH}]_{\text{av}}$ in Figure 7. Since $[\text{OH}]_{\text{av}}$ was shown to be proportional to the k_1 value in our previous study (*28*), the relative plateau value of $[\text{OH}]_{\text{av}}$ normalized to light intensity can be called the relative OH radical formation potential and recognized as one of the generalized parameters. Further, the absolute plateau value of $[\text{OH}]_{\text{av}}$ normalized to light intensity should be useful and important in comparing the smog-chamber data from different laboratories. Table II shows both the normalized absolute and relative OH formation potentials of each hydrocarbon as defined above.

Comparing the relative OH radical formation potentials shown in Table II, one finds the order to be $C_3H_6 >$ 1-C_4H_8 $> C_2H_4 >$ 1-C_5H_{10}, which is in the same order as neither the OH–olefin rate constants nor the observed ozone formation rates. Although the ozone formation rate of C_2H_4 is much slower than that of 1-C_4H_8 and 1-C_5H_{10}, its OH radical formation potential is much higher than the latter. It is very interesting to note that in the case of C_2H_4 the product of the relative OH radical formation potential, 0.68, and the relative OH rate constant, 0.40, gives roughly the relative ozone formation rate, 0.27. This result suggests that the essential reaction scheme should be very similar for C_2H_4 and C_3H_6. In the cases of 1-C_4H_8 and 1-C_5H_{10}, the relative OH formation potential agrees well with the relative ozone formation rate and the low OH formation potential mainly causes the slow ozone formation rate as compared to C_3H_6. The nitrate-forming reaction between the peroxy radicals and NO, which competes with the NO oxidation reaction, might yield the low OH radical formation potentials of 1-C_4H_8 and 1-C_5H_{10}. Analogous reactions were first proposed by Darnall et al. (*32*) for the alkylperoxy radicals whose carbon numbers are larger than four in the paraffin systems.

Although the photochemical reactivity index based on the OH radical rate constant (*20*) can intrinsically predict the correct relative hydrocarbon decay rate in the ambient air, it cannot predict the absolute rate of the hydrocarbon decay. The OH radical formation potential proposed in this work complements the former index and possibly may be used for the prediction of the absolute hydrocarbon decay rate in hydrocarbon mixture systems if the additivity of the index can be found. Evaluation of the OH radical formation potential of other classes of hydrocarbons is in progress.

Literature Cited

(1) Leighton, P. A. "Photochemistry of Air Pollution"; Academic Press: New York, 1961.
(2) Altshuller, A. P.; Kopczynski, S. L.; Lonneman, W. A.; Becker, J. L.; Slater, R. *Environ. Sci. Technol.* **1967,** *1*, 899.
(3) Romanovsky, J. C.; Ingels, R. M.; Gordon, R. J. *J. Air Pollut. Control Assoc.* **1967,** *17*, 454.
(4) Stephens, E. R.; Price, M. A. *Atmos. Environ.* **1969,** *3*, 573.
(5) Altshuller, A. P.; Kopczynski, S. L.; Wilson, D.; Lonneman, W. A.; Sutterfield, F. D. *J. Air Pollut. Control Assoc.* **1969,** *19*, 787.
(6) Glasson, W. A.; Tuesday, C. S. *Environ. Sci. Technol.* **1970,** *4*, 37.
(7) Altshuller, A. P.; Kopczynski, S. L.; Lonneman, W. A.; Sutterfield, F. D.; Wilson, D. L. *Environ. Sci. Technol.* **1970,** *4*, 44.
(8) Dimitriades, B. *Environ. Sci. Technol.* **1972,** *6*, 253.
(9) Kopczynski, S. L.; Altshuller, A. P.; Sutterfield, F. D. *Environ. Sci. Technol.* **1974,** *8*, 909.
(10) Shen, C. H.; Springer, G. S.; Stedman, F. D. *Environ. Sci. Technol.* **1977,** *11*, 151.
(11) Zafonte, L.; Bonamassa, F. *Environ. Sci. Technol.* **1977,** *11*, 1015.
(12) Winer, A. M.; Darnall, K. R.; Atkinson, R.; Pitts, J. N., Jr. *Environ. Sci. Technol.* **1979,** *13*, 822.
(13) Carter, W. P. L.; Winer, A. M.; Darnall, K. R.; Pitts, J. N., Jr. *Environ. Sci. Technol.* **1979,** *13*, 1094.
(14) Akimoto, H.; Sakamaki, F.; Hoshino, M.; Inoue, G.; Okuda, M. *Environ. Sci. Technol.* **1979,** *13*, 53.

ADDITIONS AND CORRECTIONS

1981, Volume 16, Page 671

Arthur W. Stelson and John H. Seinfeld:* Chemical Mass Accounting of Urban Aerosol.

Recently, Dr. James J. Morgan of the California Institute of Technology pointed out an error in this paper. The error occurs in the [H], [OH], [H]′, and [OH]′ concentrations calculated on the basis of electroneutrality. The original manuscript assumed the sodium is ionic and neglected that the sodium could be present as oxides in solid solutions. In revising the manuscript, the electroneutrality balance was incorrectly adjusted. The correct values are listed in the table below. By reviewing the revised values, one can see that the statement on page 677, "Samples TC and TD were the only ones that were definitely acidic, whereas WK, WL, VJ, and TE could be basic or acidic", is incorrect. The change from an acidic to basic prediction based on the electroneutrality balance method indicates the desirability of measuring the hydroxyl or hydrogen ion concentration and the sensitivity of the electroneutrality balance method to the individual ion measurements. Although this error appears in the calculations in Tables II, VI, VII, and VIII and Figure 6, the general conclusions are not affected since the numerical values only change slightly.

Table I. Hydroxyl and Hydrogen Ion Concentration Based on Electroneutrality Balance

	hydroxyl and hydrogen ion concn, $\mu g\ m^{-3}$			
sample	[H]	[OH]	[H]′	[OH]′
WK	0.3			1.5
WL	0.1			4.1
VJ		0.1		5.7
TC	0.2			5.1
TD	0.1			4.1
TE	0.1			3.7

Corrected

A J,
261013.

Accounting of Urban Aerosol.

Recently, Dr. James J. Morgan of the California Institute of Technology pointed out an error in this paper. The error occurs in the [H], [OH], [H]′, and [OH]′ concentrations calculated on the basis of electroneutrality. The original manuscript assumed the sodium is ionic and neglected that the sodium could be present as oxides in solid solutions. In revising the manuscript, the electroneutrality balance was incorrectly adjusted. The correct values are listed in the table below. By reviewing the revised values, one can see the statement on page 677, "Samples TC and TD were the only ones that were definitely acidic, whereas WK, WL, VJ, and TE could be basic or acidic", is incorrect. The change from an acidic to basic prediction based on the electroneutrality balance method indicates the desirability of measuring the hydroxyl or hydrogen ion concentration and the sensitivity of the electroneutrality balance method to the individual ion measurements. Although this error appears in the calculations in Tables II, VI, VII, and VIII and Figure 6, the general conclusions are not affected since the numerical values only change slightly.

Corrected.
A1'
260728.

(16) Glasson, W. A.; Tuesday, C. S. *Environ. Sci. Technol.* **1970,** *4*, 916.
(17) Altshuller, A. P.; Cohen, I. R. *Int. J. Air Water Pollut.* **1963,** *7*, 787.
(18) Yeung, C. K. K.; Phillips, C. R. *Atmos. Environ.* **1974,** *8*, 493.
(19) Farley, F. F. In Proceedings of the International Conference on Photochemical Oxidant Pollution and Its Control"; Jan 1977; Vol. II, p 713; EPA-600/3-77-0016.
(20) Darnall, K. R.; Lloyd, A. C.; Winer, A. M.; Pitts, J. N., Jr. *Environ. Sci. Technol.* **1976,** *10*, 692.
(21) Wolff, G. T.; Lioy, P. J.; Wight, G. D.; Meyers, R. E.; Cederwall, R. T. *Atmos. Environ.* **1977,** *11*, 797.
(22) Yukovich, F. M.; Bach, W. D., Jr.; Crissman, B. W.; King, W. J. *Atmos. Environ.* **1977,** *11*, 967.
(23) Karl, T. R. *Atmos. Environ.* **1978,** *12*, 1421.
(24) Akimoto, H.; Hoshino, M.; Inoue, G.; Sakamaki, F.; Washida, N.; Okuda, M. *Environ. Sci. Technol.* **1979,** *13*, 471.
(25) Whitten, G. Z.; Hogo, H.; Killus, J. P. *Environ. Sci. Technol.* **1980,** *14*, 690.
(28) Akimoto, H.; Sakamaki, F.; Inoue, G.; Okuda, M. *Environ. Sci. Technol.* **1980,** *14*, 93.
(29) Herron, J. T.; Huie, R. E. *J. Phys. Chem.* **1974,** *78*, 2085.
(30) Huie, R. E.; Herron, J. T. *Int. J. Chem. Kinet., Symp.* **1975,** *No. 1*, 165.
(31) Japar, S. M.; Wu, C. H.; Niki, H. *J. Phys. Chem.* **1974,** *78*, 2318.
(32) Darnall, K. R.; Carter, W. P. L.; Winer, A. M.; Lloyd, A. C.; Pitts, J. N., Jr. *J. Phys. Chem.* **1976,** *80*, 1948.
(33) Overend, R.; Paraskevopoulos, G. *J. Chem. Phys.* **1977,** *67*, 674.
(34) Atkinson, R.; Perry, R. A.; Pitts, J. N., Jr. *J. Chem. Phys.* **1977,** *66*, 1197.
(35) Nip, W. S.; Paraskevopoulos, G. *J. Chem. Phys.* **1979,** *71*, 2170.
(36) Atkinson, R.; Pitts, J. N., Jr. *J. Chem. Phys.* **1975,** *63*, 3531.

Received for review May 12, 1980. Accepted February 6, 1981.

Chemical Mass Accounting of Urban Aerosol

Arthur W. Stelson and John H. Seinfeld*

Department of Chemical Engineering, California Institute of Technology, Pasadena, California 91125

■ A chemical mass accounting technique emphasizing the importance of chemical speciation is developed for analyzing atmospheric-aerosol data. The technique demonstrates that total aerosol mass can generally be characterized from measurements of SO_4, Cl, Br, NO_3, NH_4, Na, K, Ca, Fe, Mg, Al, Si, Pb, carbonaceous material, and aerosol water, the predominant species being SO_4, NO_3, NH_4, Si, carbonaceous material, and aerosol water. Since water is the major species distributed between the gas and aerosol phases, the interrelation between water and electrolytic mass is explored. It is shown that aerosol water is significantly correlated with electrolyte mass. Calculated aerosol ionic strengths lie in the region where the relative humidity/ionic strength relation is most sensitive, thereby suggesting the importance of relative-humidity monitoring during aerosol sampling.

Introduction

The urban aerosol consists in general of a complex mixture of ionic salts, metal oxides, glasses, carbonaceous material, and water. Partitioning the aerosol into groups of materials with similar physical and thermodynamic properties can simplify the interpretation of experimental data and facilitate theoretical analysis. The main objective of this paper is to develop methods for obtaining an accurate overall aerosol mass balance from the least number of measured quantities.

The urban aerosol usually exhibits a bimodal volume distribution (see Figure 1). The fine-particle mode generally results from gas-to-particle conversion, whereas the coarse-particle mode arises from mechanically generated particles. The coarse mode is usually basic since the particles are formed from basic materials such as soil, cement, and fly ash. The fine mode can be neutral or acidic depending on the relative degree of neutralization of acidic material. In the eastern United States, the fine-particle mode in the urban aerosol generally dominates the total mass, so that the net aerosol pH is likely to be acidic, whereas Western aerosol has a greater tendency to be basic (*1, 3, 4*). Because the nature of the atmospheric aerosol depends strongly on its chemical speciation, it is important to be able to estimate its chemical composition based on measurements of elemental composition.

The atmospheric aerosol can be considered to consist of five major classes of constituents: ionic solids, electrolytes (dissolved ionic species), carbonaceous material, metal oxides and glasses, and water. An equation expressing this relation is

$$\mathrm{TSP} = \sum_i \sum_j [\mathrm{M_iO_j}] + \sum_i [\mathrm{E_i}] + \sum_i [\mathrm{CM_i}] + \sum_i [\mathrm{I_i}] + [\mathrm{H_2O}] \qquad (1)$$

where TSP = total suspended particulate matter (μg m^{-3}), $[M_iO_j]$ = mass concentration of metal oxide or glass (μg m^{-3}), $[E_i]$ = mass concentration of electrolyte i (μg m^{-3}), $[CM_i]$ = mass concentration of carbonaceous material i (μg m^{-3}), $[I_i]$ = mass concentration of ionic solid i (μg m^{-3}), and $[H_2O]$ = aerosol water concentration (μg m^{-3}). Electrolytes are dissociating ionic substances dissolved in water, whereas ionic solids are undissolved electrolytic material. Carbonaceous material refers to carbon-containing species, present as elemental carbon or organic or inorganic compounds. Metal oxides and glasses refer to oxidized elemental species, such as those present in soil and cement dust and fly ash. The water content refers to "free" water unassociated with hydrated salts.

The object of this paper is to show that, by making assumptions about each term on the right-hand side of eq 1, one can calculate the total suspended particulate mass concentration on the basis of conventional aerosol measurements.

From an accurate aerosol mass accounting, several important issues can be explored: (1) the possibility of biased total-mass measurements through alteration of the aerosol between sampling and analysis, (2) the relation between measured electrolyte mass-to-water ratios and solubilities of atmospherically significant electrolytes, (3) the aerosol ionic strength and possible dependence of aerosol water content on the prevailing relative humidity, (4) the net aerosol pH, and (5) the relative importance of different aerosol fractions—electrolytic, metal oxide and glass, carbonaceous, and aqueous—to the total aerosol mass and the possible interrelation between different fractions. Each of these issues will be evaluated and discussed with particular reference to the Los Angeles aerosol.

0013-936X/81/0915-0671$01.25/0

ACHEX

One of the most detailed urban aerosol studies involving chemical analysis was the California Aerosol Characterization Experiment (ACHEX) (*5*). Ambient atmospheric aerosol was deposited on high-volume filters (Whatman 41) and analyzed for many chemical species. In addition, β-gauge, waterometer, and total-filter (47-mm Gelman GA-1 and Gelman A) measurements were performed. During some sampling periods, the aerosol carbonaceous material was analyzed (*6*). From the ACHEX data, 6 days are chosen for individual mass-balance analyses. More sampling periods would have been desirable, but these days were the only ones in which the aerosol was chemically analyzed for the major inorganic species, water, and carbonaceous material, in addition to continuous total-mass measurements. Even for these 6 days, the aerosol water content was not measured throughout the high-volume-filter sampling period. In Table I the sampling times and locations are summarized. Only at West Covina, CA (TC), did the aerosol water concentration and high-volume-filter sampling times totally overlap. Since the waterometer measurements overlapped the majority of the high-volume sampling period, it will be assumed that the time-averaged aerosol water concentration over its sampling time typifies the time-averaged aerosol water concentration over the total high-volume-filter sampling period.

The ACHEX ambient atmospheric aerosol high-volume-filter samples were analyzed for many chemical species. When only the major species, SO_4, Cl, Br, NO_3, NH_4, Na, K, Ca, Mg, Al, Si, and Pb, were considered, greater than 90% of the measured moles, excluding water and carbonaceous material, were accounted for. Therefore, the major species will only be considered in this study. Equation 1 will be modified as

$$\mathrm{TSP} = \sum_i \sum_j [M_iO_j] + \sum_i [E_i] + \sum_i [CM_i] + \sum_i [I_i] + [H_2O] + \sum_i [N_i] \quad (2)$$

where $[N_i]$ is the concentration of minor specie i ($\mu g\ m^{-3}$). In Table II the sum of the minor species for the ACHEX data is listed. We see that this term is less than 1% of the total for the 6 days.

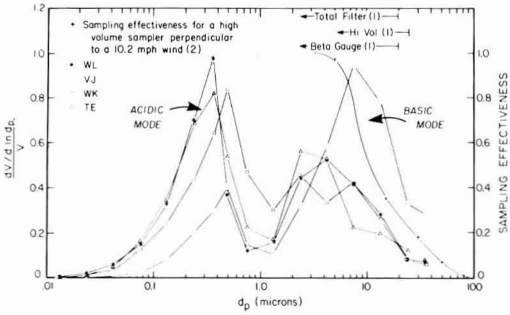


Figure 1. Time-averaged normalized aerosol volume distributions and sampler upper effective size limit (*1*, *2*, *5*). (See Table I for aerosol volume distribution sample code definition.)

A basic object of this paper is to attempt to reconcile TSP measurements with eq 2 by studying the means of estimating the contributions of each of the terms on the right-hand side of eq 2. Although we focus on the ACHEX data, the techniques to be discussed will have general applicability. To evaluate the terms on the right-hand side of eq 2 other than $\Sigma[N_i]$, one must make assumptions about the chemical form of the different species. Each term and the assumptions needed in evaluating each will now be discussed. Then, the right-hand side of eq 2 will be evaluated theoretically and compared with the total suspended particulate measurements from ACHEX.

Aerosol Components

Ionic Solids. Measurements of ionic-solid concentrations present difficult problems. In the measurement of the ion concentration in an aerosol, the filter is washed with a solvent and the ion concentration in the solvent is measured. Using this procedure, it is impossible to tell whether the ion was present in an ionic solid or an aqueous solution. Indirectly, the presence of ionic solids can be inferred. If the ambient relative humidity is less than the deliquescent humidity of the ionic solid, then it can be assumed that the salt is present as a solid. An additional check can be invoked if the solid is volatile, for example, NH_4NO_3 (*7*). The gas-phase concentrations of the precursors can be measured along with the temperature, and, if the calculated equilibrium coefficient matches the theoretical equilibrium coefficient for the ionic solid, it is assumed that the ionic solid is present. Both indirect methods fail if solid or supersaturated solutions are present.

For our analysis, it will be assumed that the ionic-solid concentration is zero. If the calculated ionic strength of the electrolytic aerosol solution is unreasonably high, then a correction must be made for the presence of ionic solids. For the mass accounting, it is immaterial whether the ionic-solid material is treated as an ionic solid or an electrolyte.

Metal Oxides and Glasses. The major elements possibly occurring in the form of oxides and glasses are Al, Ca, Fe, Si, Mg, Pb, K, and Na. When one follows the approach of Macias et al. (*8*), the chemical form of these elements can be assigned (see Table III). The majority of the oxides listed in Table III are known to be formed in combustion processes (*9*, *10*). Additionally, Biggins et al. (*11*) have identified Fe_2O_3, Al_2O_3, and

Table I. ACHEX Sampling Time and Location Summary (*5*)[a]

site	sample code	date	high-volume (HVM) sampling period	total-filter (TF, TV) sampling period	β-gauge ($\bar{\beta}$) sampling period	waterometer (H_2O) sampling period
Dominguez Hills, CA	WK	10/4–10/5/73	2100–2105	2100–2100	2100–2100	2115–1515
Dominguez Hills, CA	WL	10/10–10/11/73	2100–2100	2100–2100	2100–2100	0000–1800
Rubidoux, CA	VJ	9/24–9/25/73	2300–1802	2300–1801	2300–1900	0400–1900
West Covina, CA	TC	7/24–7/25/73	2320–1605	2300–1600	2300–1600	2300–1600
West Covina, CA	TD	7/25–7/26/73	0500–1826	0500–1800	0500–1600	0445–1545
West Covina, CA	TE	8/8–8/9/73	2100–2100	2100–2100	2100–1800	2200–1400

[a] HVM = total mass from Whatman 41 8 × 10 in. high-volume filter ($\mu g\ m^{-3}$). $\overline{TF}$ = time-averaged total mass from Gelman GA-1, 47-mm filters ($\mu g\ m^{-3}$). $\overline{TV}$ = time-averaged total mass from Gelman A, 47-mm filters ($\mu g\ m^{-3}$). $\bar{\beta}$ = time-averaged total mass from β gauge ($\mu g\ m^{-3}$). $\overline{H_2O}$ = time-averaged total water concentration from waterometer ($\mu g\ m^{-3}$).

Table II. Summary of Measured and Calculated Los Angeles Aerosol Concentrations (*5*) [a]

	metal oxide and glass concn, $\mu g\ m^{-3}$							
sample	$[Al_2O_3]$	$[Fe_2O_3]$	$[SiO_2]$	[PbO]	[CaO]	[MgO]	$[K_2O]$	$[Na_2O]$
WK	4.9	2.2	14.3	1.2	1.8	2.6	0.7	5.5
WL	3.8	2.8	13.4	4.0	2.4	1.8	0.7	3.0
VJ	8.6	5.9	28.5	0.8	4.1	1.9	1.7	1.5
TC	8.2	5.2	27.4	4.0	3.4	3.0	1.4	5.3
TD	6.4	3.7	19.8	3.2	2.8	1.8	1.0	3.9
TE	4.7	2.6	16.5	2.2	1.9	1.9	0.9	3.4

	electrolyte concn, $\mu g\ m^{-3}$												
sample	[Cl]	$[NO_3]$	[Br]	$[NH_4]$	[Na]	$[SO_4]$	[Pb]	[Ca]	[K]	[Mg]	[H]	[H]′	[OH]′
WK	0.3	0.9	0.2	6.7	4.1	31.4	1.1	1.3	0.6	1.6	0.3		1.3
WL	1.2	7.3	1.2	3.1	2.2	4.2	3.8	1.7	0.6	1.1	0.1		3.8
VJ	0.7	11.8	0.1	4.7	1.1	2.0	0.7	2.9	1.5	1.1	0.2		2.3
TC	0.6	9.9	0.7	9.5	3.9	26.3	3.8	2.4	1.2	1.8	0.5	0.1	
TD	0.9	12.0	0.5	8.1	2.9	16.6	2.9	2.0	0.8	1.1	0.4	0.1	
TE	0.7	7.2	0.4	3.2	2.5	6.5	2.1	1.4	0.7	1.2	0.2		1.5

	summations, $\mu g\ m^{-3}$							
sample	$\Sigma_i\Sigma_j[M_iO_j]$	$\Sigma_i\Sigma_j[M_iO_j]'$	$\Sigma_i[M_i]$	$\Sigma_i[E_i]$	$\Sigma_i[E_i]'$	$\Sigma_i[N_i]$	$\Sigma_i[CM_i]$	$[H_2O]$
WK	33.2	21.4	11.4	39.8	49.5	0.7	18.7	54.2
WL	31.9	20.0	10.8	17.1	30.2	0.9	16.4	24.9
VJ	52.9	43.0	23.5	19.5	28.9	0.7	8.0	34.5
TC	55.9	40.8	22.0	47.5	60.2	1.4	29.8	75.2
TD	42.6	29.9	16.1	38.5	47.9	1.1	11.7	74.4
TE	34.1	23.8	12.7	18.2	27.4	0.8	10.8	29.7

[a] [A] = mass concentration of specie A. [H] = hydrogen concentration calculated from electroneutrality when $x_{Pb} = 0$, $x_{Ca} = 0$, $x_{Na} = 0$, $x_K = 0$, and $x_{Mg} = 0$. [H]′ or [OH]′ = hydrogen or hydroxyl ion concentration when $x_{Pb} = 1$, $x_{Ca} = 1$, $x_{Na} = 1$, $x_K = 1$, and $x_{Mg} = 1$. $\Sigma_i\Sigma_j[M_iO_j]$ = sum of metal oxide and glass concentrations when $x_{Pb} = 0$, $x_{Ca} = 0$, $x_{Na} = 0$, $x_K = 0$, and $x_{Mg} = 0$. $\Sigma_i\Sigma_j[M_iO_j]'$ = sum of metal oxide and glass concentrations when $x_{Pb} = 1$, $x_{Ca} = 1$, $x_{Na} = 1$, $x_K = 1$, and $x_{Mg} = 1$. $\Sigma_i[M_i]$ = sum of metal oxide and glass forming elements assuming no oxygen is present and $x_{Pb} = 1$, $x_{Ca} = 1$, $x_{Na} = 1$, $x_K = 1$, and $x_{Mg} = 1$. $\Sigma_i[E_i]$ = sum of electrolyte concentrations when $x_{Pb} = 0$, $x_{Ca} = 0$, $x_{Na} = 0$, $x_K = 0$, and $x_{Mg} = 0$. $\Sigma_i[E_i]'$ = sum of electrolyte concentrations when $x_{Pb} = 1$, $x_{Ca} = 1$, $x_{Na} = 1$, $x_k = 1$, and $x_{Mg} = 1$. $\Sigma_i[N_i]$ = sum of minor species concentrations. $\Sigma_i[CM_i]$ = sum of carbonaceous material.

Table III. Aerosol Metal Oxides

element	oxide form	element	oxide form
Al	Al_2O_3	Mg	MgO [a]
Ca	CaO [a]	Pb	PbO
Fe	Fe_2O_3	Na	Na_2O [a]
Si	SiO_2	K	K_2O [a]

[a] Assumed.

SiO_2 in roadside aerosol. The presence of CaO, MgO, and PbO can be examined from considerations of chemical equilibrium. Equilibrium constants for the reactions of CaO, MgO, and PbO with water are given in Table IV. The equilibrium analysis indicates that CaO and MgO should readily react to form $Ca(OH)_2$ and $Mg(OH)_2$, whereas the PbO should not. Na_2O should readily react with water to form NaOH, and K_2O should react similarly to CaO and MgO to form KOH. Biggins et al. (*11*) have measured Pb_3O_4 in roadside dust in addition to elemental lead, lead sulfates, lead carbonates, and lead hydroxides. The assumed form of lead, e.g., Pb_3O_4, PbO, or Pb, will not substantially affect the mass balance because of the high molecular weight of lead. We will assume lead to exist as PbO. Reiter et al. (*13*) have measured insoluble CaO, in disagreement with the pure thermochemical analysis. $Ca(OH)_2$ has a solubility similar to that of CaO, as shown in Table V. Thus, the insoluble CaO reported by Reiter et al. (*13*) could be $Ca(OH)_2$. MgO, Na_2O, and K_2O have not apparently been identified in tropospheric aerosol.

Table IV. Equilibrium Analysis of Hydroxide Formation

free energy of formation data (*12*)

species	$\Delta G°_{298}$, kcal/(g-mol)	species	$\Delta G°_{298}$, kcal/(g-mol)
CaO(s)	−144.4	PbO(s)	−45.25,[a] −45.05[b]
$Ca(OH)_2(s)$	−214.33	$Pb(OH)_2(s)$	−100.6
MgO(s)	−136.13	$H_2O(g)$	−54.64
$Mg(OH)_2(s)$	−199.27		

oxide reactions with water

reaction	$\Delta G°_{298}$, kcal/(g-mol)	P_{H_2O}, atm
$CaO(s) + H_2O(g) \rightleftarrows Ca(OH)_2(s)$	−15.29	6.0×10^{-12}
$MgO(s) + H_2O(g) \rightleftarrows Mg(OH)_2(s)$	−8.5	6.0×10^{-7}
$PbO(s) + H_2O(g) \rightleftarrows Pb(OH)_2(s)$	−0.71,[a] −0.91[b]	0.3,[a] 0.2[b]

[a] Red form. [b] Yellow form.

MgO, Na_2O, K_2O, and CaO could exist in the atmospheric aerosol in solid solutions with SiO_2, Al_2O_3, and Fe_2O_3 in soil dust or rock flour. The ability to remove these elements by forming hydroxides depends on particle size, rock structure, and the acidic nature of the leaching agent. Goldich (*14*) measured the weathering loss in sedimentary rocks and obtained the following ordering: Na_2O, CaO, MgO, K_2O, SiO_2, Al_2O_3, and iron, where Na_2O is the easiest to remove and iron is the hardest. This ordering supports the preceding thermodynamic and qualitative discussion. An additional calculation supporting the weathering ordering is obtained by using

Table V. Solubility of Inorganic Salts

metal oxides and glasses	solubility, [a] g/100 g of H_2O	ref	metal oxides and glasses	solubility, [a] g/100 g of H_2O	ref
SiO_2	insoluble in H_2O	*12*	Na_2O	decomposes	*12*
Al_2O_3	insoluble in H_2O	*12*	MgO	0.0086^{30}	*12*
Fe_2O_3	insoluble in H_2O	*12*	PbO	0.0023^{22}	*12*
CaO	0.131^{10}, decomposes	*12*	K_2O	very soluble	*12*
electrolytes	**solubility, [a] g/100 g of H_2O**	**ref**	**electrolytes**	**solubility, [a] g/100 g of H_2O**	**ref**
NaOH	113.2^{25}	*27*	NaCl	35.91^{25}	*27*
KOH	112^{20}	*28*	KCl	34.7^{20}	*12*
NH_4OH	soluble	*12*	NH_4Cl	39.5^{25}	*27*
$Mg(OH)_2$	0.0009^{18}	*12*	$MgCl_2$	54.25^{20}	*12*
$Ca(OH)_2$	0.162^{20}	*27*	$CaCl_2$	81.9^{25}	*27*
$Pb(OH)_2$	0.0155^{20}	*12*	$PbCl_2$	1.08^{25}	*27*
$NaNO_3$	91.79^{25}	*27*	NH_4HSO_4	288^{25}	*29*
KNO_3	31.6^{20}	*28*	$MgSO_4$	44.5^{20}	*12*
NH_4NO_3	192^{20}	*12*	$CaSO_4$	0.298^{20}	*28*
$Mg(NO_3)_2$	128.2^{20}	*27*	$PbSO_4$	0.00425^{25}	*12*
$Ca(NO_3)_2$	138^{25}	*27*	H_2SO_4	∞	*12*
$Pb(NO_3)_2$	59.6^{25}	*27*	HNO_3	∞	*12*
Na_2SO_4	27.8^{25}	*27*	HCl	69.4^{25}	*18*
$NaHSO_4$	28.6^{25}	*12*	HBr	198^{20}	*28*
K_2SO_4	12^{25}	*12*	NaBr	90.5^{20}	*28*
$KHSO_4$	51.4^{20}	*28*	KBr	65.2^{20}	*28*
$(NH_4)_2SO_4$	76.9^{25}	*27*	NH_4Br	97^{25}	*12*
$MgBr_2$	101.5^{20}	*12*	$PbBr_2$	0.85^{20}	*28*
$CaBr_2$	142^{20}	*12*			

[a] For example, 0.131^{10} means a solubility of 0.131 g/100 g of H_2O at 10 °C.

Clarke and Washington's (*15*) average composition of igneous rocks. Using the measured aerosol SiO_2 concentrations and the appropriate metal oxide-to-SiO_2 ratios calculated from Clarke and Washington's analysis, one can calculate the amounts of CaO, Na_2O, MgO, and K_2O. The calculated K_2O concentrations agree within 6% of measured K_2O concentrations, whereas the calculated and measured CaO, MgO, and Na_2O concentrations differ by greater than 40%. Thus, it seems that K_2O originates from soil dust and that the CaO, MgO, and the Na_2O come from preferentially enriched sources, i.e., sea salt, cement dust, or fly ash. In light of the possibility that Pb, Ca, Na, K, and Mg are in either the glass and metal oxide or electrolytic phases, the metal oxide and glasses mass balance can be written as

$$\sum_i \sum_j [M_iO_j] = (1 - x_{Pb}) \frac{M_{PbO}}{M_{Pb}} [Pb] + (1 - x_{Ca}) \frac{M_{CaO}}{M_{Ca}} [Ca] + (1 - x_{Mg}) \frac{M_{MgO}}{M_{Mg}} [Mg] + (1 - x_K) \frac{M_{K_2O}}{M_K} [K] + (1 - x_{Na}) \frac{M_{Na_2O}}{M_{Na}} [Na] + \frac{M_{Fe_2O_3}}{2M_{Fe}} [Fe] + \frac{M_{Al_2O_3}}{2M_{Al}} [Al] + \frac{M_{SiO_2}}{M_{Si}} [Si] \qquad (3)$$

where M_A is the molecular weight of species A and x_{Pb}, x_{Ca}, x_K, x_{Na}, and x_{Mg} are the fractions of Pb, Ca, K, Na, and Mg, respectively, in the ionic-solid or electrolytic form. Determination of x_{Pb}, x_{Ca}, x_K, x_{Na}, and x_{Mg} could be based on a chemical-source balance. Even if the source signature is known, determination of the chemical form may be difficult. For example, Pb resulting from automobile exhaust may either be electrolytic or not depending on the fraction of Pb emitted as PbO or Pb vs. halogenated forms. In our analysis we will examine the two extremes: $x_{Pb} = x_{Ca} = x_K = x_{Na} = x_{Mg} = 1$, and $x_{Pb} = x_{Ca} = x_K = x_{Na} = x_{Mg} = 0$.

Electrolytes. An expression for the electrolyte mass of the atmospheric aerosol, i.e., ionic species dissolved in water, is

$$\sum_i [E_i] = [SO_4] + [Cl] + [NO_3] + [NH_4] + [Br] + x_{Pb}[Pb] + x_{Ca}[Ca] + x_K[K] + x_{Na}[Na] + x_{Mg}[Mg] + [H] + [OH] \qquad (4)$$

The [H] or [OH] must be calculated on the basis of electroneutrality. If the aerosol is acidic, then [OH] may be neglected and

$$[H] = M_H\{2[SO_4]/M_{SO_4} + [Cl]/M_{Cl} + [NO_3]/M_{NO_3} - [NH_4]/M_{NH_4} + [Br]/M_{Br} - x_{Na}[Na]/M_{Na} - x_K[K]/M_k - 2x_{Pb}[Pb]/M_{Pb} - 2x_{Ca}[Ca]/M_{Ca} - 2x_{Mg}[Mg]/M_{Mg}\} \qquad (5)$$

If $[H] < 0$ from eq 5, then $[OH] = -M_{OH}[H]/M_H$. Of course, eq 5 is an expression for the net acidity. Actually, the tropospheric aerosol would likely contain a mixture of acidic and basic particles (*16*).

Water. Ho et al. (*17*) have shown that the aerosol water content varies diurnally. Since the ACHEX chemical composition measurements were time-averaged, the aerosol water concentrations as measured by the waterometer were time-averaged. Since the average aerosol water concentrations were determined by integrating waterometer measurements, no assumptions were made concerning the amount of water on the filter material; i.e., the aerosol water is not assumed to be equal to the unaccounted mass on the filter as is typically done.

Carbonaceous Material. The carbonaceous fraction of the total aerosol mass must typically be estimated since carbonaceous aerosol concentration measurements are very limited. Interpretation of existing carbonaceous-material measurements is complicated by the different organic carbon extraction efficiencies of solvents and the mutual extraction of inorganic nitrates by polar solvents (*18*, *19*). Therefore, a calculation procedure must be devised that utilizes existing data to obtain values reflective of the actual carbonaceous-material loading.

Pierson and Russell (*20*) calculated for Denver a linear relation between the aerosol carbon, [C], and lead, [Pb], concentrations.

$$[\mathrm{C}] = (5.84 \pm 0.34)[\mathrm{Pb}] - 0.85 \pm 0.97\ \mu\mathrm{g\ m}^{-3} \qquad (6)$$

In Figure 2 this correlation is compared to data for aerosol lead and carbon measurements. The Los Angeles and Denver trends are similar except that, as [Pb] → 0, the Los Angeles data approach 10 μgC m^{-3}. The combined Los Angeles, San Jose, and Los Alamitos data indicate that eq 6 overpredicts the aerosol-carbon loading at high lead concentrations.

An additional correlation between total carbonaceous material and lead can be derived by utilizing data of Grosjean et al. (*23*), who reported an average noncarbon-to-carbon ratio of 0.37 in the organic aerosol fraction for 2 days in 1973 at Pasadena, CA. (The noncarbon material is nitrogen, oxygen, and hydrogen associated with carbon in organic molecules.) Thus, the total carbonaceous aerosol mass loading, $\Sigma_i[\mathrm{CM}_i]$, can be approximated by multiplying the Pierson and Russell correlation by 1.37

$$\sum_i [\mathrm{CM}_i] = (8.02 \pm 0.47)[\mathrm{Pb}] - 1.17 \pm 1.33\ \mu\mathrm{g\ m}^{-3} \qquad (7)$$

In Figure 3 this correlation is compared with ACHEX aerosol lead and carbonaceous-material estimates using the data of Appel et al. (*6*). The $\mathrm{CH_3OH{-}CHCl_3}$ extractables were corrected for the solubilization of ammonium nitrate by assuming that all of the nitrate measured was ammonium nitrate and subtracting the value obtained from the $\mathrm{CH_3OH{-}CHCl_3}$ extractables. Subsequently, the $\mathrm{CH_3OH{-}CHCl_3}$-extracted carbon value was subtracted from the total $\mathrm{CH_3OH{-}CHCl_3}$-extractable mass. This procedure led to negative mass concentrations in 7 out of 11 cases. To check the extreme case, we subtracted the sum of the nitrate and $\mathrm{CH_3OH{-}CHCl_3}$-extractable carbon loadings from the total $\mathrm{CH_3OH{-}CHCl_3}$-extractable mass. This procedure led to negative values in 3 out of 11 cases. Therefore, either all of the nitrate must not have solubilized in the $\mathrm{CH_3OH{-}CHCl_3}$ solution or some measurement error must have been present. Thus, the points plotted in Figure 3 represent the minimum aerosol carbonaceous material. As can be seen, the Los Angeles data are not well correlated with eq 7.

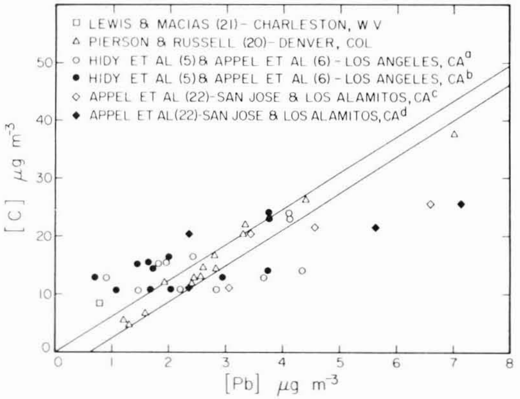


Figure 2. Relation between aerosol carbon and aerosol lead: (a) Pb from Whatman 41 high-volume filter; (b) time-averaged Pb from 47-mm Gelman GA-1 filters; (c) Pb from 47-mm Fluoropore filter; (d) Pb from Spectrograde high-volume filter. Solid lines: minimum and maximum of Pierson and Russell (*20*) correlation.

The correction for aerosol nitrate in the $\mathrm{CH_3OH{-}CHCl_3}$-extractable mass is significant and can be shown by the following approximation:

$$\begin{aligned}[\mathrm{NO_3}] = {} & (M_{\mathrm{NO_3}}/M_{\mathrm{NH_4NO_3}}) \times \\ & [\mathrm{CH_3OH{-}CHCl_3}\text{-extractable mass}] \times \\ & (1 - [\text{carbon fraction}][\text{carbon + noncarbon fraction}]/ \\ & [\text{carbon fraction}])\end{aligned}$$

$$[\mathrm{NO_3}] = {}^{62}/_{80}\ [\mathrm{CH_3OH{-}CHCl_3}\text{-extractable mass}] \times (1 - 1.37[\text{carbon fraction}]) \qquad (8)$$

assuming nitrate is present as ammonium nitrate and that the $\mathrm{CH_3OH{-}CHCl_3}$-extractable mass has the same noncarbon-to-carbon ratio as that measured by Grosjean et al. (*23*) for the organic aerosol fraction in Pasadena. The total noncarbon-to-carbon ratio of Grosjean is similar to those measured by Cukor et al. (*24*) and Ciacco et al. (*25*) in New York City. Based on their data for chloroform, 2-propanol, and methanol extractions, calculated noncarbon-to-carbon ratios varied between 1.36 and 1.49. Therefore, the total organic noncarbon-to-carbon ratio of Grosjean should approximate that in the $\mathrm{CH_3OH{-}CHCl_3}$-extractable mass. In Figure 4 nitrate

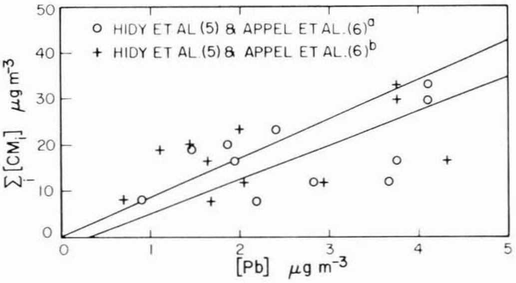


Figure 3. Relation between aerosol carbonaceous material and aerosol lead: (a) Pb from Whatman 41 high-volume filter; (b) time-averaged Pb from 47-mm Gelman GA-1 filters.

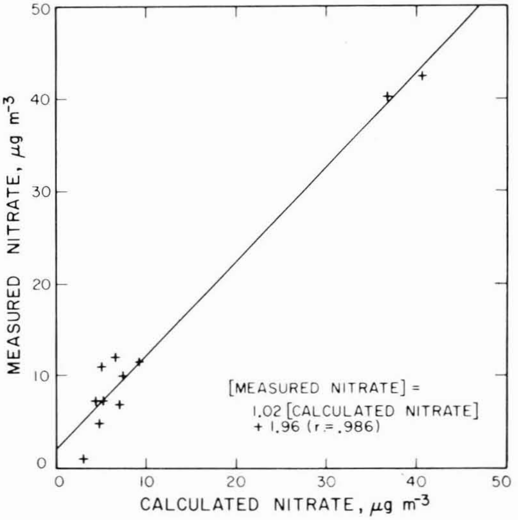


Figure 4. Measured nitrate vs. calculated nitrate. Solid line: linear least-squares fit to data.

values calculated from eq 8 are compared with the measured values of Hidy et al. (*5*).

Mueller et al. (*26*) measured aerosol carbonate carbon in Pasadena, CA, and determined it to be consistently less than 5% of the total carbon present. In light of the previously discussed inaccuracies, the carbonate fraction of the aerosol will be assumed to be negligible.

In summary, the total carbonaceous aerosol concentration can be estimated from the sum of the benzene- and CH_3OH–$CHCl_3$-extracted mass minus nitrate as ammonium nitrate plus the estimate for the maximum elemental carbon aerosol loading of Appel et al. (*6*). The carbonaceous aerosol concentration as calculated by the above procedure should generally reflect the atmospheric carbonaceous-material loading and is the best obtainable using the existing data.

Aerosol Mass Accounting

Table II presents a summary of the data used for the mass accounting calculation. The calculated and measured total-mass data are summarized in Table VI. In Table VI, M_1 is the total mass calculated by assuming $x_{Pb} = 0, x_{Ca} = 0, x_K = 0, x_{Na} = 0$, and $x_{Mg} = 0$, and M_2 is that when $x_{Pb} = 1, x_{Ca} = 1, x_K = 1, x_{Na} = 1$, and $x_{Mg} = 1$. M_3 is the calculated total mass assuming that the total mass is the sum of the measured species. Thus, no assumptions are made concerning chemical speciation in the calculation of M_3.

All three mass calculation procedures (M_1, M_2, M_3) yield similar values but disagree with the total-mass concentrations calculated from the β gauge, total filters, and high-volume filters. To evaluate the trend among these seven variables, M_1, M_2, M_3, $\overline{\beta}$, $\overline{TF}$, $\overline{TV}$, and HVM, we performed a least-squares analysis between all pairs (see Table VII). (VJ was omitted from the least-squares analysis since a $\overline{TV}$ measurement was not performed.) All measured and calculated total suspended mass techniques correlated significantly. A notable feature seen in the results in Table VII is that the β-gauge measurements are consistently lower than the other calculated and measured total-mass concentrations. (Possibly the instrument gain was set too low.)

The mass ratio, S, of electrolytic material to water can be calculated by

$$S = \left(\sum_i [E_i]/\overline{H_2O}\right) \times 100 \text{ g}/100 \text{ g of } H_2O \qquad (9)$$

Calculated values of S are listed in Table VIII for the two extreme cases of the distribution of Pb, Ca, K, Na, and Mg between the metal oxide–glass subset and the electrolyte subset. The values calculated for S and S' are within the typical range of solubilities of electrolyte materials listed in Table V. Since the calculated mass ratios vary between 50 and 125 g/100 g of H_2O, it can be inferred that the electrolyte portion of the atmospheric aerosol at these sampling locations is dominated by soluble sulfates, nitrates, and chlorides. The chemical analysis summary shows the dominance of nitrate and sulfate (Table II). Ochs and Gatz (*30*) recently measured the fraction of water-soluble material in particles of >4.6-μm radius as ~0.3. Using data from Tables II and VI, we compute the soluble fraction in the Los Angeles aerosol to lie between 0.15 and 0.35. Older Los Angeles aerosol data of Cadle (*31*) list water and volatile organics as 0.15 of the total aerosol mass, with a water-soluble fraction of 0.15.

The ionic strength of the aerosol solution can be calculated by

$$I = (1000/2\overline{H_2O})\left(\sum_i z_i^2[E_i]/M_i\right) \qquad (10)$$

where M_i is the molecular weight and z_i is the charge of species i. Calculated values of I are listed in Table VIII for the two extreme cases of the distribution of Pb, Ca, K, Na, and Mg. The range of ionic strengths at each sampling location is compared with the ionic-strength dependence of water activity

Table VI. Calculated and Measured Total Mass (μg m^{-3}) (*5*)

sample	M_1	M_2	M_3	$\overline{\beta}$	$\overline{TF}$	$\overline{TV}$	HVM
WK	146.6	144.5	133.8	105.7	113.5	127.7	148
WL	91.2	92.4	82.4	77.7	101.5	107.5	114
VJ	115.6	115.1	96.0	85.8	160.9		211
TC	209.8	207.4	192.0	173.1	210.9	215.4	241
TD	168.3	165.0	153.9	137.8	176.9	176.0	194
TE	93.6	92.5	82.3	87.1	101.0	113.4	123

Table VII. Least-Squares Analysis of Measured and Calculated Total Mass

	M_1	M_2	M_3	$\overline{\beta}$	$\overline{TF}$	$\overline{TV}$	least squares parameters [a]
HVM	0.974	0.975	0.972	0.999	0.986	0.997	*r*
	0.929	0.905	0.867	0.738	0.933	0.870	*m*
	−10.4	−8.1	−13.3	−4.8	−12.3	5.4	*b*
$\overline{\beta}$	0.976	0.977	0.974	1.00	0.981	0.995	*r*
	1.26	1.23	1.18	1.00	1.26	1.18	*m*
	−4.6	−2.4	−7.9	0.0	−5.5	−11.4	*b*
$\overline{TF}$	0.935	0.936	0.933	0.981	1.00	0.995	*r*
	0.941	0.918	0.879	0.766	1.00	0.918	*m*
	9.4	11.1	5.1	8.5	0.0	18.9	*b*
$\overline{TV}$	0.955	0.956	0.952	0.995	0.995	1.00	*r*
	1.04	1.02	0.974	0.842	1.08	1.00	*m*
	−12.5	−10.2	−15.2	−8.3	−19.0	0.0	*b*

[a] *r* = correlation coefficient; *m* = slope; *b* = intercept.

Table VIII. Calculated Electrolyte-to-Water Mass Ratios and Ionic Strengths for Los Angeles Aerosol [a]

sample	*S*	*S'*	*I*	*I'*
WK	73.4	91.3	18.6	22.2
WL	68.7	121.3	14.2	25.9
VJ	56.5	83.8	8.0	16.5
TC	63.2	80.1	13.4	15.4
TD	51.7	64.4	10.0	11.5
TE	61.3	92.3	11.6	18.3

[a] S = calculated mass ratio when $x_{Pb} = 0$, $x_{Ca} = 0$, $x_{Na} = 0$, $x_K = 0$, and $x_{Mg} = 0$, g/100 g of H_2O. S' = calculated mass ratio when $x_{Pb} = 1$, $x_{Ca} = 1$, $x_{Na} = 1$, $x_K = 1$, and $x_{Mg} = 1$, g/100 g of H_2O. I = ionic strength when $x_{Pb} = 0$, $x_{Ca} = 0$, $x_{Na} = 0$, $x_K = 0$, and $x_{Mg} = 0$, mol/1000 g of H_2O. I' = ionic strength when $x_{Pb} = 1$, $x_{Ca} = 1$, $x_{Na} = 1$, $x_K = 1$, and $x_{Mg} = 1$, mol/1000 g of H_2O.

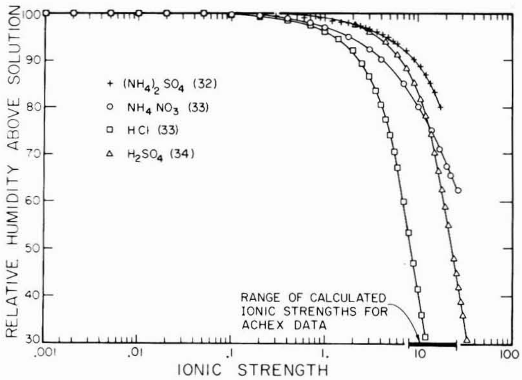


Figure 5. Water activities for typical electrolytes as a function of ionic strength (T = 25 °C).

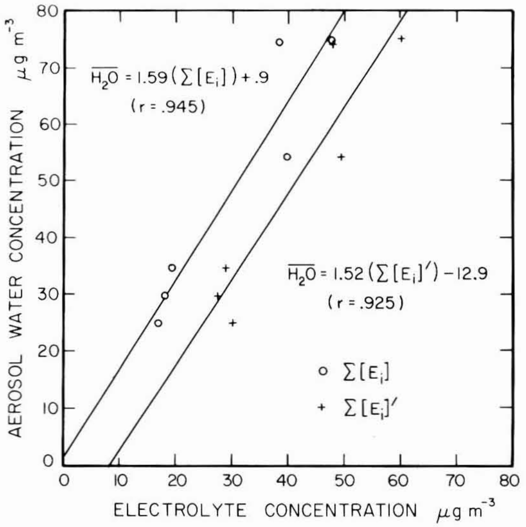


Figure 6. Aerosol water vs. electrolyte concentration. Solid lines: linear least-squares fits to data.

for several electrolytes at 25 °C in Figure 5. All of the calculated ionic strengths are in the region where the relative humidity–ionic strength variation is strongest, indicating the importance of the prevailing relative humidity and the aerosol chemical nature in determining the atmospheric aerosol water content.

The net aerosol pH was calculated for both extreme distributions of Pb, Ca, K, Na, and Mg (see Table II). Samples TC and TD were the only ones that were definitely acidic, whereas WK, WL, VJ, and TE could be basic or acidic. Although Liljestrand (*4*) measured net basic aerosol pHs in Los Angeles, his measurements and those reported in ACHEX (*5*) were taken by using quite different experimental techniques that might have different cutoff diameters. Since the coarse mode is generally basic and the fine mode acidic, a lower cutoff would lead to a lower net pH. Combining the coarse and fine modes can also lead to sampling errors (*35*).

The metal oxide–glass, electrolyte, carbonaceous, and water fractions are of equal importance in the total aerosol mass (see Table II). The dominance of different fractions at different locations and sampling periods is evident. In sample VJ the metal oxide–glass fraction was largest, and in WK, TC, and TD the water fraction predominated. In TE and WL the aerosol was fairly evenly distributed among the metal oxide–glass, electrolytic, and water fractions.

Finally, the electrolytic mass and the aerosol water concentrations are well correlated, indicating the presence of electrolytic solutions (see Figure 6).

Implications for Measurement Techniques

Several important experimental questions need to be considered when comparing the total suspended mass measurements obtained by using glass-fiber filters, cellulose filters, cellulose triacetate filters, and the β gauge: (1) Does the β gauge measure only suspended particles and not exhibit a relative-humidity interference? (2) Do filtration-efficiency differences have a significant influence on total-mass measurements? (3) Are the samplers' upper and lower aerosol size cutoffs similar? (4) What effect does equilibrating the filters to 55% relative humidity at 25 °C have on the water adsorbed or absorbed on the filter material and the water contained in the aerosol? (5) How important is filter artifact in prejudicing aerosol nitrate and sulfate measurements?

Landis (*36*) has reported a large positive interference in β-gauge measurements at high relative humidity (>75%). Data of Husar (*37*) and Yamamoto (*38*) do not show this interference but show the thermodynamically predicted absorption of water on filter-deposited NaCl and $(NH_4)_2SO_4$ aerosols as the relative humidity is increased above the deliquescence point. Additionally, ACHEX data using the β gauge do not show instrument saturation during times of high relative humidity as would be predicted by Landis' measurements. Landis' Figure 3 shows that β-gauge measurements are consistently lower than or equal to the total filter measurements. If the instrument responded to high relative humidity and had a response greater than the manufacturer's calibration for atmospheric aerosol, the filter-sample data should be less than the β-gauge measurements. Since the measured effect is the opposite of the calibration results, some inconsistency exists. Therefore, the β-gauge measurements were not considered in error and have been compared here to other mass measurement techniques.

Shown in Figure 7 is the initial filtration efficiencies of different filter materials vs. face velocity. The most recent data of John et al. (*39*) show that the efficiencies of Gelman GA-1 and Gelman A should be greater than 99% over the operating range of interest for a polydisperse room aerosol. Even though the data indicate higher efficiencies than those found by Appel et al. (*40*), the maximum discrepancy would account for an error of only 5%. The data for Whatman 41 filters do not agree as well with the other data in Figure 7. These differences can result from filter maturation, material construction variation, and different particle concentration measurement techniques. Since the filtration efficiency curves for Whatman

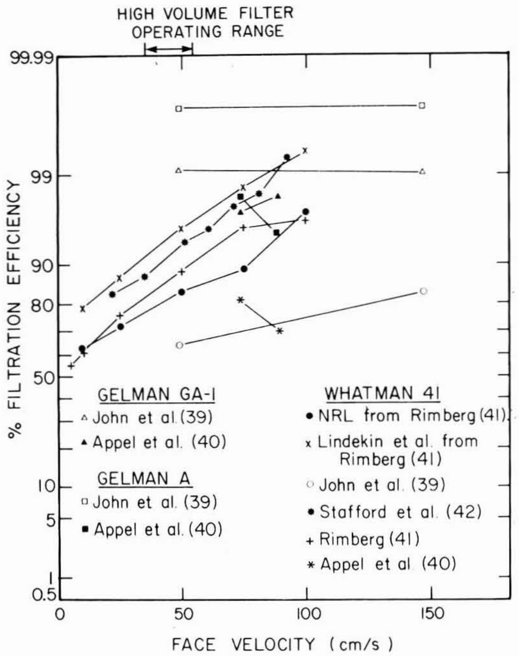


Figure 7. Filtration efficiencies for Whatman 41, Gelman A, and Gelman GA-1.

41 are lower than the curves for Gelman GA-1 and Gelman A, the effect of filtration loss must be evaluated. Lindeken et al. (*43*) and Stafford et al. (*42*) measured the increase in filter efficiency for Whatman 41 as a function of time. Using their data and making very conservative estimates, one can estimate the maximum error due to the initial filter inefficiencies as 1% for all samples. When one considers that the average standard deviation error of the three filter total suspended mass measurement techniques is 8%, initial filtration inefficiency differences cannot be the major source of error.

Shown in Figure 1 are the time-averaged normalized aerosol volume distributions for four sampling periods. Also, shown in Figure 1 are the sampler cutoffs for sampling in stagnant air (*1*). The value for the high-volume sampler is a more recent one than that reported in ACHEX (i.e., 60 μm). Wedding et al. (*2*) measured the sampling effectiveness of a high-volume sampler perpendicular to a 10.2 mi/h wind. Figure 1 shows that the presence of wind can significantly affect the fraction of the coarse mode sampled. Since the wind effect on the sampling efficiency of the total filter setup or the β gauge has not been measured, it is assumed that wind affects all samplers similarly. Thus, the ambient aerosol should not be significantly preferentially measured by any sampler.

The filters used in ACHEX were equilibrated to 55% relative humidity and 25 °C as prescribed by NASN procedures. Tierney et al. (*44*) and Demuynck (*45*) showed that glass-fiber filters lose their adsorbed or absorbed water when equilibrated to NASN conditions. Demuynck demonstrated that Whatman 41 cellulose filters irreversibly absorb water. When Demuynck's data and the ratio of filter surface areas are used, this interference would amount to 107 $\mu g\ m^{-3}$ for a 24-h high-volume filter. In Table VI, $\overline{\mathrm{HVM}}$ is consistently higher than $\overline{\mathrm{TV}}$, verifying the irreversible absorption of water by Whatman 41. The cellulose triacetate filters did not irreversibly absorb water, as seen by comparing $\overline{\mathrm{TF}}$ and $\overline{\mathrm{TV}}$ values in Table VI. Whether the filter drying process removed water from the aerosol is very important. Table II and VI show that the aerosol contains between 20 and 45% water. If the water is removed, then 20–45% of the aerosol mass is unaccountable. This fraction is unreasonably high; therefore, only the loosely held absorbed water on the filter surface is removed by the initial drying. Whether the aerosol is a supersaturated solution or more dilute cannot be determinined from existing data.

Corrections for artifact nitrate and sulfate were not performed since assigning a correction would be somewhat arbitrary with current knowledge. Maximum artifact values can be calculated from the results of Appel et al. (*22*). The maximum artifact sulfate would be ~2 $\mu g\ m^{-3}$ and nitrate would be ~26 $\mu g\ m^{-3}$ (10 ppb 24-h average $HNO_3(g)$ concentration) for Whatman 41 high-volume filters. The measured sulfate values used in this study were consistently above 2 $\mu g\ m^{-3}$, whereas the nitrate values were below 26 $\mu g\ m^{-3}$ (see Table II). Thus, the sulfate data are presumed to be more accurate than the nitrate data, but no measured values were corrected since assignment of corrections could not be quantitatively performed. Recent work by Appel et al. (*46*) indicates that positive and negative nitrate artifacts exist, making corrections even more difficult to assign.

Conclusions

The foregoing analysis demonstrates several important points concerning mass accounting, the presence of electrolytic solutions, and aerosol pH.

Mass Acccounting. A reasonably accurate mass balance for the Los Angeles aerosol has been obtained from measurements of SO_4, Cl, Br, NO_3, NH_4, Na, K, Ca, Fe, Mg, Al, Si, Pb, carbonaceous material, and aerosol water, the predominate species being SO_4, NO_3, NH_4, Si, carbonaceous material, and aerosol water. Chemical speciation was assigned, and the presence of oxygen in metal oxides and glasses was accounted for. The addition of metal oxide and glass oxygen to the mass balance did not have a significant effect on the total-mass correlations. The assignment of oxide forms to certain elements is, however, physically important, since metal oxides tend to be water insoluble. Thus, no "free" water would be associated with these oxides.

Since aerosol carbon measurements are limited, the aerosol carbon concentration typically must be estimated. The Pierson and Russell (*20*) correlation was examined and does not seem to apply to the Los Angeles aerosol data (Figure 2). In addition to quantification of the aerosol carbon concentration, determination of the associated oxygen, nitrogen, and hydrogen in the carbonaceous material is important. As indicated by Appel et al. (*6*), Grosjean (*18*), Gordon and Bryan (*19*), and this work, the CH_3OH–$CHCl_3$-extractable mass contains considerable nitrate. Thus, a correction to this measurement for dissolved inorganics would improve future mass accounting calculations.

Since certain chemical species are distributed between the gas and aerosol phases, the total aerosol mass, the aerosol water concentration, the relative humidity, and the temperature should be continuously monitored during sampling. Ideally, other volatile species that are distributed between the gas and aerosol phases should also be monitored, i.e., NH_3, HNO_3, HCl, and organics. By analyzing continuous data, one can determine the distribution of material between the gas and aerosol phases and the possibility of aerosol alteration between sampling and measurement due to volatilization, uptake of water, or displacement reactions. Since mass is reversibly distributed between the gas and aerosol phases, care must be taken when determining the total suspended particulate mass from filter samples such that the filters are equilibrated with a known relative humidity and temperature at the time of weight measurement. Ideally, filter weight measurements should be performed at several relative humidities.

Presence of Electrolyte Solutions. The calculated electrolyte-to-aerosol water mass ratios are typical of atmospherically significant electrolyte solutions near saturation (Tables V and VIII). By assigning valences to the electrolyte species, we have calculated the ionic strength. From the ionic strengths calculated and compared with typical ionic-strength dependence of water activities in binary electrolyte solutions, the electrolyte material appears to be present in highly concentrated solutions and/or ionic solids. The amount of water in the aerosol phase is very dependent on the chemical nature of the electrolytes and the prevailing relative humidity (Figure 5). Since the aerosol water and electrolyte concentrations are interdependent, a correlation between electrolyte mass and aerosol water was evaluated. The significant correlation between electrolyte mass and aerosol water highlights an important point, namely, that electrolyte material can cause greater visibility reduction per unit mass than organics or metal oxides because of hygroscopicity.

Aerosol pH. The fraction of electrolyte material for Ca, Pb, K, Na, and Mg must be determined to perform an accurate chemical mass and acidity balance. Biggins et al. (*11*) and Reiter et al. (13) recognized the importance of differentiating between water-soluble and -insoluble Pb and Ca. Depending on the assumptions of chemical speciation for Ca, Pb, K, Na, and Mg, metal oxide vs. electrolyte, the net aerosol pH may be basic or acidic (Table II). Knowing the net aerosol pH would improve the aerosol mass balance because an additional variable would exist to check chemical speciation assumptions or measurements. Recent aerosol data include aerosol pH measurements but do not have detailed chemical analyses and aerosol water measurements to perform a mass balance (*3, 47*). An additional factor important to determining the net aerosol pH is the upper cutoff of the aerosol sampler. This point is graphically illustrated by Figure 1.

Acknowledgment

We extend appreciation to Bruce Appel for his helpful comments.

Literature Cited

(1) National Research Council, Subcommittee on Airborne Particles "Airborne Particles"; University Park Press: Baltimore, MD, 1979; Chapter 1.

(2) Wedding, J. B.; McFarland, A. R.; Cermack, J. E. *Environ. Sci. Technol.* **1977,** *11*, 387.

(3) Tanner, R. L.; Cederwall, R.; Garber, R.; Leahy, D.; Marlow, W.; Meyers, R.; Phillips, M.; Newman, L. *Atmos. Environ.* **1977,** *11*, 955.

(4) Liljestrand, H. M. Ph.D. Thesis, California Institute of Technology, Pasadena, CA, 1980.

(5) Hidy, G. M., et al. "Characterization of Aerosols in California", Rockwell International Report, California Air Resources Board, ARB Contract No. 358, 1975.

(6) Appel, B. R.; Colodny, P.; Wesolowski, J. J. *Environ. Sci. Technol.* **1976,** *10*, 359.

(7) Stelson, A. W.; Friedlander, S. K.; Seinfeld, J. H. *Atmos. Environ.* **1979,** *13*, 369.

(8) Macias, E. S.; Blumenthal, D. L.; Anderson, J. S.; Cantrell, B. K. "Size and Composition of Visibility-Reducing Aerosols in Southwestern Plumes", presented at the Conference on Aerosols: Anthropogenic and Natural-Sources and Transport, New York Academy of Sciences, New York, Jan 9–12, 1979.

(9) Bryers, R. W. "Influence of the Distribution of Mineral Matter in Coal on Fireside Ash Deposition", ASME Paper No. 78-WA/CD-4, 1978.

(10) Henry, W. M.; Knapp, K. T. *Environ. Sci. Technol.* **1980,** *14*, 450.

(11) Biggins, P. D. E.; Harrison, R. M. *Environ. Sci. Technol.* **1980,** *14*, 336.

(12) Weast, R. C., Ed. "Handbook of Chemistry and Physics", 54th ed.; CRC Press: Cleveland, OH, 1973.

(13) Reiter, R.; Sladkovic, R.; Pötzl, K. *Atmos. Environ.* **1976,** *10*, 841.

(14) Pettijohn, F. J. "Sedimentary Rocks"; Harper and Brothers: New York, 1957; Chapter 11.

(15) Mason, B. "Principles of Geochemistry"; Wiley: New York, 1966; Chapter 3.

(16) Brosset, C. *Atmos. Environ.* **1978,** *12*, 25.

(17) Ho, W.; Hidy, G. M.; Govan, R. M. *J. Appl. Meteorol.* **1974,** *13*, 871.

(18) Grosjean, D. *Anal. Chem.* **1975,** *47*, 797.

(19) Gordon, R. J.; Bryan, R. J. *Environ. Sci. Technol.* **1973,** *7*, 645.

(20) Pierson, W. R.; Russell, P. A. *Atmos. Environ.* **1979,** *13*, 1623.

(21) Lewis, C. W.; Macias, E. S. *Atmos. Environ.* **1980,** *14*, 185.

(22) Appel, B. R.; Tokiwa, Y.; Wall, S. M.; Hoffer, E. M.; Haik, M.; Wesolowski, J. J. "Effect of Environmental Variables and Sampling Media on the Collection of Atmospheric Sulfate and Nitrate"; Final Report, California Air Resources Board, ARB Contract No. 5-1032, 1978.

(23) Grosjean, D.; Friedlander, S. K. *J. Air Pollut. Control Assoc.* **1975,** *25*, 1038.

(24) Cukor, P.; Ciaccio, L. L.; Lanning, E. W.; Rubino, R. L. *Environ. Sci. Technol.* **1972,** *6*, 633.

(25) Ciaccio, L. L.; Rubino, R. L.; Flores, J. *Environ. Sci. Technol.* **1974,** *8*, 935.

(26) Mueller, P. K.; Mosley, R. W.; Pierce, L. B. In "Aerosols and Atmospheric Chemistry"; Hidy, G. M., Ed.; Academic Press: New York, 1972.

(27) West, C. J., Ed. "International Critical Tables of Numerical Data, Physics, Chemistry and Technology"; McGraw-Hill: New York, 1933; Vol. IV.

(28) Lange, N. A., Ed. "Handbook of Chemistry", 5th ed.; Handbook Publishers: Sandusky, OH, 1944.

(29) Tang, I. N.; Munkelwitz, H. R. *J. Aerosol Sci.* **1977,** *8*, 321.

(30) Ochs, H. T., III; Gatz, D. F. *Atmos. Environ.* **1980,** *14*, 615.

(31) Cadle, R. D. "Particles in the Atmosphere and Space"; Reinhold: New York, 1966; Chapter 2.

(32) Wishaw, B. F.; Stokes, R. H. *Trans. Faraday Soc.* **1954,** *50*, 952.

(33) Hamer, W. J.; Wu, Y. C. *J. Phys. Chem. Ref. Data* **1972,** *1*, 1047.

(34) Robinson, R. A.; Stokes, R. H. "Electrolyte Solutions; The Measurement and Interpretation of Conductance, Chemical Potential and Diffusion in Solutions of Simple Electrolytes", 2nd ed. (revised); Butterworths: London, 1959.

(35) Brosset, C. "Possible Changes in Aerosol Composition Due to Departure from Equilibrium Conditions during Sampling"; Swedish Water and Air Pollution Research Laboratory; Goteborg, 1978; PB-298 947.

(36) Landis, D. A. *Atmos. Environ.* **1975,** *9*, 1079.

(37) Husar, R. B. *Atmos. Environ.* **1974,** *8*, 183.

(38) Macias, E. S.; Husar, R. B. In "Fine Particles. Aerosol Generation, Measurement, Sampling, and Analysis"; Liu, B. Y. H., Ed.; Academic Press: New York, 1976.

(39) John, W.; Reischl, G. *Atmos. Environ.* **1978,** *12*, 2015.

(40) Appel, B. R.; Wesolowski, J. J. In "The Character and Origins of Smog Aerosols; A Digest of Results from the California Aerosol Characterization Experiment (ACHEX)"; Hidy, G. M., Mueller, P. K., Grosjean, D., Appel, B. R., Wesolowski, J. J., Eds.; Wiley: New York, 1980.

(41) Rimberg, D. *Am. Ind. Hyg. Assoc. J.* **1969,** *30*, 394.

(42) Stafford, R. G.; Ettinger, H. J. *Am. Ind. Hyg. Assoc. J.* **1971,** *32*, 319.

(43) Lindeken, C. L.; Morgin, R. L.; Petrock, K. F. *Health Phys.* **1963,** *9*, 305.

(44) Tierney, G. P.; Conner, W. D. *Am. Ind. Hyg. Assoc. J.* **1967,** *28*, 363.

(45) Demuynck, M. *Atmos. Environ.* **1975,** *9*, 523.

(46) Appel, B. R.; Tokiwa, Y.; Haik, M. *Atmos. Environ.*, **1981,** *15*, 283.

(47) Stevens, R. K.; Dzubay, T. G.; Russwurm, G.; Rickel, D. *Atmos. Environ.* **1978,** *12*, 55.

Received for review May 16, 1980. Accepted February 17, 1981. This work was supported by U.S. Environmental Protection Agency grant R806844 and by State of California Air Resources Board contract A7-169-30.

A β-Gauge Method Applied to Aerosol Samples

Joseph M. Jaklevic,* Ray C. Gatti, Fred S. Goulding, and Billy W. Loo

Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720

■ An instrument developed for the routine measurement of aerosol mass using the β-particle attenuation method is described and evaluated. Factors affecting the precision and the accuracy of the measurement are discussed in detail. Results of intercomparison studies between the β-gauge method and conventional gravimetric methods are presented. The design of the present instrument is particularly well suited for the automatic mass measurements of membrane filters used in modern dichotomous samplers. The precision of such measurements has been shown to be less than ± 5 μg/cm^2 for counting intervals of 1 min per sample.

Introduction

The β-gauge method of mass measurement is based on the attenuation which a β-particle spectrum undergoes when traversing a thin film of matter. If one measures the total number of electrons in a continuous β-particle spectrum emanating from a radioisotope source, the number of electrons transmitted through a thin, uniform foil would be (*1, 2*)

$$I = I_0 e^{-\mu x} \tag{1}$$

where I_0 is the incident flux, μ is the mass absorption coefficient in cm^2/g, and x is the thickness of the film expressed in g/cm^2. If μ and I_0 are accurately known, then a measurement of I can be directly related to the mass of a given sample. The values of μ and I_0 are normally determined by measuring I as a function of x for several known standards.

β thickness gauges based on the above model have been used for several years in applications where continuous, nondestructive monitoring of thin films is required, for example, in certain industrial processes (*3, 4*). Several authors have recently applied the method to the measurement of particulate deposits collected from the atmospheric aerosol (*5–7*). The use of the β-gauge method has several potential advantages over direct weighings for the measurements of aerosol samples. Handling of the fragile filter samples is minimized, the risk of contamination is reduced, and the automated analysis of many samples can be facilitated. Insofar as a β gauge can be made to operate with a precision and accuracy comparable to current microbalance technology, it represents a preferred approach in modern, large-scale monitoring programs.

The measurement of the aerosol particulate deposits collected on filter substrates represents a particularly demanding mass-measurement problem. Modern air sampling techniques result in typical particulate deposits of 50–200 μg/cm^2 on filter substrates weighing 1–5 mg/cm^2. Variations in substrate mass from sample to sample require that each filter be weighed before and after exposure. A precision of ± 5 μg/cm^2 in the measurement of the aerosol deposit requires a maximum error of ± 3 μg/cm^2 in each individual weighing. A direct measurement on a 5 mg/cm^2 substrate therefore requires a precision of $\pm 0.06\%$. The calibration accuracy must be assured in the presence of potential particle size, filter nonuniformity effects, and additional artifacts unique to the β-particle attentuation method. In order to achieve the desired performance, it is important that a thorough understanding of the technique and its implications be achieved.

Description of Method

A schematic of a simple β gauge is shown in Figure 1. It consists of a radioisotope source, a detector, and a sample. The source is chosen such that β-particle emission is the predominant mode of decay. The half-life should be sufficiently long that decay corrections over the duration of a measurement cycle are avoided and frequent replacement of the source is not required. For the measurement of thin samples, the most appropriate choices are ^{14}C, ^{147}Pm, and possibly ^{63}Ni.

The detector and associated electronics must be sensitive to electrons in the energy region of interest and be capable of counting discrete events at a high enough rate to facilitate rapid measurements. Most modern applications employ solid-state semiconductor detectors which measure the total ionization produced by an incident particle. The output pulses are amplified and a discriminator circuit is used to register electrons with energies above a certain lower limit.

In order to choose a radioactive source for a particular application, the physical processes involved in the measurement should be considered. Figure 2 shows an idealized β-particle spectrum as emitted from the source. It consists of a continuous energy distribution with an end point $E_{\max}$ which is characteristic of the isotope used. The maximum number of electrons in the distribution occurs at $E \sim 0.4E_{\max}$. We have indicated a discriminator level E_{disc} below which the system is not sensitive to events; the shaded area represents the measured intensity I.

When traversing the sample material between source and detector, the incident β particles (electrons) lose energy in a continuous manner via collisions with the electrons in the sample. The energy and the direction of incident particles are both affected by repeated small energy losses. As the sample thickness is increased, the spectrum of Figure 2 is not uniformly attenuated in terms of the number of particles per unit energy but, instead, undergoes a shift to lower energies accompanied by complete stopping of the lowest-energy particles. The measurement then consists of counting the number of particles with energies remaining above the value E_{disc} after traversing the sample thickness. The exponential dependence given in eq 1 then results from the fortuitous combination of β-spectral shape and energy-loss behavior of low-energy electrons. It is expected that the exponential behavior will be only approximate for large dynamic ranges of mass.

The choice of a radioactive β-particle source depends on matching the average energy of the β spectrum to the range of mass thickness to be measured. If the electrons in the spectrum have a maximum range which is less than the thickness to be measured, very few electrons will penetrate the sample and the relationship of eq 1 is no longer valid. Similarly, if the electrons are extremely energetic relative to any losses in a thin sample, then little or no effect will be observed on the spectrum and a sensitive measurement of mass is not possible.

Figure 3 shows a curve of the maximum range of electrons in carbon, copper, and lead as a function of energy (*8*). Of most importance for the present discussion are the range curves for carbon since most filter substrates consist of hydrocarbon materials. Curves for the other elements are presented in order to show the atomic-number dependence and alert us to possible effects which this might have on the mass measurement. Indicated on the plots are the average and end-point energies for the electron distributions from the commonly employed isotopes ^{14}C and ^{147}Pm. Either of these isotopes is seen to be a practical source for measurement in the 1–10 mg/cm^2 range.

0013-936X/81/0915-0680$01.25/0

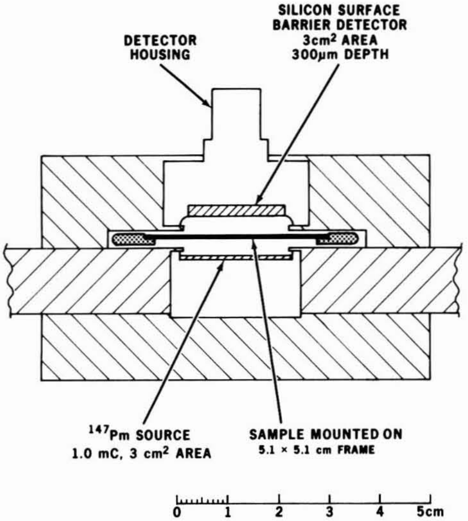


Figure 1. Schematic of a β gauge suitable for measuring thin aerosol samples.

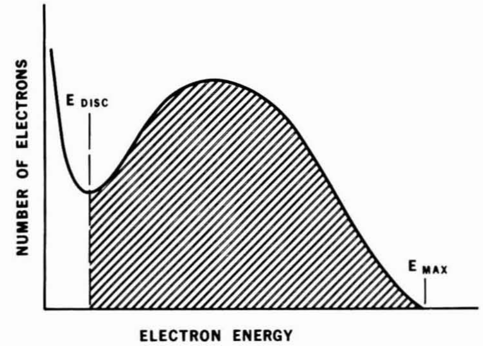


Figure 2. Idealized β-particle spectrum emitted from a radioisotope source.

Of more direct concern in the design of a β-gauge is the relative intensity vs. mass thickness described in eq 1. Figure 4 shows plots of experimental curves for ^{14}C and ^{147}Pm. These were obtained by measuring the variation in counting rates as a function of mass for a series of thin uniform films whose masses were gravimetrically determined. The dashed straight lines represent semiempirical values calculated from a relationship derived by Gleason et al. (*2*)

$$\mu(\mathrm{cm^2/mg}) = 0.017E_{\max}{}^{-1.43} \tag{2}$$

where $E_{\max}$ is the end-point energy in MeV. This expression was deduced by measuring the mass absorption coefficient for a number of isotopes with $E_{\max}$ ranging from 0.15 to 3.5 MeV and is valid for mass ranges which are small compared to the average electron range. This is consistent with the results shown in Figure 4, where the theoretical slopes are tangent to the experimental result at low mass values.

On the basis of the results shown, one would conclude that ^{14}C is the best choice for the range of 5 mg/cm² or less since the change of counting rates with mass is greater, resulting in a higher sensitivity. The ^{147}Pm source has a lower rate of attenuation and is thus better suited to cover a larger mass range. However, since the difference in sensitivity between

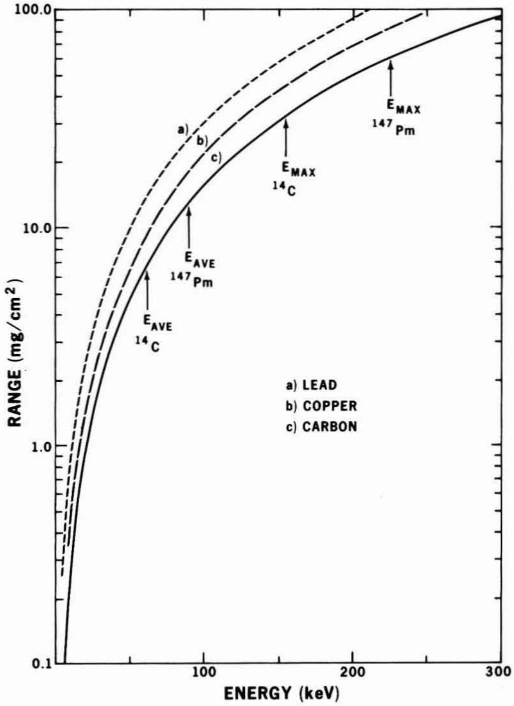


Figure 3. Range–energy curves for monoenergetic electrons with energies in the region appropriate for β-thickness gauges. Curves are shown for (a) lead, (b) copper, and (c) carbon.

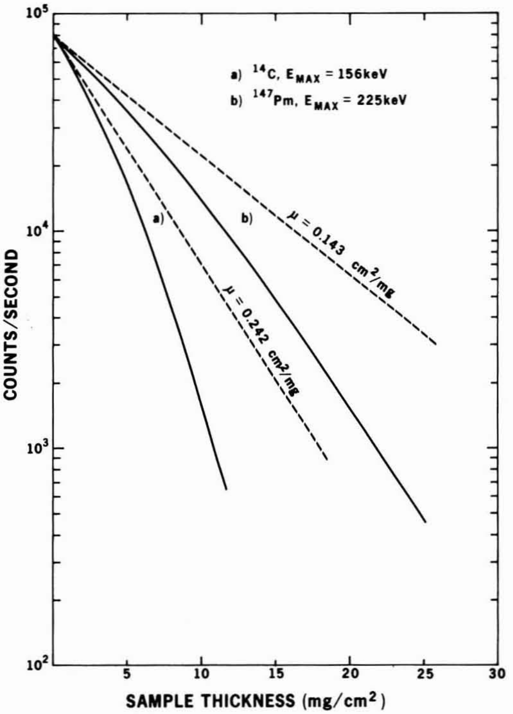


Figure 4. Attenuation curves for thin polycarbonate films using two radioisotopes: (a) ^{14}C and (b) ^{147}Pm. Solid curves are experimental measurements. Dashed curves are derived from eq 2.

the two sources is small, the use of ^{147}Pm is often preferred because of the broader range of masses over which it is sensitive. This allows the use of additional protective windows on source and detector. Furthermore, the measurements are less susceptible to artifacts arising from particle size and filter nonuniformity effects. The relatively short half-life of 2.62 yr for ^{147}Pm does not constitute a severe limitation if calibrations are performed frequently.

A close examination of the experimental curves shows that they are not purely exponential over the wide range of masses shown. However, over a relatively narrow range, a reasonable approximation can be maintained. For these reasons, the calibration curve is normally derived from a very limited range which overlaps the range of mass measurement to be made. If one assumes typical deposit to be 200 μg/cm^2 and a root mean square deviation in tare weight of ±500 μg/cm^2, a calibration range of ±1 mg/cm^2 is adequate.

In normal operation, the system can be frequently calibrated in order to minimize the effect of long-term drift. Our current procedure employs five uniform thin polycarbonate standards which span the mass range of interest. The masses of these standards are first determined by weighing. They are then processed through the β gauge, and a least-squares fit to eq 1 is performed to obtain I_0 and μ. In general, deviations from a straight line (±10 μg/cm^2) can be observed due to systematic effects in the mass measurements. After repeated measurement in the β gauge, the mass values for the thin-film standards are corrected to fit a straight line within a typical precision of ±2 μg/cm^2. The procedure whereby the gravimetric masses are adjusted to conform to the result obtained in the β gauge has little effect on the accuracy of the measurement since it involves only a slight correction to the observed slope. In effect, the accuracy of the calibration standards is determined by the average gravimetric mass. Slight systematic variations of the individual samples are adjusted according to the higher precision afforded by repeated β-gauge measurements.

Subsequent mass determinations are made by using the μ and I_0 values obtained from the least-squares fit in order to calculate the mass from the observed counting rate. The expression is

$$x = (\ln I_0 - \ln I)/\mu \tag{3}$$

The present approach to mass measurement differs from other β-gauge procedures (*7, 9*) in that the tare weights are directly calculated relative to calibration standards and stored in that fashion. Although in principle it is possible to store the counts only and compare the counts before and after exposure, the stability of a calibration over a long period of time cannot be guaranteed at the necessary level of precision. Consequently, we require that individual calibration measurements be performed with each series of measurements.

Description of Instrument

The present β-gauge design employs a source, a sample, and a detector geometry similar to that shown in Figure 1. The source is a commercially obtained ^{147}Pm source in a 2.54-cm diameter cylindrical aluminum source holder. The active area is 2.2 cm in diameter and is specified to be uniform to better than ±10%. The source is protected by a 600 μg/cm^2 foil supplied by the manufacturer; an additional 7 mg/cm^2 Al foil is used to protect the surface of the source from mechanical damage during normal handling and operation.

The detector is an Ortec Model CA-018-300-300 silicon surface barrier detector operated at room temperature. The active area is 3 cm^2 with a 300-μm (70 mg/cm^2) sensitive depth. The electronic resolution is ~12 keV at the operating temperature. The front surface of the detector is also protected by a 7 mg/cm^2 Al foil which reduces the sensitivity of the device to ambient light. The source-to-detector distance is 0.7 cm, representing an air path of ~0.9 mg/cm^2 equivalent mass.

Since the present instrument is designed for automatic operation, it is interesting to consider the associated mechanical and electronic hardware. These are illustrated schematically in Figure 5. The sample carrier is designed to accommodate two standard trays with 36 samples each plus an additional five standards at top and bottom. The two trays would typically represent the coarse- and fine-particle fractions obtained from a dichotomous sampler (*10*). The five standards at the top are normally used to calculate the thin-film calibration constants. The bottom standards are blank filters of the type used in the study and are employed as cross checks on system stability and calibration accuracy.

The detector preamplifier, amplifier, and discrimination circuitry were designed and built in our laboratory and have been extensively tested for stability. Repeated measurement of the same counting rate over extended periods of time indicate a long-term stability in the entire system of one part in 3 × 10^4.

The control of the system is incorporated into a Hewlett-Packard 9815 calculator. An interface module is used to execute the instructions from the calculator. The unit also includes a scaler and a clock which are used to count the pulses from the discriminator and communicate the result to the calculator.

Additional analysis data such as sample numbers, calibration masses, date, and time are entered via the calculator keyboard. This information is used to control the analysis procedure, calculate the calibration curve, and file the results in the proper location. The cassette facility included with the calculator is capable of storing the necessary program files and the data for 10 000 samples in each cassette. Since the tare weight must be individually stored and subsequently matched to the final weight for each slide, the large storage capability allows one considerable flexibility in the handling of samples. For a typical study which might require fewer than 10 000 total samples, the programs would accommodate the analysis of these samples in more or less random order. Final output of the data can be produced on the printer or cassette tape or the data can be transferred from the calculator to a larger facility using a standard interface.

Precision and Accuracy

The precision of the β-gauge instrument can be defined as the reproducibility with which a given value can be obtained from the measurement of an unknown mass. It will include the effects of counting statistics and electronic stability on both the measurement of the calibration standards and the unknown samples. It can also be affected by possible variations in absorption characteristics as a result of misalignment of the standards and unknowns in the instrument.

The accuracy of the measurements is defined in terms of the comparison of the β-gauge results with totally independent but equivalent methods of measurement. In the case of a single mass measurement of a given sample, the accuracy of the results depends upon the quality of the standards and the validity of the calibration procedure together with any artifacts which might affect the application of a given calibration curve to the assignment of unknown masses. Included in the category of artifacts would be particle-size effects, filter-substrate inhomogeneity, and possible atomic-number dependence of the mass absorption coefficient.

In the case of a difference measurement such as employed when determining the deposited mass on a substrate, the question of precision and accuracy must be carefully interpreted. If we can associate a root mean square variation with both precision and accuracy (σ_P and σ_A, respectively), then the total uncertainty in the measurement is obtained by combining these results in normal quadrature addition.

If the two measurements are performed on different systems or by using completely different calibration procedures, then the errors are uncorrelated, and the combined uncertainty is

$$\sigma^2 = 2\sigma_{\mathrm{P}}^2 + 2\sigma_{\mathrm{A}}^2 \qquad (4)$$

Since the uncertainty in the calibration factors is typically a few percent compared to a precision of a fraction of a percent, the error is dominated by the calibration uncertainty.

A far worse condition can exist if there is a systematic bias of the calibration curve employed in one β-gauge measurement relative to the other. If we wish to detect a deposit of 10 μg/cm^2 on a 1 mg/cm^2 substrate, a shift of 1% in calibration slope between the two weighings can completely eliminate any observed deposit. Since it is extremely difficult to maintain accuracies below this level, such errors can easily occur. For these reasons, it is important that the β-gauge system be maintained in as stable a configuration as possible so that measurement before and after exposure can be performed under identical conditions. In cases where unavoidable modifications in detector–source geometry occur, repeated measurement of standard samples should be used to determine whether any systematic calibration shifts have occurred.

Precision. The precision of the β-gauge measurement depends both on statistical fluctuations associated with normal counting experiments and on fluctuations in counting rate or sample position due to uncontrolled parameters. Ideally the contributions due to the latter effects can be minimized with the result that the precision is determined principally by counting rate and analysis time.

Beginning with eq 3, we can derive an expression for the error associated with the calculated mass as follows:

$$\sigma^2(x) = \frac{(\ln I_0 - \ln I)^2}{\mu^4}\,\sigma^2(\mu) + \frac{1}{\mu^2}\,\sigma^2(\ln I_0) - \frac{(\ln I_0 - \ln I)}{\mu^3}\,\mathrm{Covar}\,(\mu, \ln I_0) + \frac{1}{\mu^2 I^2}\,\sigma^2(I) \qquad (5)$$

The first three terms in eq 5 are associated with the errors incurred in the linear least-squares fitting procedure. The Covar (μ, ln I_0) term is the usual error term arising from the interdependence of the slope and the intercept when fitting a straight line to the ln I vs. x calibration curve. The final term in the equation represents the statistical variation associated with the counting measurement on the unknown mass.

The dependence of the error on terms involving inverse powers of μ indicates the importance of choosing a source which experiences maximum attenuation. It can also be shown that the errors obtained from the least-squares fitting procedure are proportional to the relative errors associated with the measurement of the individual I values. If we can assume that the standards and unknowns are measured at approximately the same counting rate and for the same interval, then

$$\sigma^2(x) \propto \sigma^2(I)/I^2 = 1/(IT) \qquad (6)$$

This gives the expected result that the total precision of the measurement scales as $T^{-1/2}$ where T is the counting interval.

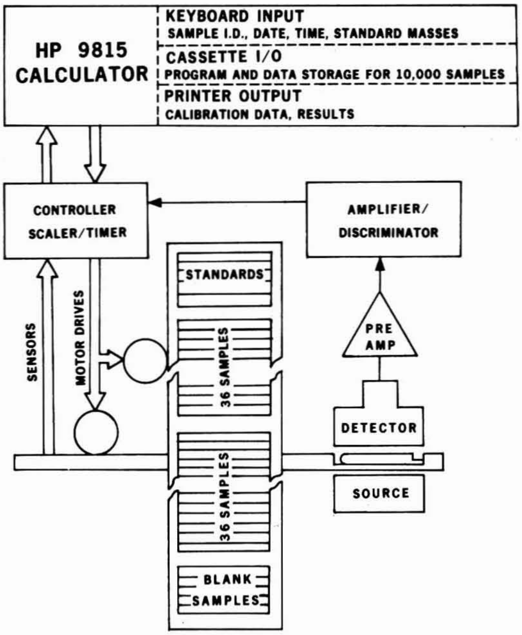


Figure 5. Automatic sample handling and data acquisition system used in conjunction with β gauge.

Table I. Stability Tests for Room-Temperature β Gauge[a]

parameter	av deviation
I_0 (blank counts)	12 145 622 ± 19 500
ln I_0 (fitted intercept)	14.0794 ± 0.0018
μ (fitted slope)	$1.5468 \times 10^{-4} \pm 2.9 \times 10^{-7}$ cm^2/μg
mass (μg/cm^2)	686.1 ± 2.9
	1093.8 ± 2.3
	697.8 ± 2.2
	729.1 ± 1.9
	773.5 ± 1.8
	341.4 ± 2.0
	301.8 ± 2.7
	357.9 ± 3.3
	302.1 ± 2.6
av deviation	± 2.5 μg/cm^2
temp range	24.6 ± 1.7 °C

[a] Measurements represent precision in the calibration parameters and the calculated masses which were observed in the repeated measurement of nine thin-film standards.

Table I gives a summary of results testing the precision of the current β-gauge design. These represent repeated measurements on a series of nine filters using the same calibration standards for each measurement. The nominal counting rate was 1.2×10^5 s^{-1}, and a 100-s interval was used. If we calculate the root mean square deviation under these conditions assuming statistical fluctuations only, we obtain a value of ±2.56 μg/cm^2. This is consistent with the experimentally measured value. The temperature range is included in the table since it is known to be the external parameter which will most seriously affect the system stability presumably through variations in detector capacitance, amplifier gain and stability, and density variations in the source-to-detector air gap.

Accuracy. Primary gravimetric mass standards in the form of thin, uniform films can normally be prepared to an accuracy of ±1 μg/cm^2 by using conventional microbalance methods. These are usually hydrocarbon films (polycarbonate, for example) which are weighed and mounted in standard sample holders. Mass values range from 600 to 6000 μg/cm^2 depending upon the average filter mass to be measured. A series of measurements of ln I vs. mass are then fitted to a straight line, and the average values of μ and I_0 are computed. The value of the standard masses are then adjusted slightly to conform to the straight-line fit. These adjustments compensate for small variations in the measured mass due to possible nonuniformities in the thin films and any nonlinearities in the mass absorption curve in the vicinity of the least-squares fit. Following these adjustments, subsequent fits to the standard typically exhibit root mean square deviations of ± 3 μg/cm^2.

Of more serious concern to measurement accuracy are possible systematic biases which arise from the application of the thin-film calibration curve to aerosol particles collected on nonuniform filter media. Effects which must be considered include particle size, filter inhomogeneity, and atomic-number dependence.

Particle Size and Filter Inhomogeneity. Particle-size and filter-inhomogeneity effects are closely related. Both arise because the measured mass per unit area represents the average over a nonuniform mass distribution arising either from a finite number of discrete particles or from a variable-thickness substrate. In gravimetric mass determinations, these nonuniformities present no problem since the average mass per unit area can be computed directly from the total mass and area. However, in the β-gauge measurement, the mass is related to the measured quantity via an exponential function. Insofar as the averaging is no longer performed linearly, possible errors can be introduced (*11*).

A simple method for estimating the effect assumes that the particles are in the form of cubes lying on a uniform substrate. If one assumes N cubes per square centimeter with linear dimensions d and density ρ, then the mass per unit area which one would measure by direct gravimetric means would be

$$x(\mathrm{g/cm^2}) = Nd^3\rho + t \tag{7}$$

where t is the substrate thickness. If the measurements are performed by using a β gauge with characteristic calibration constants of μ and I_0, then the mass must be derived from the following attenuation data:

$$I = I_0\{(1 - Nd^2) + Nd^2e^{-\mu\rho d}\}e^{-\mu\rho t} \tag{8}$$

This equation describes a model in which β particles incident on a fraction of the filter area (Nd^2) undergo an attenuation $e^{-\mu t}e^{-\mu d}$. The remainder of the beam undergoes an attenuation $e^{-\mu t}$. The application of the standard thin-film calibration curve requires that the mass x' be obtained by interpreting the observed intensity I in eq 10 according to eq 3.

The ratio of x'/x is a measure of the error introduced as a result of finite particle size. Figure 6 is a plot of this ratio as a function of d for the case of ^{14}C and ^{147}Pm sources assuming a 100 μg/cm^2 deposit of unit density particles. In the small-particle range, the number density of particles approaches that of a thin film, and the discrepancy vanishes. For very large particles, one can see that, in the limit of a few very large cubes, the attenuation is proportional to the area of the particle compared to the total filter. The mass of the particle is then practically undetected. The higher attenuation experienced by the ^{14}C source causes it to be more susceptible to particle-size effect according to the model. If we allow ourselves to interpret the linear dimension d in terms of aerosol particle size, then we see that, below 15-μm particle diameter, the discrepancy will be less than 5% for a ^{147}Pm β-gauge source. Although the model used is relatively simple, it is useful in that it gives an upper limit to the observed effect. In the data processing normally employed, no corrections for particle-size effects are made.

Inaccuracies due to filter inhomogeneities can be estimated by using a similar calculation. We assume that the small-scale inhomogeneities in the filter can be approximated by a model in which the filter thickness varies by a factor of 2. If we furthermore assume that the total area of the thicker portion is one-half the total area, then calculations similar to eq 7 and 8 can be performed to estimate the discrepancies which arise from the application of the uniform thin-film calibration curve. If we assume a 1 mg/cm^2 average thickness, then the discrepancies would be 0.976 and 0.987 for ^{14}C and ^{147}Pm, respectively. For a 5 mg/cm^2 substrate, the corresponding numbers are 0.891 and 0.939. Although the errors are small in a relative sense, the magnitude of the absolute error ranges from 13 to 109 μg/cm^2 in the least favorable case. The discrepancy vanishes when the differences between initial and final masses are calculated, although, once again, the importance of using identical systems for both mass measurements is emphasized. Discrepancies are minimized for the case of thinner substrates and higher-energy β particles.

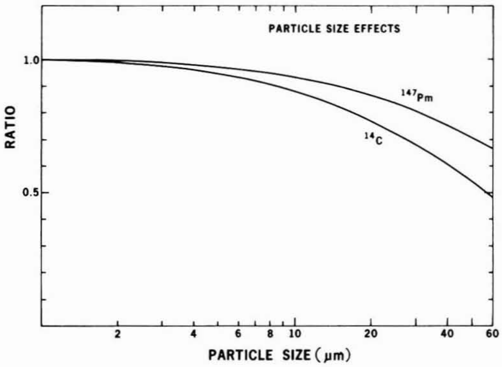


Figure 6. Discrepancy in β-gauge mass measurements as a function of particle size for the case of two commonly used isotopes.

The presence of large-scale inhomogeneities in the filter substrate coupled with a slight nonuniformity in the spacial distribution of the radioactivity emitted from the source can produce similar discrepancies. These can be observed either when nonidentical β-gauge measurements are performed or, in a much more likely case, if the filter is not placed in a reproducible geometry in the instrument. This applies both to rotations and translations of the sample relative to the axis of the source–detector system. Again the effect can be eliminated by the use of identical measurement procedures for both tare-weight and final-weight determinations.

Atomic-Number Dependence. The process by which the β particles interact within the sample depends upon the number of electrons in the sample which scatter the incident beam. The validity of the β-gauge method depends upon the proportionality between the number of electrons in the sample and the total mass and also upon the equivalence of all electrons in terms of their scattering properties. The fact that the range of electrons expressed in mg/cm^2 depends somewhat upon the atomic number of the absorber (see Figure 3) indicates that some departure from this simple behavior is expected.

We have performed measurements of the mass absorption coefficient as a function of atomic number for several substrates. The procedures were the same as those employed in normal calibration runs except different thin-film materials were used. Table II is a summary of the results. The measured mass absorption coefficients are also presented graphically in Figure 7 as a function of Z/A.

It is apparent that no simple relationship between μ and Z/A can be easily derived. For pure elemental samples we have $Z/A < 0.5$, and the data seem to follow a straight-line dependence. The values for hydrocarbon films vary only slightly for Z/A values $0.48 < Z/A < 0.57$. A smooth curve can be drawn

Table II. Measured Mass Absorption Coefficients for Substances with Varying Effective Atomic Number and Mass

material	at. no./at. mass, Z/A	mass absorption coeff, cm^2/g
gold	0.401	0.217
beryllium	0.444	0.116
copper	0.456	0.173
nickel	0.477	0.178
aluminum	0.482	0.156
poly(vinyl dichloride)	0.495	0.165
polyimide	0.517	0.141
polycarbonate	0.537	0.154
polyethylene	0.570	0.167
polypropylene	0.570	0.165

through the experimental points with the exception of the measurement for Be. Be represents a unique case in that it is an elemental sample with $Z/A = 0.44$ but is also the lightest element standard with $Z = 4$.

The atomic-number dependence of the absorption coefficient can be partially understood by considering in greater detail the energy-loss processes for electrons. As is evident in Figure 2, the total range of electrons expressed in mg/cm^2 increases as a function of atomic number. This would imply a lower mass absorption coefficient for the heavier elements, which is opposite to the behavior observed. However, as noted earlier, in addition to the discrete energy-loss processes which occur during collisions, there is also a change in the direction of the scattered particle. This average angular deflection is a function of atomic number and increases for the heavier elements. A typical trajectory for an electron in Be is relatively straight compared to the case of Au where a sizeable fraction of the electrons can actually be backscattered from the foil (*12*). It is this strong angular dependence and its relationship to atomic number which result in the observed behavior of mass absorption coefficient with Z/A. The anomalously low absorption coefficient for Be can also be explained by this simple interpretation.

Although a detailed model for the Z/A dependence cannot be easily calculated, the effect of such variations upon realistic aerosols can be estimated. If we neglect the anomaly of Be and assume a dependence described by the curve shown in Figure 7, then the errors resulting from applying a hydrocarbon thin-film calibration to variable Z particles can be estimated. Table III gives the percent error in the mass measurement for various commonly encountered aerosol compounds when the mass measurement is interpreted in terms of the normal calibration procedure.

As can be seen from the data, significant problems do not occur until one reaches the Pb compounds, where errors of 30% can be expected. However, insofar as typical urban aerosol composition normally contains much less than 10% of such Pb compounds, the error introduced in the total mass measurement is minimal. In special cases where large Pb or other heavy-element concentrations are observed, it should be possible to apply a correction to the calibration produced to reduce any discrepancy due to atomic-number dependence.

The fact that there is some variation in μ with Z/A again emphasizes the importance of maintaining a stable configuration in the β-gauge calibration and measurement system. A slight variation in effective atomic number brought about by using different standards or changes in the material used for detection windows, absorbers, etc., can cause apparent shifts in the measured masses.

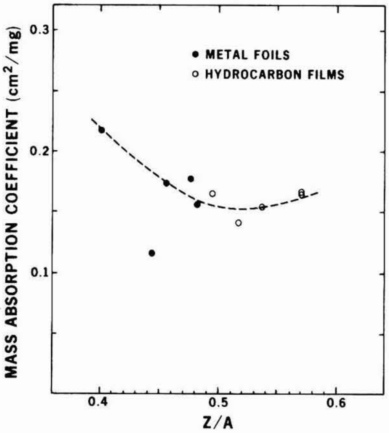


Figure 7. Measured values for the mass absorption coefficients as a function of the ratio of atomic number to atomic mass.

Table III. Effect of Atomic-Number Dependence on the Measured Mass of Several Compounds[a]

compd	Z/A	μ, cm^2/mg	ratio to standard
$(NH_4)_2SO_4$	0.530	0.153	0.99
NH_4HSO_4	0.521	0.152	0.99
$CaSO_4 \cdot H_2O$	0.511	0.152	0.99
SiO_2	0.499	0.154	1.00
$CaCO_3$	0.500	0.154	1.00
carbon	0.500	0.154	1.00
Fe_2O_3	0.476	0.163	1.06
NaCl	0.478	0.172	1.12
$PbSO_4$	0.429	0.193	1.25
$PbCl_2$	0.417	0.204	1.32
PbBrCl	0.415	0.206	1.34
calibration value		0.154	

[a] Column four gives the discrepancy with respect to the polycarbonate standards.

Results and Summary

The ultimate test of the β-gauge method for aerosol mass measurement consists in comparison of results with those obtained by more conventional methods. The commonly accepted method for mass measurement is gravimetric measurement using microbalance techniques. The results from several independent studies which involved intercomparison of β-gauge and gravimetric mass determinations are now available. Data have been selected from these studies in which the β-gauge instrumentation was equivalent to the system described in this paper.

Figure 8 shows scatter plots of data obtained in a side-by-side sampling intercomparison performed in Charleston, WV, in May 1977 (*13*). The data quoted herein and the description of the sampling and analysis protocol are taken from ref *12*. The mass concentrations are quoted in terms of μg/m^3 referred to the original atmospheric aerosol. Figure 8A compares the results of Rodes obtained by using a high-volume sampler and gravimetric weighing with results from a dichotomous sampler and β-gauge mass determinations. The total masses given for the latter case were calculated as the sum of the coarse and fine fractions. The average slope of the data in the scatter plots was calculated as the ratio of the sum of the

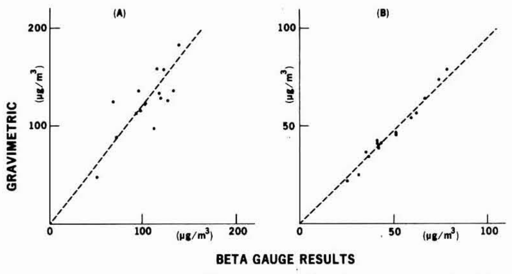


Figure 8. Comparison of β-gauge results with those obtained by gravimetric methods. These data were obtained by comparing side-by-side samples of the same atmospheric aerosol collected by different samplers. Case A represents high-volume samples vs. dichotomous. Case B was obtained with manual dichotomous vs. automatic dichotomous samplers.

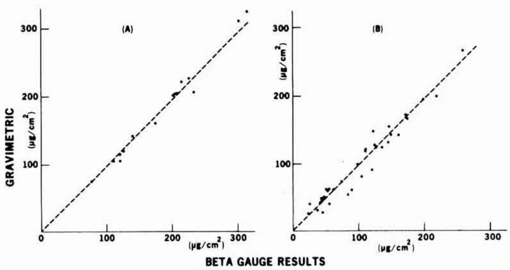


Figure 9. Comparison of β-gauge results with those obtained by gravimetric methods. These data represent duplicate mass measurements on the same sample. Samples for curve A were obtained in our laboratory. The data shown in curve B were obtained from workers at EPA (*13*).

data sets and was found to be 1.23. The higher average mass obtained with the high-volume sampler probably reflects the larger effective particle size cutoff obtained with this sampler relative to the dichotomous samples.

The plot of Figure 8B shows the results obtained from a gravimetric analysis of samples acquired with separate dichotomous samplers relative to the earlier β-gauge results. The gravimetric measurements are those quoted by Dzubay in ref *12*. The data shown are for the fine-particle fractions only since the upper cutoff for each of the dichotomous samplers was unknown. The excellent agreement between the two data sets reflects the relative precision of the two sampling methods. The calculated slope of the line shown is 0.954.

A more direct comparison which eliminates uncertainties due to nonequivalent sampling methods can be obtained by sampling with membrane filters mounted on thin frames which can be removed from the normal 5.1 × 5.1 cm carrying frame. The same sample can then be analyzed by both β gauge and direct weighing. Figure 9 shows the results of two such independent studies. The plot of Figure 9A was generated from data obtained in our laboratory by using aerosol samples collected locally. The fine- and coarse-particle fractions were analyzed separately and are included in the plot at separate points. The data are quoted directly in terms of $\mu g/cm^2$ as deposited on the thin Teflon membrane filter. The observed slope of the data was calculated to be 0.973. There were some slight systematic differences observed between the coarse- and fine-particle fractions which are not obvious in the combined data set. This is probably due to nonuniformity of the particle deposition together with possible particle-size effect, as discussed earlier.

Figure 9B shows the results of a study performed at the EPA Environmental Sciences Research Laboratory (*14*). Fine-particle samples were acquired from an indoor aerosol and subjected to the same analysis as discussed above. Again the agreement was excellent, with a calculated slope of 0.963.

Summary. The β-gauge method for the determination of the mass of atmosphere aerosol samples has been demonstrated to be equivalent in accuracy to gravimetric methods when proper attention is paid to instrumental design and calibration procedures. The advantages of automation and reduced sample handling would make β attenuation the method of choice for larger-sized monitoring programs. The present instrument design has been implemented with the capability for the automatic storage and retrieval of large data sets consistent with the large-scale approach to mass measurement.

Acknowledgment

We acknowledge the support of several other members of the Department of Instrument Techniques including D. Landis, D. Adachi, and N. Madden, who assisted in the detector and electronic development, and W. Searles, who did much of the mechanical design. We have profited from discussions with T. Dzubay of the U.S. Environmental Protection Agency and W. Courtney of Northrup Services, Inc.

Literature Cited

(1) Evans, R. D. "The Atomic Nucleus"; McGraw-Hill: New York, 1955; p 627.
(2) Gleason, G. I.; Taylor, J. D.; Tabern, P. L. *Nucleonics* **1951,** *8*, 12.
(3) Foster, G. B.; Chope, H. R. *ASTM Spec. Tech. Publ.* **1959,** 268.
(4) Compton, C. E. *Proc. Int. Conf. Peaceful Uses At. Energy, 1st, 1955* **1955–1958,** *15*, 124.
(5) Lilienfeld, P. *Am. Ind. Hyg. Assoc. J.* **1970,** *31*, 722.
(6) Lilienfeld, P. *Staub-Reinhalt. Luft* **1975,** *35*, 458.
(7) Macias, E. S.; Husar, R. B. *Proc. Int. Conf. Nucl. Methods Environ. Res., 2nd* **1974,** 413.
(8) Berger, M. J.; Seltzer, S. M. *N.A.S.–N.R.C., Publ.* **1964,** *1133*, 205.
(9) Cooper, D. W. *J. Air Pollut. Control Assoc.* **1975,** *25*, 1154.
(10) Loo, B. W.; Jaklevic, J. M.; Goulding, F. S. "Fine Particles: Aerosol Generation Measurement, Sampling and Analysis"; Liu, B. Y. H., Ed.; Academic Press: New York, 1976; p 311.
(11) Cooper, D. W. *J. Air Pollut. Control Assoc.* **1976,** *26*, 366.
(12) Archard, G. D. *J. Appl. Phys.* **1961,** *32*, 1505.
(13) Camp, D. C.; VanLehn, A. L.; Loo, B. W. "Intercomparison of Samples Used in the Determination of Aerosol Composition"; Interagency Energy–Environment Research and Development Series, Report No. EPA-600/7-78-118.
(14) Courtney, W. J. Northrup Services, Inc., Research Triangle Park, NC, private communication, 1979.

Received for review June 20, 1980. Accepted January 16, 1981. This work was supported in part by the Office of Health and Environmental Research of the U.S. Department of Energy and the Environmental Protection Agency under Contract No. W-7405-ENG-48.

Automatic Particulate Sulfur Measurements with a Dichotomous Sampler and On-Line X-ray Fluorescence Analysis

Joseph M. Jaklevic,* Billy W. Loo, and Ted Y. Fujita
Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720

■ An instrument is described which employs a dichotomous sampler to acquire fine-particulate samples on a continuous tape filter. Analyses for elemental sulfur are performed immediately following acquisition by using a sensitive X-ray fluorescence spectrometer. Sample sequencing, data acquisition, and calculation of concentrations are performed continuously by using an on-line calculator. Precision and accuracy of the method are discussed, and results obtained from ambient measurements are presented.

Introduction

The increased emission of sulfur-containing compounds into the atmosphere has become a major consideration in the design of air pollution monitoring and control strategies. This has stimulated considerable interest in the development of monitoring equipment capable of analyzing the atmospheric aerosol for sulfur-containing compounds. We describe a rapid, sensitive, and accurate X-ray fluorescence method for the analysis of elemental sulfur collected from ambient aerosol samples. The instrument includes a dichotomous sampler, an air filter transport system, and a high-sensitivity wavelength dispersive X-ray fluorescence analyzer. An associated calculator/controller enables one to obtain real-time measurements of ambient particulate sulfur concentrations over short time intervals.

Analysis Method

The technique of X-ray fluorescence analysis has been previously demonstrated to be a sensitive and accurate method for the analysis of elemental sulfur in air-particulate samples collected on thin-membrane substrates (*1*, *2*). Although much of this work has involved multiple element analysis using energy dispersive X-ray spectrometers, the use of single-channel wavelength dispersive analyzers is preferred when only one particular element is to be analyzed (*3*, *4*). The wavelength dispersive method has the advantages of simplicity and compactness when used for transportable X-ray analyzers. Figure 1 is a simplified schematic diagram of a wavelength dispersive X-ray spectrometer optimized for the detection of sulfur Kα characteristic X-rays. The spectrometer depends upon the coherent diffraction of X-rays from selected lattice planes of a critically oriented germanium crystal. X-rays incident on the crystal will be diffracted only if the wavelength (λ) satisfies the Bragg condition:

$$\lambda = 2d \sin \theta \tag{1}$$

where d is the lattice spacing of the crystal planes (in this case Ge ⟨111⟩, $2d = 6.532$ Å) and θ is the angle between the incident X-ray and the lattice plane. If the range of angles incident on the crystal is restricted by means of narrow slits, then only a limited range of wavelengths (or energies) are reflected into the proportional counter. The resolution of the spectrometer is determined by the angular divergence of the slits $\mathrm{d}\theta$ as follows:

$$\mathrm{d}E/E = \mathrm{d}\lambda/\lambda = \mathrm{d}\theta/\tan \theta \tag{2}$$

In the present design, 2.31-keV sulfur Kα X-rays are detected at $\theta = 55.4°$ with a resolution of 13 eV. In the application of the sulfur spectrometer to ambient-aerosol analysis, it is important that the energy resolution be sufficient to eliminate interfering X-rays resulting from excitation of the lead M$_\alpha$ lines at 2.34 keV. It is characteristic of wavelength dispersive spectrometers that the very good energy resolution is achieved at the expense of reduced geometrical efficiency.

In the case of small sample sizes, an improvement over the planar geometry can be achieved by using a curved crystal for the reflecting element. By appropriately bending and grinding the surface of the Ge crystal, it is possible to achieve a reflection geometry whereby all X-rays of a given wavelength which originate in a narrow slit can be refocused in a slit image at a complementary location (*5*). Different wavelengths focus at different locations in the same manner as before except that the focusing properties inherent in this geometry enable one to accept a larger solid angle of radiation emitted from the sample.

We have constructed such a spectrometer using a commercially obtained Ge ⟨111⟩ crystal that had been bent to a 15-cm diameter focusing circle. Figure 2 is a schematic diagram of the spectrometer. The narrow range of wavelengths over which the spectrometer is sensitive is determined by the orientation of the crystal with respect to the defining slit in front of the proportional counter. The Bragg condition is then satisfied for all 2.31-keV X-rays which originate from the sample and with directions within the angular spread indicated by the virtual source. The sensitivity of this spectrometer has been measured to be ~10 times the simple geometry shown in Figure 1. This increase is thought to be due both to the increased effective solid angle and to the higher transmission resulting from the elimination of the relatively inefficient collimator design employed in the planar spectrometer.

There are several other features of the spectrometer design which are important to consider. The chamber enclosing the major portion of the path between sample and counter is hermetically sealed in order to permit operation in a helium gas environment. The use of a helium environment in preference to a vacuum chamber was dictated by the presence of 50-μm Be windows on both the proportional counter and spectrometer entrance. The transmission of the helium path for 2.31-keV X-rays is 98% compared with less than 1% for an equivalent air path. Absorption of the sulfur X-rays is further reduced by exposing the top surface of the membrane-filter samples to the aerosol deposit and placing the sample within 2 mm of the Be entrance window. The transmissions of the air path and the 50-μm Be window are 94% and 92%, respectively.

Irradiation of the sample is provided by a 40-W, Ag anode air-cooled X-ray tube illuminating the sample from below. The 3-keV Ag X-rays are transmitted 86% by the ~1 mg/cm^2 filter substrate. Although the close-coupled geometry produces more scattering than normally desired, the increased efficiency for detection more than compensates.

Sampling Method

The sulfur compounds of interest in normal ambient monitoring result principally from the large-scale combustion of fossil fuels. It is well-known that the sulfur-containing particulates are concentrated in the fine-particle fraction (*6*).

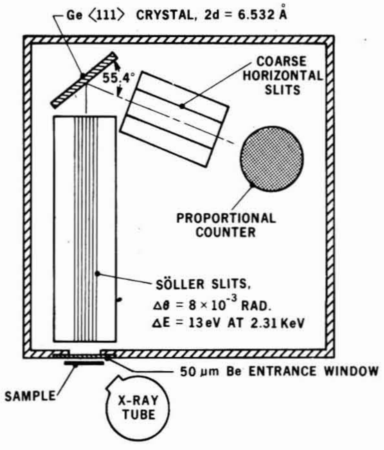


Figure 1. Schematic drawing of wavelength dispersive spectrometer. Ge ⟨111⟩ crystal is tuned to the sulfur Kα emission energy.

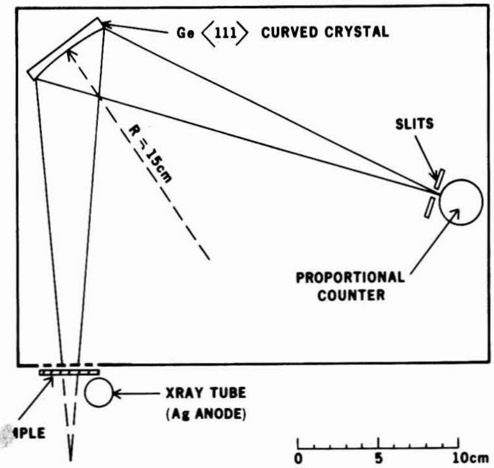


Figure 2. Wavelength spectrometer incorporating curved-crystal X-ray optics.

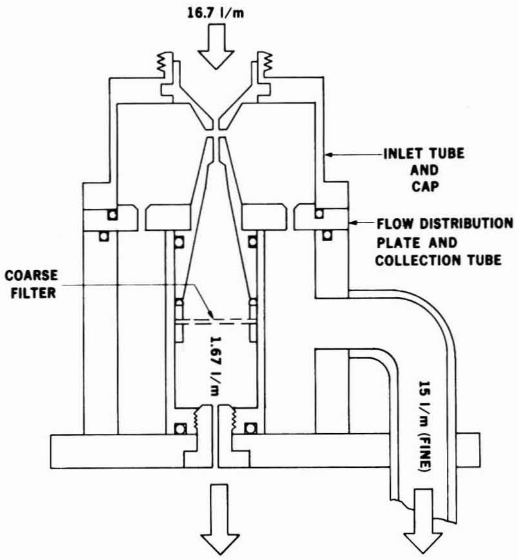


Figure 3. Diagram of modified dichotomous sampler. Coarse particles are collected within sampler; fine particles are extracted for deposition on continuous filter strip.

The sulfur monitor design includes a 16.7 L/m single-stage virtual impactor with a 2.5-μm cutpoint to separate the coarse- and fine-particle fractions before they are deposited on the filter (5). This increases the sensitivity for sulfur analysis by removing potentially interfering material from the sample and eliminates many X-ray analysis problems associated with the larger particles sizes.

Figure 3 shows a cross section of the modified impactor design. The small particles are directed onto a 1.6-cm^2 circular Teflon membrane filter area which is incorporated into a continuous 35-mm wide paper tape. The filters and associated optical locating holes are spaced at 3.81-cm intervals along the strip.

The coarse particles are collected on a 37-mm diameter cellulose filter. The filter was chosen to minimize the impedance in the coarse-particle flow circuit. Since the coarse particles are not included in the analysis, the associated filter is changed infrequently. Our operating experience has indicated that once per month is adequate under normal operating conditions. If coarse-particle loading becomes significant, it is possible to modify the flow pattern to impact the particles preferentially in the center of the filter, thereby decreasing the effects of filter clogging.

The fine-particle filters are changed frequently depending upon the experimental protocol. A pneumatic flow controller, flow-rate meters, and a diaphragm vacuum pump are incorporated into the monitor hardware. The flow controller compensates for the variation in fine-particle filter impedance as the loading increases; a vacuum-actuated switch is used to detect overload conditions and initiate filter changes where appropriate.

Sampler Operation

The filter tapes are commercially obtained in continuous rolls in lengths of 30 m corresponding to a supply of 800 filters per roll. A takeup reel is used to advance the strip past the sampling and analysis locations. Normal operating protocol calls for a sample to be acquired for the appropriate interval followed by an advance of the tape to the next sampling location. The previously exposed sample is now in the analysis position in the spectrometer sample position. Analysis results for the preceding sample are generated simultaneously with the acquisition of the subsequent filter sample. Normal operation requires that the analysis interval be equal to or less than the sample interval. However, for very short sample intervals, it is possible to operate in a mode where sample analysis is deferred for batch processing at a later time.

The sequencing of samples, timing of sampling and analysis intervals, and monitoring of experimental parameters are performed with an on-line calculator interfaced to the appropriate hardware as illustrated in Figure 4. The calculator is also used to store calibration data, perform concentration calculations, and output data to either printer or magnetic tape cassette.

The only calibration data contained in the calculator are a blank concentration obtained from an average over several unexposed filters and a sensitivity factor obtained from a carefully prepared particulate sulfur standard. The calculator automatically adjusts the result for changes in sampling and analysis intervals. Additional control features include the ability to automatically change filters if, during an air-pollu-

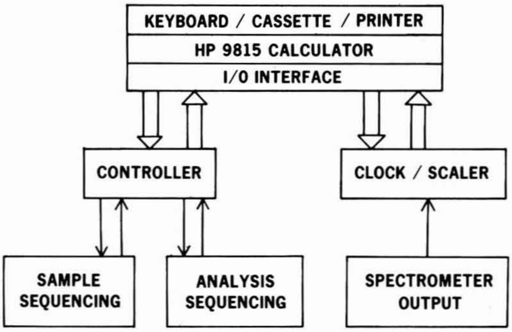


Figure 4. Block diagram of data acquisition and analysis electronics.

tion episode, the maximum filter loading is reached before the end of the regular sampling period.

Calibration and Results

The results of the X-ray analyses are calculated from the following formula:

$$C\ (\mu g/m^3) = K(N_S - N_B)/ST_S \tag{3}$$

where N_B is the background counting rate obtained as an average over several blank filters, N_S is the counting rate obtained for the sulfur peak in the exposed sample, T_S is the sampling interval, and S is the sensitivity of the spectrometer as obtained from a standard. A typical value for S is 4.2 counts s^{-1} $(\mu g/cm^2)^{-1}$ for an X-ray tube power of 30 W using the curved crystal spectrometer. N_B is 0.7 counts s^{-1} under these conditions. The factor K is a constant which includes the equivalent flow rate per unit area on the fine-particle filter. The sensitivity factor S is obtained by measuring the counting rate obtained from a known concentration of fine-particle sulfur. Standards for this measurement are prepared by generating fine 0.3-μm particle $CuSO_4$ aerosols and collecting them on a membrane filter. The concentration per unit area is measured by a carefully calibrated energy dispersive X-ray spectrometer. A cross-check on the sulfur results is obtained from a measurement of the copper concentration by assuming 1:1 stoichiometry. Agreement between these measurements verifies that particle size or filter matrix effects associated with the low-energy sulfur X-rays have been minimized. Several standards spanning the concentration range from 1 to 30 μg/cm² have been prepared and measured to ensure linearity of the calibration equation (eq 3). Although the sulfur X-rays are attenuated in their passage through the spectrometer system, the fact that the standards and unknowns experience identical conditions cancels the discrepancy.

Table I. Minimum Detectable Limits (3σ) for Elemental Sulfur

sample interval (16.7 L/m)	analysis with flat crystal (600 s),[a] μg/m³	analysis with curved crystal (600 s),[b] μg/m³
1 min	31.8	5.7
5 min	6.36	1.14
1 h	0.53	0.10
6 h	0.089	0.016
12 h	0.044	0.008
24 h	0.022	0.004

[a] 3σ = 0.21 μg/cm². [b] 3σ = 0.037 μg/cm².

If one assumes that the automatic flow controller, the X-ray current stabilizer, the helium pressure, and other easily regulated parameters are maintained within ±1%, the most serious sources of measurement error are variability in background counting rate, changes in sensitivity, and measurement artifacts associated with X-ray matrix and particle-size effects.

The variation in background from one blank filter to the next is probably due to small-scale nonuniformities in the filter structure which result in unpredictable changes in scattering probability or filter transmission characteristics. A series of 10 blank filters has been measured, and the root mean square variation has been determined. The error associated with these variations is equivalent to $\sigma = 0.030$ μg/cm².

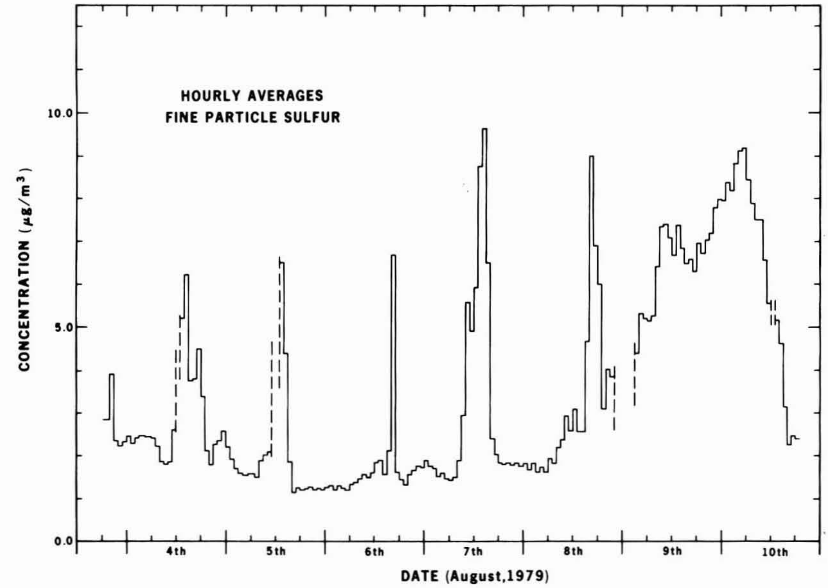


Figure 5. Plot of continuous particulate sulfur measurements obtained over a 7-day period. The sampling interval was 1 h.

Variations in sensitivity have been observed to be limited by the precision of the X-ray tube voltage and current control to a few percent. Periodic checks can be made by using the $CuSO_4$ standard to ensure that major systematic shifts have not occurred. Such shifts can be the result of defective He atmosphere in the spectrometer or changes in the proportional counter gain.

Problems associated with X-ray particle size and matrix effects are greatly reduced by the use of dichotomous size separation and thin-membrane filters. When one assumes a mean particle diameter of 0.3 μm for the sulfur aerosol particles, the correction due to particle-size effect is <1%. The larger correction for thick deposits can be estimated to be 3% for 100 $\mu g/cm^2$ up to 13% for 500 $\mu g/cm^2$. The nominal overload condition for the flow controller will trigger at 150–200 $\mu g/cm^2$. Since the particle deposit is on the filter surface facing the spectrometer, no correction for filter-attenuation effect is required. Results obtained with the current X-ray fluroescence analyzer have been cross-checked with other X-ray measurements with excellent agreement.

The precision of the measurement for short-term samples or light filter loadings is limited primarily by statistical variations in the counting rate averaged over the analysis interval. Table I is a summary of operating performance under a variety of sampling situations. The 3σ minimum detectible limits are quoted for both types of spectrometers for different sample intervals and by assuming a constant analysis time of 600 s. The improved sensitivity of the curved-crystal design is apparent.

Figure 5 is a plot of continuous sulfur measurements made on an hourly average during an 8-day interval in St. Louis. These results were a part of an intercomparison study involving several sulfur analysis methods. Results of the comparison will be published separately (*7*). The plot is shown here to illustrate the continuous monitoring capability of the present instrument. The results shown were available to the experimenters automatically on a continuous basis during the course of the study. Discontinuities in the data are the result of operator intervention in the experiment and do not reflect upon the reliability of the continuous sampler. The sensitivity of the combined sampler/analyzer system is such that a sampling time of 20 min or less could be employed. It is important to note that these results are for elemental sulfur only; equivalent sulfate concentrations would be 3 times greater. A comparison of these measurements with the minimal detectable limits given in Table I illustrates the sensitivity of the instrument for ambient-aerosol measurements. For example, using the curved-crystal spectrometer, it would be possible to perform sampling and analysis with 5-min time resolution during the peak sulfur concentration episodes.

Conclusions

Results obtained from the intercomparison of these results with other analytical methods support the validity of the present technique. The inherent advantages of the X-ray method include stability of calibration, relative immunity from chemical interferences, and the nondestructive processing of samples. Operating experience has demonstrated the ease of calibration and setup procedures. The availability of the samples following X-ray fluorescence analysis permits the use of the sampler for the collection of particulates for use with multiple analytical methods. The present instrument including sampler, X-ray analyzer, and all associated electronic hardware is ~1 m high and 0.5 m on a side, weighs less than 35 kg, and operates on a standard 115-V, 60-Hz power source.

Acknowledgment

We acknowledge the participation of W. Searles and S. Wollenburg in much of the mechanical and electronic design phases. F. S. Goulding, D. Landis, N. Madden, and other members of the Lawrence Berkeley Laboratory Department of Instrument Techniques contributed significantly to the success of the project. We appreciate the assistance of R. Gatti and R. Giauque in the preparation of standards and validation of the results.

Literature Cited

(1) Dzubay, T. G., Ed. "X-Ray Fluorescence Analysis of Environmental Samples"; Ann Arbor Science Publishers: Ann Arbor, MI, 1977.

(2) Loo, B. W.; French, W. R.; Gatti, R. C.; Goulding, F. S.; Jaklevic, J. M.; Llacer, J.; Thompson, A. C. *Atmos. Environ.* **1978**, *12*, 759–71.

(3) Birks, L. S.; Gilfrich, J. V. "Low Cost Compact X-Ray Fluorescence Analyzer for On-Site Measurement of Trace Elements in Airborne Particulate Emissions"; Environmental Monitoring Series, U.S. Environmental Protection Agency EPA-600/4-75-002, July 1975.

(4) Birks, L. S.; Gilfrich, J. V. *Spectrochim. Acta* **1978**, *33B*, 305.

(5) Johansson, T. *Naturwissenschaften* **1932**, *20*, 758.

(6) Husar, R. B.; Lodge, J. P., Jr.; Moore, D. J., Eds. *Atmos. Environ.* **1978**, *12*, No. 1–3.

(7) Loo, B. W.; Adachi, R. S.; Cork, C. P.; Goulding, F. S.; Jaklevic, J. M.; Landis, D. A.; Searles, W. L. Berkeley, CA, Jan 1979, Lawrence Berkeley Report LBL-8725.

(8) Camp, D. C., Lawrence Livermore Laboratory, unpublished results.

Received for review June 27, 1980. Accepted January 19, 1981. This work was supported in part by the Environmental Protection Agency under Interagency Agreement with the Office of Health and Environmental Research of the Department of Energy under Contract W-7405-ENG-48.

Use of Lead Isotopes in Soils To Identify the Source of Lead Contamination Near Adelaide, South Australia

Brian L. Gulson,* Kevin G. Tiller,[†] Karen J. Mizon,[‡] and Richard H. Merry[†]

CSIRO Division of Mineralogy, Institute of Earth Resources, P.O. Box 136, North Ryde, New South Wales 2113, Australia

■ Soil profiles from an urban–rural transect near Adelaide, South Australia, have been analyzed by using lead isotopes as a discriminant for the source of soil lead. Analyses of the top 10 cm of soil profiles taken from sites up to 50 km from Adelaide show that this surface horizon mainly contains Precambrian lead, such as that found in the Broken Hill or Mount Isa deposits. There is also a small amount of younger lead present, similar to that derived from Missouri and young Canadian deposits. Both types of lead are used in the manufacture of tetraethyllead for Adelaide gasoline. Natural soil lead, derived from parent rock, occurs throughout the profiles; however, it is only a relatively minor component in the surface horizons but is the major component at depths greater than 30–40 cm. Assessment of the data suggests that orchard sprays, power stations, and smelters are not the main source of lead in the surface horizons—rather, contamination derived from tetraethyllead from gasoline is indicated.

An ongoing study by the CSIRO Division of Soils of metal cycling in an urban–rural transect east of Adelaide, South Australia, is resulting in the collection of information on soils, plants, stream waters, and atmospheric accession. This transect includes a variety of soils and rocks and is ca. 100 × 30 km. It comprises urban, intensive agricultural, and extensive dryland agricultural environments, as well as an important water catchment.

A survey of surface soils in the transect suggests that, with increasing distance from Adelaide, the concentrations of lead and zinc decrease in the surface horizons, whereas the distributions of copper and cadmium show no such relationship to distance from the city (*1*). Furthermore, the decrease in concentration of lead with depth in the profiles is more pronounced closer to Adelaide, in the western part of the transect. The higher lead levels in the surface soils nearer to the city were initially considered to be related to the parent rocks and to enhanced biological activity due to higher rainfall. However, more recent investigations suggest that atmospheric fallout may have contributed significantly to the lead present in these surface soils.

Apart from some soils obviously affected by agricultural sprays or mineralization, the range of lead concentrations found in most of the surface soils taken from the transect was not significantly greater than normal.

The aim of the lead-isotope investigation was to determine the sources of the lead found throughout the soil profiles of the transect and, if possible, to evaluate the regional extent of urban pollution.

Four lead isotopes, three of which are the stable end product of the radioactive decay of a parent element, are measured. The radiogenic isotopes are ^{208}Pb (from ^{232}Th), ^{207}Pb (from ^{235}U), and ^{206}Pb (from ^{238}U). The fourth isotope, ^{204}Pb, has no known radioactive parent.

Since the formation of the earth, the three radiogenic lead isotopes have exhibited a smooth increase in abundance with time compared to the nonradiogenic isotope ^{204}Pb. The relative increase for each radiogenic isotope is in accord with the rate of radioactive decay of its parent. The various ratios of the isotopes to each other are conventionally plotted in diagrams such as those of Figures 2 and 3. By plotting the ratios of the relatively abundant radiogenic isotopes, for instance, in a diagram of ^{208}Pb/^{206}Pb vs. ^{207}Pb/^{206}Pb, one can minimize errors that may arise during mass-spectrometry measurements of the less abundant ^{204}Pb.

The growth curves are also plotted on the diagrams and represent the changing ratios of the isotopes with time in a closed system. In theory this variation in relative abundance is dependent not only on time but also on the Th/Pb and U/Pb ratios of the parent material. However, in practice there are complications, such as the mixing of lead from different sources. On the ratio plots, this is shown by the straight mixing lines.

Each lead–zinc ore body has its own specific set of isotope ratios (i.e., its "isotopic fingerprint"). For example, large "massive sulfide"-type ore bodies—such as those at Mount Isa and Broken Hill in Australia and at Sullivan in Canada—contain lead that has uniform isotope ratios. The isotopic data plot on or near to the growth curves. However, the "Mississippi Valley"-type ore bodies—such as those in Missouri in the United States—are very different and contain lead that has diverse isotope ratios. The isotopic data are of a more radiogenic nature (i.e., ^{206}Pb, ^{207}Pb, and ^{208}Pb are relatively abundant) and do not plot on the growth curves.

In soils, the lead isotopic data can show even more variable and more radiogenic isotopic patterns than "Mississippi Valley"-type ore bodies.

Study Area

The study area is shown in Figure 1. It extends from the Adelaide urban area (Adelaide Plains) in the west to the Murray River (Murray Plains) in the east. These regions are predominantly underlain by Quaternary sediments, whereas the central Mount Lofty Ranges, in the center of the area, are underlain by mainly Upper Proterozoic, Cambrian and Ordovician rocks, although a small area is underlain by lower Proterozoic rocks (e.g., at site 694).

Soils are mainly loam, sandy loam, or loamy sand surface soils overlying yellow or red clay B horizons, which vary considerably in depth to weathered rock. Average annual rainfall is largely topographically controlled and varies in amount from ca. 900 to 300 mm. The higher average rainfalls occur on the western side of the Mount Lofty Ranges, declining both to the east and to the west. Frontal rains approach from the west, the prevailing wind direction, and provide the major part of the annual rainfall, ~70–80% of which falls between April and October (*2*).

Although other winds do occur, the predominant winds in Adelaide during the wet months of the year are from the northwest to southwest direction, both close to the ground and at ~1000 m (Bureau of Meteorology, Adelaide, personal communication). Southwesterly sea breezes predominate during the daytime in the summer months.

Site Selection

The 12 soil sample sites used in this study are representative of others along the transect and are shown in Figure 1. They were chosen mainly on the basis of surface-soil lead concen-

---

[†] CSIRO Division of Soils, Institute of Earth Resources, P.B. No 2, Glen Osmond, South Australia 5064.

[‡] CSIRO Division of Fossil Fuels, Institute of Earth Resources, P.O. Box 136, North Ryde, New South Wales 2113.

0013-936X/81/0915-0691$01.25/0 © 1981 American Chemical Society

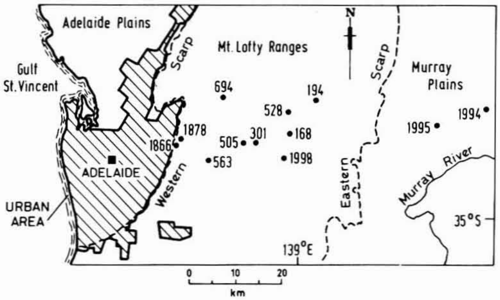


Figure 1. Locality map for soil samples from the study area.

Table I. Distance of Sites from Adelaide and from Nearest Main Road of Known Traffic Volume

site no.	distance from Adelaide,[a] km	distance to nearest main road,[b] km	vehicles/day[c]
1866	15	1.4	1500–11000
1878	16	2.2	>11000
563	20	3.6	2600
694	27	0.7	150
505	27	3.6	850
301	31	6.8	850
168	37	2.0	500
528	39	3.8	400
194	47	11.3	400
1995	68	2.0	180
1994	78	11.3	180
1998	38	3.8	600

[a] Measured from city center. [b] Toward Adelaide, in a westerly direction. [c] Data from South Australian Highways Department.

tration and for remoteness from busy roads, although the two sites nearest to the Adelaide urban area (1878 and 1866) are closer to roads carrying high traffic volumes. The sites have a westerly aspect (i.e., toward Adelaide) or are unobstructed for a considerable distance in that direction. All sites are in open grassland or pasture (except 694, which is in dry sclerophyll woodland).

The distance of each site to the nearest main road (for which the traffic volume in a westerly direction had been measured in 1974) is shown in Table I. Samples were normally collected at least 50 m from local roads and tracks, which have much lower traffic volumes (less than ~20 vehicles/day) than the nearest main road.

Soil Sampling

Soil cores were obtained by driving a steel tube (5-cm diameter) to a depth of 1 m, or less if the soil was shallow. The cores either were cut into 10-cm sections immediately on extrusion from the tube and stored in plastic bags or were extruded directly into a plastic sheath for later subsectioning in the laboratory. The individual samples were then dried at 35 °C, ground to pass a 2-mm sieve, and stored in plastic containers before analysis. The sections of the profile selected for isotope analysis were the 10-cm surface, the deepest subsample, and an intermediate subsample, which was taken either from the B horizon, where clearly defined midway down the profile, or from the 30–40-cm section if there was no clearly definable pedological change. Organic matter (such as roots and seeds) present in the surface soil was not separated.

Techniques

Contaminant lead present in surface soil is more easily removed than the lead in the lower horizons, which is an inherent part of the soil and is tightly bound in minerals such as feldspars. Consequently, for most of our analyses, only dilute HCl was used to extract the lead. To investigate the inherent lead in the whole soil, the sample was attacked with $HF–HNO_3$.

For the acid leaches, ~0.5–1 g of soil was weighed into a 10-mL PTFE beaker. Ca. 3 mL of 1.2 N HCl was added and the mixture stirred overnight (for ~16 h). The material was then transferred in 1.2 N HBr to a 10-mL polypropylene centrifuge tube and centrifuged. In most samples, the supernatant liquid was split: one aliquot was retained for isotope ratios and the other mixed with a $^{207}Pb/^{204}Pb$ spike for concentration measurements and to correct for mass fractionation during mass-spectrometric analysis. The spiked aliquot was evaporated to dryness and taken into solution with ~2–3 mL of 1.2 N HBr and 1 mL of 1.2 N HCl. The solutions were transferred to a 2-mL anion-exchange column (AG 1-X8, 200–400 mesh) previously conditioned with 1.2 N HBr. Washings (10 mL of 1.2 N HBr, 10 mL of 1.2 N HCl) were discarded, and the lead was eluted with 6 N HCl. A second-stage purification was achieved by anodic electrodeposition.

For some samples, the whole soil or the centrifuged residue from the acid leach was dissolved in $HF–HNO_3$, and the lead leached out with 1.2 N HBr–1.2 N HCl. The lead separation method was the same as that used for the supernatant from the acid leaches.

The lead was analyzed by using the silica gel–phosphoric acid method on an AVCO 35-cm radius 90°-sector mass spectrometer. Data for the preliminary study (which was carried out 18 months prior to the present results) were usually taken with the largest peak ^{208}Pb at ca. 1×10^{-11}–3×10^{-11} A, by using a peak switching unit arranged in the order 206–207–zero–208–zero–204–206. The data from a DANA digital voltmeter were recorded with a Hewlett-Packard printer taking five 20-ms readings per peak. This prototype system was less sophisticated and gave less satisfactory data than the present arrangement, which is under computer control. Also, on occasion, it was difficult to obtain a clean sample for the mass-spectrometric analysis, even with electrodeposition. For a set of 10 ratios, the internal standard deviations were as follows: $^{208}Pb/^{206}Pb$, 0.02–0.2%; $^{207}Pb/^{206}Pb$, 0.03–0.1%; and $^{206}Pb/^{204}Pb$, 0.10–0.3%. Some runs (as indicated in Table II) had a standard deviation of 0.3–0.5% for the $^{206}Pb/^{204}Pb$.

The most recent data were acquired under computer control and with small changes in the chemical separation method. Two to four blocks of 16 ratios, measured in the sequence 206–204–206–207–206–208–206, typically gave the following standard errors of the mean: $^{208}Pb/^{206}Pb \leq 0.01\%$; $^{207}Pb/^{206}Pb \leq 0.02\%$; and $^{206}Pb/^{204}Pb \leq 0.1\%$. Eight analyses of the National Bureau of Standards SRM 981 over a 2-week period gave the following results, expressed as standard error of the mean: $^{208}Pb/^{206}Pb = 0.005\%$; $^{207}Pb/^{206}Pb = 0.02\%$; $^{206}Pb/^{204}Pb = 0.035\%$. The results in Table II were normalized to SRM 981 and Broken Hill lead. Processing blanks ranged from 8 to 12 ng of lead.

Results

In view of the number of data in Table II, and to avoid confusion, we have plotted only representative sites and usually the highest-precision data in Figures 2 and 3. Mixing lines are drawn in these figures to join isotopic values of Broken Hill–Mount Isa and Missouri ("Mississippi Valley")

Table II. Lead Isotopic and Concentration Measurements for Soils from Urban–Rural Transect[f]

sample no.[a]	depth, cm	treatment	Pb[b] µg/g	$^{208}Pb/^{206}Pb$	$^{207}Pb/^{206}Pb$	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$
Mt Lofty Ranges Profiles								
694/1[c]	0–10	AL	47 (53)	2.1026	0.8414	18.87	15.87	39.67
/4[c]	30–40	AL	25.6 (25)	2.0600	0.8042	19.84	15.96	40.87
/7[c]	60–73	AL	28.9 (24)	2.0475	0.7980	20.06	16.01	41.07
/7[c]	60–73	WS	14	1.9937	0.7782	20.94	16.30	41.75
1878/1	0–10	AL	25 (30)	2.1793	0.9140	16.964	15.505	36.970
/4	30–40	AL	10 (10)	2.1159	0.8510	18.395	15.654	38.922
/9	80–93	AL	16 (12)	2.0755	0.8051	19.717	15.874	40.923
1866/1	0–10	AL	23 (15)	2.1925	0.9322	16.469	15.352	36.108
/4	30–40	AL	3.1 (—)	2.1611	0.9074	17.041	15.463	36.827
/6	50–57	AL	2.2 (1.6)	2.1221	0.8751	17.732	15.517	37.629
563/1[cde]	0–10	AL	(21)	2.183	0.915	16.98	15.54	37.06
/1-1[cd]	0–10	AL	(21)	2.172	0.910	17.08	15.55	37.09
/1-2[c]	0–10	AL	(21)	2.1769	0.9112	17.02	15.51	37.05
/1-2[cd]	0–10	res	10	2.124	0.848	18.57	15.75	39.44
/1-3	0–10	AL	23	2.1760	0.9097	17.061	15.520	37.125
/1[c]	0–10	WS		2.1538	0.8847	17.65	15.62	38.02
/4[c]	30–40	AL	(3.6)	2.1344	0.8349	18.75	15.65	40.01
/6[cd]	50–60	AL	(2.3)	2.140	0.854	18.52	15.82	39.63
/6[cd]	50–60	WS		2.119	0.820	19.34	15.86	40.98
168/1	0–10	AL	13 (12.5)	2.1901	0.9272	16.686	15.471	36.544
/3	20–30	AL	10 (11.0)	2.1532	0.8977	17.230	15.467	37.100
/9	80–90	AL	6.4 (3.7)	2.1062	0.8516	18.025	15.350	37.964
301/1[c]	0–10	AL	(12.7)	2.1785	0.9260	16.75	15.51	36.49
/4[c]	30–40	AL	(3.8)	2.0963	0.8422	18.95	15.96	39.72
/10[c]	90–100	AL	(3.9)	2.0867	0.8283	19.06	15.79	39.77
/10[c]	90–100	WS	13.8	2.0833	0.8253	19.68	16.24	41.00
528/1	0–10	AL	4.2 (3.9)	2.1871	0.9254	16.684	15.439	36.490
/5	40–50	AL	2.3 (2.1)	2.0976	0.8531	18.287	15.601	38.359
/9	80–90	AL	1.9 (0.8)	2.0868	0.8469	18.376	15.563	38.347
194/1-1[c]	0–10	AL	3.0 (3.1)	2.1608	0.8896	17.23	15.33	37.23
/1-2[c]	0–10	AL	(3.1)	2.1590	0.8875	17.55	15.58	37.90
/3[c]	20–30	AL	1.9 (1.1)	2.0690	0.7712	20.48	15.80	42.38
/10[cd]	90–100	AL	1.3 (0.73)	2.057	0.758	21.18	16.06	43.58
/10[c]	90–100	WS		2.0659	0.7686	20.49	15.75	42.33
Background Profiles								
1994/1	0–10	AL	2.4 (2.5)	2.0869	0.8424	18.504	15.588	38.616
/4	30–40	AL	1.2 (—)	2.0542	0.8193	19.006	15.572	39.042
10	90–100	AL	2.1 (2.4)	2.0647	0.8243	18.955	15.625	39.136
1995/1[d]	0–10	AL	3.6 (3.5)	2.0924	0.8486	18.34	15.56	38.36
/4[d]	30–40	AL	2.9 (—)	2.0523	0.8129	19.21	15.62	39.43
/10[d]	90–100	AL	1.5 (2.4)	2.0682	0.8319	17.55	14.60	36.30
Orchard soil								
505	0–10	AL	240 (265)	2.2174	0.9524	16.171	15.401	35.858
Mineralized Profile								
1998/1	0–10	AL	130 (120)	2.1385	0.8780	17.716	15.554	37.886
/5	40–50	AL	220 (190)	2.1412	0.8765	17.813	15.613	38.141
10	90–100	AL	300 (340)	2.1428	0.8774	17.791	15.610	38.123

[a] 1-1, 1-2, etc., replicate analyses. [b] Concentrations in parentheses are by 1 N HCl extraction, 16 h, 10 g of soil with 25 mL of HCl, analyzed by atomic absorption. [c] Data from preliminary study. [d] Analyses with standard deviation of 0.3–0.5% for $^{206}Pb/^{204}Pb$. [e] Stirred 5 h longer than 563/1-1 and 563/1-2. [f] AL = acid leach; WS = whole soil; res = residue.

lead (*3*). Part of the growth curve for "massive sulfide" deposits is also drawn (*4*).

Profiles from Mount Lofty Ranges. Profiles from eight sites in the Mount Lofty Ranges were chosen to evaluate the extent of possible urban pollution. These profiles (168, 194, 301, 528, 563, 694, 1866, and 1878) are located at varying distances from Adelaide and have differing lead concentrations. They conform to a fairly standard pattern: (1) The lead concentration is usually highest in the top 10 cm of soil and decreases by 3–4 times in the middle and lower parts of the soil profile. (2) The lead isotope ratios become more radiogenic with depth, approaching the ratio expected of the parent rocks (i.e., higher in $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{208}Pb/^{204}Pb$ ratios or, conversely, lower in $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$). (3) The samples from each profile give results that lie on well-defined arrays, the goodness-of-fit being better for the more recent, higher-quality data than for the preliminary data (Figures 2 and 3, Table II). (4) The arrays intersect the Broken Hill–Missouri mixing line and the growth curve over a restricted range of isotopic ratios. (5) The slopes of most of these arrays depart significantly from those for the Broken Hill–Missouri mixing line and the growth curve, which suggests that the lead in these samples is not a simple mixture of lead from different ore bodies, such as from Broken Hill and Missouri.

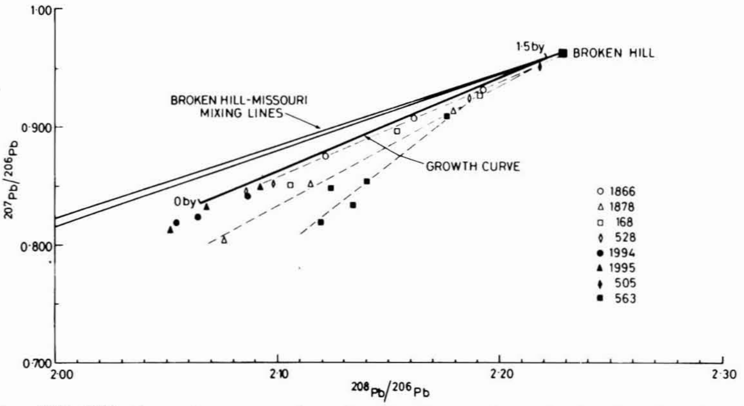


Figure 2. $^{208}Pb/^{206}Pb$ vs. $^{207}Pb/^{206}Pb$ diagram for representative soil profiles. The growth curve is taken from Cumming and Richards (*4*), and the Missouri data were taken from Sverjensky et al. (*3*). Dashed lines (eyeball fit) are the mixing lines between natural soil and contaminant leads.

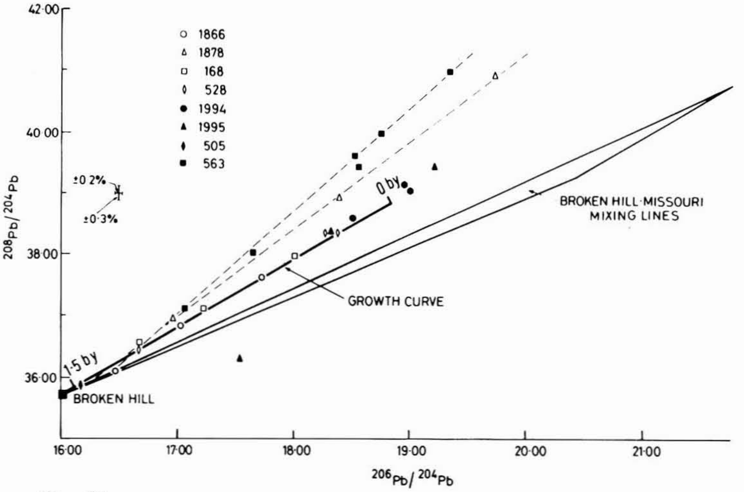


Figure 3. $^{208}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ diagram for representative soil profiles. The growth curve is taken from Cumming and Richards (*4*), and the Missouri data were taken from Sverjensky et al. (*3*).

The data clearly suggest that the surface soils in these profiles contain significant amounts of Precambrian lead from Broken Hill or Mount Isa, with a small amount of some younger lead, perhaps from Missouri or Canada. (No tetraethyllead is manufactured in Australia; both Missouri and Canadian lead—in addition to lead from Broken Hill and Mount Isa—are used to make tetraethyllead for the Australian market.) They also show that contamination of soil with this lead takes place up to at least 50 km east of the coastline at Adelaide. Calculations indicate that the Australian ore component of this contaminant lead is ~80–85% when based on Broken Hill lead ratios. The lead isotope ratios obtained from the soil profiles are essentially mixing lines of soil and contaminant Pb.

That the lead in the soils is a mixture of contaminant and soil lead is well illustrated by profile 563. The acid-leach data for the top 0–10 cm of 563/1 (the horizon with the highest amount of extractable lead) lie close to the growth curve (Figures 2 and 3). Deeper in the soil profile, the lead concentration decreases to 3.6 and 2.3 μg/g, and the data become more radiogenic. This trend would be expected of the natural soil lead, which developed in a higher U/Pb and Th/Pb environment than ore lead.

The proposal that lead in surface soils has a component of contaminant lead is further substantiated by whole-soil data and the residues from the acid leach. For 563/1, the data for acid leaching, whole soil, and residue lie approximately on a mixing line of contaminant and natural soil lead, with the residue, stripped of contaminant Pb, being more radiogenic than the acid leach or whole soil.

The whole-soil data for 694/7, 563/1, 563/6, and 301/10 (but not 194/10) are more radiogenic than their acid-leach counterparts, as expected for natural soil lead. In the case of the deepest samples, the whole-soil data (natural soil lead) define one end member of a mixing line, the other end member being the acid-leach values (contaminant lead) for the 0–10-cm samples.

The linearity of the lead-isotope data for the various profiles indicates that the soils throughout an individual profile had been weathered from source rocks of uniform isotopic composition. Local or regional transport of material of similar isotopic composition cannot be ruled out.

No relationship appears to exist between the lead isotope ratios and concentrations of lead in surface horizons or at lower depths. For example, in those soils nearest Adelaide, profile 1866 with the low lead values of 2–3 μg/g (Table II) is less radiogenic and shows less dispersion (i.e., less variation of lead isotopes throughout the profile) than profile 1878, which has 10–16 μg/g in the lower horizons. These differences are probably influenced by soil type. In profile 1866, a sandy, light-textured soil, leaching is possible to a greater depth than in profile 1878, which has a massive, heavy clay subsoil at 30 cm. In general, for a given input of contamination, the sandier soils (which tend to have both the lowest lead contents and the greatest potential for leaching) should exhibit the largest shifts toward the Broken Hill–Missouri mixing line or the growth curves.

A more general relationship describing the variation of radiogenic character of soil horizons cannot be established for the limited number of samples available, because of the extent of aerial contamination of lead, site-specific variations in original lead content of the soil, and soil properties affecting leaching. For example, profile 694 occurs in an area of high expected levels of contamination but also has high lead contents arising from the parent rocks. These lead concentrations are so high that contaminating lead does not markedly affect soil lead levels. Surface horizon isotopic data for profile 694 are thus closer to those of the lower horizons and do not exhibit the expected substantial shift toward the Broken Hill–Missouri mixing line. Despite the apparent anomalies, the majority of sites sampled in the Mount Lofty Ranges clearly indicate that there has been significant accession of aerosol lead.

Background Profiles. Site 1994 is an agricultural soil with calcareous subsoil on recent sediments and is farthest from Adelaide and remote from frequently used roads. The three samples from this profile contain 1–2 μg/g lead (Table II) and have radiogenic lead isotope ratios.

Site 1995 is also remote, but its soil has developed on metamorphosed granites. The data are similar to those for 1994, although more variable, perhaps reflecting a greater heterogeneity of lead in the source rocks or the contribution of other materials to the low lead levels present in the soil horizons. The surface soil could be expected to be similar to 1994, but at a depth of 90–100 cm it is quite different. In contrast to 1994, the acid-leachable lead concentrations of 1995 decrease down the profile from 3.6 to 1.5 μg/g.

The isotopic data for these two profiles suggest that they are uncontaminated, in that the analyses do not lie along mixing arrays but tend to form a cluster in the uncontaminated section of the soil mixing arrays (Figures 2 and 3). That is, their isotopic patterns are consistent with the deeper uncontaminated parts of the soil profiles from the Mount Lofty Ranges.

Mineralized Profile. Site 1998 is a lateritized soil (podzol) overlying the Nairne pyrite unit. Lead concentrations in the surface soil range from 130 to 300 μg/g. At the surface the mineral hinsdalite (Pb, Ba, Al phosphosulfate) is common, while at depth (up to 2 m) hinsdalite and lead sulfide occur (*5*). Lead isotopic ratios (Table II) are uniform, plot close to the growth curve, and are thus consistent with known "massive sulfide" deposits.

Sources of Contamination

The lead isotopic data from the soil profiles lie on mixing arrays whose end members are soil lead and contaminant lead. Intersection of the arrays on various isotopic plots allows the isotopic ratios of the contaminant lead to be obtained, so that its source can be determined.

The intersection of the arrays is close to Broken Hill–Mount Isa lead (Figures 2 and 3), but there is a small component of more radiogenic (probably younger) lead present. Calculations indicate that the Australian ore component of the contaminant lead is ~80–85% when based on Broken Hill isotope ratios. A number of possible sources could give contaminant lead with this isotopic signature: agricultural sprays, lead smelters, thermal power stations, and gasoline additives.

Agricultural Sprays. For many years, orchards in the study area have been sprayed with lead arsenate for control of various insect pests. It is conceivable that the contamination observed in some surface soils in the study area originates from this spray. The lead in the spray, manufactured in Australia, was undoubtedly from Broken Hill or Mount Isa.

The lead concentration for the orchard soil sample used in this study was 240 μg/g, but values of up to 600 μg/g have been measured (*6*). The lead isotope ratios for the orchard soil differed by less than 1% from Broken Hill lead (*7*) and less than 0.5% from Mount Isa lead (*8*). These small differences between the orchard soil ratios and those of Broken Hill and Mount Isa lead probably reflect a minor contribution from soil lead in the orchard soil (probably no more than 15–20 μg/g).

All of the arrays for contaminated samples intersect at, or very close to, the orchard-soil value. This may indicate that the samples are at least partly contaminated with lead arsenate spray, but there are several other factors to be considered:

(1) The main orchard area lies to the south and southeast of the study area, but the prevailing wind direction is from the northwest and southwest.

(2) Lead arsenate is no longer used as a commercial insecticide. Also, its total usage in the Mount Lofty Ranges is negligible in comparison to the amount of lead from automobile emissions in the Adelaide metropolitan area (in which there were 615 486 registered automobiles in 1975; data from the South Australian Department of Transport). In addition, lead accession to the area is a current phenomenon (*1*).

(3) Soil analyses from pastures adjoining the orchards suggest that lead from sprays does not drift more than ~30–50 m (*1*).

Lead Smelters. Lead smelters are another possible contaminating source. The feed stock for the Port Pirie smelter (which began in 1889 and is ~200 km NNW of Adelaide) is mainly Broken Hill ore. A detailed investigation by Cartwright et al. (*9*) showed that the greatest contamination from heavy metals is in the prevailing wind direction, and only background concentrations of lead can be measured beyond ~40 km from the smelter. The prevailing surface wind (at 2 m above ground level) direction in this area is from the south, with a component from the north (*9*). However, heavy-metal contamination is also significant in the hilly area to the east of the smelter, because of the prevailing high-level westerly winds (*9*).

Thermal Power Stations. Thermal power stations are another possible source of lead. However, in view of the young age of the coal used in power stations (compared with the Precambrian age of the major contaminant lead) and the expected radiogenic lead isotopes in coal (*10*), they are not considered a major source.

Gasoline Additives. On a worldwide basis, almost all of the isotopic data for gasoline additives (*11*) lie on the fan between the Broken Hill–Missouri mixing lines and the growth curve. Most of the tetraethyllead added to gasoline at the Port Stanvac (Adelaide) refinery is manufactured by a company that uses mainly Broken Hill and Mount Isa lead, with some Canadian lead. The isotopic ratios of this tetraethyllead are consistent with those estimated from the intersection of the arrays in Figures 2 and 3, but they are also consistent with the presence of up to 20% Missouri lead in the contaminant.

As it is impossible to obtain precise information on the isotopic composition of tetraethyllead used in Australia over a long time period, we can only conclude that, at the present stage of our investigation, gasoline additives appear to be the major source of contamination.

In fact, the absence of significant sources of contaminant lead other than automobile exhaust in the Adelaide metropolitan area provides a unique opportunity to assess the spread of urban pollutants into adjoining areas. The long-range transport of the finest lead aerosols is exemplified by studies of accumulation of lead in the Greenland icecap (*12*) and by estimates of the long atmospheric residence times (7–30 days) of lead (*13*). The very short-range transport (less than 100 m) of coarser lead particles away from highways is also well documented. Intermediate-range transport of lead aerosols arising from automobiles is not as well understood, but Reiter et al. (*14*) concluded that nearly half of the lead emitted from automobiles was still airborne at the perimeter (>20 km) of their urban study area. Chow and Johnstone (*15*) showed that the high concentrations of lead in snow at the Lassen Volcanic National Park were derived from gasoline aerosols probably transported from San Francisco.

The spread of automobile lead aerosols with atmospheric residence times of some hours, and the precipitation of lead as dust or by rainfall, should indicate the potential for dispersal of many other urban pollutants which are emitted into the atmosphere. Because of the limited mobility of lead in soils, levels of contaminant lead in soils provide an approximation of the historic record of the extent of pollutant fallout. This approach was used by Cartwright et al. (*9*) in their assessment of accumulated fallout of heavy metals around a lead–zinc smelter in South Australia. The current isotopic study shows that surface soils are contaminated with lead at distances of ~50 km east of the city in the general direction of the prevailing winds. In other situations, this distance would be influenced by local topography and climate.

Comparison with Other Isotope Studies of Soils

Ault et al. (*16*) analyzed surface samples across the New Jersey Turnpike, in a rural area approximately midway between New York City and Philadelphia. The isotope ratios of the topsoil close to the turnpike were less radiogenic (i.e., more similar to those measured for tetraethyllead) than samples more than 150 m from the turnpike. Soil samples from a depth of 12.5 cm had very similar isotope ratios to surface soils, implying further contamination at greater depths. The isotopic ratios of samples from a forested area in the Ringwood State Park, away from major roads, at depths of 0–2.5, ~19, and ~39 cm, showed trends similar to those observed in our samples. That is, isotope ratios of surface soils are more akin to those measured for lead in gasoline additives, but the ratios become progressively more radiogenic with depth and resemble those of the parent rock.

Rabinowitz and Wetherill (*17*) carried out a detailed study in southern Missouri and California, where they found that, although the lead concentrations from hot 6 N HCl acid leaches decreased 13 cm beneath the surface, the isotopic data showed no consistent trend. However, because some of the deeper soils were more radiogenic than the surface samples, they suggested that the surface soils were contaminated by automobile exhaust.

The data of Chow et al. (*18*) for Californian sediments show similar trends to our data. Their isotopic data for the top layers lie close to a "pollution line" plotted from isotopic data for lead ores and gasoline additives (*11*). Also, Chow (*19*) had earlier sampled soils adjacent to major highways in the United States. He found that the 7 N HCl leaches of the 10–15-cm profile had a lower lead concentration and were more radiogenic than those of the 0–5-cm profile. Our data are consistent with this finding.

Conclusions

A lead-isotope study of soil profiles on an urban–rural transect extending east from Adelaide, South Australia, suggests that, up to ~50 km from Adelaide in the prevailing westerly wind direction, the top 10-cm horizon at least is contaminated with lead from gasoline additives. The data indicate that appreciable lead contamination does not extend deeper than 30–40 cm. Using automobile lead as an indicator of urban pollution, this study indicates that pollutants have spread at least 50 km from their source.

Acknowledgment

We thank M. J. Korsch, J. R. Richards, S.-S. Sun, M. Vaasjoki, and D. J. Whitford for criticism of the manuscript.

Literature Cited

(1) Tiller, K. G.; Smith, L. H.; Merry, R. H., CSIRO Division of Soils, 1978, unpublished data.
(2) Coote, G. C.; Cornish, E. A. *CSIRO, Div. Math. Stat. Tech. Pap.* **1958,** *4*.
(3) Sverjensky, D. A.; Rye, D. M.; Doe, B. R. *Econ. Geol.* **1979,** *74*, 149.
(4) Cumming, G. L.; Richards, J. R. *Earth Planet. Sci. Lett.* **1975,** *28*, 155.
(5) Norrish, K. "Trace Elements in Soil–Plant–Animal Systems"; Nicholas, D. J. D., Egan, A. R., Eds.; Academic Press: New York, 1975.
(6) Merry, R. H., CSIRO Division of Soils, unpublished data, 1978.
(7) Cooper, J. A.; Reynolds, P. H.; Richards, J. R. *Earth Planet. Sci. Lett.* **1977,** *6*, 467.
(8) Gulson, B. L.; Mizon, K. J., CSIRO Institute of Earth Resources, unpublished data, 1979.
(9) Cartwright, B.; Merry, R. H.; Tiller, K. G. *Aust. J. Soil Res.* **1977,** *15*, 69.
(10) Chow, T. J.; Earl, J. L. *Science* **1972,** *176*, 510.
(11) Chow, T. J.; Snyder, C. B.; Earl, J. L. "Isotope Ratios as Pollutant Source and Behaviour Indicator"; Joint FAO–IAEA Symposium, Vienna, 1974.
(12) Murozumi, M.; Chow, T. J.; Patterson, C. *Geochim. Cosmochim. Acta* **1969,** *33*, 1247.
(13) National Research Council, National Academy of Sciences. "Airborne Lead in Perspective"; National Academy of Sciences: Washington, DC, 1972.
(14) Reiter, E. R.; Henmi, T.; Katen, P. C. "Lead in the Environment"; Boggess, W. R., Ed.; National Science Foundation: Washington, DC, 1977; Chapter 3.
(15) Chow, T. J.; Johnstone, M. S. *Science* **1965,** *147*, 502.
(16) Ault, W. U.; Senechal, R. G.; Erlebach, W. E. *Environ. Sci. Technol.* **1970,** *4*, 305.
(17) Rabinowitz, M. B.; Wetherill, G. W. *Environ. Sci. Technol.* **1972,** *6*, 705.
(18) Chow, T. J.; Bruland, K. W.; Bertine, I.; Soutar, A.; Koide, M.; Goldberg, E. D. *Science* **1973,** *181*, 551.
(19) Chow, T. J. *Nature (London)* **1970,** *225*, 295.

Received for review July 7, 1980. Accepted February 6, 1981.

Alkylpyridines in Surface Waters, Groundwaters, and Subsoils of a Drainage Located Adjacent to an Oil Shale Facility

Robert G. Riley,* Thomas R. Garland, Kazumi Shiosaki, Dale C. Mann, and Raymond E. Wildung

Environmental Chemistry Section, Pacific Northwest Laboratory, Battelle Memorial Institute, P.O. Box 999, Richland, Washington 99352

■ Soil extracts, surface waters, and groundwaters were analyzed for the presence of water-soluble organic compounds in a drainage located adjacent to the retorted shale disposal pile at the Department of Energy Anvil Points Oil Shale Facility, Rifle, CO. The C_3–C_6 alkylpyridines were positively identified in water from one of several alluvial wells, and in a surface seep. Surface waters of the stream below the seep contained alkylpyridines but in lower concentration. Alkylpyridines were detected in a moist subsoil sampled adjacent to the well, in retort water, and in aqueous extracts of shale oil. They were not detected in aqueous extracts of raw shale, retorted shale, or Prudhoe Bay crude oil. The absence of the alkylpyridines in a petroleum suggests that the compounds may be unique to shale oils, perhaps allowing their use as diagnostic indicators of water in contact with shale oils at sites of oil shale production and processing.

Introduction

Because of the uncertain status of current world petroleum prices and supplies, emphasis is being placed in the United States on the development of processes for the production of synthetic fuels from oil shale and coal. The above-ground oil shale retorting processes produce liquid and solid wastes that, in many respects, are unique to the industry (*1*). Current protocols call for the disposal of retorted shale to the ground, possibly in association with retort water used for compaction and dust control. Recent investigations (*2–4*) have indicated that a high percentage of organic compounds comprising retort water and retorted shale are polar, accounting for their high water solubility. Mono- and dibasic organic acids, a class of compounds that fit this category, have been identified in retort water, but these identified compounds account for only 0.4% of the soluble organic carbon (*2*). Compounds with relatively low affinity for retorted shale, with sufficient leaching, could subsequently enter surface water and groundwater adjacent to oil shale operations (*5–10*). There is a need to further define the composition of retort water as identification of organic compounds in leachates from retorted shale and codisposed materials early in the development of commercial production processes will allow development of control measures necessary to minimize environmental and human health effects resulting from waste disposal.

Studies were initiated at the Department of Energy Anvil Points Oil Shale Facility at Rifle, CO, in the spring of 1979 to evaluate the environmental fate of mobile residues from the wastes disposed during shale oil production. This site has been utilized for development of oil shale mining and production processes since the 1940s. The stream and drainage basin characteristics have been described (*11*). Solid wastes, principally retorted shale and raw shale fines, produced by several experimental processes have been disposed to the West Sharrard drainage adjacent to the facility. Furthermore, retort water and shale oil have been stored periodically on the site for a number of years. Current investigations are directed toward determination of the concentration of water-soluble organic compounds in materials disposed of or stored at the site and in surface waters, groundwaters, and subsoils above and below the site. Continuing studies are underway to aid in defining the source and hydrologic transport of water-soluble compounds which may result from nearly 40 yr of operations and waste disposal.

Experimental Section

Sample Collection. To identify changes in water composition, we collected samples of surface waters, alluvial groundwaters (well waters), and seeps from above and below the disposal location in West Sharrard drainage for organic chemical analysis. Water samples from West Sharrard stream and several alluvial wells and a seep located adjacent to the stream were collected in Teflon bottles in May 1979. The samples were immediately frozen (−20 °C) and transported to the laboratory for chemical analysis.

Samples of shale oil, retorted shale (<6.3 mm), raw shale, and retort water were obtained from the Department of Energy Anvil Points Oil Shale Facility, Rifle, CO. The retort was being operated in the direct mode at the time that the oil, retorted shale, and retort water were produced; i.e., retort gases recycled to the retort and combustion of a portion of the carbonaceous fraction provided the heat for the process. Before use, the untreated retort water was filtered through glass wool and a 0.45-μm filter. Filtered samples were stored in capped bottles at 2 °C when not in use. Prudhoe Bay crude oil was obtained from Atlantic Richfield Co., Cherry Point, WA.

Subsoil core samples were obtained at selected levels adjacent to the drainage stream during the installation of new alluvium water wells by using either "standard penetration tests" or "California type" split spoon barrels (5.1-cm o.d.) driven 30.5–45.7 cm by a 63.6-kg bumper falling freely a distance of 76.2 cm.

Preparation of Aqueous Extracts of Shale Oil, Prudhoe Bay Crude Oil, Raw Shale, and Retorted Shale. Ten-milliliter samples of shale oil and Prudhoe Bay crude oil were extracted with 100 mL of distilled water, and the aqueous extracts were filtered through a 0.45 μm filter. Hexane extracts of the filtered aqueous extracts were analyzed by gas chromatography. Samples of raw shale and retorted shale (50 g) were shaken in 250-mL Corex centrifuge tubes containing 150 mL of 0.05 M $NaHCO_3$ for 18 to 36 h. After being shaken, the samples were centrifuged, and 100 mL of the aqueous solutions was extracted with hexane and analyzed by gas chromatography.

Preparation and Gas-Chromatographic Analysis of Well Water Extracts for Saturate and Aromatic Hydrocarbons. A sample of well water was passed through a stainless-steel column (1.6-cm o.d. × 22.9 cm in length) containing XAD-2 resin. Adsorbed hydrocarbons were eluted from the resin column with ethyl ether. The ether extract was dried (Na_2SO_4) and concentrated by using a Snyder column, and the saturate and aromatic hydrocarbons were separated by silica gel chromatography and analyzed by gas chromatography according to a previously described procedure (*12*).

Preparation and Gas-Chromatographic Analysis of Well Water Extracts for Phenols. Samples of well water (50 mL) were made basic by the addition of 0.2 g of NaOH and extracted with 20 mL of hexane. Following removal of the hexane layer, 0.5 mL of acetic anhydride was added to the aqueous layer. The aqueous layer was shaken for 1 min and then extracted with 5 mL of hexane. The hexane extract was concentrated to 4 mL following addition of 0.5 mL of a 400-

0013-936X/81/0915-0697$01.25/0

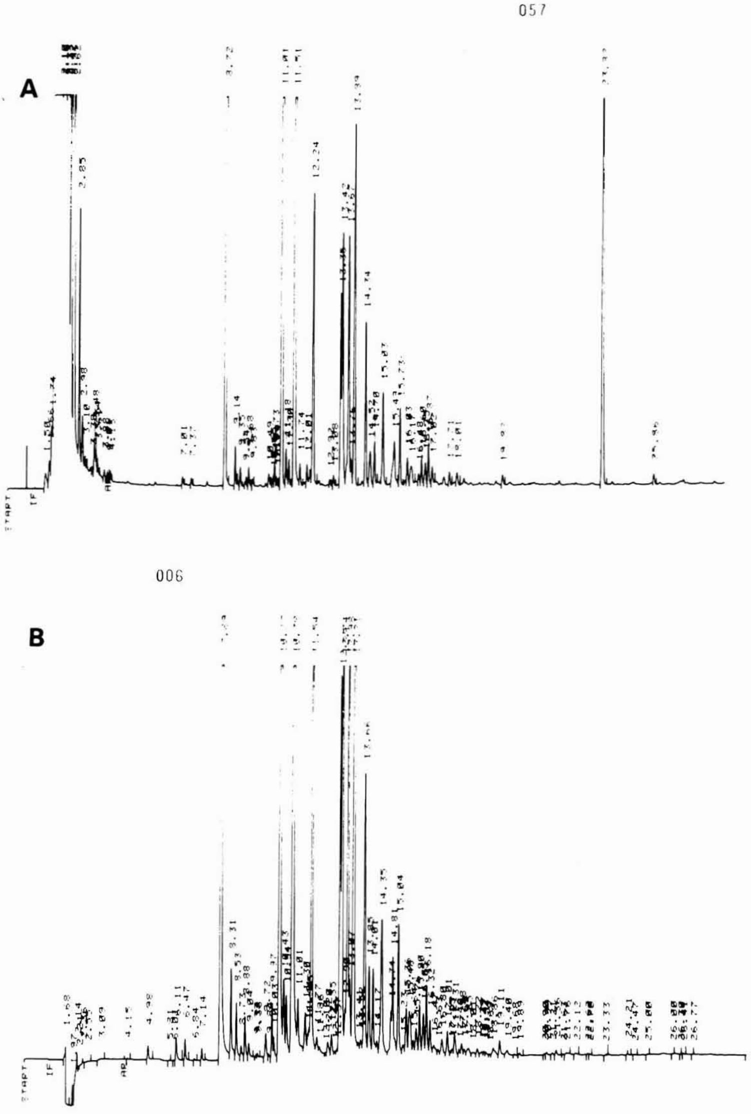


Figure 1. Capillary gas chromatograms of hexane extract of water from well below the oil shale disposal area: (A) separation using flame-ionization detector; (B) separation using nitrogen–phosphorus detector.

ppm internal standard (*n*-dodecane) and analyzed on a 30M SP-2250 glass capillary column. After an initial hold at 65 °C of 4 min, the column was programmed from an initial temperature of 65 °C to 250 °C at a rate of 4 °C/min. Details of this procedure will be published elsewhere.

Preparation and Gas-Chromatographic Analysis of Well Water for Organic Acids. Freeze-dried samples of well water (100 mL) were refluxed in the presence of 20 mL of BF_3/MeOH for 4 h. The reaction mixture was cooled, and the excess BF_3 decomposed with 50 mL of H_2O. The aqueous solution was extracted twice with 5-mL portions of CH_2Cl_2. The CH_2Cl_2 extracts were combined and concentrated to 1 mL after addition of 0.5 mL of a 44-ppm hexamethylbenzene internal standard. Samples were analyzed for acid methyl esters on a 30-m SP-2250 glass capillary column according to the gas-chromatographic conditions described for phenol analysis.

Preparation and Gas-Chromatographic Analysis of Extracts of Well and West Sharrard Stream Waters, Aqueous Extracts of Raw Shale, Retorted Shale, Prudhoe Bay Crude Oil, and Shale Oil for Alkylpyridines. Samples of well and West Sharrard stream waters (100 mL), aqueous extracts of raw shale, retorted shale, Prudhoe Bay crude oil, and shale oil were extracted twice with hexane (1 × 20 mL, 1 × 10 mL). The hexane extracts were combined and subsampled (1 mL) or concentrated (20, 10, 4, and 1 mL) before subsampling (1 mL). The 1-mL samples were analyzed for alkylpyridines on a 30-m SP-2250 glass capillary column according to gas-chromatographic conditions described for the analysis of phenols and acids, except the initial temperature was 70 °C. Alkylpyridine concentrations were corrected for losses based on the average recovery of 2-C_3-alkylpyridine and 2-C_4-alkylpyridine analytical standards. The average recovery of these four analytical standards from water was 83.5 ± 3.9%.

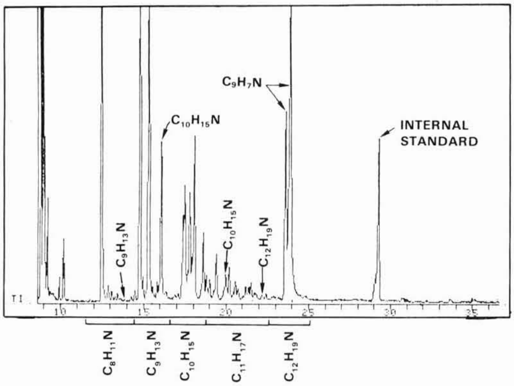


Figure 2. Total ion mass chromatogram of volatile nitrogen compounds in hexane extract of water from well below the oil shale disposal area.

All reported alkylpyridine concentrations in water are corrected for this loss.

Preparation and Gas-Chromatographic Analysis of Extracts of Subsoil Cores for Alkylpyridines. Samples of subsoil (50 g wet weight) in beakers were stirred in the presence of 50 mL of hexane for 15–30 min. The hexane was removed and an additional 25 mL of hexane was added. The mixture was stirred and allowed to sit 1–2 h. The hexane extracts were combined, concentrated under a stream of nitrogen, transferred to vials, and returned to the PNL-Richland Laboratories for analysis by capillary gas chromatography as previously described for analysis of alkylpyridines in water. Average recovery of 2,3,6-trimethylpyridine and *tert*-butylpyridine from subsoils using the above procedure was 23.5 ± 3.5% and 60.2 ± 9.7%, respectively. All reported alkylpyridine concentrations in sediments are corrected for these losses.

Infrared Spectroscopy, Capillary Gas Chromatography, and Capillary Gas Chromatography–Mass Spectrometry. Carbon tetrachloride (CCl_4) extracts of seep waters were analyzed on a Beckmann Acculab 6 spectrophotometer using a microcavity cell (9 μL, Barnes Engineering). Analytical standards of alkylpyridines and alkylanilines (Aldrich, Pfaltz and Bauer) were appropriately diluted in CCl_4 and similarly analyzed.

To compare the response of organic compounds to flame ionization and nitrogen–phosphorus detectors, we first separated a hexane extract of well water on a 30-m SP-2100 glass capillary column connected to a flame-ionization detector (FID) after which the back end of the column was coupled to a nitrogen–phosphorus detector and the sample was reana-

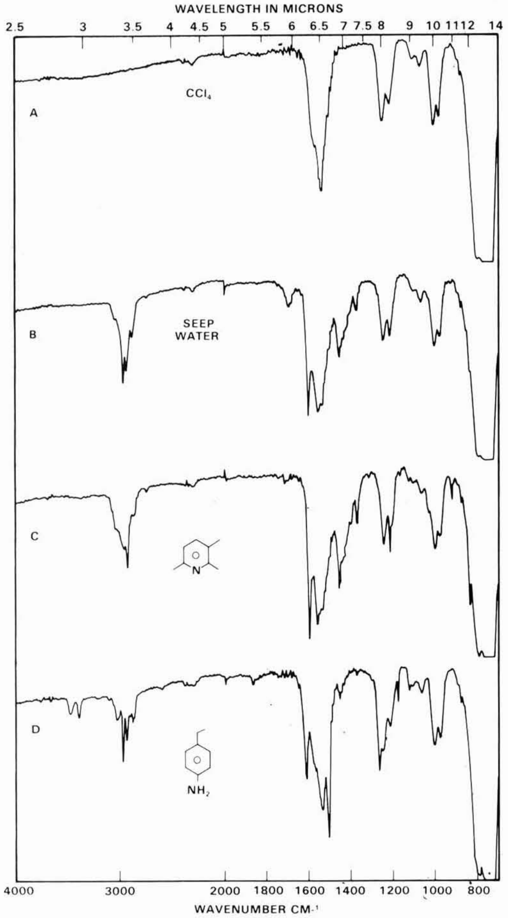


Figure 3. Infrared spectra of blank, extract of surface seep water, and nitrogen standards: (A) CCl_4; (B) CCl_4 extract of surface seep water; (C) 2,3,6-trimethylpyridine in CCl_4; (D) 4-ethylaniline in CCl_4.

Table I. Alkylpyridine Concentrations (μg/mL (ppm)) in Retort Water and Aqueous Extracts of Shale Oil, Raw Shale, Retorted Shale, and Prudhoe Bay Crude Oil

compd	retort water	shale oil	raw shale	retorted shale	Prudhoe Bay crude
C_3-pyridine	106.8	9.0	<0.003	<0.002	<0.01
C_4-pyridine 1	33.9	3.2	<0.002	<0.002	<0.01
2	84.4	4.9	<0.002	<0.002	<0.01
C_5-pyridine 1	<1.6	0.2	<0.002	<0.002	<0.01
2	18.6	1.8	<0.002	<0.002	<0.01
3	42.6	2.5	<0.002	<0.002	<0.01
4	70.4	5.3	<0.002	<0.002	<0.01
5	12.3	1.1	<0.002	<0.002	<0.01
6	14.5	1.0	<0.002	<0.002	<0.01
7	9.6	1.1	<0.002	<0.002	<0.02
C_6-pyridine 1	<1.6	<0.06	<0.002	<0.002	<0.01
2	18.3	2.4	<0.002	<0.002	<0.04
3	4.4	0.5	<0.002	<0.002	<0.09
4	<1.6	1.4	<0.002	<0.002	<0.11
5	3.2	0.9	<0.002	<0.002	<0.01
total alkylpyridines	419.0	35.3	<0.03	<0.03	≲0.37

lyzed. The column program conditions were 70 °C to 250 °C at 4 °C/min with an initial hold of 4 min at 70 °C. Results of this analysis are reported in Figure 1.

Extracts of samples of well water in which the hexane had been exchanged for heptane were analyzed on a Hewlett Packard 5985 GC–mass spectrometer equipped with 7900A and 7920 disk drives operating in methane chemical ionization and electron impact modes. A 30-m SP-2250 glass capillary column was used to resolve the individual components in the complex mixture. Glass capillary column conditions were those described for phenols and acid analyses, except the initial temperature was 70 °C.

Results and Discussion

Elevated levels of total dissolved organic carbon occurred in water from seeps and alluvial groundwaters downstream of the retorted shale disposal pile as compared to waters collected upstream. In addition, water from one well and one seep below the retorted shale pile had an odor similar to that of shale oil and retort water.

The well water exhibiting the odor as well as other well water samples did not contain detectable levels of aliphatic or aromatic hydrocarbons, phenols, or carboxylic acids. However, a hexane extract of the well water exhibiting the odor contained volatile organic compounds which were not present in waters collected from an adjacent well. Comparison of capillary gas-chromatographic separations of the components of the extract using flame-ionization and nitrogen–phosphorus detector systems showed all the components to contain nitrogen (Figure 1). Capillary gas chromatographic–mass spectrometric analysis (methane chemical ionization and electron impact) of the components in the water extract led to the preliminary molecular formula assignments in Figure 2. These molecular formulas were consistent with those of alkyl-substituted pyridines and/or anilines. The mass-spectral data were not sufficient to differentiate compounds comprising these classes of compounds in the complex environmental sample. Infrared analysis of a CCl_4 extract of the surface seep water, which contained higher concentrations of these compounds, based on relative GC retention time matches with the nitrogen components found in the well water (Figure 3b), showed the spectrum to be very similar to 2,3,6-trimethylpyridine (Figure 3c). The significant absorption bands included C–C and C–N ring stretching bands (1600, 1558, and 1455 cm^{-1}) and aromatic C–H stretch (3040 cm^{-1}, broad). Primary alkylanilines were ruled out as possible structures because of the absence of N–H stretching bands at 3465 and 3385 cm^{-1} as exemplified by the infrared spectrum of 4-ethylaniline (Figure 3d) although such compounds have been detected in a hydrocracked shale oil naphtha (*13*). *N*-Methyl- and *N*,*N*-dimethyl-substituted anilines were ruled out because of the absence of bands in the region of 2820–2790 cm^{-1} indicative of C–H stretching of methyl groups attached to nitrogen on an aromatic ring (*14*).

This combination of GC/MS and infrared spectrometric methods produced absolute confirmation of the presence of alkylpyridines in water from surface seep and well water. This is consistent with a previous study that identified these compounds in shale oil naphtha (*15*) and another study in which nonaqueous titritmetric analysis of fractions isolated from oil shale retort waters had indicated the presence of weak and very weak bases (*16*).

Total alkylpyridine concentrations in water discharging from the seep and water from a well below the shale disposal pile in June 1979 were 30.8 and 4.1 μg/mL, respectively. The surface stream waters at locations below the seep discharge also contained trace levels of alkylpyridines (0.1–0.2 μg/mL). Alkylpyridines were not detected (<0.1–0.2 μg/mL) in a sample of surface sediment from the stream located adjacent to the seep discharge; however, alkylpyridines were detected (2.3–55.1 μg/g dry weight) with depth in cores of subsoil collected adjacent to the well containing alkylpyridines.

Although the distributions were different, alkylpyridines were detected in retort water (419 μg/mL) and an aqueous extract of shale oil (35.3 μg/mL); however, they were not detected in aqueous extracts of raw shale, retorted shale, or Prudhoe Bay crude oil (≤0.37 μg/mL) (Table I).

Conclusions

Alkylpyridines were positively identified, by using a combination of infrared and gas chromatographic–mass spectrometric techniques, in water from one of several alluvial wells and in a surface seep located adjacent to the oil shale facility. Stream waters sampled below the seep contained alkylpyridines, but in lower concentrations, likely due to dilution of the seep discharge. Alkylpyridines were also detected in a moist subsoil at concentrations that ranged from 0.5 to 13.8 times the concentration detected in water collected from the adjacent well. Other water-soluble compounds also known to be present in shale oil and retort water (organic acids, phenols) were not detected in the well containing the alkylpyridines. If one assumes that the source was shale oil or retort water, the presence of alkylpyridines and the absence of these other water-soluble compounds suggest that the alkylpyridines were less subject to sorption on the soil or were more persistent during hydrologic transport. This class of compounds therefore requires further investigation to define the factors governing transport to surface water and groundwater to aid in evaluation of use of retort water for dust control and compaction of retorted shale disposal piles. Shale oils and retort waters from other processes need to be examined for the alkylpyridines. However, their absence in aqueous extracts of petroleum indicates that they may be unique and perhaps useful in environmental studies as diagnostic indicators of water which has been in contact with shale oils. Laboratory and field investigations are currently in progress to determine the hydrologic transport and fate of this class of organic compounds at the facility.

Literature Cited

(1) Routson, R. C.; Wildung, R. E.; Bean, R. M. *J. Environ. Qual.* **1979,** *8*, 14.

(2) Riley, R. G.; Shiosaki, K.; Bean, R. M.; Shoengold, D. M. *Anal. Chem.* **1979,** *51*, 1995.

(3) Wildung, R. E.; Riley, R. G.; Garland, T. R.; Bean, R. M.; Li, S. W. "Terrestrial Effects of Oil Shale Development"; NTIS BNWL-2100, Part 2, 1977; pp 2.1–2.8.

(4) Wildung, R. E.; Garland, T. R.; Riley, R. G.; Silviera, D. J.; Rogers, J. E.; Bean, R. M.; Li, S. W. "Terrestrial Effect of Oil Shale Development"; NTIS BNWL-2500, Part 2, 1978; pp 6.3–6.15.

(5) Ho, C. H.; Clark, B. R.; Guerin, M. R. *J. Environ. Sci. Health* **1976,** *7*, 481.

(6) Cook, E. W. *Chem. Ind.* **1971,** 485.

(7) Wen, C. S.; Yen, T. F.; Knight, J. B.; Poulson, R. E. *Prepr. Pap.—Am. Chem. Soc., Div. Fuel Chem.* **1976,** *21*, 290.

(8) Kwan, J. T.; Tang, J. I.; Wong, W. H.; Yen, T. F. *Prepr., Div. Pet. Chem., Am. Chem. Soc.* **1977,** *22*, 823.

(9) Felix, W. D.; Farrier, D. S.; Poulson, R. E. "High Performance Liquid Chromatographic Characterization of Oil Shale Retort Waters"; USERDA, Omega-9 CIP Document No. 3, 1977.

(10) Poulson, R. E. *J. Chromatogr. Sci.* **1969,** *7*, 152.

(11) Ecker, R. M.; Walters, W. H.; Skaggs, R. L. "Hydrologic Monitoring Program, Paraho Oil Shale Development Site, Colorado"; NTIS PNL-3220, 1979.

(12) Riley, R. G.; Thomas, B. L.; Bean, R. M. "Trace Analysis of Organic Pollutants in Duwamish River Intertidal Sediment"; NTIS PNL-SA-7690, 1979.

(13) Brown, D.; Earnshaw, D. G.; McDonald, F. R.; Jensen, H. B. *Anal. Chem.* **1970,** *42*, 146.

(14) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. "Spectrometric Identification of Organic Compounds", 3rd ed.; Wiley: New York, 1974.

(15) Dinneen, G. U.; Van Meter, R. A.; Smith, J. R.; Bailey, C. W.; Cook, G. L.; Allbright, C. S.; Ball, J. S. Washington, DC, 1961, Bureau of Mines Bulletin 593.

(16) Jackson, L. P.; Poulson, R. E.; Spedding, T. J.; Philips, T. E.; Jensen, H. B. In "Proceedings of the Environmental Oil Shale Symposium"; Colorado School of Mines: Golden, CO, 1975; Vol. 70, p 125.

Received for review September 2, 1980. Accepted February 20, 1981. This work was supported by the U.S. Department of Energy under Contract DE-AC06-76RLO 1830.

Evaluation of Tenax-GC and XAD-2 as Polymer Adsorbents for Sampling Fossil Fuel Combustion Products Containing Nitrogen Oxides

Ray L. Hanson,* Charles R. Clark, Robert L. Carpenter, and Charles H. Hobbs

Inhalation Toxicology Research Institute, Lovelace Biomedical and Environmental Research Institute, P.O. Box 5890, Albuquerque, New Mexico 87115

■ Tenax-GC and Amberlite XAD-2 are porous polymer adsorbents used to sample organic vapors in effluents from fossil fuel combustion technologies. Both polymers decompose in the presence of oxides of nitrogen which are also present in the combustion effluent streams. We report here that the major NO_2-decomposition products of Tenax-GC are 2,6-diphenyl-*p*-quinone and diphenylquinols, which are not mutagenic and do not interfere with the gas-chromatographic elution and analysis of vapor-phase organics adsorbed on the polymer. The NO_2-decomposition products of XAD-2, however, are of lower molecular weight and elute with retention characteristics similar to the vapor-phase organics. Dichloromethane extracts of XAD-2 exposed to NO_2 were mutagenic and preclude the use of this material for the detection and bioassay of vapor-phase organics in effluent streams. Results for efficiency of collection of vapor-phase organics by Tenax-GC are presented from field sampling studies. The first two stages of a three-stage polymer adsorbent sampler filled with Tenax-GC collected greater than 90% of the gas-chromatographable, vapor-phase organics which were collected.

Introduction

Tenax-GC and Amberlite XAD-2 have been used as adsorbents for sampling combustion effluents and ambient air for organic vapors (*1–6*). For sampling higher-boiling species (>120 °C) and for sampling at elevated temperatures, Tenax-GC has been recommended because of its greater thermal stability compared to XAD-2 (*7*). Nitrogen oxides present in fossil fuel combustion products may react with sampling media. The decomposition of Tenax-GC when sampling stack gases has been attributed to reaction with the nitrogen oxides (*8*). Neher and Jones (*9*) reported the formation of 2,6-diphenyl-*p*-quinone (DPQ) as a result of reactions of Tenax-GC with nitric oxide, higher oxides of nitrogen, or nitric acid present in stack gases. Chromosorb 102, which is a styrene–divinylbenzene polymer very similar to XAD-2, has been found to react with NO_2 and oxygen at elevated temperatures (*10, 11*).

However, reactions of nitrogen oxides with XAD-2 have not been reported. Therefore, the decomposition products of Tenax-GC and XAD-2 formed by reaction with nitrogen dioxide and nitric oxide were examined. The results of these investigations indicated that both adsorbents decomposed but that the products from Tenax-GC did not interfere with gas-chromatographic analysis of vapor-phase organics which elute before 1,2-benzofluorene (bp, 398 °C).

The *Salmonella* mutagenicity assay has been used to aid in identifying environmental chemicals causing mutations and cancer (*12–14*). Extracts of samples of fossil fuel combustion products have been found to be mutagenic in the *Salmonella* mutagenicity assay (*15, 16*). This bioassay is useful for identifying mutagenic samples of combustion products. Pellizarri et al. (*17*) recommend field sampling of pollutants as part of the evaluation of adsorbent samplers. The evaluation of the collection characteristics of Tenax-GC were undertaken by sampling the flue gases from combustion of Paraho oil shale. Tenax-GC has been used in an uncooled adsorbent trap for stack temperatures from ambient to 50 °C (*18*). Three adsorbent samplers were placed in series to ensure complete sample collection. Analysis of these samples revealed that vapor-phase organics were present with large quantities of Tenax-GC decomposition products.

Experimental Section

Materials. Tenax-GC, a polymer of 2,6-diphenyl-*p*-phenylene oxide 60/80 mesh (Figure 1) (Enka N.V., the Netherlands), and Amberlite XAD-2, a styrene–divinylbenzene polymer 20/50 mesh (Figure 1) (Rohm and Hass Co.) were used in the studies. The Tenax-GC was Soxhlet extracted with glass-distilled *n*-pentane for 24 h and dried in an oven at 110 °C before use. The XAD-2 was Soxhlet extracted with glass-distilled dichloromethane to achieve less than 10 μg of extractable residue per gram of polymer for 24-h extraction and then dried in an oven at 110 °C before use. Tenax-GC is soluble in polar solvents; therefore, an aliphatic hydrocarbon (*n*-pentane) is used to extract traces of residues before use. The XAD-2 contains more residues than Tenax-GC, and XAD-2 can be extracted with polar solvents to clean it before use.

Sampling. The adsorbent was packed in brass tubes (Figure 2, 15-cm long, 2.5-cm i.d.) which were placed in series. Stainless-steel screens at each end of the tube kept the adsorbent in place. A 47-mm glass-fiber filter was mounted in a filter holder for the studies with nitrogen oxides (Figure 2). A silver-membrane filter was used as the filter for sampling oil shale combustion flue gases from a fluidized bed combustor (FBC). The filters were used to collect the particles. The experimental conditions for the study of the decomposition products from Tenax and XAD-2 are given in Table I. The adsorbents were Soxhlet extracted for 24-h by using *n*-pentane for Tenax-GC and dichloromethane or *n*-pentane for XAD-2. The sampling of organics in (FBC) combustion effluents has been previously described (*19–21*). Generally, 10 L/min of diluted stack gases was sampled from 36 to 103 min. The NO_x concentration of the undiluted effluent ranged from 460 to 810 ppm. A second and a third sampler were placed behind the first to collect any organics that pass through the first adsorbent sampler.

Sample Analysis. Qualitative identifications of compounds were made by using a Finnigan Model 4023 gas chromatograph–mass spectrometer (GC–MS) with an INCOS data

0013-936X/81/0915-0701$01.25/0

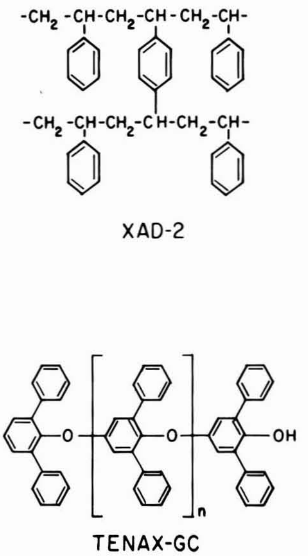


Figure 1. Chemical structure of polymer sorbent resins.

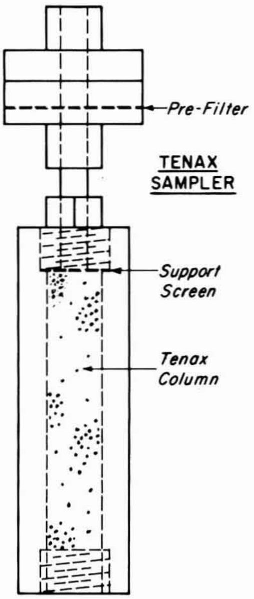


Figure 2. Brass polymer adsorbent sampler. Prefilter is 47 mm in diameter. Adsorbent chamber is 15-cm long and 2.5-cm i.d.

system. A 25-m and SE-52 fused silica capillary column was used with a temperature program of 50 °C for 2 min, a ramp of 5 °C/min to 270 °C, followed by 15-min hold at 270 °C. Helium was used as the carrier gas at a linear velocity of 30 cm/s. Tentative identifications were based upon (a) retention characteristics which were compared to standards and (b) the mass-spectral fit of the sample spectra to the library spectra. Quantitation of FBC effluents by gas chromatography has been described (*21*, *22*).

Mutagenicity Assay. The *Salmonella* mutagenicity assay was conducted as described by Ames et al. (*23*). Only two strains were used because of the small sample sizes available. Strain TA-100 and TA-100 FRI, a nitroreductase-deficient strain (kindly supplied by B. N. Ames), was used to determine the involvement, if any, of bacterial nitroreductase in the mutagenicity of the extracts. Survival in the presence of nitrofurazone was used to confirm nitroreductase deficiency. Aroclor-induced rat liver homogenate fractions (S9) were prepared from male Fischer 344 rats (*23*). Sodium azide and 2-aminoanthracene were used to confirm the reversion properties of TA-100 and the activity of the S9. Test materials were delivered to the assay in 0.1 mL of glass-distilled dimethyl sulfoxide (Me_2SO), and revertant colonies were counted by using an Artek automatic colony counter.

Results

The weights of residue extracted from the polymers from the various exposure conditions are given in Table II. Greater decomposition was found with NO_2 than with NO. Dichloromethane was a more efficient solvent than *n*-pentane for the XAD-2 decomposition products.

Reconstructed ion chromatograms of the decomposition products of XAD-2 and Tenax exposed to nitrogen dioxide are shown in Figure 3. Many XAD-2 decomposition products have retention times near those of the vapor-phase organics from combustion samples. Therefore, gas-chromatographic analysis of vapor-phase organics from combustion products containing nitrogen oxides would include the XAD-2 decomposition products in the gas chromatograms. The reconstructed ion chromatogram for the decomposition products of XAD-2 and Tenax exposed to nitric oxide are shown in Figure 4. The major product from Tenax-GC following exposure to NO or NO_2 is DPQ; a small quantity of 2,6-diphenyl-*p*-quinol is also formed. Both of these compounds elute after 1,2-benzofluorene with the chromatographic conditions described above. Therefore, Tenax-GC can be used to adsorb vapor-phase organics that eluted before 1,2-benzofluorene. Tables III and IV list the compounds tentatively identified in the decomposition products of XAD-2 and Tenax exposed to nitric oxide and nitrogen dioxide.

Residues extracted from Tenax and XAD-2 after exposure to NO, NO_2, and filtered room air were evaluated for mutagenicity in *Salmonella typhimurium* TA-100. XAD-2 exposed

Table I. Experimental Polymer Adsorbent Exposure Conditions [a]

				wt of adsorbent, g		
gas	concn, ppm	rel humidity, %	sampling time, h	Tenax [b]	XAD-2 [b]	XAD-2 [c]
air			1.5	3.3		15.5
NO_2	85	20	2.5	13.2	31.4	32.2
NO_2	99	29	2	13.2		63.1
air			1.5	6.5		7.9
NO	102	31	1.5	13.2	31.8	31.3
NO	98	30	3			94.4

[a] Sampling rate was 5 L/min for all samples. [b] Extracted with *n*-pentane. [c] Extracted with dichloromethane.

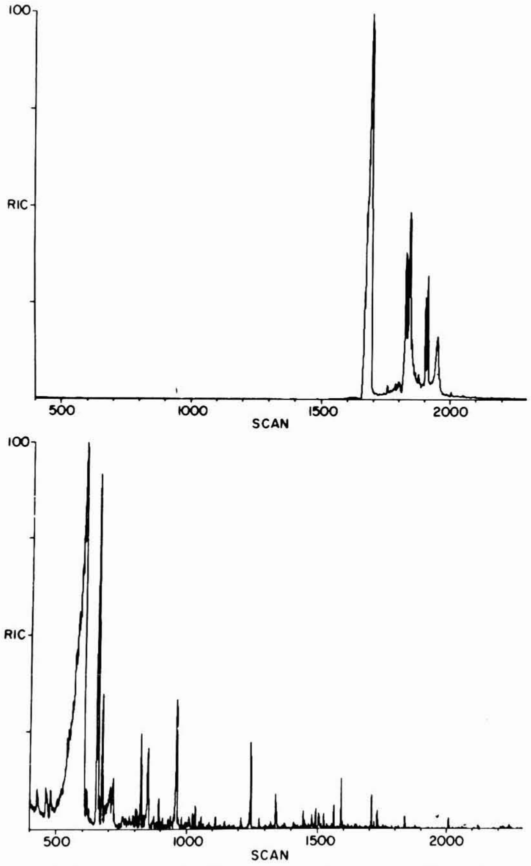


Figure 3. Reconstructed ion chromatograms for decomposition products from XAD-2 (bottom) extracted with dichloromethane and Tenax (top) exposed to NO_2. Chromatographic conditions: 25-m SE-52 fused silica capillary column, 30 cm/s helium carrier gas. Temperature program: 50 °C for 2 min, 5 °C/min to 270 °C, 15 min at 270 °C.

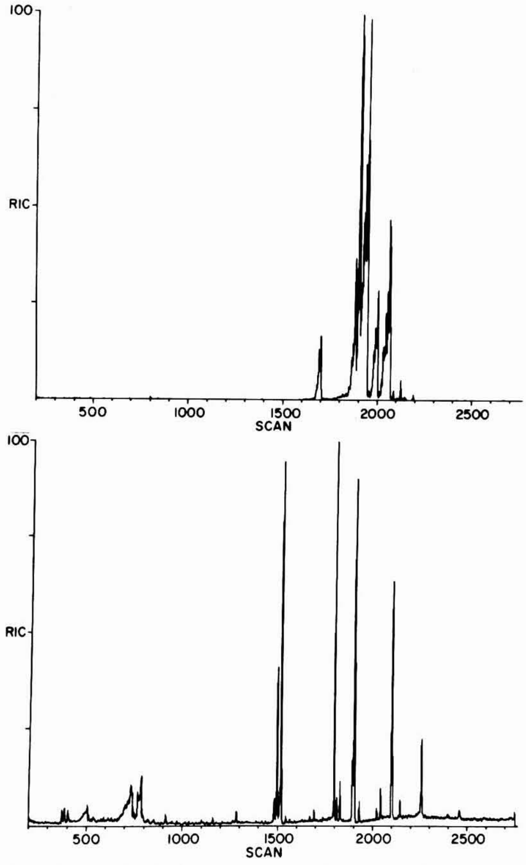


Figure 4. Reconstructed ion chromatograms for decomposition products from XAD-2 extracted with dichloromethane (bottom) and Tenax (top) exposed to NO. Chromatographic conditions same as Figure 3.

Table II. Weights of Residue (mg) Extracted from Adsorbents

		adsorbent, solvent		
gas	concn, ppm	Tenax, pentane	XAD-2, pentane	XAD-2, CH_2Cl_2
air		0.10		0.36
NO_2	85	29.6	2.47	11.8
NO_2	99	22.7		9.12
air		0.33		0.36
NO	102	11.5	0.36	1.86
NO	98			2.75

to NO_2 and extracted with dichloromethane contained direct-acting mutagens (Table V); the mutagenicity of the extract decreased somewhat when a liver homogenate fraction (S9) was added. No difference in the mutagenicity of the residue extracted from XAD-2 exposed to NO_2 was observed between strains TA-100 and TA-100 FRI, the nitroreductase-deficient counterpart. None of the other extracts, including the solvent extractions used to clean the adsorbents, were mutagenic. No mutagenic activity was detected when up to 1000 μg of the NO-exposed XAD-2 and NO- and NO_2-exposed Tenax extracts were tested in strain TA-100.

Table III. Decomposition Products from XAD-2 and Dichloromethane Extracts

NO exposure		NO_2 exposure	
mol wt	tentative identification	mol wt	tentative identification
122	benzoic Acid	122	benzoic Acid
134	ethylbenzaldehyde	134	ethylbenzaldehyde
134	dimethylbenzaldehyde	134	(C_4)-benzene
148	ethylphenylethanone or (C_5)-benzene	139	nitrophenol
150	dimethylbenzoic acid	150	ethylbenzoic acid
164	(C_3)-benzoic acid	150	ethyl ester of benzoic acid or ethoxyethylbenzene
183	2-hydroxy-3-nitrobenzoic acid	182	dinitrotoluene
222	diethylphthalate		
262	diphenoxybenzene		
278	dibutylphthalate		

Figure 5 is the reconstructed ion chromatogram of a Tenax sample extract of combustion effluents from Paraho oil shale for the compounds eluting before DPQ. The compounds tentatively identified in this extract are listed in Table VI. Many of these vapor-phase compounds eluted in the same

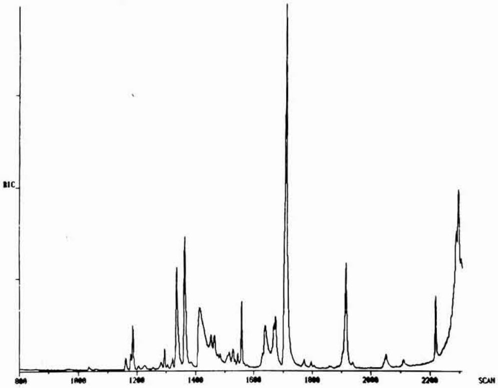


Figure 5. Reconstructed ion chromatogram of extract of Tenax-GC sample of FBC stack effluent burning Paraho oil shale for components eluting before DPQ. Table VI lists tentative identifications of compounds in this reconstructed ion chromatogram.

Table IV. Decomposition Products from Tenax-GC

NO exposure		NO_2 exposure	
mol wt	tentative identification	mol wt	tentative identification
260	2,6-diphenylquinone	260	2,6-diphenylquinone
262	2,6-diphenylquinol	262	2,6-diphenylquinol
330	C_3H_7CO or C_5H_{10} adduct to 2,6-diphenylquinone	330 (2 peaks)	C_3H_7CO or C_5H_{10} adduct to 2,6-diphenylquinone
323 (3 peaks)	C_3H_7CO or C_5H_{10} adduct to 2,6-diphenylquinol	332 (2 peaks)	C_3H_7CO or C_5H_{10} adduct to diphenylquinol

Table V. Mutagenicity of XAD-2 and Tenax-GC Exposed to NO_2

	no. of revertants (TA-100) [a]	
extract, μg	without S9	with S9 [b]
	Dichloromethane Extract of XAD-2	
0 [c]	93 ± 1	95 ± 2
100	177 ± 27	126 ± 8
250	208 ± 25	133 ± 17
500	299 ± 29	218 ± 28
1000	444 ± 62	308 ± 21
	Pentane Extract of Tenax-GC	
0 [c]	104 ± 9	123 ± 1
125	168 ± 7	136 ± 22
250	162 ± 22	133 ± 16
500	174 ± 24	139 ± 24
1000	148 ± 14	129 ± 22

[a] Mean ± SD from triplicate plates. [b] Aroclor-induced rat liver S9. [c] Me_2SO solvent blank (spontaneous mutation rate).

Table VI. Tentative Identification of Compounds in Extract of Tenax from Sampling FBC Stack Effluents from Paraho Oil Shale

1-methylnaphthalene
2-methylnaphthalene
biphenyl
dimethylnaphthalenes (3 peaks)
fluorene
dibenzofuran
hydroxynaphthalenedione
phenanthrene
fluorenone
dibenzothiophene
methylphenylhexanone
methylphenanthrene
fluoranthene
pyrene
1-phenylnaphthalene
2-phenylnaphthalene
trimethylphenyldihydroindene

Table VII. Organic Penetration through Tenax Vapor-Phase Sampler

Tenax sampler stages	sampling time, min	mass extractable residue, mg	gas-chromatographable organics, [a] μg	% collected
first	100	23.28	394	62
second	100	14.60	203	94
third	100	5.58	41	100
first	36	6.76	50	81
second	36	4.36	8.5	95
third	36	3.74	3.2	100
first	103	3.28	116	70
second	103	3.34	35	91
third	103	2.81	15	100

[a] Organics eluting before DPQ.

retention window as the decomposition products from XAD-2 exposed to NO or NO_2 in the laboratory.

The collection efficiencies of Tenax adsorbent samplers for vapor-phase organics collected during Paraho oil shale combustion are given in Table VII. The weight of residue extracted from each of the three stages of the Tenax-GC sample and the gas-chromatographable organics that eluted before DPQ are also given in Table VII. For these samples 91–95% of the gas-chromatographable organics were collected on the first two stages. The majority of the extractable residue is decomposition product (98.2–99.6%) with only a small portion of the residue (0.4–1.8%) being vapor-phase organics detected by the hydrogen flame ionization detector.

Discussion

The GC–MS analysis of decomposition products from reaction of Tenax-GC and XAD-2 with nitrogen dioxide and nitric oxide indicated that Tenax would be more suitable than XAD-2 for the sampling of stack effluents from fossil fuel combustion. The decomposition products from Tenax-GC enabled analysis of many vapor-phase organics that elute from the capillary column before DPQ. This type of analysis is not possible with XAD-2 because of the large number of decomposition products which elute in the same retention window as the vapor-phase organics in combustion effluents. It has been reported that Chromosorb 102, which is a polymer similar to XAD-2, reacts with nitrogen dioxide to give products with nitrated aromatic rings (*9*). We found decomposition products from XAD-2 that may have these nitrated rings (Table III). Three peaks have been tentatively identified as nitrophenol, dinitrotoluene, and 2-hydroxy-3-nitrobenzoic acid. Aromatic ketones have been reported to be formed on Chromosorb 102 columns when heated above 100 °C from depolymerization reactions with oxygen adsorbed on the surface of the packing (*10*). Aromatic ketones and aldehydes and benzoic acids also were found in the XAD-2 decomposition products.

The finding that dichloromethane extracts of XAD-2 exposed to NO_2 contained decomposition products mutagenic in the *Salmonella* assay has important implications. The widespread use of the *Salmonella* assay to detect mutagenic activity in fossil fuel combustion effluents (**15, 16**) which contain nitrogen oxides may preclude the use of XAD-2 for sampling these effluents. The presence of nitro-containing decomposition products in the mutagenic extract (Table III) suggested that the mutagenicity might be the result of activation of these compounds by nitroreductase enzymes present in the *Salmonella* tester strains. No difference, however, was seen in the mutagenicity of the XAD-2 exposed to NO_2 decomposition residue in TA-100 and its nitroreductase-deficient counterpart, TA-100 FRI.

Although it has been reported that DPQ decomposed when Tenax decomposition products were analyzed by GC or GC–MS using packed columns (*11*), this decomposition was not observed when using a fused silica capillary column coated with SE-52 and a glass-lined injection port heated at 270 °C. The DPQ gas-chromatographic interference was reported to be greatest in the region between the elution of pyrene and chrysene using packed columns (*11*), the region where DPQ eluted from our capillary column.

The Tenax-GC polymer adsorbent has been evaluated for sampling organics in FBC effluents. Much of the mass of extractable residue from Tenax-GC was DPQ. For a sampling time of 103 min, 91% of the gas-chromatographable, vapor-phase organics were collected on the first two stages of the Tenax adsorbent. It seems desirable to use at least two stages for sampling vapor-phase organics in fossil fuel combustion stack effluents. If only one stage is used, we have found that collection efficiency could be as low as 62%.

Conclusion

Our results indicate that Tenax-GC is more suitable than XAD-2 for sampling vapor-phase organics in combustion effluents containing oxides of nitrogen. The decomposition products from the reaction of XAD-2 with nitrogen dioxide interfere with gas-chromatographic analysis of vapor-phase organics and produce a positive mutagenic response in a *Salmonella* assay. Greater than 90% of vapor-phase organics were collected by the first two stages of a Tenax-GC adsorbent sampler collecting effluents from fluidized bed combustion of Paraho oil shale.

Acknowledgment

The assistance of S. H. Weissman, D. D. Horinek, R. L. Beethe, T. R. Henderson, C. T. Schnizlein, R. E. Royer, J. M. Benson, E. B. Barr, A. J. Federman, P. E. Wenner, R. F. Henderson, and E. E. Goff of the staff of the Inhalation Toxicology Research Institute is acknowledged.

Literature Cited

(1) Pellizzari, E. D.; Bunch J. E.; Berkley, R. E.; McRae, J. *Anal. Chem.* **1976**, *48*, 803.

(2) Bertsch, W.; Chang, R. C.; Zlatkis, A. *Chromatogr. Sci.* **1974**, *12*, 175.

(3) Jones, P. W.; Giammar, R. D.; Strup, P. E.; Standford, T. B. *Environ. Sci. Technol.* **1976**, *10*, 806.

(4) Russel, J. W. *Environ. Sci. Technol.* **1975**, *9*, 1175.

(5) Snyder, A. D.; Hodgson, F. N.; Kammer, M. A.; McKendree J. R. "Utility of Solid Sorbents for Sampling Organic Emissions from Stationary Sources", EPA-600/2-76-201, 1976.

(6) Gallant, R. F.; King. J. W.; Levins, P. L.; Piecewicz, J. F. "Characterization of Sorbent Resins for Use in Environmental Sampling", EPA-600/7-78-054, 1978.

(7) Adams, J.; Nezies, K.; Levins, P. "Selection and Evaluation of Sorbent Resins for the Collection of Organic Compounds", EPA-600/7-77-044, 1975.

(8) Neher, M. B.; Jones, P. W.; Perry, P. J. "Performance Evaluation of a Solid Sorbent Hydrocarbon Sampler", EPRI EA-959, 1979.

(9) Neher, M. B.; Jones. P. W. *Anal. Chem.* **1977**, *49*, 512.

(10) Neumann, M. G.; Morales, S. *J. Chromatogr.* **1972**, *74*, 332.

(11) Trowell, J. M. *J. Chromatogr. Sci.* **1971**, *9*, 253.

(12) Ames, B. N. *Science* **1979**, *204*, 587.

(13) de Serres, F. J.; Shelby, M. D. *Environ. Mutagen.* **1979**, *1*, 87.

(14) Fox, J. L. *Chem. Eng. News* **1977**, *55*, 34.

(15) Chrisp, C. E.; Fischer, G. L.; Lammert, J. E. *Science* **1978**, *199*, 73.

(16) Clark, C. R.; Hobb, C. H. *Environ. Mutagen.* **1980**, *2*, 101.

(17) Pellizzari, E. D.; Bunch, J. E.; Carpenter, B. H.; Sawicki, E. *Environ. Sci. Technol.* **1975**, *9*, 552.

(18) Feairheller, W.; Marn, P. J.; Harris, D. H.; Harris, D. L. "Technical Manual for Process Sampling Strategies for Organic Materials", EPA-600/2-76-122, 1976.

(19) Carpenter, R. L.; Weissman, S. H. Newton, G. J.; Hanson, R. L.; Peele, E. R.; Mazza, M. H.; Kovach, J. J.; Green, D. A.; Grimm, U. "Characterization of Aerosols Produced by an Experimental Fluidized Bed Coal Combustor Operated with Sub-bituminous Coal", LF-57, 1978.

(20) Newton, G. J.; Carpenter, R. L.; Yeh, H. C.; Weissman, S. H.; Hanson, R. L.; Hobbs, C. H. "Sampling of Process Streams for Physical and Chemical Characterization of Respirable Aerosols", Symposium on Potential Health Effects of Synthetic Fossil Fuel Technologies, Oak Ridge National Laboratory, CONF-780903, 1978.

(21) Hanson, R. L.; Carpenter, R. L.; Newton G. J.; Rothenberg, S. J. *J. Environ. Sci. Health, Part A* **1979**, *14*, 223.

(22) Hanson, R. L.; Carpenter, R. L.; Newton, G. J. In "Polynuclear Aromatic Hydrocarbons: Chemistry and Biological Effects"; Bjørseth, A., Dennis, A. J., Eds.; Batelle Press: Columbus, OH, 1980; pp 599–616.

(23) Ames, B. N.; McCann, J.; Yamasaki, E. *Mutat. Res.* **1975**, *31*, 347.

Received for review September 22, 1980. Accepted February 18, 1981. This research was performed under U.S. Department of Energy Contract DE-AC04-76EV01013.

Modeling the Flux of Atmospheric Polychlorinated Biphenyls across the Air/Water Interface

Paul V. Doskey and Anders W. Andren*

Water Chemistry Program, University of Wisconsin, Madison, Wisconsin 53706

Introduction

Polychlorinated biphenyls (PCBs) are ubiquitous in the environment. A recent National Academy of Sciences report (*1*) indicates a total cumulative PCB use in the United States of 6.1×10^8 kg as of 1976. Of this amount, 8.3×10^7 kg (~14%) has entered a "mobile environmental reservoir." The report also states that the Atlantic Ocean appears to be the major sink for PCBs, accounting for 80–90% of the PCB burden in the environment. Many freshwater lakes also serve as sinks for PCBs. Fish taken from Lake Michigan often exceed the 2 μg/g standard set by the FDA. This has resulted in a closing of the commercial fishing industry.

Recent data have indicated that atmospheric transport is important in distributing PCBs, on both a local and global basis (*1–7*). Much of the transport of PCBs to the North Atlantic is thought to be atmospheric. Similarly, PCB transport to freshwaters, such as Lake Michigan, is thought to have an important atmospheric component. Quantification of the total

0013-936X/81/0915-0705$01.25/0 © 1981 American Chemical Society

■ Problems involved in measuring and modeling polychlorinated biphenyl (PCB) fluxes across the air/water interface are addressed. Speciation of airborne PCBs, operationally defined by partitioning through a glass-fiber filter, indicate that greater than 90% exist in the vapor phase. Indirect calculations based on semiempirical expressions predict that particle-bound Aroclors are primarily associated with submicrometer-size aerosols. Mono- and dichlorobiphenyl vapor is collected poorly by available collection methodologies. Quantification of environmental samples is further complicated by weathering of individual Aroclor components. A model of the PCB flux across the air/water interface, employing Lake Michigan as an example, is presented which includes the processes of vapor and particle deposition, volatilization, and bubble ejection. The importance of vapor deposition and volatilization is dependent upon the magnitude of the Henry's law constant. Henry's law constants derived from laboratory and environmental data are used to elucidate the flux of atmospheric PCBs to Lake Michigan.

PCB flux across the air/water interface is, however, difficult. The wet flux can be measured with a reasonable degree of confidence. Murphy and Rzeszutko (*8*) measured a wet flux for PCBs to Lake Michigan by determining a volume-weighted mean concentration for a number of precipitation samples. The annual amount of rainfall was then used to calculate an atmospheric loading. To measure dry fluxes of PCBs, researchers have employed silicone oil coated surfaces (*9–13*). Whether these surfaces can reflect deposition onto a body of water is currently a matter of speculation (*1*). Södergren (*14*) has stated that this collection methodology is most appropriately used to compare depositional patterns. Most estimates of dry fluxes of PCBs to aquatic systems are made via various models. The purpose of this paper is to examine possible sources of error associated with sampling and modeling PCB fluxes across the air/water interface. Lake Michigan will be used as an example of our own modeling efforts.

Problems Associated with Sampling Atmospheric PCBs

Accurate measurements of PCBs in the atmosphere have been hampered by technical and analytical problems, the most important being the following: (1) particulate and vapor-phase PCBs are only differentiated in an operational sense; i.e., that fraction which passes through a glass-fiber filter is called vapor phase, and that which is retained is judged as particulate; (2) insufficient collection of the most volatile PCB fraction leads to an underestimation of the total PCB burden; and (3) most quantification methodologies fail to indicate the extent of PCB mixture weathering.

There is presently no airborne PCB collection method which is uniformly accepted. High-volume filtration systems utilizing a glass-fiber filter in combination with adsorbent material is the most common choice. Determinations by different high-volume methods have usually shown that greater than 90% of the airborne PCBs pass through a glass-fiber filter and are subsequently collected on an adsorbent material (*3, 8, 15, 16, 22*). Whether these PCBs are associated with particles too small to be collected by glass-fiber filters, which have a particle diameter cutoff of ~0.3 μm (*18*), or are present in ambient air as vapor is uncertain. It has also been suggested that this collection method may be further hampered by vaporization of PCBs associated with particulates during the collection process (*1*). The measured partitioning of PCBs between rainwater and air was used by Murphy and Rzeszutko (*8*) to calculate vapor/particulate partitioning. They estimated that 27% of the total atmospheric PCB burden around Lake Michigan was associated with particulates. Junge (*19*) has made theoretical estimates of the vapor/particulate partitioning of chlorinated hydrocarbons (CHCs) based upon the number of particles per unit volume, the surface area of particles, and the saturation vapor pressure of CHCs. Calculations for rural air using his approach indicate that 10–45% of Aroclors 1254 and 1260 and less than 5% of Aroclors 1242 and 1248 should be associated with particulate matter. The vapor/particulate partitioning will continue to be defined by filtration through a glass-fiber filter until further refinements in sampling methodology are achieved.

The nonuniform collection efficiency of PCB adsorbent materials for individual Aroclor components is another sampling-related problem. Lewis et al. (*20*) employing polyurethane foam and Doskey and Andren (*17*) using XAD-2 have observed that these materials collect the most volatile PCB vapors less efficiently. Consequently, calculations of total PCB loadings will be underestimated.

The third problem is due to a lack of uniformity in analytical techniques. Since each commercial mixture contains a number of PCB isomers exhibiting a wide range of vapor pressures and water solubilities, the most common quantification techniques involve the comparison of gas chromatograms with Aroclor standards. However, this approach is not entirely applicable unless both the number of peaks recorded and the interpeak height ratios are identical for the sample and the standard being compared (*1*). The situations where these conditions hold are rare. PCB concentrations are thus often reported as "most closely resembling" or "similar to" a certain Aroclor standard. It thus becomes difficult to discern whether, or to what extent, individual component fractionation occurs in the environment. Single-component analysis of PCBs (*21*) using glass capillary columns may resolve some of this problem although sensitivity might be limiting.

Atmospheric PCB Flux Models

Recent atmospheric flux models have been developed on the basis that PCBs exist in the atmosphere in both a particulate and a vapor state (*5, 6, 8, 22*). The model by Doskey (*22*) includes transport both to and from the air/water interface.

Table I. Washout Coefficients for Selected Particle and Raindrop Sizes [a]

particle diam, μm	collision efficiency, E_0	washout coefficient, r
	Raindrop Size = 1 mm	
10	6.0×10^{-1}	1.5×10^{5}
2	1.3×10^{-3}	3.3×10^{2}
1	5.0×10^{-4}	1.3×10^{2}
0.2	1.4×10^{-4}	3.5×10^{1}
0.1	1.5×10^{-4}	3.8×10^{1}
0.02	6.2×10^{-4}	1.5×10^{2}
0.01	1.8×10^{-3}	4.5×10^{2}
0.002	2.0×10^{-2}	5.0×10^{3}
	Raindrop Size = 0.1 mm	
10	5.0×10^{-1}	1.3×10^{6}
2	3.1×10^{-3}	7.8×10^{3}
1	1.2×10^{-3}	3.0×10^{3}
0.2	6.2×10^{-4}	1.6×10^{3}
0.1	9.3×10^{-4}	2.3×10^{3}
0.02	7.9×10^{-3}	2.0×10^{4}
0.01	2.0×10^{-2}	5.0×10^{4}
0.002	2.4×10^{-1}	6.0×10^{5}

[a] $C = 0.5$; $h_w = 500$ m.

Air-to-water transport consists of wet and dry deposition of particulate and vapor-phase PCBs. Water-to-air transport includes the processes of volatilization and bubble ejection.

Dry Deposition of Particulate PCBs. The following equation is most commonly used to calculate particulate fluxes (*23*):

$$F = V_D\overline{C}_B \qquad (1)$$

where F = flux, V_D = deposition velocity, and $\overline{C}_B$ = average concentration of the contaminant in air at a selected reference height. The deposition velocity depends upon several factors, including particle size and wind velocity. Sehmel and Sutter (*24*) studied monodispersed particle deposition to water surfaces in a wind tunnel as a function of particle diameter and wind speed. Similar measurements have been made for ambient aerosols in natural atmospheres. Gatz (*25*) summarized his work and that of Cawse (*26*) in fashioning a relationship between deposition velocity and mass mean diameters. Results from these measurements indicate that aerosol size data are essential for making deposition calculations.

Size data are lacking for particulate-associated PCBs and must thus be determined indirectly. An indication of the size range may be inferred from washout coefficients derived from PCB concentrations in air and rain. The washout coefficient is a function of many parameters, including particle size. The following equation has been used to calculate washout coefficients (*27*):

$$r = W/P_0\overline{C}_b \qquad (2)$$

where r = washout coefficient, W = annual wet flux of the contaminant, P_0 = annual rainfall, and $\overline{C}_b$ = average concentration of the contaminant in air. Slinn et al. (*27*) also derived a relationship between the washout coefficient and the collision efficiency of the particle and raindrop:

$$r = ch_wE_0/R_{m0} \qquad (3)$$

where c = 0.5 (an empirical constant), h_w = effective height from which the pollutant is removed by wet processes (500 m), E_0 = collision efficiency, and R_{m0} = the drop radius. A semiempirical relationship exists between the collision efficiency and particle size (*27*). From this relationship and eq 3 washout coefficients can be calculated for a number of particle sizes (Table I).

Since PCBs have been hypothesized to be present in ambient air in both a particulate and vapor phase and it is uncertain whether a glass-fiber filter can define the partitioning, certain assumptions have to be made when calculating a PCB washout coefficient. Murphy and Rzeszutko (*8*) reported that an average of 66% of the total PCBs in rain collected in Chicago passed through a glass-fiber filter. Several assumptions can be made when calculating washout coefficients for PCBs. However, the most reasonable assumption is that air and rain samples contain both particulate and vapor-phase components which are operationally defined by filtration through a glass-fiber filter. Using this assumption, one can determine both particulate and vapor-phase washout coefficients. A washout coefficient for PCBs may be calculated by using the above assumption and eq 2. Employing data from Murphy and Rzeszutko (*8*), we calculated the average washout coefficient (r) to be 1.3×10^5, which corresponds to a particle size range of 0.002–0.01 μm in Table I.

It is evident that the washout coefficients generated by the preceding assumption correspond to particles which are extremely small. It must be emphasized that the relationship between collision efficiency and particle size is semiempirical. Particle sizes estimated by using this relationship may include some error. The calculations do, however, indicate that PCBs are most likely associated with submicrometer-size particles. Agreement was also found between washout coefficients calculated for particles between 2 and 10 μm in diameter. The association of PCBs with particles of this size range are doubtful. Measurements of total organic carbon in aerosols over Lake Michigan (*28*) and the ocean (*29*) have shown that organic carbon associates predominantly with submicrometer-size particles. It is expected that PCBs would be associated with particles enriched in organic carbon. Particles included in the range of those calculated for PCBs have a deposition velocity of ~0.005 m/s at wind speeds of 14 m/s (*24*, *25*).

Dry Deposition of Vapor-Phase PCBs. Vapor deposition may be approximated by employing the Whitman two-layer model (*30*) as applied by Mackay and Leinonen (*31*), Duce and Duursma (*6*), and Bidleman et al. (*5*). The basic assumption of this model is that the solute concentrations on either side of the air/water interface are in steady state. The magnitude of the driving force depends upon the concentration difference and the Henry's law constant (H).

Depending upon the magnitude of H, the contaminant may be either gas- or liquid-phase controlled. The contaminant flux under the gas-phase control model can be approximated by employing the following equation:

$$N_{GPC} = K_{OG}(P - CH)/(RT) \qquad (4)$$

where N_{GPC} = the flux, K_{OG} = the overall gas-phase, mass-transfer coefficient, C = the contaminant concentration in water, P = the partial pressure of the contaminant in air, R = the ideal gas law constant, and T = the absolute temperature. The overall gas-phase, mass-transfer coefficient is defined by the following equation:

$$1/K_{OG} = 1/k_G + H/(k_LRT) \qquad (5)$$

where k_G and k_L are the individual gas- and liquid-phase, mass-transfer coefficients, respectively. The contaminant flux under the liquid-phase control model can be calculated by employing the following equation:

$$N_{LPC} = K_{OL}(C - P/H) \qquad (6)$$

where K_{OL} (the overall liquid-phase, mass-transfer coefficient) is defined by the following equation:

$$1/K_{OL} = 1/k_L + 1/(Hk_G/RT) \qquad (7)$$

From the preceding discussion it is evident that values of H and K_{OL} are essential if one is to estimate the flux of a gas across the air/sea interface. Examination of Henry's law indicates that each solute in an aqueous solution has its own value of H, provided the solution is dilute in all solutes. An aqueous solution of an Aroclor contains a mixture of PCB isomers. Consequently, the behavior of the mixture can only be modeled if H and K_{OL} have been determined for each PCB isomer. Strictly speaking, any H determined for Aroclor mixtures should be termed an air/water partition coefficient. However, in the remainder of the text, they will be referred to as Henry's law constants. A review of calculations and experiments designed to determine H for Aroclor mixtures follows.

Mackay and Leinonen (*31*) calculated H for Aroclors 1242 and 1254 by using published aqueous solubility and vapor-pressure data. However, in order to calculate H, the vapor pressure and aqueous solubility must refer to the same state of matter. Individual PCB isomers are solids at room temperature while Aroclors, which are complex mixtures of PCB isomers, are viscous liquids. Aroclors, when present in the environment, will be partitioned between water and air as individual isomers and must be treated accordingly. Thus the above approach may have to be modified.

Another approach to indirectly calculate H is to experimentally determine either of the overall mass-transfer coefficients and use estimates of the individual mass-transfer

Table II. Experimentally and Theoretically Derived Overall Liquid-Phase Mass-Transfer Coefficients (K_{OL}), Henry's Law Constants (H), and Air/Water Partition Coefficients for Aroclor Mixtures

		K_{OL}, m/h				H,[a] atm m^3/mol			
ref	Aroclor	1221	1016	1242	1254	1221	1016	1242	1254
31				5.7×10^{-2}	6.7×10^{-2}			5.7×10^{-4}	2.8×10^{-3}
36			$(7.9 \pm 8.3) \times 10^{-2}$	$(8.3 \pm 8.5) \times 10^{-2}$			$(1.4 \pm 0.7) \times 10^{-2}$	$(7.6 \pm 4.5) \times 10^{-3}$	
34		$(8.9 \pm 0.6) \times 10^{-4}$	$(8.7 \pm 1.6) \times 10^{-4}$			$(7.4 \pm 10) \times 10^{-6}$	$(2.7 \pm 0.5) \times 10^{-6}$		
atmospheric[b]				1.3×10^{-3}	2.8×10^{-4}			4.0×10^{-6}	9.8×10^{-7}
22[c]				$(9.0 \pm 5.9) \times 10^{-5}$	$(4.1 \pm 2.1) \times 10^{-5}$				

	air/water partition coefficients, atm m^3/mol	
ref	Aroclor 1242	Aroclor 1254
22[c]	$(2.8 \pm 1.8) \times 10^{-7}$	$(1.4 \pm 0.7) \times 10^{-7}$

[a] At 25°C. [b] Determined from precipitation and air samples collected by Murphy and Rzeszutko (*8*). [c] Determined in unfiltered lake water solutions.

coefficients in eq 5 or 7. Typical values for the individual mass-transfer coefficients of CO_2 ($k_L = 0.2$ m/h) and H_2O ($k_G = 30$ m/h) have been reported (*32*). Estimates of k_L and k_G for gases other than CO_2 and H_2O may be calculated by multiplying these values by the ratio of the square roots of the molecular weights of H_2O or CO_2 and the other gas (*32*). However, the dependence of k_L and k_G on the chemical species remains to be established. Values for K_{OL} may be determined by monitoring the amount of PCB lost from an aqueous solution vs. time. The equation describing this behavior can be derived from eq 6 (*31*):

$$C = C_O \exp(-K_{OL}t/L) \qquad (8)$$

where t = time, L = the depth of water, C_O = the original soluble concentration, and C = the soluble concentration at time t.

An experiment was designed (*22, 33*) to examine the volatilization rates of Aroclors 1242 and 1254 under conditions similar to those found in the environment. The experiment was performed with 1 L of unfiltered lake water (Lake Emrick, Wisconsin) in a 4-L flask. The air space above the water level was continuously purged with a flow of compressed air through a glass frit at 50 mL/min. The outlet of the microenvironment consisted of two glass columns filled with XAD-2 resin to capture volatilized PCB. The water was stirred with a Teflon stir bar at a slow enough rate to prevent formation of a vortex but, at the same time, keep the particulate matter in suspension. Two concurrent experiments were performed. Each was designed so that the solubilities of Aroclors 1242 and 1254, reported to be 0.240 and 0.012 mg/L, respectively (*31*), were not exceeded. In one flask 10 mg of fly ash coated with 1050 ng of 1242 and 1530 ng of 1254 was added to 1 L of lake water. In another flask 10 μL of acetone containing 2087 ng of 1242 and 2239 ng of 1254 was introduced into 1 L of lake water. Ten milligrams of fly ash was also added to keep the suspended-solid load in each flask identical. Analysis of the XAD-2 traps was performed over regular intervals for 1 month. The concentration of PCBs remaining in the lake water after each sampling interval was not determined analytically. Concentrations were calculated by using the amount of PCB recovered by the vapor traps and the original spike. Since the soluble PCB concentrations of the lake water after each sampling interval were not known, total concentrations were used in eq 8 to calculate K_{OL}. Hence, K_{OL} is only defined for the system under study. H, which is defined for PCBs in actual solution and partial pressures in air, cannot be derived from an experiment of this nature. However, using K_{OL} in eq 7, it is possible to arrive at an air/water partition coefficient for the lake water used in the experiment.

Hetling et al. (*34*) performed similar volatilization experiments using saturated water solutions of Aroclors 1016 (175 ppb) and 1221 (1 ppm). The volatilized PCB was monitored with polyurethane foam plugs over a 4-day period. They reported their results in percent loss of PCBs vs. time. We used their data to arrive at a K_{OL} and H for Aroclors 1016 and 1221.

Paris (*35, 36*) used a direct approach to calculate H for Aroclor mixtures. Saturated and dilute aqueous solutions of Aroclors 1016 and 1242 were contained within a closed system. Samples of headspace and water were taken after 96-h equilibration and after 1, 2, and 4 weeks. Determination of both vapor and aqueous concentrations permitted a direct determination of H.

Another possible approach to calculate H is to utilize washout coefficients for PCB vapor. If a gas forms a simple solution, molecular diffusion to the raindrop is rapid enough for equilibrium to occur within the atmosphere (*27*). The washout coefficient (r) becomes equal to (RT/H) for vapors (*27*). A vapor washout coefficient may then be calculated from eq 2 based upon the assumption that the nonfilterable fraction of precipitation and air samples is composed of PCB vapor. H and K_{OL} values were calculated from an average of precipitation and air-sample data collected by Murphy and Rzeszutko (*8*). A better estimate might be obtained if data were available for air and precipitation samples taken concurrently.

Data for K_{OL} and H for various Aroclor mixtures are presented in Table II. The values from Hetling et al. (*34*) and Doskey (*22*) are averages based upon the number of vapor samples analyzed during the experiments. The values of Doskey (*22*) are included to indicate that air/water partition coefficients and mass-transfer coefficients may be affected by environmental factors. These air/water partition coefficients should not be confused with Henry's law constants.

The phase (gas or liquid) which controls the flux of PCB vapor may be established by calculating the liquid ($1/k_L$) and gas-phase resistances (RT/Hk_G). Using the values of Hetling et al. (*34*), those derived from the data of Murphy and Rzeszutko (*8*), and the coefficients found by Doskey (*22*), we find that the resistance to transfer in the gas phase is much larger than that in the liquid phase. This indicates that PCB vapor may be gas-phase controlled. Performing the same calculation with the data of Mackay and Leinonen (*31*) and Paris et al. (*36*) indicates liquid-phase control.

The large variations in K_{OL} and H values reported in Table II and the uncertainty in the phase controlling PCB vapor indicates that additional experimentation in this area is needed. The mass-transfer and air/water partition coefficients determined in lake water may be more indicative of environmental partitioning than the values reported for aqueous solutions. They are approximately 3 orders of magnitude lower than K_{OL} and H values reported for aqueous solutions. However, the suspended-solid load, the dissolved organic carbon (DOC) content, and the particulate organic carbon (POC) content of a lake may all have an effect upon mass-transfer and air/water partition coefficients. Therefore, different lakes may have different volatilization and vapor deposition rates. The values of Paris et al. (*36*) and Mackay and Leinonen (*31*) seem to agree even though those of the latter were calculated by using a liquid vapor pressure.

Cohen et al. (*37*) found that the liquid-phase, mass-transfer coefficients of benzene and toluene were a function of the wind and stirring speeds in an experimental wind–wave tank. They found that K_{OL} is best correlated with the roughness Reynolds number which depends upon the wind friction velocity and surface roughness. A more accurate estimate of the PCB flux across the air/water interface must involve calculations under different wind speed conditions. These considerations have not been included in our calculations of PCB flux across the air/water interface in Lake Michigan. A limited data base on temporal and spatial atmospheric PCB concentrations and some additional modeling constants (*37*) probably does not warrant their use.

Bubble Ejection

Erickson (*38, 39*) and Blanchard (*40*) have estimated that the ocean produces between 10^{15} and 10^{16} g/yr of atmospheric sea salt particles. Rising bubbles skim off a very thin layer of the air/sea interface known as the surface microlayer (*41, 42*). The composition of the surface microlayer and also the bubble skin contribute to the final composition of the ejected material.

Employing controlled laboratory experiments, Wallace and Duce (*43*) have shown that rising bubbles can transport particulate organic carbon and particulate trace metals to the sea surface. Laboratory experiments performed by Hoffman and Duce (*44*) showed that the organic carbon (OC)/Na ratio of ejected particulate matter was a function of bubble path length and the dissolved organic carbon (DOC) content of the seawater. The OC content of the ejected aerosols increased with increasing DOC concentrations in the seawater. On the basis of the OC/salt ratio found in aerosols collected in Bermuda (0.05) and the amount of ejected sea salt from the ocean (10^{15}–10^{16} g/yr), Duce and Hoffman (*45*) estimated that the ocean ejects between 5×10^{13} and 5×10^{14} g of OC/yr.

Table III. Parameters for PCB Flux Calculations

	Aroclor 1242	Aroclor 1254
concn in air [a]		
vapor, [b] atm	5.6×10^{-14}	1.5×10^{-14}
particulate, [c] ng/m³	0.13	0.13
concn in L. Michigan water [d]		
dissolved, mol/m³	7.7×10^{-9}	2.6×10^{-8}
total, mol/m³	4.7×10^{-8}	6.8×10^{-8}
aerosol deposition velocity (V_D), m/s	0.005	0.005
air/water partition coeff, [e] atm m³/mol	2.8×10^{-7}	1.4×10^{-7}
Henry's law constants (H), [f] atm m³/mol	5.7×10^{-4}	2.8×10^{-3}
overall gas-phase mass-transfer coeff (K_{OG}), [e] m/h	7.9	7.0
overall liquid-phase, mass-transfer coeff (K_{OL}), [f] m/h	5.7×10^{-2}	6.7×10^{-2}
RT (at 25 °C), atm m³/mol	2.45×10^{-2}	2.45×10^{-2}

[a] Average concentrations from eight cruises (*22*). [b] Mol wt of Aroclors 1242, 1254, and 1260 taken as 256, 324, and 358, respectively. [c] Total concentration of Aroclors 1242, 1254, and 1260. [d] From Murphy and Rzeszutko (*8*). [e] From Doskey (*22*). [f] From Mackay and Leinonen (*31*).

Table IV: Total Atmospheric PCB Flux to Lake Michigan

	gas-phase control, [b] kg/yr	liquid-phase control, [c] kg/yr
dry deposition [a] particulate	1200	1200
vapor	2800	0
wet deposition [d]	2500	2500
volatilization	0	270000
net input	6500	−266000

[a] Area of Lake Michigan, 5.6×10^{10} m². [b] Using air/water partition coefficients from Doskey (*22*). [c] Using H and K_{OL} from Mackay and Leinonen (*31*). [d] From Murphy (*48*).

The present lack of knowledge of the significance of the bubble ejection of particulate matter from freshwater lakes makes it difficult to determine its influence upon the ejection of PCBs from Lake Michigan. This lake has an average DOC content of 2 mg/L (*46*) while that of the ocean is 0.5 mg/L (*47*). On the basis of the findings of Hoffman and Duce (*44*), the aerosols produced by Lake Michigan would be expected to be more enriched in organic carbon than those produced by the ocean. Strand (*28*) found that the total organic carbon (TOC) content of aerosols collected over Lake Michigan ranged from 7.5% to 54%. Additionally, TOC percentages of 73% and 78% were obtained under conditions when lake spray was evident. These values may be more representative of aerosols produced by bubble ejection. Surface organic microlayers in Lake Michigan have been found to be enriched in PCBs. Elzerman (*46*), employing the screen technique to sample the microlayer, found average concentrations of 245 ng of Aroclor 1254/L while that of the bulk water was 22 ng of Aroclor 1254/L. The average concentration of PCBs in particulate matter collected over Lake Michigan is 4.0 ppm (*22, 33*). It might be expected that the concentration of PCBs in bubble-ejected particulate matter may be even greater.

PCB Fluxes across Lake Michigan Air/Water Interface

An estimate of the atmospheric PCB flux to Lake Michigan was made by using model concepts discussed above and data from Doskey (*22*) and Murphy and Rzeszutko (*8*). The data set from Doskey (*22*) represents eight samples collected on Lake Michigan in 1977. These samples showed an average concentration of 1.0 ng/m³, with an average of 13% being captured by the glass-fiber filter. Adsorbed vapor showed an average composition of 75% Aroclor 1242 and 25% Aroclor 1254, while the material collected on the glass-fiber filter was composed of 69% Aroclor 1242, 23% Aroclor 1254, and 8% Aroclor 1260. Murphy (*48*) found that the total annual PCB input via precipitation to Lake Michigan was ~2500 kg in 1975–76. Parameters employed to calculate the atmospheric PCB flux are presented in Table III.

Results from calculations of the vapor and particulate PCB flux are presented in Table IV. Since uncertainties still exist in the value of H for PCBs, calculations were made for both gas- and liquid-phase control of PCB vapor deposition. The air/water partition and mass-transfer coefficients determined by Doskey (*22*) were used to calculate the flux assuming gas-phase control. The H and K_{OL} derived by Mackay and Leinonen (*31*) were used in the liquid-phase-control calculations.

Several interesting results emerge from these calculations. Particulate deposition is quite important although the major fraction of the total atmospheric PCB burden is thought to exist in the vapor form. When one assumes gas-phase control, dry deposition may be similar in importance when compared to wet deposition. Under this assumption, Lake Michigan would essentially act as a sink for PCBs. Using the K_{OL} and H derived by Mackay and Leinonen (*31*) indicates that the lake may actually be a source of PCBs. The outputs far outweigh the inputs even if an estimate of 750 kg/yr for stream input (*8*) is added. If we assume an average concentration of ~10 ng/L (Table III) for Lake Michigan, the total amount of PCB in the lake water would be ~50 000 kg. The volatilization rate is 1 order of magnitude greater than the lake burden of PCB. Finally, examination of the PCB input inventory compiled by Murphy and Rzeszutko (*8*) indicates that the atmospheric route is presently of major importance.

The uncertainty in the direction of flux may possibly be the result of either inaccurate values of K_{OL} and H or a lack of knowledge of the speciation of PCBs in air and water. Speciation is operationally defined by a glass-fiber filter in most instances. Because of their hydrophobic nature, PCBs in the nonfilterable fraction of a natural water sample may actually be associated with DOC. If PCB vapor is deposited onto a body of water and rapidly associates with DOC, it may become unavailable for volatilization. Applying a Henry's law constant to this situation would lead to an error in any determination of vapor deposition or volatilization. Another problem may arise from the operational definition of PCB vapor (i.e., that fraction which passes through a glass-fiber filter). That which is operationally defined as PCB vapor may actually be particulates which are able to pass through a glass-fiber filter.

Conclusions

Problems involved in measuring and modeling PCB fluxes across the air/water interface are discussed. Although vapor- and particulate-phase PCBs are presently differentiated by an operational definition (i.e., partitioning by a glass-fiber filter), indications are that greater than 90% exist in the vapor phase. Indirect calculations also indicate that particle-bound Aroclors are associated with submicrometer-size aerosols.

Nonuniform collection efficiencies for various PCB isomers prevent accurate air-concentration determinations. Doskey and Andren (*17*) have shown that mono- and dichlorobiphenyls are collected poorly by available collection methodologies. Atmospheric collection and quantification problems are further compounded by individual Aroclor component weathering.

Analysis of Henry's law constants generated from laboratory and environmental data indicate that the phase (gas or liquid) which controls the PCB vapor flux is still unknown. Further investigation, possibly with individual PCB isomers, are needed to determine parameters which are necessary for flux modeling efforts. These investigations may show that the degree of chlorination or positions of the chlorines on the biphenyl molecule influence the phase controlling the flux. Also, further investigations of the speciation of PCBs in air and water are needed for future modeling efforts. Air/water partition coefficients determined in systems containing DOC and POC may be more useful in atmospheric flux modeling than Henry's law constants.

The role of bubble ejection in transferring PCBs from freshwater lakes back into the atmosphere is uncertain. This phenomenon should be investigated since PCBs are enriched in surface organic microlayers.

PCB measurements in air over Lake Michigan were used to model the flux across the air/water interface using the qualifications developed above. Calculations indicate that atmospheric input presently plays a major role in comparison to other inputs.

It must be emphasized that an accurate picture of the atmospheric PCB flux can only be made by using a combination of approaches. One obvious route would be to measure the PCB sedimentation rate in a lake.

Acknowledgment

We thank Dr. Robert Bowden of the Environmental Protection Agency for allowing us to use the R/V Roger Simons. We also thank Dr. Donald Mackay for helpful comments on the manuscript. Ms. Jean Schneider's help in typing the manuscript is also appreciated.

Literature Cited

(1) National Academy of Sciences "Polychlorinated Biphenyls"; NAS: Washington, DC, 1979; pp 18–25.
(2) Risebrough, R. W.; deLappe, B. W.; Walker, W., II *Mar. Pollut. Transfer* **1976,** 261–321.
(3) Harvey, G. R.; Steinhauer, W. G. *Atmos. Environ.* **1974,** *8*, 777.
(4) Fuller, B.; Gordon, J.; Kornreich, M. "Environmental Assessment of PCBs in the Atmosphere"; The Mitre Corp.: McLean, VA, 1977; EPA Report No. EPA-40/3-77-045.
(5) Bidleman, T. F.; Rice, C. P.; Olney, C. E. *Mar. Pollut. Transfer* **1976,** 323–51.
(6) Duce, R. A.; Duursma, E. K. *Mar. Chem.* **1977,** *5*, 319.
(7) Nisbet, I. C. T.; Sarofim, A. F. *Environ. Health Perspect.* **1972,** *1*, 21.
(8) Murphy, T. J.; Rzeszutko, C. P. *J. Great Lakes Res.* **1977,** *3*, 305.
(9) Risebrough, R. W.; Huggett, R. J.; Griffin, J. J.; Goldberg, E. D. *Science* **1968,** *159*, 1233.
(10) Seba, D. B.; Prospero, J. M. *Atmos. Environ.* **1971,** *5*, 1043.
(11) Södergren, A. *Nature (London)* **1972,** *236*, 395.
(12) Bengston, S. A.; Södergren, A. *Ambio* **1974,** *3*, 84.
(13) Young, D. R.; McDermott-Erhlich, D.; Heesen, T. C. "Polychlorinated Biphenyl Inputs to the Southern California Bight"; Southern California Coastal Research Project: El Segundo, CA, 1975.
(14) Södergren, A. *Environ. Qual. Saf.* **1975,** *3*, 803.
(15) Bidleman, T. F.; Olney, C. E. *Bull. Environ. Contam. Toxicol.* **1974,** *11*, 442.
(16) Bidleman, T. F.; Olney, C. E. *Science* **1974,** *182*, 516.
(17) Doskey, P. V.; Andren, A. W. *Anal. Chim. Acta* **1979,** *110*, 129.
(18) Lockhart, L. B., Jr.; Patterson, R. L., Jr.; Anderson, W. L. "Characteristics of Air Filter Media Used for Monitoring Airborne Radioactivity"; U.S. Naval Research Laboratory: Washington, D.C., 1964; NRI Report 6054.
(19) Junge, C. E. In "Basic Considerations about Trace Constituents in the Atmosphere as Related to the Fate of Global Pollutants"; Suffet, I. H., Ed.; Wiley-Interscience: New York, 1977; Part I, pp 7–25.
(20) Lewis, R. G.; Brown, A. R.; Jackson, M. D. *Anal. Chem.* **1977,** *49*, 1668.
(21) Zell, M.; Neu, H. J.; Ballschmiter, K.; Fresenius Z. *Anal. Chem.* **1978,** *292*, 97.
(22) Doskey, P. V. M.S. Thesis, Water Chemistry Program, University of Wisconsin, Madison, WI, 1978.
(23) Chamberlain, A. C. *Proc. R. Soc. London, Ser. A* **1966,** *236*, 45.
(24) Sehmel, G. A.; Sutter, S. L. *J. Rech. Atmos.* **1974,** *3*, 911.
(25) Gatz, D. F. *Water, Air, Soil Pollut.* **1975,** *5*, 239.
(26) Cawse, P. A. "A Survey of Atmospheric Trace Elements in the U.K. 1972–1973"; United Kingdom Atomic Energy Authority: Harwell, 1974; AERE-R7669; p 78.
(27) Slinn, W. G. N.; Hasse, L.; Hicks, B. B.; Hogan, A. W.; Lal, D.; Liss, P. S.; Munnich, K. O.; Sehmel, G. A.; Vittori, O. *Atmos. Environ.* **1978,** *12*, 2055.
(28) Strand, J. W. Ph.D. Thesis, Water Chemistry Program, University of Wisconsin, Madison, WI, 1978.
(29) Hoffman, E. J.; Duce, R. A. *Geophys. Res. Lett.* **1977,** *4*, 449.
(30) Whitman, W. G. *Chem. Metall. Eng.* **1923,** *29*, 146.
(31) Mackay, D.; Leinonen, P. J. *Environ. Sci. Technol.* **1975,** *9*, 1178.
(32) Liss, P. S.; Slater, P. G. *Nature (London)* **1974,** *247*, 181.
(33) Andren, A. W.; Doskey, P. V.; Strand, J. W. "Atmospheric Chemistry of PCBs and PAHs"; International Joint Commission, Menomononee River Pilot Watershed Study, Draft, Final Report; Vol. 9, March 1980.
(34) Hetling, L.; Horn, E.; Tofflemire, J. Albany, NY, 1978, New York State Department of Environmental Conservation, Technical

Report No. 51.
(35) Paris, D. F., Research Chemist, Environmental Processes Branch, U.S. EPA, Environmental Research Laboratory, Athens, GA 30613, personal communication, 1980.
(36) Paris, D. F.; Steen, W. C.; Baughman, G. L. *Chemosphere* **1978,** *4*, 319.
(37) Cohen, Y.; Cocchio, W.; Mackay, D. *Environ. Sci. Technol.* **1978,** *12*, 553.
(38) Eriksson, E. *Tellus* **1959,** *11*, 375.
(39) Eriksson, E. *Tellus* **1960,** *12*, 63.
(40) Blanchard, D. C. "Electrification of the Atmosphere by Particles from Bubbles in the Sea"; Pergamon: Oxford, 1963; Vol. 1, pp 71–202.
(41) MacIntyre, F. *J. Phys. Chem.* **1968,** *72*, 589.
(42) MacIntyre, F. *J. Geophys. Res.* **1972,** *77*, 4211.
(43) Wallace, G. T.; Duce, R. A. *Mar. Chem.* **1975,** *3*, 157.
(44) Hoffman, E. J.; Duce, R. A. *J. Geophys. Res.* **1976,** *81*, 3667.
(45) Duce, R. A.; Hoffman, E. J. *Rev. Earth Planetary Sci.* **1976,** *4*, 187.
(46) Elzerman, A. W. Ph.D. Thesis, Water Chemistry Program, University of Wisconsin, Madison, WI, 1976.
(47) Menzel, D. W. In "Primary Productivity, Dissolved and Particulate Organic Matter, and the Sites of Oxidation of Organic Matter"; Goldberg, E. D., Ed.; Wiley-Interscience: New York, 1974; Vol. 5, pp 659–78.
(48) Murphy, T. J. "Atmospheric Inputs of Polychlorinated Biphenyls to the Great Lakes", presented before the Division of Environmental Chemistry, American Chemical Society, Washington, DC, Sept 1979.

Received for review October 29, 1979. Accepted February 12, 1981. This work was supported in part by Sea Grant NOAA and U.S. EPA Grant No. R803971020.

NOTES

Comparison of Automated Segmented-Flow and Discrete Analyzers for the Determination of Nutrients in Water

Vicenti C. Marti

U.S. Geological Survey, National Water Quality Laboratory, Arvada, Colorado 80002

David R. Hale*

Coulter Electronics, Inc., Hialeah, Florida 33010

■ Water samples with specific conductances ranging from 66 to 6950 μmho/cm at 25 °C were analyzed for ammonia-N (NH_3-N), nitrate plus nitrite-N ($NO_3 + NO_2$-N), nitrite-N (NO_2-N), and phosphate-P (PO_4-P) by using both a "segmented-flow" analyzer and a "discrete" analyzer. Plots of the discrete vs. the segmented-flow results showed linear correlation coefficients of 0.9980 for NH_3-N, 0.9997 for $NO_3 + NO_2$-N, 0.9998 for NO_2-N, and 0.9950 for PO_4-P. The significances of the slope and the y intercept of each plot are discussed in terms of possible biases which may exist between the two systems. Data concerning precision and accuracy for both analyzers are presented. For the four analytes, the rate of sample analysis was 60 samples per hour on the discrete analyzer and 40 samples per hour on the segmented-flow analyzer.

Introduction

Automated colorimetric analyses have been made extensively by using "segmented-flow" systems. Many such automated methods have become accepted and referenced as standard techniques (*1–3*). However, colorimetric analyses on automated "discrete" systems generally can be made at a faster rate of analysis for most of the chemical species determined by the reference methods (*4*).

This paper presents a comparison of the analytical results obtained with two commercially available instruments, one using a segmented-flow technique (Technicon AAII (AutoAnalyzer System II)), which automatically moves a sample through a closed system of tubing and mixing coils using air-segmented streams of reagents and sample, and the other a discrete technique (Coulter IKL (Industrial Kem O Lab)), which automatically moves a sample and reagents in an open reaction tube through a water bath.

The determinations of nutrients were chosen because of the environmental significance of these constituents in natural waters and because they commonly are best determined by colorimetric methods. The analyses were performed at the U.S. Geological Survey's water quality laboratory, Arvada, CO. The comparison study included 39 water samples randomly chosen from among the hundreds of samples received at the facility daily. They included surface waters from Alaska, California, Colorado, Hawaii, Oklahoma, and Utah.

Materials and Methods

Standards and reagents were prepared with analytical-grade chemicals and reagent-grade (ASTM type II or better) water. Standard U.S. Geological Survey-approved methods (*2*) I-2523-78, I-2545-78, and I-2600-78 were used as the guidelines for the reagents and configurations of the AAII for the various tests. Coulter methods (based on accepted methods (*1*)) were used as a reference for the reagents and configurations used on the IKL.

Specific conductance measurements were made with a standard 1-cm cell. These data quantify the relative ionic strengths of the waters tested. Reference solutions were made from concentrates provided by the U.S. Environmental Protection Agency, Quality Assurance Branch, Cincinnati, OH.

The IKL and AAII ammonia channels both used the phenate method. The IKL ($NO_3 + NO_2$-N) channel was set up for the hydrazine reduction method, while the AAII was configured for the cadmium–copper reduction technique. For both methods nitrate is reduced to nitrite and then reacted with the same reagents as in the nitrite test. Cadmium granules obtained from E. Merck, Cat. No. 2001, were used for filling the reductor columns. The ion-exchange material used to remove calcium and magnesium (hydrazine method only) was Dowex-50W-XB (Na^+) 20–50 mesh. Nitrite was analyzed by the diazotization method, and phosphate by the phosphomolybdate method, on both analyzers.

Experimental Section

The IKL was operated in a 4-channel test mode at the rate of 240 test results per hour or 60 samples per channel per hour

(5). The colorimeters of the IKL modules used 1-cm cuvettes.

The AAIIs were configured for routine measurements of nutrients (2). The rate of analysis for the 4-channel system was 40 samples per channel per hour. The rate-determining channel in this system is the $NO_3 + NO_2$-N because efficient reduction of NO_3 to NO_2 by the cadmium–copper column is achieved at this rate.

Ten-point standard curves were calculated for each channel by linear regression, and the concentration of unknown samples was determined from them.

Six natural water samples with nutrient concentrations covering the entire analytical range of each instrument were randomly placed in workloads of ~150 samples and analyzed for 5 consecutive days by both instruments to generate precision data. As a check for accuracy, determinations included the analysis of known nutrient reference samples provided by the U.S. Environmental Protection Agency.

Results and Discussion

The results for each analysis as determined by each system were compared by plotting the corresponding pairs on a graph having the IKL values as the ordinate and the AAII values as the abscissa. The slope, the *y* intercept, and the correlation coefficient were determined by linear least-squares regression, and the best-fit line was drawn.

The plot for the NH_3-N results is shown in Figure 1. Most of the concentrations were less than 0.15 mg/L. These low concentrations for the NH_3-N are not unusual for most unpolluted surface waters. The remaining few points conform to the line well; however, they may have caused the slope value of 0.969 to be significantly less than 1.00 ($P = 0.01$). There is some statistical evidence that the NH_3-N determinations by the IKL may differ from the actual concentrations by ~3% for the range studied; however, the distribution of the data points was not even, and some weighting of the results may have occurred inadvertently. This conjecture is supported by the fact that the determinations of NH_3-N included in the nutrient reference standards and in the six natural water samples indicated no bias in the results of either instrument. Most of the natural water samples tested contained little NH_3-N; therefore, the comparison took place mainly at the lower end of the dynamic ranges of the methods.

The comparison for the $NO_3 + NO_2$-N analyses is shown on Figure 2. Although two different reduction methods were used for these analyses, the results show remarkable similarity. The slope is not different from 1.0, and the *y* intercept is not significantly different from 0.0 ($P = 0.01$).

Results for the NO_2-N analyses are shown in Figure 3. All but one pair of NO_2-N data were less than 0.15 mg/L, the lowest 15% of the dynamic range of the method; the remaining pair (2.34, 2.35) are not included in this graph. The value of the slope (0.938) is not significantly different from 1.00, but the *y* intercept is significantly different from zero. Positive

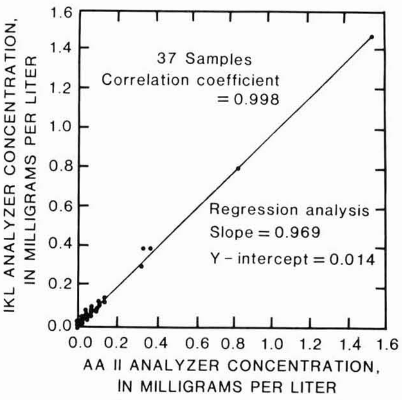


Figure 1. Comparison plot for ammonia-nitrogen determinations by AAII and IKL analyzers.

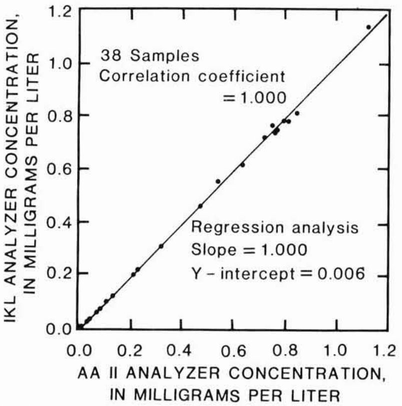


Figure 2. Comparison plot for nitrate and nitrite-nitrogen determinations by AAII and IKL analyzers.

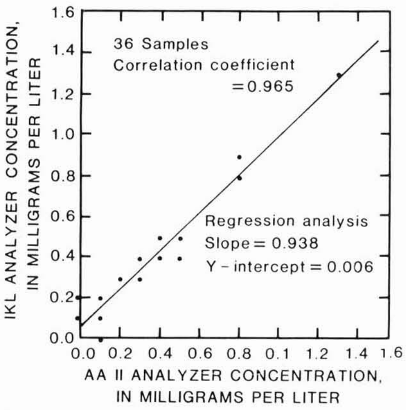


Figure 3. Comparison plot for nitrite-nitrogen determination by AAII and IKL analyzers. (Values: mg/L × 10.)

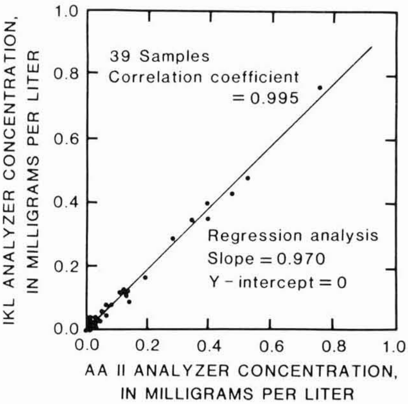


Figure 4. Comparison plot for dissolved phosphate-P determinations by AAII and IKL analyzers.

Table I. Precision as Determined by Analyses of Natural Water Samples [a]

	ammonia-N		nitrate + nitrite-N		nitrite-N		phosphate-P	
	AAII	IKL	AAII	IKL	AAII	IKL	AAII	IKL
1a	0.12 ± 0.003	0.15 ± 0.006	0.20 ± 0.005	0.19 ± 0.009	0.11 ± 0.015	0.08 ± 0.009	0.07 ± 0.014	0.05 ± 0.010
2a	0.29 ± 0.007	0.26 ± 0.006	0.40 ± 0.010	0.40 ± 0.015	0.13 ± 0.018	0.16 ± 0.001	0.07 ± 0.013	0.09 ± 0.013
3a	0.32 ± 0.008	0.32 ± 0.008	1.09 ± 0.087	0.99 ± 0.032	0.33 ± 0.045	0.32 ± 0.011	0.12 ± 0.024	0.16 ± 0.013
4a	0.76 ± 0.019	0.78 ± 0.016	1.27 ± 0.102	1.22 ± 0.039	0.65 ± 0.090	0.56 ± 0.011	0.39 ± 0.027	0.34 ± 0.029
5a	1.33 ± 0.033	1.30 ± 0.027	2.50 ± 0.200	2.34 ± 0.040	0.72 ± 0.094	0.73 ± 0.031	0.43 ± 0.031	0.50 ± 0.011
6a	1.29 ± 0.032	1.30 ± 0.029	2.52 ± 0.203	2.52 ± 0.111	1.00 ± 0.131	1.00 ± 0.047	0.70 ± 0.038	0.80 ± 0.017

[a] All results in mg/L ± SD.

Table II. Analysis of Reference Standards [a]

	ammonia-N		nitrate + nitrite-N		phosphate-P	
	AAII	IKL	AAII	IKL	AAII	IKL
	Nutrient Reference Standard I					
concn ± 1 SD	0.232 ± 0.010	0.224 ± 0.005	0.104 ± 0.005	0.111 ± 0.008	0.058 ± 0.006	0.066 ± 0.006
actual concn	0.23	0.23	0.11	0.11	0.052	0.052
	Nutrient Reference Standard II					
concn ± 1 SD	1.64 ± 0.026	1.63 ± 0.021	0.398 ± 0.010	0.370 ± 0.011	0.193 ± 0.006	0.186 ± 0.005
actual concn	1.59	1.59	0.38	0.38	0.19	0.19

[a] All values in mg/L.

bias amounting to less than 1% is indicated by this statistic; however, the weighting of results at the detection limits of both instruments may be responsible for this observation. When the point (2.34, 2.35), which is not shown in Figure 3, is included, then the value for the correlation coefficient changes to 0.9998 with no significant change in the slope or *y*-intercept values.

The results for the dissolved phosphate (PO_4-P) analyses are shown in Figure 4. Again the slope was not different from 1.0; the *y* intercept was not different from 0.0; and the correlation coefficient was 0.995.

The mean values ± one standard deviation (mg/L) obtained for each analyte by both instruments during a 5-day period are listed in Table I. As evidenced by the data, the precision of the discrete analyzer is usually better than the precision of the segmented-flow analyzer. The main reason for this is probably the diminution of "carry-over" from sample to sample noted in the discrete analyzer. The precision of the segmented-flow system can be improved by increasing the wash-to-sample ratio; but in doing so, the rate of sample analysis is decreased.

The results obtained for 11 determinations during 2 weeks using the nutrient reference standards I and II provided by the U.S. Environmental Protection Agency are shown in Table II. These standards did not contain nitrite. The results that were obtained by both instruments show good agreement with the actual values.

Summary

More than 30 natural water samples were analyzed, colorimetrically, for NH_3-N, NO_3 + NO_2-N, NO_2-N, and PO_4-P, by the Technicon AAII and the Coulter IKL analyzers. The former uses segmented-flow analysis, while the latter uses discrete analysis. The discrete analyzer provided a 50% increase in rate of analysis compared with the segmented-flow analyzer for the four determinations studied.

Comparable accuracy and precision of the two analyzers were indicated by the results of the standard reference analyses, by the results of the six natural samples used for the precision study, and also by the regression statistics pertaining to the 39 unknown water samples.

Literature Cited

(1) *Fed. Regist.* **1976,** *41,* 52780–5.
(2) Skougstad, M., Fishman, M., Friedman, L., Erdmann, D., and Duncan, S., Eds. "Methods For Determination of Inorganic Substances in Water and Fluvial Sediments"; Techniques of Water Resources Investigations of the United States Geological Survey, 1979; Book 5, Chapter A1.
(3) "Methods Chemical Analysis of Water and Washes"; Environmental Monitoring and Support Laboratory: Cincinnati, OH 1978; NTIS No. PB 297 686.
(4) Hale, D. R. *Am. Lab. (Fairfield, Conn.)* **1979,** *11,* 117–30.
(5) "Coulter Industrial Kem-O-Lab Reference Manual"; Coulter Electronics, Inc.: Hialeah, FL 33010.

Received for review August 26, 1980. Accepted February 25, 1981.

Automobile Traffic and Lung Cancer. An Update on Blumer's Report

Lincoln Polissar* and Homer Warner, Jr.

Fred Hutchinson Cancer Research Center, 1124 Columbia Street, Seattle, Washington 98104

In widely circulated reports (*1*, *2*), Blumer et al., studied the cancer mortality of a small Swiss town and calculated that residents living on a busy highway during 1958–70 had a cancer death rate 9 times greater than the rate for residents of a newer section of town with much less automobile traffic (*3*). They tentatively linked the higher rate to automobile exhaust, including PAH, which was found in a high concentration in the soil near the highway (*1*). Because of the obviously significant public health implications of such a large relative risk, we believed that testing of Blumer's results was essential.

To do this, we examined traffic volume at the residences of

■ A study carried out in Switzerland showed a high cancer risk for persons heavily exposed to automobile exhaust. An attempt to corroborate these findings was carried out. Exposure to automobile exhaust was imputed from the average daily traffic flow (ADT) at the residence of 664 lung cancer cases and 666 nonmelanotic skin cancer controls living in Seattle. There was a nonsignificant positive risk of lung cancer for female cases living on busy streets but no excess risk for males. The analysis included factors to control for the effects of age, sex, socioeconomic status, and other variables.

lung cancer cases and nonmelanotic skin cancer controls. Lung cancer was chosen as the malignancy with the greatest likelihood of correlation with exposure to automobile exhaust. We expected the milder nonmelanotic skin cancer to show little, if any, correlation. We hypothesized that the lung cancer cases would have been exposed to a higher volume of traffic than the skin cancer controls. The cases were identified from the records of the Cancer Surveillance System, a population-based tumor registry which covers 2.4 million people in the Seattle area; over 98% of the new cancer cases in the reporting area are registered. We chose a systematic random sampling of 373 males and 291 females from among the 1328 lung cancer cases diagnosed in Seattle during 1974–77. For the controls, we drew a systematic random sample of 373 males and 293 females from an incidence survey of 2229 nonmelanotic skin cancer cases diagnosed in the greater Seattle area during 1977–78. Exposure to automobile exhaust was estimated by the average daily traffic (ADT) flow (vehicles per 24 h) at the residence of each case and control at the time of diagnosis. We used traffic flow figures from a 1977 map prepared by the City of Seattle Engineering Department. Although the diagnosis dates spanned a 5-yr period, we found that the traffic flow maps differed little from year to year.

Using the Mantel and Haenszel method for pooling odds ratios (*4*), we stratified by age, by a socioeconomic (SES) indicator for the census tract, and by the geographic district of Seattle. The district variable controlled for a geographic gradient in the ratio of cases to controls. The mean size of the nine districts studied was 56 000 people. We did not stratify by race, since over 95% of the cases and the controls were white.

In sharp contrast to Blumer (*3*), we found no significant associations between traffic volume and cancer risk (Table I). Our sample size provided a 95% probability that a pooled odds ratio of 1.6 or larger (indicating a 1.6-fold increase in lung cancer risk for persons living on streets with at least 5000 ADT) would have been significant at the 5% level for both sexes combined. The pooled odds ratios for several definitions of high vs. low exposure are all fairly close to 1.0 (with one exception), and all have significance levels greater than 5%. The strongest result, a nonsignificant odds ratio of 1.97, implies that women living on streets with at least 15 000 vehicles passing per day are at almost twice the risk of developing lung cancer as women who live on streets with <15 000 ADT. There is the barest hint in the odds ratio that female lung cancer cases lived on busy streets more often than female controls. It is not surprising that the carcinogenic effects of automobile exhaust would be more likely to appear in women, for it is still generally true that smoking is less of a confounding factor for women and that they probably spend more time at home than men.

Table I. Mantel–Haenszel Pooled Odds Ratio for Lung Cancer vs. Nonmelanotic Skin Cancer in Relation to Automobile Traffic Exposure by Sex

exposure categories, vehicles/24 h		odds ratio of lung cancer risk for high vs. low exposure	
high	low	males	females
≥5 000	<5 000	1.09 (p = 0.38)	1.43 (p = 0.07)
≥10 000	<10 000	1.03 (p = 0.51)	1.36 (p = 0.18)
≥15 000	<15 000	0.65 (p = 0.22)	1.97 (p = 0.08)

These results were supplemented by two additional analyses, the Mantel–Haenszel procedure for stratified 2 × K tables (*5*) and a discriminant analysis (*6*). All results were similar: no relationship between lung cancer risk and auto traffic for men and a nonsignificant relationship for women. Further, we found only a negligible and nonsignificant difference in traffic exposure between cases and controls for two subgroups: (1) 154 cases with adenocarcinoma (the lung cancer with a histologic type least related to smoking) compared to all 666 controls and (2) 110 cases living in census tracts with lower migration rates compared to 131 controls living in the same tracts. The actual migration rates of cases and controls—a potentially important variable—is unknown.

Several differences exist between the two studies. Blumer found an elevated risk for all types of cancer; we studied only lung cancer, as the most likely tumor. Blumer's retrospective cohort study followed exposed and unexposed people forward in time, while we imputed the level of past exposure from the traffic volume at the current address. He controlled for the effect of SES on cancer by tagging each individual by occupation; we imputed as SES level for each person from the average education and income for the census tract. Blumer's Swiss town and Seattle may also have dissimilar rates of automobile exhaust dilution in the atmosphere due to wind and rain. It could be argued that these various differences preclude any reasonable comparison of the two studies. Nevertheless, we would have expected Blumer's high relative risk of 9.0 to have yielded a significant excess risk in our study.

Because of the slight, but intriguing, positive risk for women and because so many people are exposed to a possible health hazard from automobile exhaust, we suggest the necessity of two types of studies: (1) a study of the health of persons who have lived for at least 5–10 yr on heavily traveled streets and (2) retrospective case-control studies of specific cancers, in which past exposure to auto traffic could be determined by residence histories.

Literature Cited

(1) Blumer, M. et al. *Environ. Sci. Technol.* **1977,** *11*, 1082–4.
(2) *Sci. News* **1977,** *112*, 296.
(3) Blumer, W.; Jauman, T.; Reich T. *Schweiz, Rundsch. Med./Prax.* **1972,** *61*, 514–8.
(4) Mantel N.; Haenszel, W. *J. Natl. Cancer Inst.* (*U.S.*) **1959,** *22*, 719–48.
(5) Mantel, H. *J. Am. Stat. Assoc.* **1963,** *58*, 690–700.
(6) Cooley, W. W.; Lohnes, P. R. "Multivariate Data Analysis"; Wiley: New York, 1971; Chapter 9.

Received for review December 1, 1980. Accepted February 9, 1981.

Solubility Behavior of Three Aromatic Hydrocarbons in Distilled Water and Natural Seawater[†]

Steven S. Rossi* **and William H. Thomas**

Institute of Marine Resources, Scripps Institution of Oceanography, La Jolla, California 92093

■ The solubilities of three aromatic hydrocarbons were determined at 25 °C in natural seawater and distilled water. Saturation was achieved by equilibration of water and an excess of hydrocarbon by mechanical agitation. All three hydrocarbons, toluene, acenaphthene, and pyrene, were less soluble in seawater than in distilled water. The magnitude of the "salting out" effect increased with increasing molar volume of hydrocarbon. Temperature effects on aromatic-hydrocarbon solubility in seawater, studied at 15, 20, and 25 °C, were also directly related to molar volume. Temperature, rather than salinity, variations during toxicological studies with aqueous solutions of aromatic hydrocarbons would appear to present a greater challenge to toxicant concentration stasis, particularly so for experiments utilizing concentrations near the solubility limit.

Introduction

As part of a study designed to ascertain the effects of selected petroleum refinery effluent hydrocarbons on wild phytoplankton populations, we have determined the solubilities of three aromatic hydrocarbons in aqueous solution and 35‰ salinity natural seawater. The hydrocarbons chosen for study were toluene, acenaphthene, and pyrene, the latter two of which exhibit aqueous solubilities in the μg of solute/L range (*1*, *2*). Use of saturated hydrocarbon solutions in experiments with the algae was anticipated on the basis of earlier toxicological studies with related marine organisms (*3*). Since experimental design entailed the use of media of variable temperature and salinity, it was necessary to establish the effect of these variables on hydrocarbon solubility.

Experimental Section

Saturated solutions were generated by equilibrating water with an excess of hydrocarbon in an all-glass apparatus consisting of a 1-L Erlenmeyer flask, fitted with a ground-glass stopper and a side-arm tap which was plugged with glass wool. Flasks containing 500 mL of water and hydrocarbon were placed in a constant-temperature (±0.1 °C) gyrotary shaker (200 rpm) for at least 24 h. Following a 12-h stationary equilibration period, an aliquot (100 mL) of saturated solution was drained through the glass-wool plug and into a volumetrically calibrated separatory funnel. Acenaphthene and pyrene were isolated from solution by triplicate extraction with 10 mL of *n*-hexane, which recovered over 99% of hydrocarbon as determined in experiments with spiked solutions. Toluene was extracted by passing measured volumes through 0.6 × 6 cm columns of a superficially porous bonded C_{18} stationary-phase adsorbent (Bondapak C_{18}, Water Associates, Milford, MA), which provided better than 99% extraction efficiency for volumes of toluene solution less than 50 mL. Toluene was eluted from columns with trichlorofluoromethane (Freon-11).

Hydrocarbon levels in concentrated extracts (or eluates) were determined on a Hewlett-Packard Model 5840A gas chromatograph equipped with a flame ionization detector and an electronic integrator. Detector and inlet port temperatures were 350 and 250 °C, respectively. Two columns were employed: a $\frac{1}{8}$ in. × 8 ft stainless-steel column of 10% TCEP on 10/120 Chromsorb for toluene analyses and a WCOT SP-2100 glass column (30 m × 0.25 mm i.d.) for acenaphthene and pyrene determinations. The oven temperature and the programming rate were variable depending on the hydrocarbon under study. Concentrations were determined by peak-area comparison with that of external standards. All values were corrected for evaporation and handling losses, as determined by use of internal-standard hydrocarbons. Hydrocarbon concentrations in extracts (or eluates) were additionally determined by peak-height comparison with standards via ultraviolet spectrophotometry on a Beckman ACTA MVI recording spectrophotometer. Agreement between gas-chromatographic and spectrometric analyses was typically within 2%.

Analytical-grade aromatic hydrocarbons were used following purification. Toluene (Burdick & Jackson, Muskegon, MI) was purified by triple distillation in glass. High-purity (99.9%) acenaphthene (Aldrich Chemical Co.) was obtained by double recrystallization from distilled methanol. Pyrene (Aldrich Chemical Co.) was separated from its major contaminant, 2,3-benzanthracene, by derivitization with 2,4,6-trinitrophenol. Water used for solubility determinations and cleaning of glassware was doubly distilled in an all-glass system and was free of trace organics. Extraction solvents were also doubly distilled in glass. Seawater collected off the Scripps pier was filtered twice through a 0.22-μm membrane and twice extracted with *n*-hexane (10:1, v/v) before use. Salinity was adjusted to 35‰ with doubly distilled water or NaCl by use of an American Optical refractive-index salinometer. All seawater blanks failed to exhibit chromatographic response after a 100-fold concentration. All glassware was rinsed with water and hexane, soaked in a dichromate–sulfuric acid bath for 6 h, rinsed with doubly distilled water, and dried at 200 °C until just before use.

Results

Table I shows solubilities of the aromatic hydrocarbons in distilled water and seawater at 25 °C. Values obtained in this work are compared with those of Eganhouse and Calder (*1*), May et al. (*2*), and Sutton and Calder (*4*). Agreement is quite good, with the exception of the acenaphthene data. This may be due, in part, to the inclusion of naphthalene in solute analyses of previous studies. Naphthalene is the major contaminant of high-purity acenaphthene, and these two hydrocarbons are not easily distinguished with conventional (noncapillary column) chromatographic equipment. All measurements give the precision as the standard deviation of the mean for six replicates.

Table II gives data demonstrating the effect of temperature on solubility of three aromatic hydrocarbons in seawater. All values represent means for six determinations. Standard deviations were ±1% or less. Since experimental temperatures during our toxicity studies (with surface seawater) were not anticipated to be significantly below 15 °C, this temperature was chosen as a lower limit (*5*).

Discussion

To explain the dissolution process, investigators have correlated certain properties of aromatic hydrocarbons with their solubilities. Molar volume and surface area have provided the

---

[†] Contribution from the Scripps Institution of Oceanography.

Table I. Solubilities of Three Aromatic Hydrocarbons in Freshwater and Seawater at 25 °C

molecule	solubility in distilled water		solubility in seawater		solubility in distilled water from lit., mole fraction
	mole fraction	μg/g	mole fraction	μg/g	
toluene	5.5×10^{-6}	506.7 ± 6.1	4.5×10^{-6}	418.5 ± 5.0	5.8×10^{-6} (*4*)
acenaphthene	1.6×10^{-8}	2.42 ± 0.02	1.2×10^{-8}	1.84 ± 0.04	2.3×10^{-8} (*1*)
pyrene	6.4×10^{-10}	0.13 ± 0.01	4.6×10^{-10}	0.09 ± 0.01	6.5×10^{-10} (*2*)

Table II. Solubilities of Three Aromatic Hydrocarbons in Seawater at Various Temperatures [a]

hydrocarbon	molar vol., mL	log solubility (μg/kg)		
		15 °C	20 °C	25 °C
toluene	109 (*6*)	5.61	5.61	5.62
acenaphthene	150 (*7*)	2.33	2.74	3.26
pyrene	172 (*8*)	1.75	1.85	1.95

[a] Salinity = 35‰, 0.5 M.

Table III. Salt Parameters for Three Aromatic Hydrocarbons at 25 °C

hydrocarbon	K_s (obsd), L/mol	K_s (calcd), L/mol
toluene	0.166	0.190
acenaphthene	0.238	0.253
pyrene	0.319	0.304

most accurate correlations, particularly for a homologous series of compounds (*4, 6*). The logarithm of solubility is frequently observed to be directly correlated with molar volume. Our data for three nonhomologous aromatic hydrocarbons exhibit a linear relation between molar volume and log of solubility (Table II).

Solubility in distilled water and higher ionic strength media may be related by the Setschenow equation which empirically describes the magnitude of the "salting out effect":

$$\log (S_0/S_s) = K_s C_s \qquad (1)$$

where S_0 and S_s are concentrations of the solute in fresh and salt water, respectively, K_s is the Setschenow constant for the salt solution, and C_s is the molar salt concentration. Values of K_s calculated for the aromatic hydrocarbons investigated in this work are shown in Table III and compared to values calculated from the McDevit and Long (*9*) equation, as supplemented by Gordon and Thorne (*10, 11*). Gordon and Thorne (*10, 11*) demonstrated that the effect of sea salt upon hydrocarbon solubility is additive; that is, the value of K_s for sea salt can be calculated by knowing the values of K_s for the component salts and using the equation

$$\log S_i = \log S_i{}^0 - \sum_{i=1}^{n} N_i K_i C_s \qquad (2)$$

where S_i is the solubility of the hydrocarbon in salt solution. $S_i{}^0$ is the solubility of the hydrocarbon in pure water, N_i is the mole fraction of the ith salt component in sea salt, K_i is the salting parameter of the ith salt component in sea salt, C_s is the sum of the individual salt molarities, and n is the number of major salts in sea water. Agreement between observed and theoretical salting-out constants was quite good. Thus, only large changes in salinity would result in significant alterations of maximum obtainable concentrations of these aromatic hydrocarbons when dissolved in natural seawater.

Except for toluene, when the ionic strength of an aqueous solution was constant, maximal solute dissolution was strongly influenced by temperature (Table II). This conclusion was also made by Schwarz (*12*) in studies with polynuclear aromatic hydrocarbons and 0.5 M NaCl solutions. Reductions in maximal solubility due to lower temperature appear to be linearly related to enthalpy of solution, which is generally greater for hydrocarbons of greater molar volume (*13*). As seen in previous work, the solubility of toluene is little affected by temperatures in the range 15–25 °C (*14*). Data in Table II suggest that seawater solutions of different temperature will vary somewhat in their ability to solubilize aromatic hydrocarbons, particularly when nominal concentrations are near the solubility limit. These data may be useful in planning future toxicological studies with such compounds on communities in areas of the sea where different temperatures are found.

Acknowledgment

We are grateful to Professors A. A. Benson and F. T. Haxo for the use of their facilities.

Literature Cited

(1) Eganhouse, R. P.; Calder, J. A. *Geochim. Cosmochim. Acta* **1976,** *40*, 555.
(2) May, W. E.; Wasik, S. P.; Freeman, D. H. *Anal. Chem.* **1978,** *50*, 997.
(3) Winters, K.; O'Donnell, R.; Batterton, J. C.; VanBaalen, C. *Mar. Biol. (Berlin)* **1976,** *36*, 269.
(4) Sutton, C.; Calder, J. A. *J. Chem. Eng. Data* **1975,** *20*, 320.
(5) Scripps Institution of Oceanography, University of California, Marine Life Research Group, SIO Ref 79-9, 1979.
(6) McAuliffe, C. *J. Phys. Chem.* **1966,** *70*, 1274.
(7) Klevens, H. B. *J. Phys. Colloid. Chem.* **1950,** *54*, 283.
(8) Davis, H.; Gottlieb, S. *Fuel* **1962,** *8*, 37.
(9) McDevit, W.; Long, F. *J. Am. Chem. Soc.* **1952,** *74*, 1773.
(10) Gordon, J. E.; Thorne, R. L. *J. Phys. Chem.* **1967,** *71*, 4390.
(11) Gordon, J. E.; Thorne, R. L. *Geochim. Cosmochim. Acta* **1967,** *31*, 2433.
(12) Schwarz, F. P. *J. Chem. Eng. Data* **1977,** *22*, 273.
(13) Wauchope, R.; Getzen, F. *J. Chem. Eng. Data* **1972,** *17*, 38.
(14) Bohon, R. L.; Claussen, W. F. *J. Am. Chem. Soc.* **1951,** *73*, 1571.

Received for review September 29, 1980. Accepted January 19, 1981. This work was supported by Grant No. R806260010 from the U.S. Environmental Protection Agency.

Best-Sellers from the American Chemical Society

Substantial Savings Over Hardbound Prices

NOW AVAILABLE IN PAPERBACK!

Your rights, problems, obligations

LEGAL RIGHTS OF CHEMISTS AND ENGINEERS

By Warren D. Niederhauser and E. Gerald Meyer. Basics of employment contracts, trade secrets, rights in layoffs and grievances, retirement plans, unions, patents and inventions. Also taxes, affirmative action, whistle blowing. Advances in Chemistry Series No. 161, 109 pages. Hardback edition (still available) $18.25.
Now in paperback . . . $8.50.

Up-to-date review of a fast-moving topic

BIOINORGANIC CHEMISTRY—II

Kenneth N. Raymond, Ed. Background material and reports of original research by international experts cover 24 subjects in three areas: biological transport of iron; biological electron transport and copper-containing molecules; molybdenum-containing molecules. Advances in Chemistry Series No. 162, 448 pages. Hardback edition (still available) $57.25.
Now in paperback . . . $25.00

A valuable reference for libraries

INORGANIC COMPOUNDS WITH UNUSUAL PROPERTIES

R. Bruce King, Ed. Thirty-two chapters fall into two categories: inorganic compounds exhibiting a specific property, and recent developments in the synthetic chemistry of a class of inorganic compounds. Metal alkyls, metal alkoxides, metal alkylamides, metal chalates, and metal clusters. Advances in Chemistry Series No. 150, 437 pages. Hardback edition (still available) $51.00
Now in paperback . . . $30.00

Helping the marine chemist manage and revitalize coastal marine resources

MARINE CHEMISTRY IN THE COASTAL ENVIRONMENT

Thomas M. Church, Ed. The first attempt to collate the most recent advances in the field of marine chemistry in the coastal environment, the book covers physical, organic, and tracer marine chemistry; hydrocarbons and metals in the estuarine environment; ocean disposal forum; applications and resources in marine chemistry; and organic and biological marine chemistry. ACS Symposium Series No. 18, 710 pages. Hardback edition was $41.25.
Now in paperback . . . $20.00

Toxicant-medicated changes in plant life

AIR POLLUTION DAMAGE TO VEGETATION

John A. Naegele, Ed. "This volume has been structured to develop a total concept of the known effects of air pollutants on plants. The subject is well treated, in a short but quite informative manner. The problems are depicted clearly . . ." *Agro-Ecosystems.* 2 (1975) 95–97. Advances in Chemistry Series No. 122, 137 pages. Hardback edition (still available) $15.00.
Now in paperback . . . $8.50

Wine production from vineyard to goblet

CHEMISTRY OF WINEMAKING

By A. Dinsmoor Webb. "For the serious student of wine." *Wine Internat'l Letter & Digest.* "This excellent reference book should be especially valuable because of the extensive literature citations." *Am. J. Enol. Viticult.* "This is a volume of value to all those seriously interested in enology . . ." *Choice.* Advances in Chemistry Series No. 137, 311 pages. Hardback edition (still available) $26.00
Now in paperback . . . $9.00

Past, present & future of pest control chemicals

PESTICIDE CHEMISTRY IN THE 20TH CENTURY

Jack R. Plimmer, Ed. Chlorinated insecticides and resistance mechanisms; herbicides; fungicides; insect and plant growth regulators. Also effects of pesticides on organisms; pesticide transformations in environment, environmental fate of xenobiotics. ACS Symposium Series No. 37, 310 pages. Hardback edition was $23.00.
Now in paperback . . . $12.00

The latest information for polymer researchers

ULTRAVIOLET LIGHT INDUCED REACTIONS IN POLYMERS

Santokh S. Labana, Ed. The 29 chapters in this volume focus on photopolymerization reactions (the role of photoinitiators and photosensitizers), and photodegradation (the use of photostabilizers and photodegradable polymers). ACS Symposium Series No. 25, 495 pages.
Now in paperback . . . $17.25

A complete revision of Volumes I and II!

AZEOTROPIC DATA III

Compiled by Lee H. Horsley. Revised, updated data on azeotropes, nonazeotropes, vapor-liquid equilibria for over 17,000 systems. Binary, ternary, quaternary, quinary system tables; formula index; charts for predicting azeotropism and calculating composition. Advances in Chemistry Series No. 116, 628 pages. Hardback edition was $45.50.
Now in paperback . . . $19.50.

Geochemistry and environmental science

TRACE ELEMENTS IN THE ENVIRONMENT

Evaldo L. Kothny, Ed. Theory and applied science of geochemistry; the chemical composition, route and concentration of substances and elements on earth; origins, dilutions, concentrations, transformations of emissions into atmosphere, water, land. Advances in Chemistry Series No. 123, 149 pages. Hardback edition (still available) $16.00.
Now in paperback . . . $9.00.

Understanding and improving pesticides

MECHANISM OF PESTICIDE ACTION

G.K. Kohn, Ed. Interactions of organism (including man), host plant, environment, and pesticidal composition, mechanism, metabolism; insecticides, herbicides, fungicides, acaricides, sterilants; analysis of cellular and model systems. ACS Symposium Series No. 2, 180 pages. Hardback edition was $14.75.
Now in paperback . . . $8.75.

An indispensable tool for anyone who works in a chemical laboratory or pilot plant

CHEMICAL TECHNOLOGY HANDBOOK

Robert L. Pecsok, Kenneth Chapman, and Wade H. Ponder, Eds. ". . . a well-illustrated manual with up-to-date information on aspects of laboratory work." *Electrochemical Progress.* "The material presented is excellent . . . of considerable use to commercial and industrial laboratories as a reference. It is written simply and is easy to comprehend." *Food Technology.* ". . . an informative, easy to understand guide book on all aspects of chemical laboratory work." *National Safety News.* Hardback edition (still available) $15.75
Now in paperback . . . $10.00

CALL TOLL FREE 800—424-6747
CHARGE TO YOUR VISA OR
MASTER CHARGE CARD

American Chemical Society, 1155 Sixteenth Street, N.W., Washington, D.C. 20036
Please send me the following ACS best-selling books:

Quantity	Title	Price

☐ Master Charge/Interbank Code: ________ Total number of books ordered: ________
☐ Visa
Account Number: ________ Total cost of these books: ________
Expiration Date: ________ California residents add 6% sales tax: ________
Signature ________ Total Payment (Enclosed): ________
Send books to:
Name ________
Address ________
City ________ State ________ Zip ________

20

HRM

Houston Regional Monitoring

Photo courtesy of Port of Houston Authority

Technical Approach

The monitoring plan as approved by EPA Region VI consists of twelve (12) air quality and meteorological monitoring systems and two upper air acoustic sounding devices. The air monitoring stations are identical in the parameters that are measured. Each system measures ambient concentrations of sulfur dioxide, ozone, nitrogen oxides, and carbon monoxide continuously; total suspended particulate matter daily; and the meteorological parameters of wind speed, wind direction, temperature, net radiation, and rainfall. Lead analyses are performed every sixth day at each of the twelve sites. Radian Echosonde acoustic sounding systems to measure upper air patterns are located at two of the sites. These systems measure upper air wind field characteristics including three-dimensional wind speed/wind direction and multiple layering for accurate on-site modeling input data. A UV pyranometer, humidity sensor, and bivanes are also located at the two sites with the Echosondes. Extensive quality assurance consistent with all guidelines of the Federal and State organizations is utilized throughout the program for both air quality and meteorological instruments. A minimum of 90% data capture is guaranteed on all data channels.

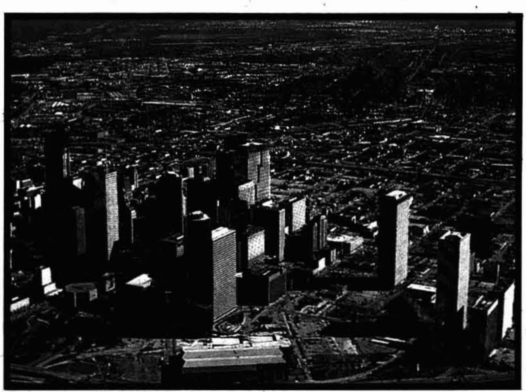
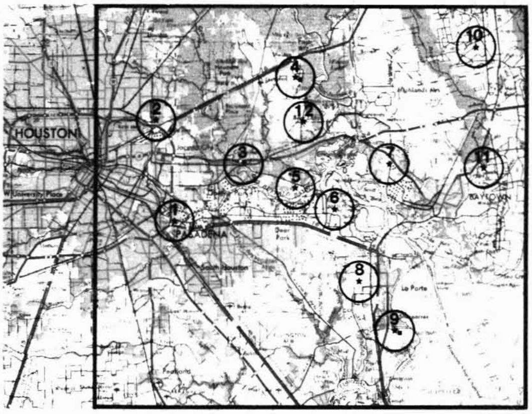


Photo courtesy of Port of Houston Authority

Objectives

The Houston Regional Monitoring Corporation, HRM, is a Texas corporation formed by a group of industries to conduct regional air quality monitoring in eastern Harris County and western Chambers County. The approach is consistent with guidelines from both EPA's national office and Region VI office in Dallas. The Texas Air Control Board, City of Houston and Harris County have been involved in the formulation of the approach that was ultimately presented to EPA for approval. Conceptually, the project is to share the cost of a continuous ambient monitoring program among multiple companies to provide the data necessary for more cost-effective and timely permit applications. The results will provide dispersion model calibration data and PSD increment consumption measurement over the term of monitoring. During the initial three-year period of monitoring, this program will develop extensive information concerning the ambient air quality of the Houston area. The program is currently underway and the first year's monitoring begins July, 1981. Information concerning air quality results will be given to the appropriate governmental agencies on a quarterly basis. The initial contract to perform three years of monitoring has been awarded to Radian Corporation, an Austin, Texas firm with offices in Houston.



Organization

HRM is acting for manufacturing companies representing more than 20,000 manufacturing employees in the area. Cost-sharing in the monitoring group is accomplished through a prorata share determined by the number of manufacturing employees. It is expected that by the time the data collection is underway, July 1, 1981, more than 30 firms with more than 30,000 manufacturing employees in the area will have joined the Corporation. The HRM Corporation is not a part of the Houston Chamber of Commerce nor directly affiliated with any other industrial organizations in the area. However, the concept of such a group was developed by the Environment Committee of the Houston Chamber of Commerce. Inquiries from several groups of industries in other geographical regions have indicated interest in similar programs at other industrialized areas.

RADIAN
CORPORATION

For further information please contact: F. Scott LaGrone, 8501 Mo-Pac Blvd., P.O. Box 9948, Austin, Texas 78766-0948, (512) 454-4797

CIRCLE 13 ON READER SERVICE CARD