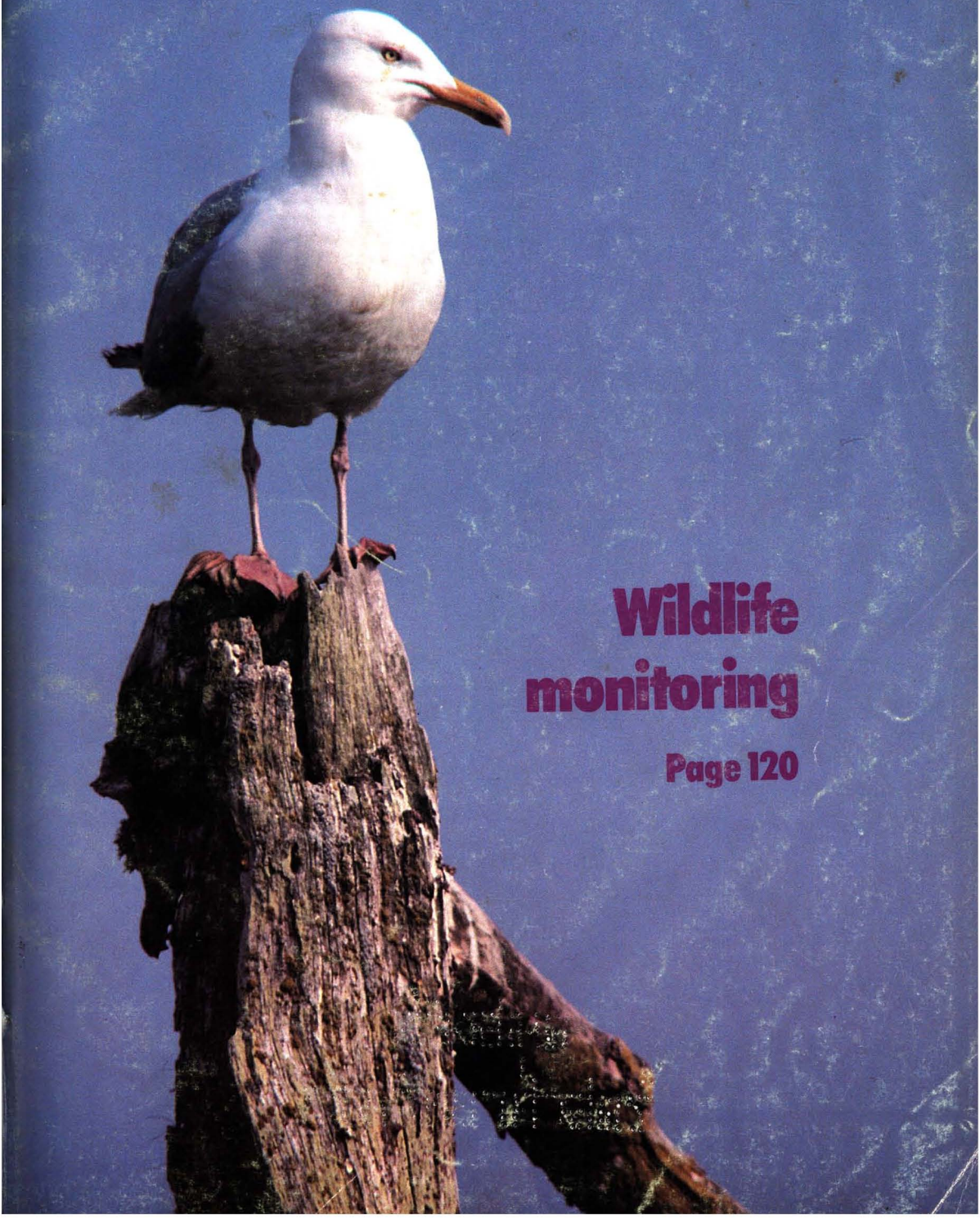
FEBRUARY 1988
ENVIRONMENTAL SCIENCE & TECHNOLOGY

ES&T



Wildlife monitoring

Page 120

Environmental Scientists And Engineers

ENVIRON® Corporation, a leading scientific and technical consulting firm providing a broad range of environmental services, invites you to consider the challenging opportunities for career growth with our firm. ENVIRON is a 120-person, multidisciplinary scientific and regulatory affairs consulting firm with offices in Washington, D.C. and Princeton, N.J. We are expanding rapidly in response to the growing demand for our services in the field of environmental risk management through environmental assessments of facilities where chemicals have been used, hazardous waste disposal and treatment, planning and design of remedial action programs, and scientific support for litigation and regulatory proceedings. Our clients include industry, trade associations, insurance professionals, law firms, and government agencies. We are looking for individuals who are eager to contribute new and creative ideas to innovative problem-solving in an increasingly complex area of science, technology, and regulatory policy.

ENVIRON's expanding practice in the field of environmental science and engineering emphasizes comprehensive exposure assessment including analyses of toxicity of materials at the site, the means and media through which contaminants may move through the environment, the population at risk, the routes of potential exposure, and the environmental management practices at the site. We also design and execute ground water studies to delineate the extent of contamination, evaluate remedial technologies, and identify actions necessary to reduce exposures and resulting liabilities.

Environmental Scientists and Engineers

Strong technical background with experience in chemical and hazardous waste management practices, control technologies, regulatory issues, site investigations, environmental auditing.

Hydrogeologists

Strong technical background with experience in comprehensive assessments of ground water contamination associated with industrial activity and hazardous waste sites, field experience in soil and ground water flow and contaminant transport.

ENVIRON offers competitive salaries and excellent benefits and the excitement of working closely with other highly motivated skilled professionals in providing environmental consulting services to private industry and government. Career opportunities are available at both the Washington, D.C. and Princeton, N.J. offices.

For an evaluation of your potential at ENVIRON and a confidential interview, send resume and salary history to Personnel, ENVIRON Corporation, Dept. EST-288, 1000 Potomac Street, N.W., Washington, D.C. 20007. ENVIRON is an equal opportunity employer.

ENVIRON

Counsel in Health and Environmental Science

Environmental Science & Technology
© Copyright 1988 by the American Chemical Society

Editor: William H. Glaze
Associate Editor: John H. Seinfeld
Associate Editor: Philip C. Singer

ADVISORY BOARD
Roger Atkinson, Fritz H. Frimmel, Nicholas E. Gallopoulos, Roy M. Harrison, George R. Helz, Ronald A Hites, James Leckie, Donald Mackay, Walter J. Weber, Jr., Richard G. Zepp

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

MANUSCRIPT REVIEWING
Manager: Monica Creamer
Associate Editor: Yvonne D. Curry
Assistant Editor: Diane Scott
Editorial Assistant: Marie Crunkleton

MANUSCRIPT EDITING
Assistant Manager: Mary E. Scanlan
Assistant Editor: Darrell McGeorge

GRAPHICS AND PRODUCTION
Production Manager: Leroy L. Corcoran
Art Director: Alan Kahan
Designer: Amy J. Hayes
Production Editor: Victoria L. Contie

BOOKS AND JOURNALS DIVISION
Director: D. H. Michael Bowen
Head, Journals Department: Charles R. Bertsch
Head, Production Department: C. Michael Phillippe
Head, Research and Development Department: Lorrin R. Garson

ADVERTISING MANAGEMENT
Centcom, Ltd.
For officers and advertisers, see page 154.

Please send *research* manuscripts to Manuscript Reviewing, *feature* manuscripts to Managing Editor. For editorial policy, author's guide, and peer review policy, see the January 1988 issue, page 31, or write Monica Creamer, Manuscript Reviewing Office, *ES&T.* A sample copyright transfer form, which may be copied, appears on the inside back cover of the January 1988 issue.

Environmental Science & Technology, ES&T (ISSN 0013-936X), is published monthly by the American Chemical Society at 1155 16th Street, N.W., Washington, D.C. 20036. Second-class postage paid at Washington, D.C., and at additional mailing offices. POSTMASTER: Send address changes to *Environmental Science & Technology,* Membership & Subscription Services, P.O. Box 3337, Columbus, Ohio 43210.

SUBSCRIPTION PRICES 1988: Members, $30 per year; nonmembers (for personal use), $55 per year; institutions, $192 per year. Foreign postage, $8 additional for Canada and Mexico, $16 additional for Europe including air service, and $24 additional for all other countries including air service. Single issues, $15 for current year; $19 for prior years. Back volumes, $219 each. For foreign rates add $2 for single issues and $10 for back volumes. Rates above do not apply to nonmember subscribers in Japan, who must enter subscription orders with Maruzen Company Ltd., 3-10 Nihon bashi 2 chome, Chuo-ku, Tokyo 103, Japan. Tel: (03) 272-7211.

COPYRIGHT PERMISSION: An individual may make a single reprographic copy of an article in this publication for personal use. Reprographic copying beyond that permitted by Section 107 or 108 of the U.S. Copyright Law is allowed, provided that the appropriate per-copy fee is paid through the Copyright Clearance Center, Inc., 27 Congress St., Salem, Mass. 01970. For reprint permission, write Copyright Administrator, Books & Journals Division, ACS, 1155 16th St., N.W., Washington, D.C. 20036.

REGISTERED NAMES AND TRADEMARKS, etc., used in this publication, even without specific indication thereof, are not to be considered unprotected by law.

SUBSCRIPTION SERVICE: Orders for new subscriptions, single issues, back volumes, and microform editions should be sent with payment to Office of the Treasurer, Financial Operations, ACS, 1155 16th St., N.W., Washington, D.C. 20036. Phone orders may be placed, using Visa, Master Card, or American Express, by calling the ACS Sales Office toll free (800) ACS-5558 from anywhere in the continental U.S. (In the Washington, D.C., area call 872-4600.) 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."

The American Chemical Society assumes no responsibility for statements and opinions advanced by contributors to the publication. Views expressed in editorials are those of the author and do not necessarily represent an official position of the society.

ES&T

CONTENTS

Volume 22, Number 2, February 1988

FEATURES

120
Wildlife monitoring, modeling, and fugacity. They are indicators of chemical contamination. Tom Clark, Kathryn Clark, Sally Paterson, and Donald Mackay, University of Toronto, Toronto, Ont., Canada; and Ross Norstrom, Canadian Wildlife Service, Ottawa, Ont., Canada

128
Eastern Lake Survey. The chemistry of lakes in New England and New York state is of special interest. Dixon H. Landers, Environmental Protection Agency, Corvallis, Ore.; W. Scott Overton, Oregon State University, Corvallis, Ore.; Rick A. Linthurst, Environmental Protection Agency, Research Triangle Park, N.C.; and David F. Brakke, Western Washington University, Bellingham, Wash.

136
Hazardous organic compound analysis. Lost analytical data and misinformation hamper decision-makers and site managers. Kathleen C. Swallow and Neil S. Shifrin, Gradient Corp., Cambridge, Mass.; and Philip J. Doherty, Energy and Environmental Engineering, Inc., Somerville, Mass.

REGULATORY FOCUS

150
EPA's new pesticide–groundwater strategy. Richard Dowd explains how EPA plans to protect drinking-water supplies from pesticide contamination.

VIEWS

144
Health effects from radiation. Robert E. Alexander examines probabilities of health effects from the Three Mile Island and Chernobyl mishaps.

145
Numerical data for scientists. Stephen R. Heller and Lewis H. Gevantman discuss several on-line computerized data bases.

148
Causation in forest decline. Richard M. Klein addresses problems in proving the causes of forest decline statistically and legally.

DEPARTMENTS

115 Editorial
116 Guest Editorial
117 Currents
151 Books
152 Classified
154 Consulting services

UPCOMING

Immunoassays as a means of evaluating exposure to chemical contaminants

Fate and transport of airborne toxic pollutants

RESEARCH

155
Chemical and physical characteristics of lakes in the northeastern United States. David F. Brakke,* Dixon H. Landers, and Joseph M. Eilers

The data collected during the Eastern Lake Survey support the hypothesis that regional lake acidification has occurred in the northeastern United States.

ESTHAG 22(2)113–232 (1988)
ISSN 0013 936X

Cover: Pierre Mineau
Credits: Julian Josephson, p. 120; Tom Clark, p. 121; David F. Brakke, p. 128

164
Chemical and physical characteristics of lakes in the upper Midwest, United States. Joseph M. Eilers,* David F. Brakke, and Dixon H. Landers

A statistical sampling of 592 lakes is used to quantify the number of lakes with surface area greater than 4 ha that are acidic or have low acid neutralizing capacity.

172
Chemical and physical characteristics of lakes in the southeastern United States. Joseph M. Eilers,* Dixon H. Landers, and David F. Brakke

The lakes in the Southern Blue Ridge showed a high degree of chemical homogeneity, in contrast to a high degree of heterogeneity for Floridian lakes.

178
Acidification of lakes in the eastern United States and southern Norway: a comparison. Richard F. Wright

The major-ion chemistry of lakes in the eastern United States and southern Norway indicates that acidification of lakes entails similar chemical changes in both regions.

182
Estimation of non-carbonato protolytes for selected lakes in the Eastern Lakes Survey. James R. Kramer* and Steven S. Davies

Acid and base titration data from the EPA Eastern Lakes Survey are used to estimate the importance of organic acids in lake acidity.

185
Evaluation of the role of sea salt inputs in the long-term acidification of coastal New England lakes. Timothy J. Sullivan,* Charles T. Driscoll, Joseph M. Eilers, and Dixon H. Landers

Deposition of sodium from sea spray does not appear to play a significant role in the long-term acidification of coastal lakes in the northeastern United States, although episodic acidification may occur.

190
Reactions that modify chemistry in lakes of the National Surface Water Survey. Sijin Lee and Jerald L. Schnoor*

A mass balance equation is used to determine which reactions are most important in controlling the acid–base chemistry of selected lake watersheds.

196
Parametric distributions of regional lake chemistry: fitted and derived. Mitchell J. Small,* Michael C. Sutton, and Mark W. Milke

This work extends the analysis of regional distributions by providing methods for fitting parametric probability models to the observed frequency distributions.

205
Long-term fate of organic micropollutants in sewage-contaminated groundwater. Larry B. Barber, II,* E. Michael Thurman, Michael P. Schroeder, and Denis R. LeBlanc

Trace levels of volatile organic compounds are shown to persist for more than 30 years in groundwater contaminated by rapid-infiltration sewage disposal.

212
Source resolution of the fine carbonaceous aerosol by principal component–stepwise regression analysis. Sotiris E. Pratsinis,* Melvin D. Zeldin, and Elizabeth C. Ellis

A receptor modeling methodology that combines gas and aerosol data is presented for quantitative source apportionment of fine carbonaceous aerosols in Los Angeles.

216
Alkaline precipitation in Bahía Blanca, Argentina. M. Cintia Piccolo,* Gerardo M. E. Perillo, and Pedro Varela

The characteristics of the spatial and seasonal variations in precipitation pH for Bahía Blanca and its surroundings are reported.

219
A ferrous cysteine based recyclable process for the combined removal of No_x and SO_2 from flue gas. David K. Liu, Lawrence P. Frick, and Shir-Ger Chang*

The use of ferrous cysteine for NO removal in wet flue gas scrubbing systems is described, and a scheme for cysteine regeneration is presented.

224
Isolation and detection of genotoxic components in a black river sediment. W. Raymond West, Philip A. Smith, Gary M. Booth,* and Milton L. Lee

Polycyclic aromatic compounds isolated from a river sediment are identified by GC–MS and assayed for genotoxicity using the Ames assay and unscheduled DNA synthesis.

CORRESPONDENCE

229
Comment on "Estimation of the atmospheric and nonatmospheric contributions and losses of polychlorinated biphenyls for Lake Michigan on the basis of sediment records of remote lakes." Thomas J. Murphy

Deborah L. Swackhamer* and David E. Armstrong

231
Comment on "Reaction products and rates of disappearance of simple bromoalkanes, 1,2-dibromopropane, and 1,2-dibromoethane in water." H. Anson Moye* and Randy Weintraub

Martin Reinhard* and Timothy M. Vogel

*To whom correspondence should be addressed.

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

ES&T
EDITORIAL

Needed: a speedier time to publication

I received my first letter welcoming me as the new editor of *ES&T* about four weeks before my term began. Perhaps it was fitting that the letter was primarily a complaint over the delay in the publication of a manuscript. No other aspect of author–editor relationships seems to raise more emotions than this one, except perhaps the decision of an editor to reject a manuscript. I expect there will be more letters on this subject in the coming months.

My reply to the author was that we will take very seriously his complaint. Having served as a member of the Editorial Advisory Board for several years, I am aware of the problems that *ES&T* has had in reducing the publication time of research articles. In fact, the original contact I had with the journal years ago involved this issue. A major goal during my five-year term as editor will be to reduce the review and publication time to a period that is competitive with all major journals in our field. We have not yet set a specific target or timetable for reaching my goal, but we do know that some significant reductions must be achieved.

During the past few years former editors have given considerable attention to this problem. For papers published in 1987, the average time from receipt of a manuscript to publication was 49 weeks. Since the production stage on the average required only 14 weeks, the largest portion of that time was spent reviewing and revising the paper. With this in mind we will focus our efforts on reducing the time from receipt to acceptance. In 1978 we began using electronic mail between the editors and the Washington staff, and this resulted in some time savings. We are now evaluating our system to determine other operations that can be streamlined. We are aware of the hurdles ahead, and we know that the desired improvements will not occur overnight. In addition, other unforeseen delays may occur because the *ES&T* office handles three other American Chemical Society journals and must strike a balance between each journals' priorities. However, it is most important that we decrease the time from receipt to publication and strive for the minimum period that is humanly possible given our editorial budget.

My colleagues at the journal tell me that authors and reviewers are responsible for some of the delay in the publication of articles. All who publish and review are aware that this is the case. *ES&T* has established sound procedures, I believe, for expediting the review process, including sending a red bag to facilitate return of reviews. Nonetheless, there are still reviewers who hold a manuscript well past the deadline and, in some cases, return it without a review. There are also several authors who hold a manuscript after review for several weeks or months. These are extreme cases, but they serve to skew the time to publication distribution. In the case of the manuscript that was the subject of my first letter of complaint, it apears that the unacceptably long delay was caused by a combination of factors, including some staff delays. The latter were caused in part by some staffing problems that have now been rectified.

The time to publication is one criterion of a good scientific journal. In the environmental field it is particularly significant because most of our scientific work has a direct impact on public understanding. The associate editors, the Washington, D.C., editorial staff, and I are committed to improving the editorial process and the time to publication. We ask that authors and reviewers cooperate with us in achieving this goal.

0013-936X/88/0922-0115$01.50/0 © 1988 American Chemical Society

ES&T
GUEST EDITORIAL

On reviewing environmental models

Since the turn of the century scientific progress has gone hand-in-hand with the evolution of a subtle and effective review system in which reports of original work are subjected to anonymous criticism by peer reviewers prior to publication. This system, as followed by *Environmental Science & Technology* and steered by its editorial staff, is fair, vigilant, and successful. It depends heavily on the goodwill of reviewers who voluntarily devote time to the process for the collective benefit of the entire environmental science community.

Most research reports can be judged by a thorough reading—looking for appropriate techniques and reasonable results—and a check of the mathematics and statistics. However, environmental science and management rely increasingly on complex models to describe, for example, the complex behavior of chemicals in a multimedia environment, routes to human exposure, spill damages, atmospheric dispersion in complex terrain, or extensive ionic equilibria. The intellectual contribution is often the selection and assembly of equations and parameter values of a lengthy computer program. Few reviewers are likely to check the coding line by line to detect mistakes. Normally all that can be accomplished is a cursory check of reasonableness and a comment on the assumptions used. How can we ensure that such models are valid, free from mistakes, and thus reliable tools in the hands of scientists and managers?

Perhaps there are two ways. Agencies that fund the development of models should also accept the obligation to fund thorough, impartial, time-consuming, and thus expensive peer reviews. Such reviews require allocation of time and money—more than even the persuasive *ES&T* reviewing staff can hope to achieve.

Second, agencies and professional societies could sponsor "round robins" (so deservedly popular in analytical chemistry) in which the same modeling task is addressed by independent groups who can then come together to compare and criticize approaches and results in detail. Recently the International Joint Commission sponsored an event of this type, in which three groups (from Manhattan College, Limno-Tech Inc. of Ann Arbor, and the University of Toronto) compiled rival models of PCB behavior in Lake Ontario over the period 1940–2000. The models were then compared and criticized during a two-day intensive session. Fortunately they gave similar results despite quite substantial differences in approach. No doubt the better features of each model will become incorporated into the others. More confidence is established that the models are faithfully describing the same environmental reality. Mistakes should be exposed and eliminated. A free market is encouraged in which the best models will evolve and flourish. The science of describing complex environmental phenonema is advanced.

Complex, computer-based models can play an important role in environmental science, but we cannot expect the existing review system to give them the scrutiny they need and deserve. Those who fund, develop, and ultimately use models must be willing to seek, encourage, and sponsor novel peer reviewing approaches to ensure the scientific rigor of the published word, which is at the core of scientific progress.

Don Mackay

Don Mackay *is a professor of chemical engineering and applied chemistry at the University of Toronto. His research interests include the environmental fate and transport of toxic substances with a special emphasis on modeling, the volatization of organic compounds from water, and the measurement of physical and chemical properties. He has been a member of the ES&T* Editorial Advisory Board since 1984.

0013-936X/88/0922-0116$01.50/0 © 1988 American Chemical Society

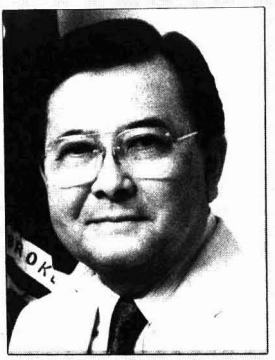
INTERNATIONAL

The People's Republic of China has drafted its first water law to tighten control over its water resources. Qian Zhengying, China's Minister of Water Resources and Electric Power, says this law is "extremely urgent." Qian notes that although China's water resources are estimated at 2.8 trillion m^3, the amount of water available per capita is much lower than the world average. Moreover, water resources are distributed unevenly, with the result that some areas are frequently plagued by water shortages. Widespread water pollution and overexploitation of groundwater are other serious problems in China, Qian says. Qian expresses the hope that the new law will build up "a comprehensive management system of water resources and help guard against disasters." Several agencies of the Chinese government will host the Watertech China '88 Exposition and Congress to be held in Beijing June 3–8, 1988.

FEDERAL

The hazardous waste exemption currently allowed for municipal incinerator ash may be extended to include ash from commercial waste incinerators. Moreover, commercial waste burned in a municipal incinerator would qualify for the "household exclusion" under the Resource Conservation and Recovery Act (RCRA), regardless of how toxic the ash may be after incineration. Currently, ash from commercial waste is not exempt under the household exclusion. If commercial ash contains hazardous materials and is mixed with household waste, however, all the ash loses the household exemption and is treated as hazardous waste. EPA has the authority to broaden the household exemption under Subtitle C of RCRA.

Sens. Bob Kasten (R-Wis.) and Daniel Inouye (D-Hawaii) want to reduce U.S. funding of the Inter-American Development Bank (IDB) by as much as 80% for fiscal year



Inouye: Cut violators' funds

1988. If their proposal becomes law, funding would drop from $258 million for the fiscal year to $50 million. Kasten and Inouye object to "the bank's inability to enforce contracts that send tax-supported funds to programs which destroy key environmental resources." Kasten voiced special concern about a road-building project in Acré, Brazil. He noted that IDB had promised in August to suspend funding for the project because of environmental abuses but did not do so. The senators' legislation also provides for "conservation easements," which require that conservation be a component of any rescheduling of debt owed by developing nations.

The U.S. Supreme Court ruled Dec. 1 that citizens may not sue under the Clean Water Act for alleged violations that took place entirely in the past. A suit, rather, must be brought against a defendant alleged to be committing continuous or intermittent violations, according to the decision written for the court by Justice Thurgood Marshall. He wrote that the "most natural reading of the citizen suit provision [of the Clean Water Act] is in the present tense," thereby applying a strict interpretation of Section 505 of the act. The unanimous decision resolved the case of Gwaltney of Smithfield Ltd. vs. Chesapeake Bay Foundation Inc. The meat-packing company had been fined $1.3 million even though its violations had ceased by the time environmental advocacy groups brought suit.

EPA has provided guidelines to show how parties that made *de minimis* contributions to Superfund sites can settle their share of liability and cleanup costs (*Fed. Regist.* 1987, *52*, 43393). *De minimis* contributors may be assessed on the basis of factors such as amount and toxicity of their wastes. After they have settled and paid, they are exempt from suits for response costs by the United States and by other potentially responsible parties. The United States may, however, sue for costs associated with damage to natural resources if it turns out that the *de minimis* contributor deposited more waste to the site than was originally thought, if cleanup costs exceed the expected maximum, or if response action at a site fails to protect public health.

EPA may propose a tighter long-term ozone standard to reduce damage to crops and forests. The agency is considering a standard of 0.04–0.06 ppm based on a three-month average of the eight hours of a day that have the highest ozone levels. This secondary standard would be in addition to the current 0.12-ppm one-hour standard now in force, which is designed to protect human health. Although the new standard would apply to rural areas, controls likely would be imposed on urban areas, which are the suspected source of ozone and its precursors. Because of uncertainties in evaluating long-term ozone concentration data, however, a standard probably would not be promulgated until at least 1990, according to an EPA spokesman.

Because of budget restrictions, EPA is discontinuing a program of measuring the accumulation of toxic substances in body fat. Scientists regard these measurements as a principal means of measuring human exposure to toxic substances. The program, known as the National Human Adipose Tissue Survey, reportedly costs less than $2 million a

0013-936X/88/0922-0117$01.50/0 © 1988 American Chemical Society

year. The survey has shown, for example, that almost every American has polychlorinated biphenyls (PCBs) in his or her body fat—a finding that led to the ban on the production of PCBs in 1977. The survey also has shown that PCB levels in body fat have decreased markedly since the ban was imposed. Budget restrictions likely will force EPA to drop or delay its project for measuring the accumulation of the toxic substances in human blood that do not tend to accumulate in fatty tissue.

STATES

The legal doctrine of sovereign immunity does not protect a state against claims for cleaning up hazardous-waste contamination for which it is responsible, according to a decision by the 3rd U.S. Circuit Court of Appeals. The court found that Congress has stipulated in the Superfund Amendments and Reauthorization Act (SARA) of 1986 that a state or local government will be subject to all provisions of SARA, including liability provisions. The court also found that this stipulation in SARA satisfies the requirement of the 11th Amendment to the Constitution that Congress must use specific language abrogating a state's sovereign immunity. The case in point arose from a spill that occurred in 1980 when employees of the Commonwealth of Pennsylvania struck a large coal tar deposit. The state and EPA cleaned up the spill under Superfund and then sued a company for allegedly depositing the tar. The company brought the state into the suit.

Air pollution officials and senators from several northeastern states blasted EPA for giving many metropolitan areas additional time (beyond Dec. 31, 1987) to comply with federal standards for ozone and carbon monoxide. Sen. Robert Stafford (D-Vt.) said the agency's move is "not only undesirable, it's illegal." Sen. Daniel Patrick Moynihan added that even if the action were desirable, it would require congressional approval. They and other members of Congress and public officials believe EPA had no legal authority to take its Nov. 17 action. They also fear that taking pressure off nearly 70 metropolitan areas to meet air cleanup deadlines may take away or reduce Congress's incentive to enact Clean Air Act amendments expeditiously.

Maryland's Department of the Environment will take no legal action against persons who are making a good-faith effort to comply with new reporting provisions of Superfund that concern gasoline and other "extremely hazardous substances." Owners and operators of sites at which these substances are present in excess of a "threshold planning quantity" should have turned in reports by May 17. Failure to report can result in heavy fines and even prison terms. The reports are required by the Emergency Planning and Community Right-to-Know provisions of the 1986 Superfund amendments. Reports must be made in writing to the SARA State Response Commission, Department of the Environment, 201 W. Preston St., Baltimore, Md. 21201.

AWARDS

The $100,000 Vetlesen Prize for 1987 has been awarded to Wallace Broecker of Columbia University's Lamont–Doherty Geological Observatory and Harmon Craig of the Scripps Institution of Oceanography. The two scientists will share the prize in recognition of the "achievement in the sciences resulting in a clearer understanding of the Earth, its history, or its relation to the universe." More specifically, Broecker was recognized for his work that heightened interest in the "greenhouse effect"—the global warming believed to be caused by the burning of fossil fuels and the resulting increase in atmospheric carbon dioxide levels. Craig was cited for showing that levels of methane—another "greenhouse gas"—have doubled over the past 300 years. The last Vetlesen Prize was awarded in 1981.

SCIENCE

A comprehensive computer model should provide a means of simulating acid rain-creating processes in the atmosphere, says Kenneth Demerjian of the State University of New York at Albany (SUNY). Because of the intricacy of the model, it must be run on a Cray X-MP, one of the most powerful scientific computers. Demerjian believes that once the model is operational, it should demonstrate the relationship between sulfur emissions in one area, for example, and the amount of acid deposition in another area. This study, called the Acid Deposition Modeling Project, is being conducted at SUNY's Atmospheric Sciences Research Center and is being funded at more than $1 million a year by EPA.

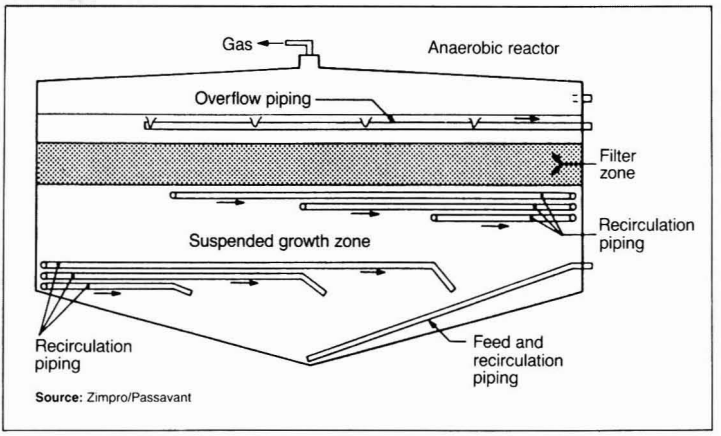
Computer simulations suggest that the reduction of power plant NO_x actually might increase ozone levels in the Los Angeles basin, whereas reduction in ROG reactive hydrocarbon emissions would decrease ozone levels. For St. Louis, the simulation indicates that a 90% reduction in NO_x emissions would bring about almost no change in ozone levels. In rural areas, reduction in NO_x would decrease ozone formation in a plume migrating from urban areas but would have a negligible effect on total tropospheric ozone. The computer simulations were carried out by the Electric Power Research Institute (Palo Alto, Calif.) using the plume airshed reactive interacting system (PARIS) model.

TECHNOLOGY

Electrotechnologies may offer promising approaches to wastewater treatment, according to the Electric Power Research Institute (EPRI). Among the technologies cited are pyrolysis, including plasmas and infrared heaters; electrochemical methods, including electrodialysis; freeze concentration; and supercritical-fluid oxidation. Other electrical methods entail ion exchange, reverse osmosis, and ultrafiltration. Although the costs of using electricity for these methods currently is relatively high, they could become lower as other energy costs and the costs of other wastewater disposal methods increase. Moreover, electrotechnologies may have applications in resource recovery, according to EPRI.

Microbes that "eat" agricultural pesticides may provide ideas for the degradation of toxic substances such as polychlorinated biphenyls (PCBs) and hazardous waste, says Jim Mueller, a doctoral candidate at Clemson University. The organisms under study feed on the organic herbicides used to control weeds in corn, peanut, and soybean fields. The microbes attack the chemicals and reduce their potency as weed killers. Mueller hopes to isolate the gene that controls the organisms' appetite for herbicides. He then wants to find a genetic engineering technique that curbs the microbes' appetite for herbicides but makes them "hungry" for substances such as PCBs and other hazardous wastes instead.

An anaerobic reactor for treating high-strength wastewaters and producing methane fuel has been introduced by Zimpro/Passavant



Source: Zimpro/Passavant

(Rothschild, Wis.). Zimpro spokesman Jim Force explains that the combination of suspended and fixed zones in one treatment tank controls the loss of biomass—a problem that bedevils many other anaerobic processes. Moreover, the technique eliminates plugging of the filter media by solids, he says. Force notes that the process, called MULTI-ZONE, uses less than 25% of the electricity needed for aerobic treatment of the same wastewater and that the organic pollutant load can be reduced by more than 90%. He says that in one installation, enough methane fuel will be generated to pay back capital costs in 41 months. Force adds that the process has proven effective in cleaning up landfill leachates.

Smog-induced crop losses can be reduced by treating the susceptible crop with sodium erythorbate, say spokesmen for Pfizer (New York). The chemical is the basis of a water-soluble antioxidant formula that is recognized as safe, according to company officials. The antioxidant, to be marketed as Ozoban, has been shown to protect seedless grapes in California, a state in which smog-caused crop losses normally exceed $300 million annually. Tests on the grapes near Arvin and Reedley, Calif., began in 1984, and effective chemical concentrations and spraying schedules were determined by 1986. Further demonstrations were begun last year, with resulting crop savings expected to show up this year, say Pfizer spokesmen.

Insect pests could be killed with a "dessert" made of cornstarch laced with microbes or small amounts of chemical insecticide, says Richard Dunkle of the U.S. Agricultural Research Service (Manhattan, Kan.). Dunkle tested a mixture of cornstarch, cucurbitacin (derived from plants in the cucumber family), and the insecticide carbaryl on the corn rootworm. The insects gorged on the meal, thereby ingesting fatal amounts of carbaryl, and were dead within 20 minutes. Another approach is to inject *Bacillus thuringiensis* (B.t.) into portions of the corn plant on which corn borers feed. Dunkle says that borer larvae eating the plant or moist starch injected with B.t. died within a week. The general technique is to use gelatinized starch with the pesticide or microbe trapped inside. The mix is air-dried and it crumbles, making an inviting meal for the target insect.

BUSINESS

Drinking-water utilities in the United States will spend an additional $10 billion a year to comply with requirements of the Safe Drinking Water Act amendments of 1986. For a system serving 10,000 persons, this could be translated to $100 more each year per household. Current average water bills nationwide are estimated at $125 a year. Requirements for the removal of volatile organic compounds could cost 50 cents per 1000 gal. Additional disinfection might cost 10 cents per 1000 gal more, and if granular activated carbon must be used, costs rise by yet another 40 cents per 1000 gal. These additional costs pertain to groundwater. If a water utility is treating surface water, proper filtration alone could cost 90 cents per 1000 gal. These figures represent estimates by the American Water Works Association (Denver, Colo.).

The Great Plains Coal Gasification Project (Beulah, N.D.) remains in existence despite the default on a $1.54 billion government-guaranteed loan by the project's initiators, Great Plains Gasification Associates (GPGA). GPGA is a consortium of five energy companies. The project is the first in the United States to produce clean substitute natural gas from coal on a commercial scale; it uses low-sulfur coal mined in North Dakota. During 1987 the plant produced 137.1 million–149.8 million ft^3 of gas per day, often in excess of its design capacity of 137.5 million ft^3 per day. The project has been taking in an average of nearly $4 million a month over expenses. The facility, currently managed by ANG Coal Gasification Co., sells gas at $3.82 per million Btu to buyers that are required to purchase the gas under a federal court decision. The average wellhead price of natural gas was $1.81 per million Btu as of early December, 1987.

One of the major problems hampering hazardous-waste management is a shortage of qualified personnel, according to Paul Busch, president of the American Academy of Environmental Engineers (Annapolis, Md.). He estimates that the total number of qualified graduates with bachelor's and advanced degrees probably will meet 5–10% of the total need during the next five years, and even less than that over the following five years. Busch suggests that educational institutions aim their curricula at helping graduates evolve into "leading problem solvers." He also recommends that employers of environmental engineers provide additional "on-the-job education and realize that education is a life-long process."

By 1995, revenues of hazardous-waste management companies could reach $10 billion annually; revenues for 1986 are estimated at $2 billion–$2.3 billion, according to Lee Fox and Fred Iannazzi of Arthur D. Little (Cambridge, Mass.). They expect that American industry will spend increasing sums on professional management of its hazardous wastes off-site. Industry's principal motivation will be that the disposal of untreated hazardous waste, even on-site, carries a long-term legal and financial liability. Fox and Iannazzi expect landfill company revenues to grow 20% a year, and incinerator operators' earnings to increase 30% annually. The two consultants forecast that companies engaged in aqueous treatment of wastes, including deep-well injection, will see their revenues rise from $575 million in 1986 to $2.6 billion in 1995.

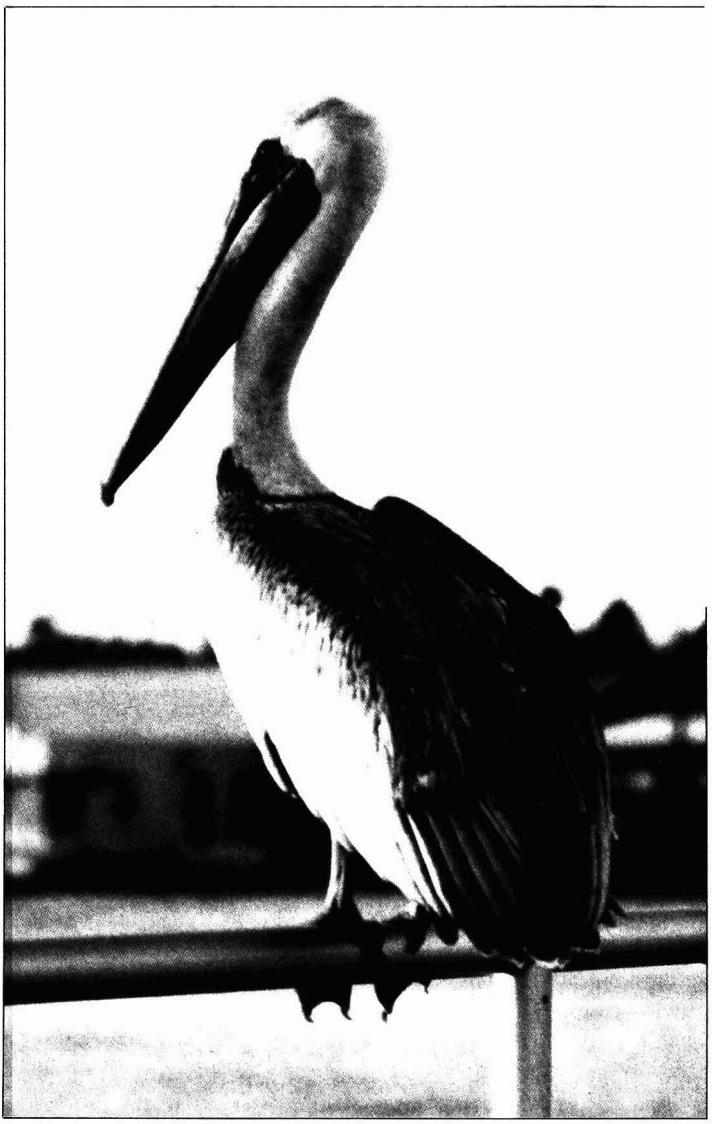
ES&T
FEATURES

Wildlife monitoring, modeling, and fugacity

They are indicators of chemical contamination

Tom Clark
Kathryn Clark
Sally Paterson
Donald Mackay
Institute for Environmental Studies
University of Toronto
Toronto, Ontario M5S 1A4, Canada

Ross J. Norstrom
Canadian Wildlife Service
Environment Canada
Ottawa, Ontario K1A 0E7, Canada

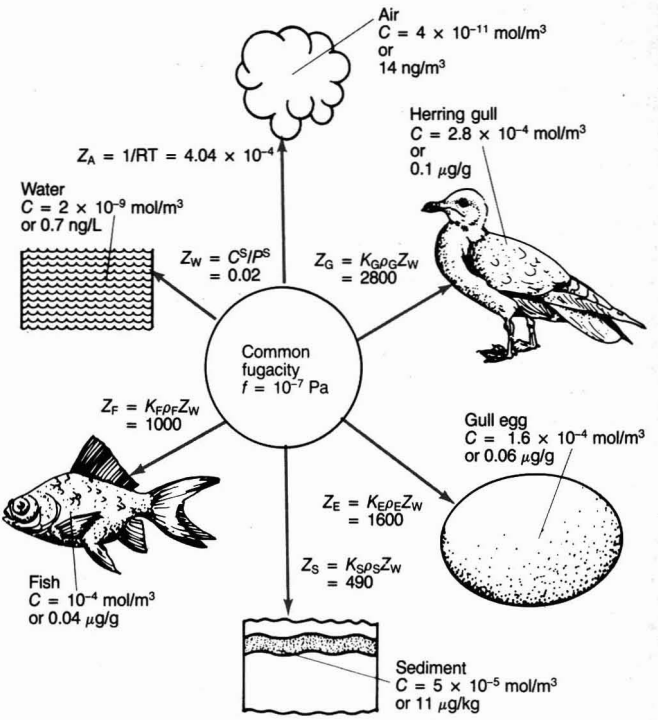


Observations of wildlife populations and their state of health have played a key role in identifying situations in which chemical contaminants have reached unacceptable concentrations in the environment. The reproductive failure of several species—including the peregrine falcon (*Falco peregrinus*), the double crested cormorant (*Phalocrocorax auritus*), the brown pelican (*Pelicanus occidentalis*), and the osprey (*Pandion haliaetus*)—has been attributed to organochlorine contamination (*1–6*). Other examples have been cited by Kendall in his review of wildlife toxicology (*7*), and by Wren in a discussion of mammals as monitors of metal contamination (*8*). As the mine canary can warn of the presence of a poisonous gas in a coal mine, wildlife populations can act as sentinels for excessive chemical contamination.

This blunt and often tragic exploitation of wildlife as a sentinel is, to be sure, an extreme example of the more subtle and far-reaching issue of the extent to which wildlife tissues can be used to indicate general levels of environmental contamination and provide guidance to the scientific and regulatory communities about the state of the environment. There are two quite sepa-

0013-936X/88/0922-0120$01.50/0 © 1988 American Chemical Society

FIGURE 1
Equilibrium distribution of a hypothetical compound[a]



[a]The compound is distributed between various media in the Lake Ontario region.

Properties of compound used to calculate Z values (mol/m³ Pa):
Molecular weight = 350 g/mol
Solubility $C^S = 10^{-5}$ mol/m^3
Vapor pressure $P^S = 5 \times 10^{-3}$ Pa

Partition coefficients:
Octanol/water $K_{ow} = 10^6$
Fish/water $K_F = 0.05\ K_{ow}$
Gull/water $K_G = 0.14\ K_{ow}$
Gull egg/water $K_E = 0.08\ K_{ow}$
Sediment/water $K_S = 0.411\ K_{ow}\ F_{oc}$

Densities (kg/L)
Fish $\rho_F = 1.0$
Gull $\rho_G = 1.0$
Gull egg $\rho_E = 1.0$
Sediment $\rho_S = 1.5$

F_{oc} = fraction of organic material in sediment = 0.04
Concentration $C = fZ$ (mol/m^3)
R = 8.314 J/mol K
T = 298 K

rate motives for exploring this issue.

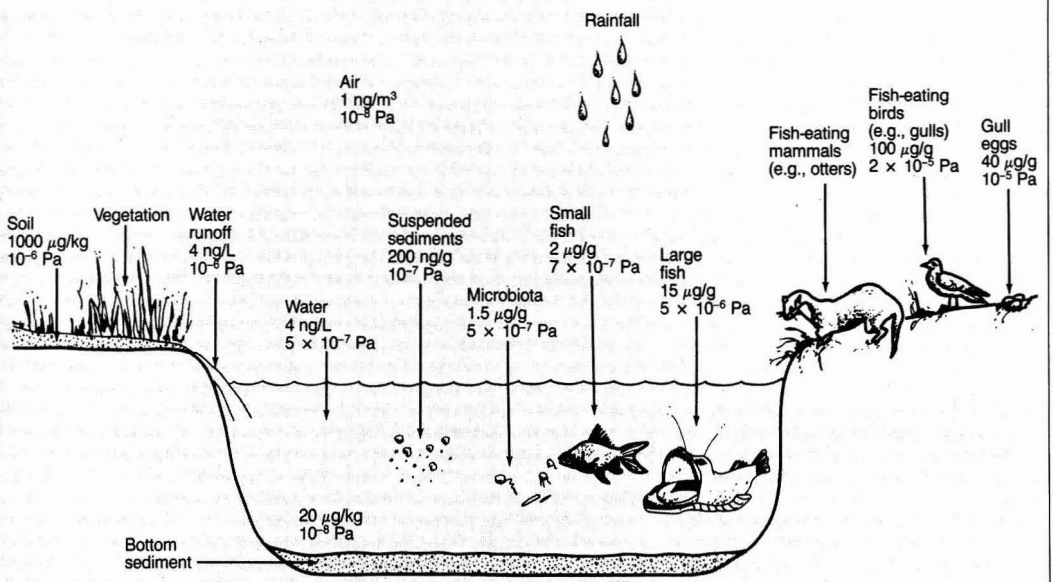
First, we value wildlife for its own sake, both aesthetically and economically. Restrictions on sport and commercial fishing in the Great Lakes basin have had dramatic effects on many small communities. The public is particularly angered by evidence that charismatic species (the ones with big, brown, sad eyes) are at risk. The extinction or extirpation of a species such as the peregrine falcon in eastern North America also is a genetic tragedy. Surely, it is argued, we should be able to ensure a continuing healthful environment for species that have carved out a niche for themselves over evolutionary millennia, long before the advent of organochlorines. Many would insist that we have an obligation to preserve these species and their ecological niches.

Second, analysis of tissues of wildlife or other sentinel organisms can provide a long-term picture of the state of contamination, its increase or decrease, and the arrival (often unexpected) of new contaminants. Tissues can be archived for retrospective analysis. For certain instances of contamination, conventional abiotic analyses can be complemented or even replaced by tissue analyses of organisms that integrate and concentrate contaminants. This can lead to easier, less expensive, and more representative analyses.

One example is the Mussel Watch program (*9*) in which bivalves from over 100 stations in the United States are monitored for concentrations of petroleum hydrocarbons, chlorinated hydrocarbons, and heavy metals that may affect the health of the public or marine life. Another example is the herring gull program in the Great Lakes (*10*). After the recent Chernobyl disaster, the West German monitoring program used archived lichen samples to determine levels of radioactivity that existed before the accident. Biological monitoring is well-established as an invaluable component of environmental surveillance (*11*).

The use of contaminant concentrations in wildlife tissue as an indicator of environmental concentrations is predicated on an assumption that for each chemical there exists some fairly constant ratio of tissue to environmental concentration; that is, a type of bioconcentration factor. For example, contaminant concentrations in fish presumably are related to concentrations in water and food (and possibly in sediment) in a predictable, quantifiable way. Establishing a picture of the bioconcentration

FIGURE 2
Concentrations and corresponding fugacities of the chemical[a]



[a]The compound is the chemical depicted in Figure 1 and distributed between various environmental media; fugacities are expressed in Pa.

pathway from source to target, however, can be tortuous and subject to many pitfalls.

Avoiding these pitfalls requires two sets of basic information. The fundamental biology, ecology, or natural history of the animal must be thoroughly understood because factors such as feeding habits, migration or mobility, and changes in lipid content can influence concentrations in tissues. Second, the rates of uptake, clearance, and metabolism (toxicokinetics) must be understood so that the status of the organism with respect to equilibrium or steady state may be determined. For example, the uptake time for some chemicals may exceed the lifetime of the organism, and a steady state is never reached. These rates are chemical-specific, but it is likely that extrapolations can be made from chemical to chemical through the careful use of structure–activity relationships.

A wildlife biomonitor must have a well-understood natural history and toxicokinetics in addition to other desirable features such as ease of sampling, tendency to remain in a locality, and ability to survive exposure to the levels of contaminant being monitored. Other factors to be considered are commercial importance or charismatic appeal.

Monitoring and modeling

Recent advances in biomonitoring sophistication have coincided with increases in the use and acceptance of multimedia environmental models (*12*). It is now recognized that the regulation of chemicals in the environment must be based on an understanding of the mass balances that are established as chemicals originating from various sources migrate between water, air, sediments, soil, and biota. Accordingly, attempts are being made to repeat the success of the Lake Erie phosphorus models for other chemicals in the entire Great Lakes basin, notably for polychlorinated biphenyls (PCBs) and other persistent organic compounds (*13, 14*). During the next decade, a capability of constructing verifiable mass balance models for most chemicals in defined regions likely will emerge.

Such models undoubtedly will exploit wildlife biomonitoring data; for many chemicals, such data may be the primary source of information. This is not to suggest that air, water, and sediment sampling will become unimportant. If reliable bioconcentration relationships can be shown to exist between water, fish, gulls, and gull eggs it may then become more convenient to monitor the state of the water by a strategy of routine analysis of gull eggs, coupled to a less comprehensive, confirmatory program of water analysis. Such procedures could result in considerable economies because biotic concentrations are higher and fewer analyses may be needed.

Currently, monitoring or investigative programs that involve various biotic and abiotic media are conducted by different agencies for different purposes, and they usually employ different methods. These programs often are poorly coordinated. Much fish sampling is done from the human food and health perspective. Bird sampling often is related to concerns about pesticide application. Water sampling may be done to ensure the safety of drinking water. Analysis of contaminants in wildlife usually is done by agencies with a mandate to preserve wildlife, not to control chemical effluents.

This lack of integration is understandable but unfortunate because wildlife monitoring and general environmental monitoring can be mutually supportive. With the aid of environmental models both types of monitoring can provide a much clearer picture of contaminant trends, pathways, and dynamics. We will explore how these disparate activities may come together and how fugacity modeling could play a key role in linking these methods of monitoring.

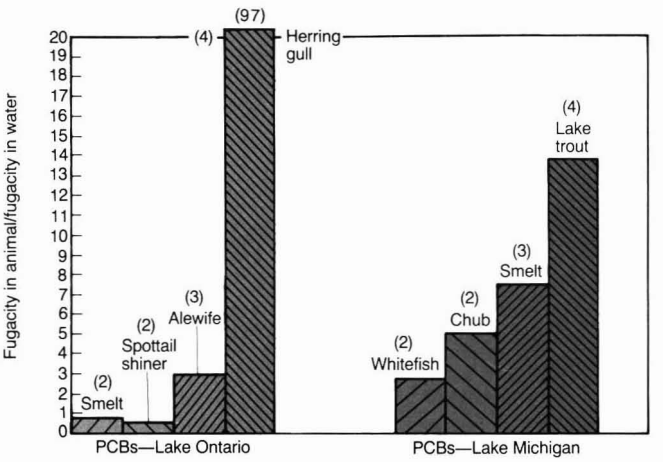
Fugacity

The concept of fugacity and its role in environmental models has been discussed in a series of papers (*15–17*).

Briefly, fugacity is analogous to chemical potential as it pertains to the tendency of a chemical to escape from a phase (e.g., from water). It is expressed in units of pressure (pascals) and is essentially a partial pressure exerted by the chemical in each medium. If a chemical attains concentrations in various media that are in equilibrium, its fugacity is equal in these media.

Fugacity f (Pa) is linearly related to concentration C (mol/m^3) through a proportionality constant, the fugacity capacity Z (mol/m^3 Pa), the value of which can be estimated for each chemical in each medium using established procedures (*15*). If we assume that a constant fugacity applies between various media and we can obtain the various Z values, it is possible for us to calculate the equilibrium concentrations and express them in commonly accepted units such as μg/kg, ppm, or ng/L (Figure 1). A nonequilibrium state usually exists in nature, however, because of localized emissions, ever-changing meteorological and hydrological conditions, and the nature and re-

FIGURE 3
Fugacity ratios of polychlorinated biphenyls (PCBs) in biota and water[a]



[a]Approximate trophic levels are indicated in parentheses.
Source: Reference 18.

TABLE 1
Concentrations and fugacities of selected organochlorine chemicals[a]

	Hexachlorobenzene	Mirex	*p,p'*-DDT	*p,p'*-DDE	Dieldrin	PCBs
Herring Gull (9.8–18% fat)[b]						
Total body concn (ppm)	0.18–0.26[b]	4.4–9.4[b]	0.029–0.15[b]	14–30[b]	0.18–0.53[b]	100–200[b]
Fat concn (mol/m^3)	0.0027–0.0076	0.042–0.14	0.00053–0.0037	0.23–0.79	0.0038–0.011	1.7–4.8
Fugacity (10^{-7} Pa)	700–2000	0.24–0.80	0.015–0.10	160–560	0.013–0.037	120–330
Egg (6.4–8.8% fat)[b]						
Total body concn (ppm)	0.068–0.14[b]	0.81–2.0[b]	0.013–0.050[b]	3.3–8.0[b]	0.067–0.18[b]	23–51[b]
Fat concn (mol/m^3)	0.0027–0.0060	0.016–0.043	0.00041–0.0016	0.11–0.27	0.002–0.0058	0.72–1.7
Fugacity (10^{-7} Pa)	720–1600	0.092–0.24	0.011–0.043	80–190	0.0065–0.019	51–120
Fish (alewife, 2.8% fat)[b]						
Total body concn (ppm)	0.005[b]	0.047[b]	0.015[b]	0.16[b]	0.017[b]	0.90[b]
Fat concn (mol/m^3)	0.0006	0.0029	0.0015	0.017	0.0015	0.087
Fugacity 10^{-7} Pa)	160	0.016	0.040	12	0.0051	6.1
Fish (smelt, 5.6% fat)[b]						
Total body concn (ppm)	0.005[b]	0.020[b]	0.014[b]	0.12[b]	0.016[b]	0.46[b]
Fat concn (mol/m^3)	0.0003	0.00061	0.00068	0.0061	0.00072	0.022
Fugacity (10^{-7} Pa)	77	0.0034	0.019	4.3	0.0024	1.5
Water						
Concn (ng/L)	0.01–0.12[c]	0.002[d]	0.03–0.27[e]	0.10[f]	0.26–0.63[e]	0.3–6
Fugacity (10^{-7} Pa)	3.7–44	0.0002	0.0022–0.020	0.022	0.0036–0.0088	0.29–5.7
Air						
Concn (ng/m^3)	0.1–0.3[g]	—	0.01–0.05[g]	—	0.01–0.1[g]	0.4–3.0[g]
Fugacity (10^{-7} Pa)	0.0087–0.026	—	0.00072–0.0036	—	0.000066–0.00066	0.03–0.21
Bottom sediment						
Concn (μg/kg)	10–320[h]	2–1600[i]	—	—	—	N.D. – 113 ng/g[j]
Fugacity (10^{-7} Pa)	200–7200	0.0004–0.3	—	—	—	<0.55
Suspended sediment						
Concn (ng/g)	12–94[k]	3.9–18[k]	—	5.8–18[k]	—	0.1–4.0 ng/L[l]
Fugacity (10^{-7} Pa)	270–2100	0.011–0.049	—	0.31–0.97	—	0.8–3.2

[a]In environmental media and wildlife in the Lake Ontario region.
[b]Reference 19.
[c]Reference 21.
[d]Reference 29.
[e]References 21 and 27.
[f]Reference 23.
[g]Reference 22.
[h]Reference 20.
[i]References 24 and 25.
[j]Reference 28.
[k]Reference 26.
[l]Reference 27.

TABLE 2
Physical–chemical properties and *Z* values of organochlorine compounds[a,b]

	Hexachlorobenzene	Mirex	*p,p'* – DDT	*p,p'* – DDE	Dieldrin	PCBs
Molecular weight	284.8	545.59	345.5	318	373.9	349.5[c]
Solubility (mol/m³)	1.65×10^{-5}[d]	1.84×10^{-4}[e]	7.6×10^{-6}[f]	1.26×10^{-4}[g]	4.9×10^{-4}[h]	1.10×10^{-4}[c]
Vapor pressure (Pa)	0.173[i]	8.0×10^{-4}[j]	1.94×10^{-5}[k]	8.67×10^{-4}[l]	2.57×10^{-4}[m]	3.67×10^{-3}[c]
Log K_{ow}	5.6[n]	6.89[o]	5.97[p]	4.99[p]	6.20[q]	6.68[c]
K_p (sediment)	1.64×10^4	3.9×10^5	3.84×10^4	4.02×10^3	6.51×10^4	1.967×10^5
***Z* Values** (mol/Pa m³):						
Air	4.03×10^{-4}	4.03×10^{-4}	4.03×10^{-4}	4.03×10^{-4}	4.03×10^{-4}	4.03×10^{-4}
Water	9.54×10^{-5}	0.23	0.392	0.145	1.91	0.0301
Sediment	2.34	1.34×10^5	2.25×10^4	876	1.86×10^5	8868
Gulls	5.16	2.43×10^5	4.97×10^4	1930	4.11×10^5	1.96×10^4
Gull eggs	2.91	1.37×10^5	2.8×10^4	1090	2.31×10^5	1.1×10^4
Alewife	1.07	5.02×10^4	1.03×10^4	399	8.49×10^4	4050
Smelt	2.16	1.01×10^5	2.08×10^4	807	1.72×10^5	8180

[a]Physical–chemical properties are estimated.
[b]*Z* values are calculated. The lipid contents given for biota in Table 1 are assumed in the calculations. The *Z* value for biota has been determined by assuming the lipid behaves as though it were octanol: *Z* biota = lipid content × K_{ow} × *Z* water.
An organic carbon content of 0.10 was assumed for the bottom and suspended sediments. Thus, $K_p = 0.411(K_{ow})(0.10)$
[c]Reference 45.
[d]Reference 30.
[e]References 35 and 36.
[f]References 31 and 36–39.
[g]Reference 36.
[h]References 36–38.
[i]References 31 and 32.
[j]Reference 35.
[k]References 31 and 40.
[l]Reference 41.
[m]References 38, 40, 42, and 43.
[n]References 30, 33, and 34.
[o]Reference 33.
[p]References 33 and 36.
[q]Reference 44.

sistance of transfer processes between the various phases such as air, water, sediment, and fish (*15*).

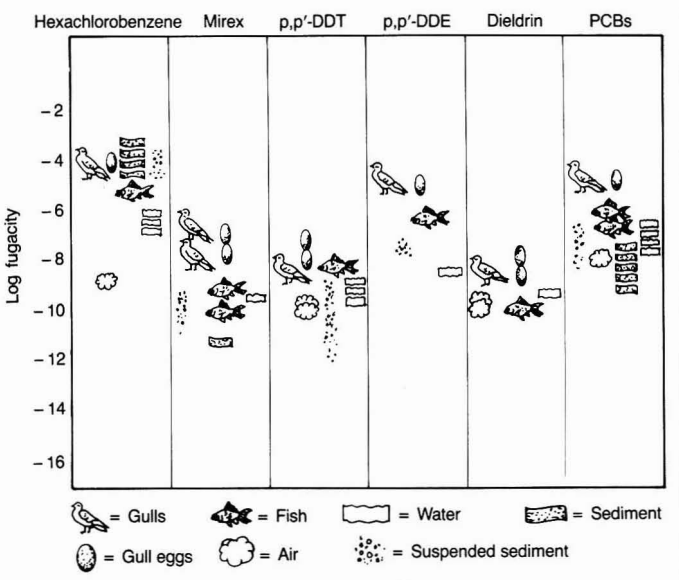
Levels of contamination in many media may be compared within a consistent single-unit system by converting reported environmental concentrations to fugacity. This synoptic fugacity approach reveals the equilibrium status of each medium with respect to the others. Hot spots that probably are sources of contamination can be identified, as well as areas that are relatively free of contamination. Compartments that approach equilibrium fugacity, or "equifugacity," are clearly identified; this is illustrated in a hypothetical example in Figure 2. The same information can be obtained by comparing phase concentrations with respect to their partition coefficients, but fugacity provides a simple, elegant, comprehensive multimedia picture of equilibrium status.

The synoptic fugacity concept

What roles can fugacity play in assessing concentrations of chemicals in the environment and in wildlife? To answer this question we will examine two sets of data. The first is a study from Connolly and Pedersen (*18*) in which concentrations of chemicals in varying trophic levels of fish were converted to fugacity and compared with water fugacity. These data, as presented in Figure 3 for PCBs in Lake Michigan, show that fugacity in water and fish generally are similar, but also that there is a definite trend for fugacity to increase with increasing trophic level. Also shown in Figure 3 in a similar manner are data from Lake Ontario (Table 1).

Table 1 presents concentrations of various organochlorine chemicals in environmental media and wildlife in the Lake Ontario region, as well as ranges of percentage lipid content for herring gulls and their eggs, alewife, and smelt. Using the data in Table 2 we may convert these concentrations to fugacities; it is assumed that the contaminant is

FIGURE 4
Fugacity of compounds in various media[a]



[a]In the Lake Ontario region.

present primarily in the lipid. Both sets of data broadly show that fugacity appears to increase with trophic level.

These examples reveal some of the benefits derived from using fugacity. Table 1 presents concentration units typical of most studies; for instance, herring gull contamination is reported in mg/kg and water contamination in ng/L. Data expressed in these units are not easily compared. The PCB level in herring gulls (Table 1), for example, is about 150 mg/kg (whole-body wet weight basis) or 3 mol/m^3 (fat weight basis), whereas the water concentration is about 3 ng/L or 9 x 10^{-9} mol/m^3. Fugacities, however, are directly comparable and may be reduced to a range which, at most, extends over 2 orders of magnitude. In terms of fugacity, gull PCB contamination is 2 × 10^{-5} Pa and water contamination is 3 × 10^{-7} Pa. Fugacity thus converts these disparate concentration units into one common unit.

Moreover, the fugacity levels for a persistent chemical in a region appear to fall in a consistent pattern within a relatively narrow range. Thus we can anticipate likely concentrations in one medium from fugacity data for another and develop a predictive capability. This is shown graphically in Figure 4. The biotic components of the environment have a tendency to have the highest fugacities, as shown by fish and by gulls and their eggs.

Several terms are used to describe this phenomenon. The bioconcentration of chemicals usually refers to the uptake of a chemical from water in which equal fugacities for fish and water are approached. Biomagnification refers to a further increase in concentration attributable to uptake from food. It results in a fugacity that may be five times that of the contaminant fugacity in food and water (Figure 3). Bioaccumulation is a broader term that indicates uptake from all sources and thus includes both effects.

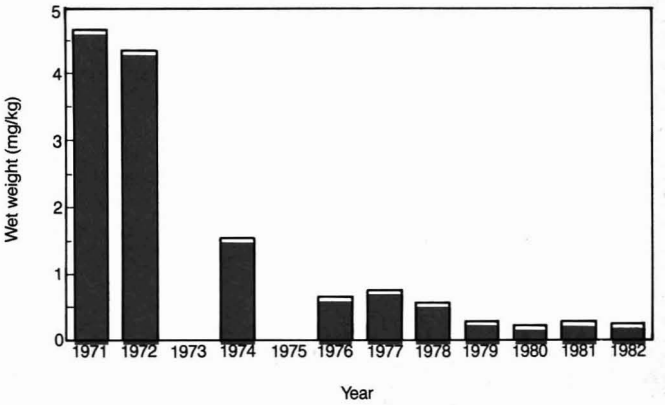
From Figure 4 it is apparent that the gulls show the highest fugacity. Fish also show a high fugacity compared with the physical environment. The generally low fugacity of contaminants in air may be explained by the movement of air from areas of lesser contamination. We are concerned with the chemicals that have a long life in the environment. Short-lived chemicals that are subject to rapid environmental reactions are more often controlled by kinetic factors; these chemicals will have lower fugacities and therefore are generally of less concern.

On the basis of the foregoing, we suggest a framework for analysis and interpretation of environmental- and wildlife-monitoring data. Measured concentrations of contaminants first are converted to fugacities; the fugacities in adjoining media then are compared. In simple situations of rapid exchange, the data should exhibit equifugacity. In other, more complex situations, the fugacities may have fairly constant ratios.

In the case of PCBs, for example, trout may develop a fugacity 15 times that of water and twice that of smelt (Figure 3). These fugacity ratios, which are functions of the chemical itself, also are functions of the nature of the environmental and biological media, but they may be quite constant between localities and they may be relatable to chemical properties.

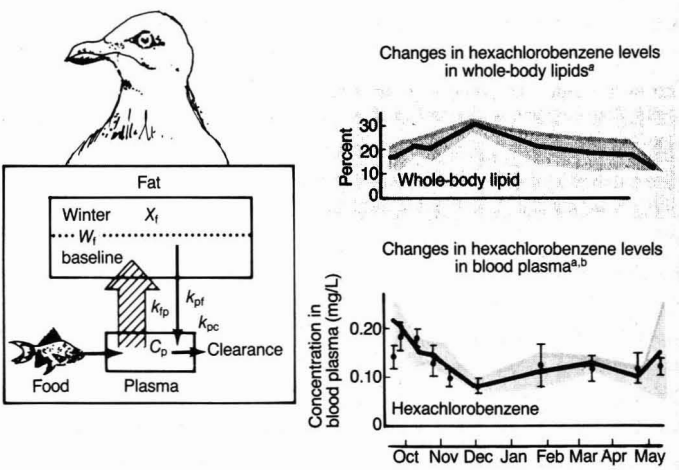
For a chemical that is readily metabolized, such as a polynuclear aromatic hydrocarbon (PAH), the fish's fugacity may be one-tenth to one-hundredth of that of the water (*46*). On the other

FIGURE 5
Hexachlorobenzene residues in herring gull eggs[a]



[a]Eggs were taken from Scotch Bonnet Island, Lake Ontario.

FIGURE 6
Two-compartment model of chemical uptake by herring gulls



[a]Model involves four test animals. Solid line represents model values; shaded area represents standard deviation (SD). Changes are recorded through autumn and winter.
[b]Solid circles in curve for blood plasma represent actual observations (*48*). Error bars in curve for blood plasma represent SD for actual observations (*48*).

hand, wildlife species that lack the enzymes necessary to degrade a specific organic chemical may show elevated fugacities. With the analysis of data sets for many regions it should be possible to explain the entire process of organic chemical transfer from the abiotic environment to wildlife.

The role of toxicokinetics

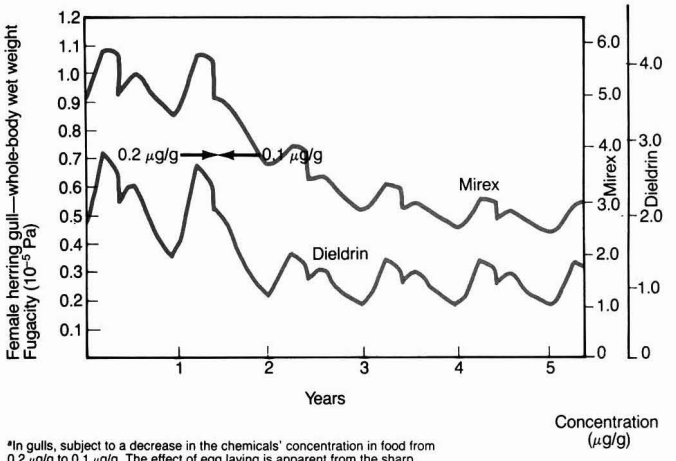
Interpreting these fugacity ratios requires a detailed understanding of the toxicokinetics of chemicals as they migrate through food chains. Such a study is now under way on organochlorine chemicals in herring gulls, smelt, and coho salmon in Lake Ontario (*10, 47*). These monitors have been used by the International Joint Commission; an example of data derived from samples is shown in Figure 5.

The gulls and their eggs are effective monitors. Most of their food comes from aquatic sources. Only the immature birds migrate out of the Great Lakes basin, and adults live to 20 years or more. Gull biology and bioenergetics have been studied extensively (*48*). A relatively simple two-compartment model provides an excellent description of the concentration dynamics as the bird's lipid levels change throughout the year in response to temperature changes (*49*).

To test the validity of the two-compartment model for gulls, a group of birds was injected with a number of organochlorine compounds. Plasma levels then were monitored from autumn to the following spring. Figure 6 shows some experimental data, a fitted curve for one compound (hexachlorobenzene), and a schematic representation of the partitioning of this contaminant between fat and blood plasma through the annual cycle. In practical terms this model allows us to quantify the annual cycle in concentration and fugacity of a contaminant and avoids the pitfalls of comparing winter and summer concentrations.

The model can be used to explore or simulate how a change in environmental contaminant levels or in the food of herring gulls results in a time response toward a new steady-state level for gulls. Figure 7 presents a scenario in which the food levels (concentrations in fish) of dieldrin and mirex, 0.2 mg/kg, rapidly decreased to 0.1 mg/kg. The curves represent free-living females subject to temperature fluctuation and egg laying. Egg laying results in a sharp annual drop in body fugacity as contaminants are cleared via the eggs. The time lag between the change in prey level and the corresponding change in the steady-state level of the monitor species is a function of the rates of metabolism and excretion.

FIGURE 7
Changes in whole-body concentrations of dieldrin and mirex[a]



[a]In gulls, subject to a decrease in the chemicals' concentration in food from 0.2 μg/g to 0.1 μg/g. The effect of egg laying is apparent from the sharp drop in fugacity or concentration in the bird just after the annual peak. The sinusoidal appearance of the curves is caused by the annual lipid fluctuation.

This time lag may be about three years for slow-clearing compounds such as mirex (half life 231 days), compared with less than one year for compounds such as dieldrin (half life 82 days) (*49*).

It is important to determine this time lag because it controls the lag between environmental and tissue concentration changes. The monitored tissue concentration thus is a function of the exposure history over a determinable time period and of the bird's growth, lipid content, and metabolism. It should be possible (and it is a fascinating scientific puzzle) to interpret tissue concentration changes in birds by back-calculating the exposures that caused these levels. This requires a time-dependent toxicokinetic model; indeed, it probably is misleading to interpret wildlife tissue data without such a model.

Assessing human health effects

Fugacity also may play a role in interpreting the nature of extreme contamination events in which wildlife populations were reduced by toxicity. It is possible for gulls to thrive when they obtain food from an aquatic environment contaminated by PCBs at fugacity levels of approximately 10^{-5} Pa. At this level, concentrations of PCBs in water typically are 1 ng/L; in fish, 1 mg/kg; in gull lipids, 30 mg/kg; and in eggs, 10 mg/kg.

If the fugacity is increased by a factor of 10, to 10^{-4} Pa, the concentrations of PCBs increase proportionately and toxic effects become apparent, possibly resulting in population declines. It thus may be possible to determine the fugacities at which populations are adversely affected by each chemical and even by chemicals in combination. The strategy for protecting wildlife then would be to ensure that the chemical's fugacity in the environment is kept below a threshold level at which adverse effects are manifest. Laboratory experiments may be used to help establish these levels.

With this approach, it may be possible to establish a dose–response relationship for a population of wildlife existing within a defined ecosystem. Wildlife can be protected from excessive contamination, and hence danger. It is noteworthy that we humans also occupy a place within these ecosystems and are subject to the same dangers.

In the design of monitoring programs, it is important to allocate resources for analyzing the findings in terms of the contaminant status throughout the entire biotic and abiotic environment. Fugacity provides a convenient tool for such analyses and helps to integrate disparate environmental monitoring efforts. We believe that such syntheses are a fruitful area for research.

Viewed from this perspective, wildlife takes on an enhanced value as a component of the overall environmental monitoring and surveillance effort. We can identify vulnerable species for each chemical in each region. We can observe their condition, periodically analyze their tissues, and confirm that levels (fugacities) of chemical contamination are being maintained below certain targets. Trends can be established and early warning can be obtained about increases that ultimately may affect wildlife populations and human

health. This is essentially a reiteration of the opinion frequently expressed by wildlife enthusiasts that the best guarantee of continued human health is to maintain an environment in which wildlife will flourish.

It is now possible to use environmental and toxicokinetic models to establish quantitative links between emissions, abiotic concentrations, concentrations in wildlife, and ecological viability. The disparate scientific efforts of environmental modeling, toxicology, toxicokinetics, and fundamental wildlife biology and ecology thus become mutually supportive and can contribute to a rational strategy for ensuring that we create and maintain a healthful environment.

Acknowledgments

This work was supported by the Wildlife Toxicology Fund of Environment Canada, the Ontario Ministry of the Environment, and the Natural Sciences and Engineering Research Council. We thank H. Won, C. Weseloh, J. Elliott, P. Angehrn and Y. Ouellette. A. J. Keith and P. G. Wells provided helpful comments.

This article was reviewed for suitability as an *ES&T* feature by Ronald J. Kendall, Western Washington University, Bellingham, Wash. 98255; and by Yoram Cohen, University of California, Los Angeles, Los Angeles, Calif. 90024.

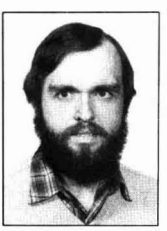
References

(1) Ratcliffe, D. A. J. Appl. Ecol. 1970, 7, 67–116.
(2) Risebrough, R. W.; Teeple, S. M.; Gilbertson, M. *Can. J. Zool.* **1983,** *61,* 427–36.
(3) Blus, L. J. et al. *Nature* **1972,** *240,* 164–66.
(4) Spitzer, R. R. et al. *Science* **1978,** *202,* 333–35.
(5) Gilbertson, M. R.; Fox, G. A. *Environ. Pollut.* **1977,** *12,* 211–16.
(6) Norstrom, R. J.; Gilman, A. P.; Hallett, D. J. *Sci. Total Environ.* **1981,** *20,* 217–30.
(7) Kendall, R. J. *Environ. Sci. Technol.* **1982,** 16, 448A–453A.
(8) Wren, C. D. *Environ. Monit. and Assessment* **1986,** *6,* 127–44.
(9) Goldberg, E. D., *Environ. Monit. and Assessment.* **1986,** *7,* 91–103.
(10) Mineau, P. et al. In *Toxic Contaminants in the Great Lakes;* Nriagu, J. O.; Simmons, M. S., Eds.; Wiley: New York, 1984; pp. 425–52.
(11) Phillips, D. J. *Quantitative Aquatic Biological Indicators;* Applied Science Publishers: London, 1980.
(12) Cohen, Y. C. In *Pollutants in a Multimedia Environment;* Cohen, Y. C., Ed.; Plenum: New York; 1986; pp. 7–48.
(13) *J. Great Lakes Res.* **1987,** *13,* 387–96.
(14) Thomann, R. V.; DiToro, D. M. *J. Great Lakes Res.* **1983,** *9,* 474–96.
(15) Mackay, D.; Paterson, S. *Environ. Sci. Technol.* **1982,** *16,* 654A.
(16) Paterson, S.; Mackay, D. In *The Handbook of Environmental Chemistry;* Hutzinger, O., Ed.; Springer-Verlag: Heidelberg, 1985; Vol. 2, Part C, pp. 121–40.
(17) Mackay, D. et al. *Chemosphere* **1985,** *14,* 335–74.
(18) Connolly, J. P., Pedersen, C. J. *Environ. Sci. Technol.*, in press.
(19) Braune, B. et al. "Dynamics of Organochlorine Substances in Herring Gulls: III. Tissue distribution of PCB congeners, PCDD's, DDE, HCB, Mirex and Cyclodiene compounds in Lake Ontario"; Technical Report; National Wildlife Research Center, Canadian Wildlife Service, Ottawa, 1987.
(20) Strachan, W.M.J.; Edwards, C. J. In *Toxic Contaminants in the Great Lakes;* Nriagu, J. O.; Simmons, M. S., Eds.; Wiley: New York, 1984; pp. 239–64.
(21) Biberhofer, J.; Stevens, R.J.J. "Organochlorine Contaminants in Ambient Waters of Lake Ontario"; Inland Waters Directorate, Scientific Series Bulletin 159; Inland Waters Directorate: Ottawa, Ontario, Canada, 1987.
(22) Eisenreich, S. J.; Looney, B. L.; Thornton, J. D. *Environ. Sci. Technol.* **1981,** *15,* 30.
(23) Oliver, B. G.; Nicol, K. D. *Sci. Total Environ.* **1984,** *39,* 57–70.
(24) Scrudato, R. J.; Del Prete, A. J. *Great Lakes Res.* **1982,** *8,* 695–99.
(25) Mackay, D.; Paterson, S. *Environ. Sci. Technol.* **1984,** *18,* 207A–214A.
(26) Oliver, B. G.; Charlton, M. N. *Environ. Sci. Technol.* **1984,** *18,* 903–8.
(27) McCrea, R. C.; Fischer, J. D.; Kuntz, K. W. *Water Poll. Res. J. Canada* **1985,** *20,* 67–78.
(28) Kauss, P. B.; Suns, K.; Johnson, A. F. In *Physical Behavior of PCBs in the Great Lakes;* Mackay, D. et al., Eds.; Ann Arbor Science: Ann Arbor, Mich., 1983; pp. 385–410.
(29) Yin, C.-Q. Ph.D. Dissertation, State University of New York, Syracuse, 1985.
(30) Miller, M. M. et al. *Environ. Sci. Technol.* **1985,** *19,* 522–29.
(31) Melinikov, N. N. *Residue Rev.* **1971,** *36,* 68–69.
(32) Weast, R. C. In *Handbook of Chemistry and Physics,* 53rd ed.; CRC Press: Boca Raton, Fla., 1973.
(33) Veith, G. D.; Defoe, D. L.; Bergstedt, B. G. *J. Fish. Res. Board Can.* **1979,** *36,* 1040–48.
(34) Neely, W. B.; Branson, D. R.; Blau, G. E. *Environ. Sci. Technol.* **1974,** *8,* 1113–15.
(35) Smith, J. H. et al. "Environmental Pathways of Selected Chemicals in Freshwater Systems, Part II: Laboratory Studies"; EPA Report 600/7-78-074; EPA: Washington, D.C., 1978.
(36) In *Handbook of Environmental Data on Organic Chemicals,* 2nd ed.; Verschueren, K., Ed.; Van Nostrand Reinhold: Toronto, 1983; pp. 432, 434, 437, 513.
(37) Gunther, F. A.; Westlake, W. E.; Jaglan, P. S. *Residue Rev.* **1968,** *20,* 1.
(38) Weil, L.; Dure, G.; Quantin, K.E.Z. *Wasser Abwasser Forsch.* **1974,** *7,* 169.
(39) Triggan, J. W.; Dutt, G. R.; Riggs, R. L. *Bull. Environ. Contam. Toxicol.* **1967,** *2,* 90.
(40) Edwards, C. A. *Residue Rev.* **1966,** *13,* 83.
(41) Spencer, W. F. *Residue Rev.* **1975,** 59, 91–117.
(42) Harris, C. R.; Mazurek, J. H. *J. Econ. Entomol.* **1964,** *57,* 698.
(43) Zimmerli, B.; Marek, B. *Mitt. Geb. Lebensmittelunters Hyg.* **1974,** *65,* 55.
(44) Briggs, G. C. *J. Agric. Food Chem.* **1981,** *29,* 1050–59.
(45) Mackay, D. et al. In *Physical Behavior of PCBs in the Great Lakes;* Mackay, D. et al., Eds.; Ann Arbor Science: Ann Arbor, Mich., 1983; pp. 59–70.
(46) Southworth, G. R.; Keffer C. C.; Beauchamp, J. *J. Environ. Sci. Technol.* **1980,** *14,* 1529–31.
(47) Norstrom, R. J.; Hallett, D. J.; Sonstegard, R. A. *J. Fish. Res. Board Can.* **1978,** *35,* 1401–9.
(48) Norstrom, R. J. et al. *Ardea* **1986,** 74, 1–23.
(49) Clark, T. P. et al. *Environ. Toxicol. Chem.* **1987,** *6,* 547–59.

Donald Mackay *is a professor in the Institute for Environmental Studies and the Department of Chemical Engineering at the University of Toronto. His research interest is in the environmental fate and modeling of organic chemicals.*

Sally Paterson *(l) is a research associate in the Institute for Environmental Studies and the Department of Chemical Engineering at the University of Toronto. Her research is concerned with modeling the environmental and pharmacokinetic fate of organic chemicals.*

Kathryn Clark *(r) is a doctoral candidate in the Department of Chemical Engineering and Applied Chemistry at the University of Toronto. She is studying the biomagnification of organic chemicals in food chains, focusing on fish.*

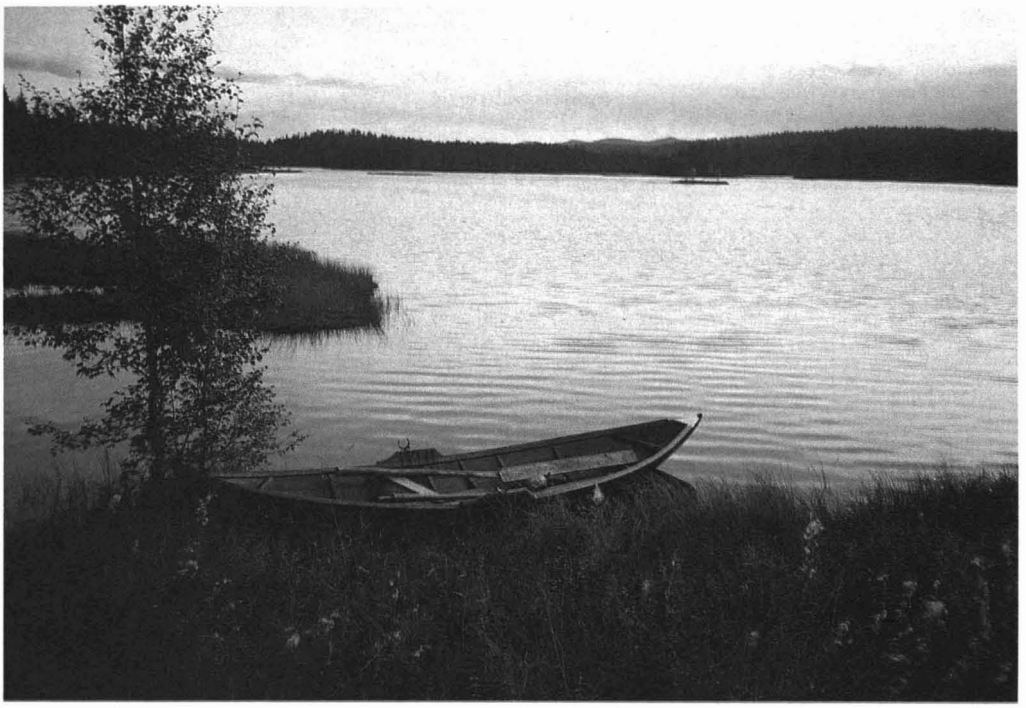


Tom Clark *(l) received his B.Sc. from the University of Ottawa and his M.Sc. in zoology from the University of Guelph, Ontario. He has worked on wildlife-related environmental problems, usually including computer simulation, for the Canadian Wildlife Service and for the provincial government.*

Ross J. Norstrom *(r) is chief of chemistry research at the National Wildlife Research Center of Environment Canada in Hull, Quebec. His areas of expertise include the modeling, pharmacodynamics, bioaccumulation, and analysis of organochlorine environmental contaminants in fish and birds.*

Eastern Lake Survey

Regional estimates of lake chemistry



Dixon H. Landers
Environmental Research Laboratory
Corvallis, Ore. 97333

W. Scott Overton
Oregon State University
Corvallis, Ore. 97331

Rick A. Linthurst
Environmental Monitoring Support Laboratory
Research Triangle Park, N.C. 27711

David F. Brakke
Western Washington University
Bellingham, Wash. 98225

The relationship between acidic deposition, the acidification of surface waters, and the loss of biological resources has become an important regional environmental issue in the United States and other nations. The question of whether the pH, alkalinity (or acid neutralizing capacity, ANC), and other chemical attributes of surface waters have been affected by acidic inputs of anthropogenic origin has been extensively reviewed, analyzed, and debated (*1–4*). Published evidence from site-specific, intensive studies in the United States and Canada is consistent with the hypothesis that declines of pH and ANC in surface waters have occurred over time and that these conditions have been caused by acidic deposition. In the analyses of chemical trends in lakes in New England and in the Adirondack region of New York, several authors have concluded that pH or alkalinity, or both, have declined from around the 1930s to the 1970s (*5–7*).

Despite these attempts to quantify changes in aquatic chemistry, the extent to which surface waters in the United States are threatened or may have been affected by acidic deposition has only recently been quantified. There remains considerable uncertainty in extrapolating the results of site-specific studies to a regional or national scale. Factors contributing to this uncertainty include the degree to which individual study sites represent larger regional populations, the unknown bias in lake selection, the absence of measurements of chemical variables that are critical in assessing chemical or biological effects, the difficulty in comparing data collected by different and sometimes unknown methods, and the inconsistent documentation of quality assurance protocols.

Recognizing the limitations associated with available data and the complexity of predicting surface water response to acidic deposition, EPA initiated the National Surface Water Survey in 1983. This survey, which includes both the National Lake Survey and the National Stream Survey, has three primary goals:

- to quantify the present chemical status of surface waters in the United States in regions potentially susceptible to the effects of acidic deposition (Phase I),
- to assess the temporal and spatial variability in aquatic chemistry and define the key biological resources associated with surface waters (Phase II), and

This article not subject to U.S. copyright. Published 1988 American Chemical Society

- to quantify long-term temporal trends in surface water chemistry and biology (Phase III).

Each phase provides specific information and contributes to later phases. The National Lake Survey will ultimately provide information that will identify those lake or stream populations appropriate for a regionally characteristic, statistically valid monitoring project designed to quantify long-term trends in chemistry and ecological resources.

The National Lake Survey includes both the Eastern Lake Survey and the Western Lake Survey. This article presents the key design features of the first phase of the Eastern Lake Survey and the regional estimates of the chemical status of lakes that resulted from its implementation. Additional details of Phase I (*8*), which was completed in 1984, the resulting population estimates for all variables (*9*), and individual lake data (*10*) are available. The results of the companion Western Lake Survey, completed a year later, are presented elsewhere (*11–13*).

Survey approach

A critical issue in the design of the survey was the chemical characterization of regional lake populations. If a single water sample can represent the chemistry of a lake well enough to satisfy the specific objectives of a study, then a large number of lakes can be sampled. If multiple water samples are needed because of temporal or spatial variability, then the number of sample lakes must be reduced proportionally.

One sample from one location at one time of the day during a specific season of a particular year cannot characterize the complex chemical dynamics of a lake. A single sample is justified only from the perspective that it is an index to the essential characteristics of the lake. Even if two or three samples are taken, they remain only indexes, because understanding the dynamics of a single lake requires a far more detailed study. Because the survey was designed in a three-phase approach, it was not essential that the synoptic sample from Phase I capture the lake chemistry at a time of worst-case condition, such as during spring snowmelt.

It was more important that the index sample be collected at a time when within-lake variability is small. Subsequent studies (Phase II) will be used to establish the relationship between the index and other sources. Data from lakes in EPA's Long-Term Monitoring Program have subsequently shown that there is a strong relationship between fall and spring ANC (*14*). The National Lake Survey was designed to describe populations of lakes from a defined statistical framework. The index sample, maximizing both lake number and spatial coverage on a large geographic scale, was therefore the most appropriate choice for addressing the collective objectives of Phase I of the Eastern Lake Survey.

The perspective that each lake is represented by an index sample rather than mean annual chemistry or some other integration over time and space is important in interpreting the results. The population descriptions represent and characterize the chemistry of a defined population of lakes as though data had been collected for every lake in the population in the same manner as for the sampled lakes. Thus the resulting frequencies and areal distributions for the chemical parameters represent a synoptic index to water chemistry for the population of lakes.

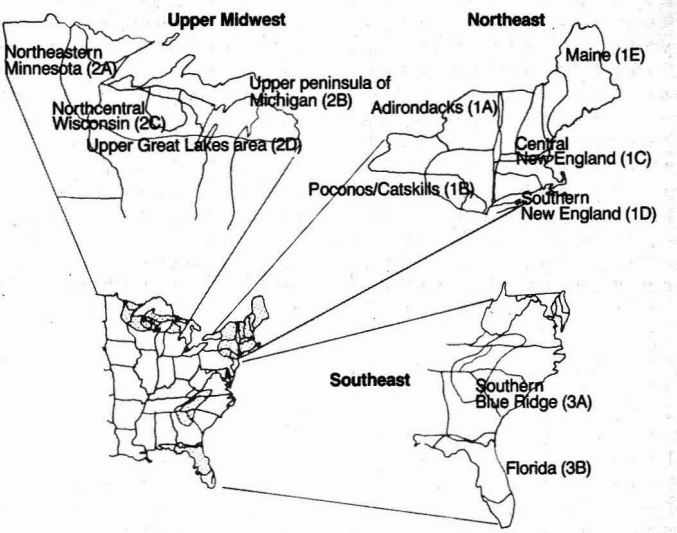
The fall season after turnover was selected as the sampling window. During this period, spatial variation within a lake is reduced as the lake undergoes a period of mixing that may last four to eight weeks in temperate climes. Samples were collected at what appeared to be the deepest part of the lake to represent the dominant water mass. Studies of temporal and spatial patterns in a subsample of the Phase I lakes are being conducted as part of the Phase II studies and will assess temporal variation within the fall and among the spring, summer, and fall seasons.

Survey design and lake selection

Because the objective of the survey was to quantify the number of low-ANC and acidic lakes, any allocation of samples to areas dominated by high-ANC lakes would result in fewer samples designated to quantify the areas of greatest interest (i.e., those with low-ANC lakes). Therefore, the study area was restricted to those parts of the country where the majority of lakes were expected to have ANC < 400 μequiv/L (*15*). Within the study area, the number of samples could have been allocated in several ways. Many surveys use a random allocation or a proportional allocation of samples. But because the number of acidic lakes was expected to be a small percentage of the total, random allocation of samples would provide few samples from the lakes of greatest interest for this project. The precision with which the acidic and low-ANC lakes could be quantified probably would be poor. We therefore decided to use a stratified design whereby sample lakes were allocated equally among strata. The populations of lakes within each of the strata are described with roughly the same precision.

Figure 1 shows the three regions—Northeast, Upper Midwest, and South-

FIGURE 1
Regions and subregions of the Eastern Lake Survey–Phase I



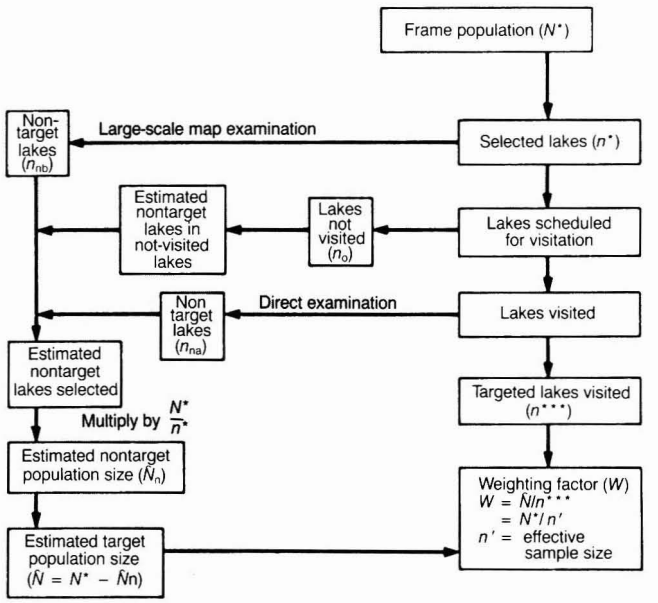
Region	No. of subregions	Designations
Upper Midwest	4	2A–2D
Northeast	5	1A–1E
Southeast	2	3A and 3B

east—and represents the first level of stratification in the design. The second stratification factor, subregion, identifies areas within each region that were expected to be relatively homogeneous with respect to water quality, physiography, vegetation, climate, and soils. Subregional stratification ensured that a representative sample was drawn from each geographically distinct portion of a region. Based on geographic homogeneity, five subregions were identified in the Northeast, four in the Upper Midwest, and two in the Southeast. On the basis of the observed physical and chemical differences between lakes in the Southern Blue Ridge and Florida, we have chosen to treat them as independent regions (3A and 3B, respectively) in this discussion.

The third stratification factor, alkalinity map class, is based on the range of surface water alkalinity values expected to dominate in different areas. The alkalinity map classes used in the stratification were < 100 μequiv/L (class 1), 100–200 μequiv/L (class 2), and > 200 μequiv/L (class 3). Spatial representations of the three alkalinity classes within each region were derived from preliminary versions of regional surface water alkalinity maps (*16–18*). Thus each stratum is an alkalinity map class within a subregion within a region. All 3 alkalinity map classes were found within each of the 11 subregions, so that a total of 33 strata (15 in the Northeast, 12 in the Upper Midwest, and 6 in the Southeast) were defined.

Map class boundaries according to region, subregion, and alkalinity were delineated and labeled on U.S. Geological Survey (USGS) topographic maps with a scale 1:250,000. Each lake represented on the maps was assigned a unique number and the set of lake areas were consecutively ordered within strata. Lakes were selected in such a way that each lake in a stratum had an equal probability of inclusion (*8*). Lake numbers were entered into a computer file in numerical order as labeled on the maps and a systematic random sample was used to select lakes within each stratum. A sample size of 50 or more target lakes per stratum was chosen, based on the judgment that this sample size would yield adequate precision for describing the chemical characteristics of lakes within each stratum (*8*). Figure 2 shows the population of lakes represented by the sample and explains how the sample was refined through several steps. All lakes identified on the USGS maps constitute the statistical "frame"— hence the term frame population. The actual population for which estimates are computed is a subset of this population and is termed the target population. Target lakes are those lakes

FIGURE 2
Estimating target population size for the Eastern Lake Survey–Phase I[a]



[a]Detailed definitions of the symbols within the boxes and their relationship to one another are provided in reference 8.

remaining in the frame population after elimination of lakes of noninterest.

Definitions for nontarget lakes included six possibilities: areas with no lakes present; areas with flowing water; bays or estuaries (high conductance); lakes affected by intense urban, industrial, or agricultural activities; marsh/swamp; and lakes too small to be consistently identified with the available maps (< 4 ha). From this approach, a weighting factor (W) was computed for each lake, such that all lakes within a given stratum had the same weighting factor. This factor represents the estimated number of target lakes within a stratum divided by the number of target lakes from which a water sample was collected. Where $W = 1$, all target lakes were sampled; where W is large (e.g., 82), only a small fraction of the lakes were visited. Consequently, most applications of the sample data must be adjusted by the stratum-specific weights (*19*).

There is substantial evidence that surface water chemical characteristics during spring may be less favorable for biota than during fall (*20*). Furthermore, short-term episodic increase in acidity from snowmelt or rain events may impose stress on biota in addition to chronic conditions. When ongoing studies of temporal variability under Phase II are complete, population estimates for spring conditions will be made for lakes with ANC ≤ 400 μequiv/L. However, population descriptions apply only to those lakes included in the original frame population. Lakes with a surface area of < 4 ha (and up to 10 ha for some maps) are generally not shown on the USGS maps that were used to establish the frame population; therefore, these lakes represent an important resource that was not considered in this survey. Small lakes are often lower in pH and ANC than larger lakes in the same geographic area. Ongoing research also is directed at this important issue.

Essential to the accurate interpretation of the data is a clear identification of any population for which inferences are made. However, the design of Phase I permits considerable flexibility in defining a subpopulation of interest (*19*), provided it is a subset of the original target population.

Sampling, analyses, data quality

Field sampling was conducted by helicopter from Oct. 7 to Dec. 14, 1984. Water samples were collected from a depth of 1.5 m to avoid the influence of the helicopter pontoons and rotor wash (0.5 for shallow lakes). Samples were stored in coolers at approximately 4 °C until processed at a nearby mobile field laboratory and

shipped by overnight mail to contract analytical laboratories. Details of field sampling and analytical techniques are described elsewhere (*21*, *22*).

Measurements were taken on-site for pH, specific conductance, Secchi disk transparency, and temperature; measurements were also taken at the field laboratory within 16 hours of sample collection. Twenty-one additional parameters were measured at an analytical laboratory within prescribed holding times of 7–28 days. Dissolved inorganic carbon (DIC), pH, and specific conductance were measured on multiple occasions.

Extensive quality assurance and quality control procedures for sampling and analytical operations were implemented during Phase I (*23*, *24*). Table 1 presents estimates of overall and analytical laboratory within-batch precision for selected measurements. Precision estimates for field laboratory measurements were calculated, using all available duplicate data, regardless of measurement value. No significant data-quality problems were noted for the major variables of interest. Precision for some chemicals present in low concentrations (e.g., nitrate, aluminum, and chloride) failed to meet the initial goals, but these deficiencies in the data were judged to have a negligible effect on regional data interpretation. The Environmental Sciences Division of Oak Ridge National Laboratory designed and implemented data base management activities (*25*) using the Statistical Analysis System (SAS) software (*26*). Analyses were prepared according to algorithms provided by Overton (*27*).

Estimates for variables

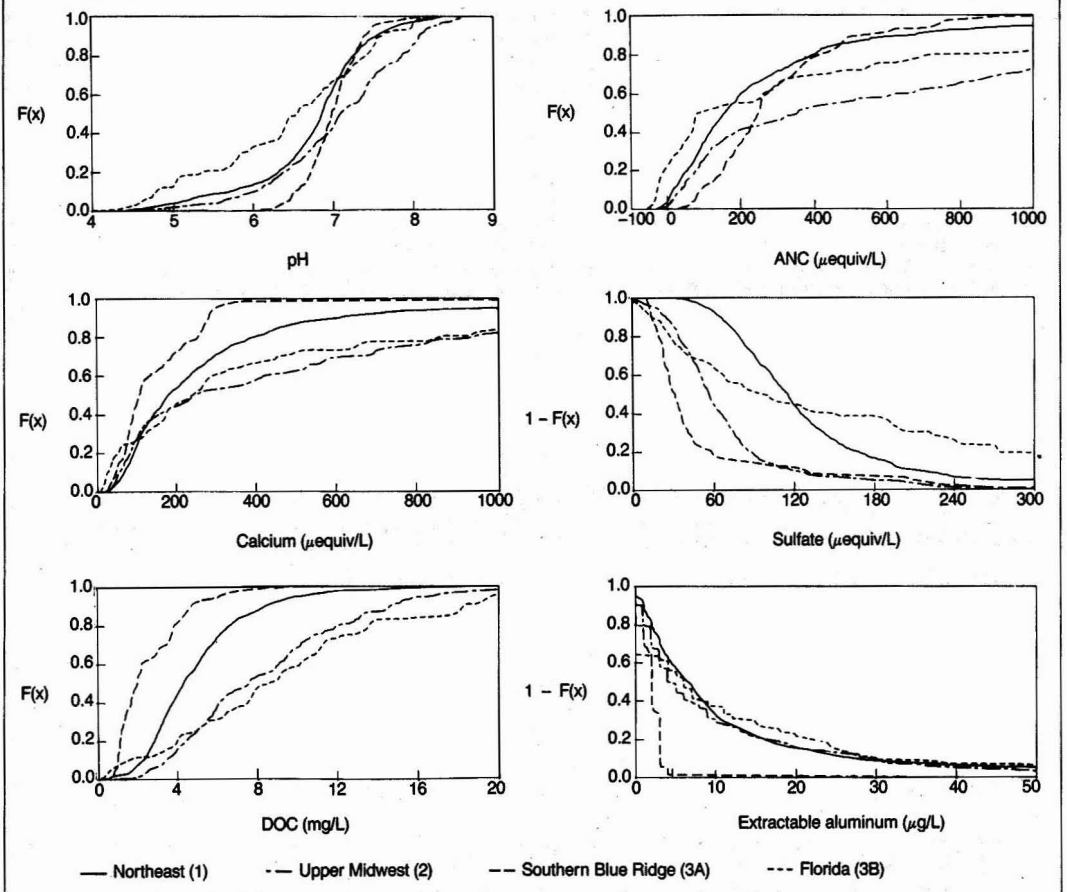
Only the primary variables are summarized herc; these include closed-system pH, ANC, sulfate, calcium, extractable Al, and dissolved organic carbon (DOC). Of the 26 variables measured, these 6 primary variables

TABLE 1
Estimated within-batch precision from field and laboratory duplicate data, Eastern Lake Survey–Phase I[a]

	Intralaboratory precision goal	Overall within-batch precision (field duplicates)		Analytical within-batch precision (laboratory duplicates)	
Parameter	%RSD	n[b]	RMS of %RSD[c]	n[b]	RMS of %RSD[c]
Field Laboratory					
pH, closed system	0.1[d]	124[e]	0.04	93[e]	0.01
DIC, closed system	10	123[e]	16	116[e]	4.6
True Color	10	125[e]	22	118[e]	1.5
Turbidity	10	125[e]	19	117[e]	8.4
Analytical Laboratory					
pH, open system (initial ANC)	0.05[d]	125[e]	0.05	127[e]	0.04
pH, air equilibrated	0.05[d]	125[e]	0.09	127[e]	0.08
ANC	10	90	10	86[f]	2.1[f]
Specific conductance	3, 1[g]	125	1.9	123	10
DIC, air equilibrated	10	94	5.0	94	2.2
DIC, initial	10	85	3.7	113	3.5
DOC (≤5 mg/L)	10	46	5.6	73	2.5
(> 5 mg/L)	5	59	12	41	2.4
Ca	5	125	2.3	123	0.88
Fe	10	32	10	101	4.3
K	5	82	3.7	121	1.5
Mg	5	125	2.3	121	0.64
Mn	10	6	11	73	1.7
Na	5	121	4.3	121	0.96
Cl^-	5	85	17	124	7.1
SO_4^{-2} (mg/L)	5	115	6.5	124	11
NO_3^- (mg/L)	10	5	60	86	3.6
F, total dissolved	5	62	8.9	123	2.5
NH_4^+ (mg/L)	5	0	—[h]	54	2.3
Al, extractable (>0.010 mg/L)	10	9	11	45	18
(≤0.010 mg/L)	20	0	—	0	—
Al, total (>0.010 mg/L)	10	1	24	9	5.4
(≤0.010 mg/L)	20	0	—	0	—
SiO_2	5	50	2.7	64	2.2
P, total (>0.10 mg/L)	10	4	9.7	95	10
(≤0.10 mg/L)	20	0	—	9	8.6

[a]RSD = relative standard deviation; RMS = root mean square
[b]*n* = number of duplicate pairs with mean > quantitation limit (*24*).
[c]Calculated as the root mean square (RMS) of the relative standard deviation of the duplicate pairs (for pH, RMS of the absolute standard deviation was calculated).
[d]Absolute standard deviation (pH unit).
[e]*n* = total number of duplicate pairs.
[f]Analytical laboratories were not required to analyze calibration blanks for ANC. Values for routine and duplicate pairs with means greater than the quantitation limit (56.6 ueq L^{-1}) were calibrated using field blanks.
[g]Overall intralaboratory precision goal (field duplicate pairs) = 3%; analytical intralaboratory precision goal (laboratory duplicate pairs) = 1%.
[h]All pairs had mean values ≤ quantitation limit. For all pairs with mean > 0 (*n* = 113), the precision was 34%.
[i]Only one pair had a mean greater than the quantitation limit; therefore, the calculated precision (RMS of %RSD) for that pair was equivalent to the actual %RSD. For all pairs with mean > 0 (*n* = 125), the precision was 35%.

FIGURE 3
Cumulative frequency distributions—F(x) and 1 – F(x)—for primary variables within major regions of the Eastern Lake Survey–Phase I[a]



[a]These are population estimates for lakes with surface areas > 4 ha and < 2000 ha.

were emphasized because of their direct relevance to the effect of acidic deposition on water chemistry. Some of these primary variables, such as pH, Ca^{2+}, and Al, are perhaps the most biologically relevant chemical indicators (*28*) and, in the case of SO_4^{2-}, can be indicative of regional anthropogenic acidification from atmospheric deposition.

Here we use estimated frequency distributions (F[x] curves) of the survey results to describe and compare the proportion of the regional lake populations equal to or less than a particular value of a variable. Inverse frequency distributions (1-F[x]) are shown for SO_4^{2-} and extractable aluminum to estimate the proportion of lakes equal to or greater than a particular reference value. Of the 1612 probability lakes sampled in the three regions of the eastern United States, 20 had a surface area > 2000 ha. We excluded these large lakes from the data presentations because their inclusion inordinately influenced lake areal data. The lowest pH measured for any of these 20 lakes was 6.64.

Figure 3 shows the estimated frequency distributions for each of the primary variables for regions 1 and 2 and subregions 3A and 3B. Figure 4 shows descriptive statistics (bar graphs) summarizing the regional chemical status of lakes for selected reference values of the primary variables. Reference values for each of the primary variables were chosen to facilitate comparisons among strata, subregions, regions, or subpopulations.

For the purpose of this article, ANC ≤ 0 has been used as a definition of an acidic lake. This is unambiguous because when ANC is zero or lower (generally corresponding to a pH value of about 5.2 or less), the lake has limited ability to neutralize acidic inputs. It should be emphasized, however, that biological damage to fish and other aquatic organisms has been documented at pH values of 5.8 to 6.0 (*29*). A reference value ≤ 200 μequiv/L is also provided for ANC to represent that population of lakes with low ANC suspected of being susceptible to acidic deposition. Various reference values are reported for other variables of interest to scientists and policy-makers. These variables are not restrictive; the data base is easily manipulated to compute population estimates for other values.

Findings

The Northeast had the largest estimated number (4258) and percent (60%) of lakes with ANC ≤ 200 μequiv/L. Florida (subregion 3B) was estimated to have the greatest number (463) and highest proportion (22%) of lakes with ANC ≤ 0. The Northeast was estimated to have 326 lakes (4.6%) with ANC ≤ 0. In the Upper Midwest, 1.7% (148) of the lakes had ANC ≤ 0 and 41.4% (3518) had ANC ≤ 200 μequiv/L. No acidic lakes were found in the Southern Blue Ridge (subregion 3A), but more than half (54.6%) of the lakes were estimated to have ANC ≤ 200 μequiv/L.

In the Northeast only 3.4% (240) of the lakes had pH ≤ 5.0, but at pH ≤ 6.0 this estimate increased to 12.9%. This region had the highest number of lakes (916) and the largest surface area (25,800 ha) estimated to have a pH ≤ 6.0. In the Upper Midwest, less than 10% (818) of the lakes had pH ≤ 6.0, and 1.5% (130) of the lakes had pH ≤ 5.0. The lakes in the Southern Blue Ridge were estimated to have only one lake with pH ≤ 6.0. Florida had the greatest percentage (32.7%) of lakes with pH ≤ 6.0, but this was a smaller estimated number (687) than in the Northeast. Florida had the largest percentage (12.4%), number (259), and surface area (7936 ha) of lakes with pH ≤ 5.0. To put these numbers in perspective, only 1% of the lakes in the West, a region receiving low levels of acidic deposition compared with the East, had pH ≤ 6.0 (*11*).

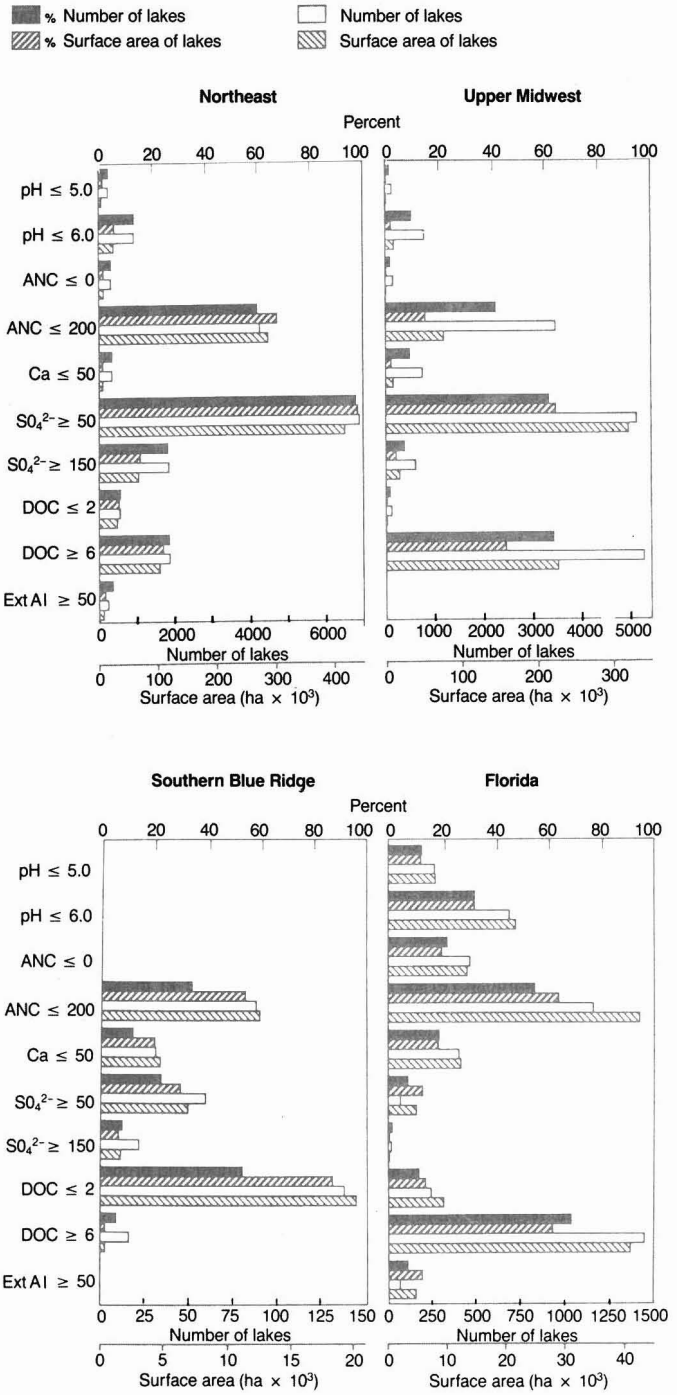
Sulfate values were by far the highest in the Northeast, where 97.3% and 26% of the lakes were estimated to have sulfate ≥ 50 μequiv/L and ≥ 150 μequiv/L, respectively. Sulfate values in Upper Midwest lakes were second-highest in this survey; 61.1% of the lakes were estimated to have sulfate ≥ 50 μequiv/L, and 7% were estimated to have sulfate ≥ 150 μequiv/L. In both of the Southeast subregions, less than 25% of the lakes were estimated to have sulfate ≥ 50 μequiv/L. By comparison, in the Western Lake Survey (*11*) it was found that only 13.5% of the lakes had sulfate ≥ 50 μequiv/L in this region of low SO_4^{2-} deposition.

Florida was estimated to have the greatest percentage (19.2%) of lakes with calcium ≤ 50 μequiv/L, whereas the Upper Midwest was estimated to have the greatest number of lakes (776 or 9.1%) in this category. In subregion 3A, an estimated 12% (31) of the lakes had calcium ≤ 50 μequiv/L. In the Northeast, 359 lakes (5.1%) had calcium ≤ 50 μequiv/L.

Often used as an indication of organic acidity, dissolved organic carbon was highest in the surface waters of

FIGURE 4

Data on lakes in the Eastern Lake Survey–Phase I[a]



[a]Includes data on percent number of lakes, percent surface area of lakes, number of lakes, and surface area of lakes. These data represent regional estimates of lake populations (4 ha < surface area < 2000 ha). Note that the scales for number of lakes and surface areas are not the same among regions.

Florida, where 68.9% of the lakes were estimated to have DOC ≥ 6 mg/L, although the Upper Midwest had the most lakes estimated to fall in this DOC category, 5351 (62.9%). The Northeast was estimated to have the greatest number (572 or 8.1%) of low-DOC (≤ 2 mg/L) systems, but the Southern Blue Ridge lakes were estimated to have the greatest proportion (53.6%) of these low-DOC lakes. Acidic lakes in the Northeast have been shown to be low-DOC systems (*30*). Other regions showed a greater influence of organics on the acidic lakes (*30*).

Some aluminum species have been shown to be toxic to some fish species (*31*), and aluminum was measured here as an indication of the habitability of waters to fish. The highest extractable aluminum values were found in the Northeast, predominantly associated with lakes having pH ≤ 6.0, where 5.2% or 237 of the clear-water lakes were estimated to exceed 50 μg/L. These estimates are reported for clear-water lakes only (i.e., those lakes with true color < 30 platinum cobalt units [PCU]) because in the presence of organic carbon (i.e., high color), aluminum is chelated and its toxicity to fish declines. The Upper Midwest and the Southern Blue Ridge had virtually no lakes with extractable aluminum in excess of 50 μg/L. Lakes in Florida had 7.4%, or an estimated 69 lakes, with extractable aluminum > 50 μg/L.

Implications

One way to measure the success of the lake survey is to evaluate its contributions to our understanding of acid deposition effects. Prior to the survey, scientists had a clear understanding that acidic lakes were present in most of the areas sampled. However, this survey provided regional estimates of the number, area, and location of these lakes within specified levels of confidence. Manuscripts by Brakke et al. (*32*) and Eilers et al. (*33*) discuss the characteristics of lakes in the Northeast and Upper Midwest in greater detail. Furthermore, Florida has been shown to have a surprisingly high percentage of acidic lakes (22%). This finding presents a challenge to the research community to explain why an area receiving only moderate loadings of sulfur contains the highest percentage of acidic lakes in the United States. This paradox is examined further in the manuscript on lakes in the Southeast (*34*). Because the chemical characterization of the lakes was relatively complete, this survey provides a first-time capability for assessing the ionic composition of acidic and low-ANC lakes in areas of greatest interest.

These new data make it possible to explore the importance of organic acids to the current status of lakes (*35*) and to test the hypothesis of regional-scale lake acidification caused by neutral salts (*36*). The complete ionic characterization also makes it possible to apply empirical models to evaluate lake acidification associated with loadings of sulfate deposition (*37*). The survey design was not optimized for analysis of fine-scale spatial patterns in lake chemistry. However, poststratifying the data into various geographic units (*32–34*) provides a clearer understanding of the physiographic factors associated with the distribution of low-ANC lakes. The problems in evaluating spatial patterns caused by use of unequal weighting among strata are currently being addressed in the Adirondacks with approaches that can be applied to other areas sampled in Phase I of the Eastern Lake Survey.

The survey represents a major advance in our understanding of the current status and extent of acidic and low-ANC lakes in the eastern United States. However, it does not provide answers to all aspects of descriptive lake chemistry. Small lakes (generally those < 4 ha and up to about 10 ha) are not included or are poorly represented in the design because a consistent set of large-scale maps for the study regions do not exist. This was not a problem for the Western Lake Survey, in which lakes as small as 1 ha could be represented using 1:100,000-scale maps (*18*). Surveys of small lakes are currently underway in several areas of the Northeast and will provide an opportunity to supplement the Eastern Lake Survey–Phase I estimates of acidic lakes.

The Phase I survey was conducted in the fall, and estimates of the number of acidic lakes are lower than what we expect to observe in the spring samples collected for Phase II of the survey. Furthermore, nitrate and aluminum concentrations are expected to be higher in the spring than those observed in the fall survey. The survey was therefore designed to incorporate seasonal variability into revised estimates for the number and properties of acidic lakes.

Because it provides a "snapshot" of lake chemical attributes, the data collected for Phase I can be extremely useful in estimating the status and extent of chronic regional acidification of lakes. Furthermore, the flexible statistical design permits extrapolation from sampled lakes to a defined population or any inclusive subpopulation of interest (e.g., high-elevation, acidic, or seepage lakes). Additional interpretations of these data—other than the regional results presented here—have already been made. For the first time in North America, limnological investigations can be quantitatively interpreted on a regional scale beyond the sample lakes themselves.

In other surveys, the design often becomes expendable upon completion. However, we view the National Surface Water Survey design as a suitable framework for additional applications. Resurveys of these lakes may be an excellent way to document future chemical changes in surface water chemistry. Other environmental issues, such as nutrient enrichment, may also be evaluated using the sampling frame developed for the Eastern Lake Survey.

Acknowledgment

The dedication and assistance of EPA regional personnel, private contractors, colleagues, and state representatives in planning and implementing this study are gratefully acknowledged. The scientific contribution of our colleague Joseph M. Eilers was instrumental in all aspects of data base design, analysis, and interpretation. The effort and expertise of J. M. Omernik, P. Kanciruk, K. Thornton, E. P. Meier, R. E. Crowe, M. D. Best, and P. Kellar are appreciated. The research described in this article was funded as part of the National Acid Precipitation Assessment Program by the U.S. Environmental Protection Agency. This research is a contribution from the National Surface Water Survey of the EPA Aquatic Effects Research Program. It has been subjected to the agency's peer and administrative review and approved for publication.

This article has been reviewed for suitability as an *ES&T* feature article by Joseph DePinto, Clarkson University, Potsdam, N.Y. 13676; and by Charles Driscoll, Syracuse University, Syracuse, N.Y. 13210.

References

(1) *"Proceedings of the International Conference on Ecological Impact of Acid Precipitation";* Drablos, D.; Tollan, A., Eds.; Sandefjord, Norway, March 1980.

(2) National Academy of Sciences (NAS). *Atmospheric-Biosphere Interaction: Toward a Better Understanding of the Ecological Consequences of Fossil Fuel Combustion;* National Academy Press: Washington, D.C., 1981; pp. 1–263.

(3) *Acidification in the Canadian Aquatic Environment;* National Research Council Canada; NRCC Publication No. 18475, 1981; pp. 1–369.

(4) "U.S./Canada Memorandum of Intent on Transboundary Air Pollution: Impact Assessment, Working Group I"; final report, January 1983.

(5) Schofield, C. L. *Ambio.* **1976,** *5,* 228–30.

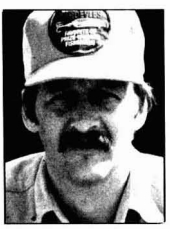
(6) Davis, R. B. et al. *Verh. Int. Ver. Limnol.* **1978,** *10,* 532–37.

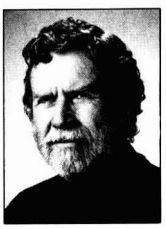
(7) *Acid Deposition Long-Term Trends;* National Research Council; National Academy Press: Washington, D.C., 1986; pp. 1–506.

(8) Linthurst, R. A. et al. In *Characteristics of Lakes in the Eastern United States: Population Descriptions and Physico-Chemical Relationships;* EPA600/4-86/007a, U.S. Environmental Protection Agency: Washington, D.C., 1986; Vol. 1, pp. 1–136.

(9) Overton, W.S. et al. In *Characteristics of Lakes in the Eastern United States: Lakes Sampled and Descriptive Statistics for Physi-*

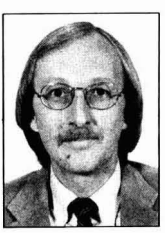
cal and Chemical Variables; EPA/600/4-86/007b, U.S. Environmental Protection Agency: Washington, D.C., 1986; Vol. 2, pp. 1–374.
(10) Kanciruk, P. et al. In *Characteristics of Lakes in the Eastern United States: Data Compendium of Site Characteristics and Chemical Variables;* EPA/600/4-86/007c, U.S. Environmental Protection Agency: Washington, D.C., 1986; Vol. 3, pp. 1–439.
(11) Landers, D. H. et al. In *Characteristics of Lakes in the Western United States: Population Descriptions and Physico-Chemical Relationships;* EPA600/3-86/054a, U.S. Environmental Protection Agency: Washington, D.C., 1987; Vol. 3, pp. 1–293.
(12) Eilers, J. M. et al. In *Characteristics of Lakes in the Western United States: Data Compendium for Selected Physical and Chemical Variables;* EPA600/3-86/054b, U.S. Environmental Protection Agency: Washington, D.C., 1987; Vol. 2, pp. 1–425.
(13) Eilers, J. M. et al. *Verh. Int. Ver. Limnol.* (in press).
(14) Newell, A. D. In *Acid Rain: Scientific and Technical Advances;* Perry, R.; Harrison, R. M.; Bell, J.N.B.; Lester, J. N., Eds; Selper: London, 1987; pp. 353-56.
(15) Omernik, J. M.; Powers, C. F. *Annals of the Association of American Geographers,* **1983,** *73,* 133–36.
(16) Omernik, J. M.; Kinney, A. J. "Total Alkalinity of Surface Waters: A Map of the New England and New York Region"; EPA-600/D-84-216, U.S. Environmental Protection Agency: Corvallis, Ore., 1985.
(17) Omernik, J. M.; Griffith, G. E. *Environ. Manage.* **1986,** *10,* 829–39.
(18) Omernik, J. M. "Total Alkalinity of Surface Waters: A Map of the Appalachian Region (draft)"; U.S. Environmental Protection Agency: Corvallis, Ore., 1985.
(19) Blick, J. D.; Overton, W. S.; Messer, J. J.; Landers, D. H. *Lake and Reservoir Management* **1987,** *3,* 470–75.
(20) Driscoll, C. T.; Schafran, G. C. *Nature* **1984,** *310,* 308–10.
(21) Morris, F. A.; Peck, D. V.; Bonoff, M. B.; Cabble, K. J. "National Surface Water Survey, Eastern Lake Survey-Phase I, Field Operations Report"; EPA-600/4-86/010, U.S. Environmental Protection Agency: Las Vegas, Nev., 1986.
(22) Hillman, D.C.J.; Potter, J. F.; Simon S. J. "National Surface Water Survey, Eastern Lake Survey–Phase I, Analytical Methods Manual"; EPA600/4-86/009, U.S. Environmental Protection Agency: Las Vegas, Nev., 1986.
(23) Drouse, S. K.; Hillman, D.C.J.; Creelman, L. W.; Simon, S. J. "National Surface Water Survey, Eastern Lake Survey–Phase I, Quality Assurance Plan"; EPA600/4-86/008, U.S. Environmental Protection Agency: Las Vegas, Nev., 1986.
(24) Best, M. D.; Drouse, S. K.; Creelman, L. W.; Chaloud, D. J. "National Surface Water Survey, Eastern Lake Survey–Phase I, Quality Assurance Report"; EPA600/4-86/011, U.S. Environmental Protection Agency: Las Vegas, Nev., 1986.
(25) Kanciruk, P.; Olson, R. J.; McCord, R. A. In *Research Data Management in the Ecological Sciences;* Michener, W. K., Ed.; University of South Carolina Press: Columbia, S.C., 1985; pp. 193–207.
(26) *The Statistical Analysis System;* SAS Institute: Cary, N.C., 1982.
(27) Overton, W. S. "Working Draft, Analysis Plan for the EPA Eastern Lake Survey"; Technical Report 113; Oregon State University: Corvallis, Ore., pp. 1–46.
(28) Overrein, L. N.; Seip, H. M.; Tollan, A. "Acid Precipitation: Effects on Forest and Fish"; SNSF final report: Oslo, 1980; pp. 1–175.
(29) Schindler, D. W. et al. *Science,* **1985,** *228,* 1395–1401.
(30) Landers, D. H. et al. *Verh. Int. Ver. Limnol.,* in press.
(31) Baker, J.; Schofield, C. *Water, Air, Soil Pollut.* **1982,** *18,* 289–309.
(32) Brakke, D. F.; Landers, D. H.; Eilers, J. M. *Environ. Sci. Technol.* **1988,** *22,* 155–63.
(33) Eilers, J. M.; Brakke, D. F.; Landers, D. H. *Environ. Sci. Technol.* **1988,** *22,* 164–72.
(34) Eilers, J. M.; Landers, D. H.; Brakke, D. F. *Environ. Sci. Technol.* **1988,** *22,* 172–77.
(35) Kramer, J. R.; Davies, S. S. *Environ. Sci. Technol.* **1988,** *22,* 182–85.
(36) Sullivan, T. J. et al. *Environ. Sci. Technol.* **1988,** *22,* 185–90.
(37) Wright, R. F. *Environ. Sci. Technol.* **1988,** *22,* 178–82.

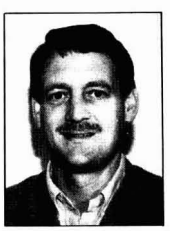




Dixon H. Landers *(l) is research director of EPA's National Surface Water Survey at the EPA Environmental Research Laboratory in Corvallis, Ore. He is a limnologist whose past work has included investigations of nutrient and elemental cycling in low-alkalinity and acidic lakes. He recently coordinated and contributed to interdisciplinary research efforts to evaluate regional acidification of surface waters in the United States.*

W. Scott Overton *(r) is a professor in the department of statistics at Oregon State University. He has had experience in designing sampling strategies for a variety of environmental and ecological problems.*





Rick A. Linthurst *(l) is program director of EPA's aquatic effects research program at the Environmental Monitoring Support Laboratory. He is an environmental scientist responsible for several of EPA's projects focused on regional assessment and interpretation of the effects of acid precipitation on surface waters.*

David F. Brakke *(r) is professor and director of the Institute for Watershed Studies at Western Washington University. His research has included interpretation of paleolimnological data for the effects of acidification, analysis of chemical status of lakes in the Pacific Northwest, and regional assessments of lake acidification in the United States and Norway.*

Receive your personal subscription to C&EN as part of your membership

when you join ACS

The subscription to C&EN you now pay $40 a year for will be yours as part of your membership, when you join ACS.

And that's only one of the benefits!

Consider a few of the others:

- National Meetings—at special member rates
- Local and Regional meetings to meet your colleagues, learn what is going on in your area
- Divisional Meetings and publications to keep pace with your specific disciplines
- Professional Development Courses at special member rates
- Substantial member savings on 22 ACS journals and periodicals
- Impressive insurance and retirement benefits

Find out how to receive your **personal subscription to C&EN** along with other member benefits. Write, use coupon below, or **CALL 1-800-ACS-5558**

American Chemical Society
1155 Sixteenth Street, N.W.
Washington, DC 20036

YES!
Please send me details on how to receive my personal subscription to C&EN as well as other advantages of membership in ACS

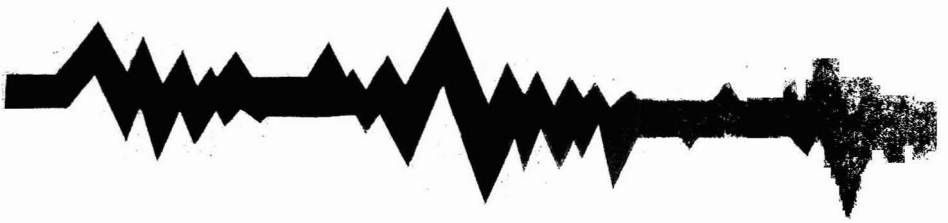
Name _____

Address _____

City _____

State, ZIP _____

Hazardous organic compound analysis



Decision-makers and site managers are hampered by lost analytical data and misinformation on analyses

Kathleen C. Swallow
Neil S. Shifrin
Gradient Corp.
Cambridge, Mass. 02138

Philip J. Doherty
Energy and Environmental Engineering, Inc.
Somerville, Mass. 02143

The assessment of the source, extent, and nature of hazardous-waste contamination relies on sophisticated chemical analyses to identify and quantify a wide range of pollutants. For organic compounds, these analyses are most often performed using combined gas chromatography/mass spectroscopy (GC/MS). These GC/MS data are used by environmental scientists and engineers for site evaluations, design of ongoing monitoring programs, and remedial activities.

Once tabulated in engineering reports or stored in data bases, the data are often reviewed interpretively but rarely scrutinized to determine if compounds have been accurately identified or quantified. It is usually assumed that this has been done in the laboratory by the analyst. In reality, GC/MS data are most often produced using highly automated instruments with very little intervention by experienced spectroscopists. With the exception of priority pollutants, qualitative and quantitative inaccuracy is a widespread problem in environmental chemical data.

This problem has become clearly evident in our work over the past several years in hazardous-waste site assessment and remedial design. Our work has involved interpreting data for both private and government clients to determine the transport and fate of chemicals in the environment. Most of the data we reviewed were generated for site owners by commercial laboratories who performed the standard priority pollutant scans.

For every case in which we reviewed the raw data (including chromatograms and mass spectra) we found one or both of the following problems for nonpriority pollutants: *misinformation*—incorrect compound identification due to poorly automated mass-spectral matching and inadequate data review, and *lost data*—observed compounds, sometimes the predominant ones, reported as "unknowns" to eliminate incorrect compound identification while minimizing time demands on the analyst.

If these problems are undetected or ignored, the results may be faulty or limited conclusions regarding site contamination and inappropriate remedies. The most notable case in our experience involved a RCRA (Resource Conservation and Recovery Act) facility located adjacent to a CERCLA (Comprehensive Environmental Response Compensation and Liability Act) site. Samples from each of the sites contained virtually identical priority pollutants.

The accurate identification of nonpriority pollutant compounds and the subsequent interpretation of compound distribution patterns and concentration gradients were critical to distinguishing between potential leakage from the RCRA facility and known leakage from the CERCLA site. This was accomplished only after the raw data was reinterpreted in detail by a mass spectroscopist who identified many of the misidentified compounds and unknowns.

The roots of this problem lie in the difficulties inherent in developing standardized GC/MS methods for universal application to complex and highly variable environmental samples. To be truly versatile, such analyses must be broad in scope yet sensitive and reproducible. The EPA attempted to achieve such versatile, standardized methods by focusing on a limited number of organic compounds, the priority pollutants, which represent a cross section of contaminants found in environmental samples.

Although originally developed for water and wastewater samples (*1, 2*), the priority pollutant methods were adopted with minor modifications for use in hazardous-waste analysis (*3, 4*). To address the nationwide need for analyzing a tremendous number of samples quickly, instrument manufacturers produced GC/MS systems that could be marketed as turnkey units to perform highly automated analyses. The automated analytical procedures rely heavily on the GC/MS instrumentation linked to dedicated computers. Compound identities and concentrations can be determined with very little need for the expertise or scientific judgment of the analyst.

The automated instruments produce reasonably high-quality data for the priority pollutants and for the slightly ex-

0013-936X/88/0922-0136$01.50/0 © 1988 American Chemical Society

panded EPA Contract Laboratories Program Hazardous Substance List because analytical standards (referred to as "external standards") are used to confirm compound identities and to perform accurate quantitation (*5*). Unfortunately, these instruments are not as successful in identifying and quantifying unknown, nonpriority pollutant compounds.

This is a serious problem because nonpriority pollutants are predominant constituents of most samples taken from hazardous-waste sites (*6–8*). The identification of such compounds requires highly skilled interpretation of mass-spectral and chromatographic data—a job for which today's instruments and computer programs remain inadequate.

In an effort to obtain high-quality chemical data on a national scale, regulatory agencies have developed standardized methods for sample handling and preparation as well as standardized instrument-operating conditions. Elaborate quality assurance and quality control (QA/QC) procedures specify and require the use of field blanks, laboratory blanks, surrogate spikes, matrix spikes, duplicate samples, and internal standards to assure that performance standards are met (quality control). In addition, comprehensive documentation and scientific review are required to assure not only that QC procedures were followed but that their results were acceptable (quality assurance). These procedures are aimed at guaranteeing that samples are representative, that priority pollutants are measured accurately within established limits of precision, and that cautious attempts are made at identifying nonpriority pollutants.

Most laboratories adhere reasonably well to all of these procedures. However, these general QA/QC procedures are laboratory housekeeping issues and are not the topic of this article. They have little or no impact on the correct identification of nonpriority pollutants.

Although these problems are familiar to most analytical chemists, environmental decision-makers also need to understand them in order to use properly the vast amount of chemical data generated on the nation's hazardous-waste sites.

Fundamentals of analysis

Figure 1 shows the main components of a GC/MS system. A mixture of chemicals is separated into its individual components as it travels through the column in the gas chromatograph. The time a compound spends on a specific column, the retention time, is reproducible and characteristic of the compound. The GC detector generates an electrical signal, which is displayed as a peak on a recorder, as a compound passes through. The GC detector gives no further information about the eluting chemical, except for its retention time.

For samples in which the components of the mixture are known, the retention time can be used to identify each component as it elutes by comparing it to the retention time of a standard run on the same instrument. If the components are unknown, however, retention time alone cannot be used to identify them unequivocally.

Combining a mass spectrometer with a gas chromatograph adds the ability to identify compounds as they elute from the GC column. In the mass spectrometer operating in the electron-ionization mode, the eluting compound is fragmented into a set of ions of various masses. The fragmentation of a molecule is not a random process, but follows readily discernible and reproducible patterns. The fragments are directed through a mass analyzer and detected sequentially as a function of their mass-to-charge ratios. The resulting mass spectrum is equivalent to a fingerprint of the molecule and can be used to determine its structure and identity.

The GC/MS systems used in routine environmental sample analysis are equipped with computer data systems and extensive libraries of reference mass spectra to identify nonpriority pollutant compounds. They can perform in a fully automated mode to separate the components of a mixture, generate a mass spectrum for each component, search the library for a matching spectrum, make an identification, and perform a quantitative analy-

FIGURE 1
Components of a GC/MS system

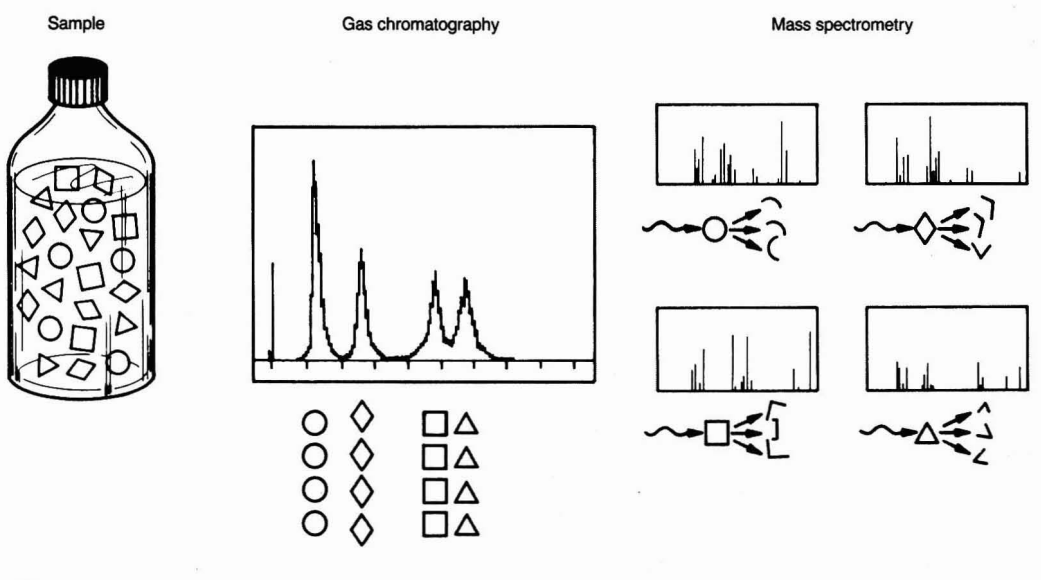
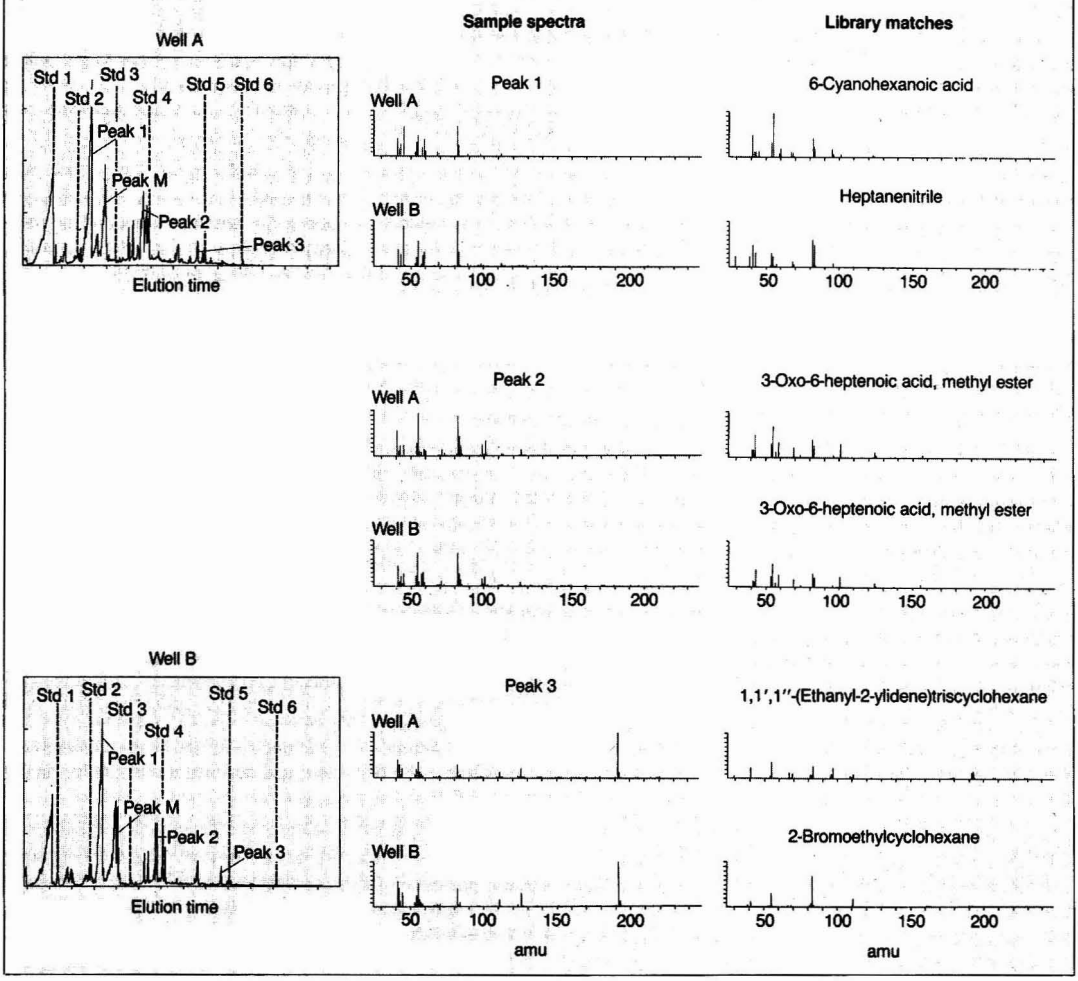


FIGURE 2
Analytical results for samples from two monitoring wells at the same site



sis. The standardized methods include instrument-tuning requirements designed with ensure that each mass spectrometer will generate mass spectra comparable with the library spectra and with each other (*9*).

The problems

Figure 2 shows the results of an actual automated environmental sample analysis performed on two samples from two different groundwater-monitoring wells at a hazardous-waste site. These examples are from the semivolatile fraction of the standardized priority pollutant analytical scheme. Only two priority pollutants were identified in these samples, both eluting before the large peaks at the beginning of the chromatograms for Wells A and B and not present in sufficient concentration to be visible on these chromatograms.

The two chromatograms show similar elution patterns and relative retention times for the remaining nonpriority pollutant compounds, suggesting that the components of the two samples are similar. Mass spectra for peaks 1, 2, and 3 are given for each sample and support the interpretation that the two samples contain the same components; however, the results of the computerized library matches for the two samples are startlingly inconclusive. Only one compound, indicated by peak 2, was identified as the same compound in both well samples. The other two compounds were identified as different chemicals in each sample. Although both samples from wells A and B yielded the same mass spectra, only seven of the fourteen paired peaks from their chromatograms were matched by the computer with the same library spectrum. Most of the computer matches were poor as illustrated by peak 3 in Figure 2. The large ion at *m/z* 192 in the unknown spectrum is completely missing from both library-matched spectra, and the overall fragmentation patterns are generally dissimilar.

The compound identified by peak 1 in Figure 2, a major component of samples taken from this site, was found in 43 of the 72 wells sampled and produced the largest peak in 21 of the chromatograms. The computer-matching program identified this component as eight different compounds in 13 of the wells, although the actual mass spectra are virtually identical except for small differences that can be attributed to background interferences. The library spectra with which the sample spectra were matched were all very different

and produced a tabulated set of data consisting of a seemingly random spatial distribution of compounds even though a clear pattern truly existed.

An issued report on this site merely tabulated the compounds incorrectly identified by computer matching. The recipient of this report therefore believed that the samples were dissimilar. Essentially all of the information on this site was lost until a review of the raw data uncovered numerous recurring compounds that produced strikingly similar elution patterns for the samples and reproducible mass spectra, which indicated that the same compounds were present in most of the wells. A clear pattern of contaminant transport and fate emerged that had previously been obscured.

To produce a library match for an unknown spectrum, the computer compares the masses and relative abundance of the ions in the sample spectrum to the masses and relative abundance of the ions in candidate library spectra. The matches are scored. If the scores are high enough to justify confidence that it is valid, the best match is reported. Other high-scoring matches are usually given as second and third alternatives. Small differences in the sample spectra can change the relative scores of closely related library spectra and therefore change the order of the candidates.

Even if the matches are reproducible and high-scoring, however, they often are poor. A manual review of data generated by the computerized library-matching routine usually results in rejection of most of the tentative identifications. As a result, many compounds are reported as unknowns. For environmental samples in which most of the constituents are not priority pollutants, very little information about the chemical composition of the sample is generated despite this costly and time-consuming analysis.

In some cases a far worse problem exists: The manual review of the data is not performed by an experienced chemist, and laboratory reports are released containing the computer-matched, tentative identifications that are often incorrect. Several other problems result from applying a standardized and automated method to environmental samples that are complex and variable at best.

Unresolved Multiplets. The peaks marked "M" on the chromatograms for Wells A and B in Figure 2 are examples of multiplets, partially resolved compounds that elute together. Figure 3 shows the mass spectra from these multiplets and corresponding library matches. Two mass spectra were generated for the multiplet in Well A and one for the multiplet in Well B.

The spectra from Well A have some common ions, but each also has unique ions. There are at least two different compounds coeluting in this peak. The corresponding peak from Well B gives a spectrum with some characteristics of each—again, probably a mixture.

All three library matches for these spectra are different. Mass spectra obtained from multiplet peaks frequently contain a mixture of ions derived from more than one compound. Cleaner spectra can be obtained by subtracting the individual component spectra from each other. In this way the multiplet can be resolved and each component can be identified. Without this resolution the information stored in the multiplet is lost, and compounds are likely to be misidentified.

Multiplet resolution is rarely performed in the automated laboratory. Fine-tuning of the analytical conditions requires a chemist's judgment and additional instrument adjustments, both of which increase the time and cost of analysis. It is impractical to include such procedures in the standardized methods used for broad screening programs. In fact, most laboratories simply have too many samples to afford the time.

Interferences. Figure 4 shows a common error resulting from background interference. The large "bump" in the baseline of this chromatogram is a hydrocarbon envelope. It occurs when the sample contains a complex mixture of hydrocarbons such as those found in petroleum products and residues. The typical gas chromatograph does not completely resolve the components of such mixtures into individual peaks but spreads them across a range of retention times as an undifferentiated mass.

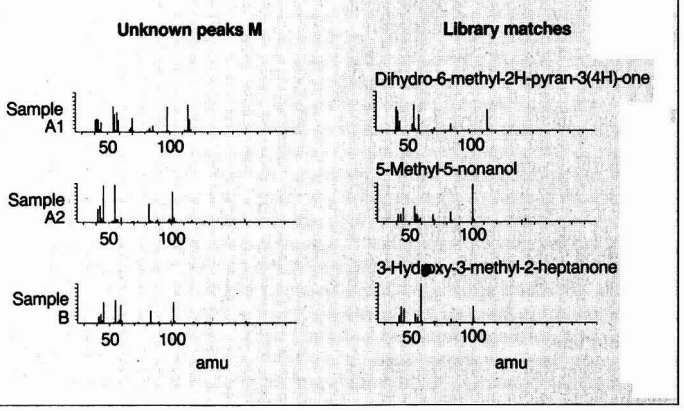
The peaks superimposed on the envelope may be part of the hydrocarbon component of the sample, or they may be unrelated compounds that happen to elute at the same time as the envelope. The mass spectra obtained from such samples are usually readily identifiable as hydrocarbon spectra, which have a characteristic fragmentation pattern. If another compound is coeluting with the hydrocarbon envelope, it may contribute some extraneous fragments to the spectrum, but generally the hydrocarbon pattern is predominant.

It is very difficult to correctly identify hydrocarbons on the basis of mass spectra alone, as the fragmentation patterns are similar for many different hydrocarbons. In Figure 4, for example, three different peaks have been identified as the same large hydrocarbon; this cannot be correct. Although obvious to scientists familiar with GC/MS analysis, this problem produces confusion when data is presented to users unaware of the difficulties with differentiation of hydrocarbon spectra. It is especially mystifying when the quantitative data on a sample indicates that the same compound has three different concentrations.

Sample Dilution. Mass spectrometers are sensitive instruments and cannot tolerate large quantities of material. To protect the instruments, samples often are first screened by GC alone to determine the concentration of the components and the need for sample dilution prior to GC/MS analysis.

Frequently a few compounds are present in much higher concentration than the others, although many compounds may be present in lower, yet significant, concentrations. It is possible that one or more of the less concentrated compounds may be more important or toxic than the more concentrated

FIGURE 3
Spectra for multiplet peaks in chromatograms for Wells A and B



compounds, but after dilution of the sample to accommodate the very high concentration compounds, the less concentrated compounds may no longer be detectable by the instrument.

Much of the valuable information about the sample will be lost in the form of numerous "nondetects" if the diluted sample alone is analyzed. With care, the more concentrated sample can be analyzed as well as the diluted one.

Quantitation

Quantitative analysis is based on the use of a set of internal standards which are usually deuterated or fluorinated analogues of the priority pollutants. For each priority pollutant a response factor relative to an appropriate internal standard is experimentally determined using a set of known external standards of the priority pollutants themselves. Subsequent analyses are performed by adding a known concentration of the internal standards to the samples. A mathematical proportionality between the instrument's responses to the unknown and to the internal standard, corrected by the relative response factor, is used to calculate the concentration of the unknown.

For priority pollutants the accuracy should be excellent; for nonpriority pollutants it is inherently poorer. Because external standards are seldom used for nonpriority pollutants a relative response factor of 1 is assumed. Considering that for priority pollutants the relative response factors range from 0.05 to 10, an error of more than 1 order of magnitude can result from this assumption alone.

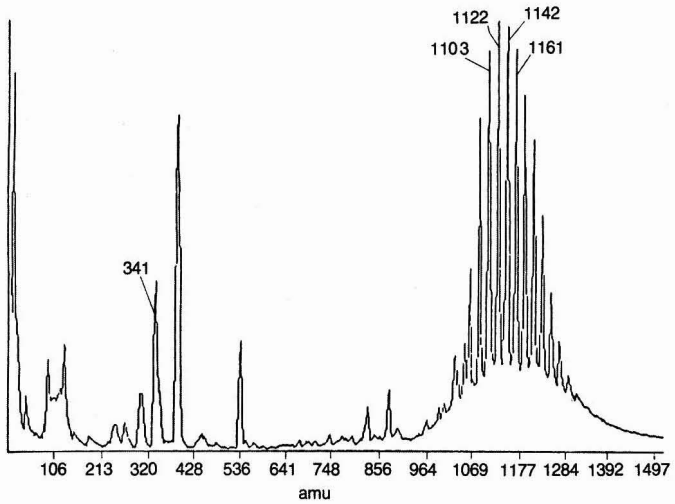
The potential error is compounded when other sources of error, such as coelution of analytes and internal standards, are considered. In addition, the use of internal standards that have properties similar to the priority pollutants is not necessarily optimum for nonpriority pollutants and may contribute substantially to the overall error. At best the analysis of nonpriority pollutants by this technique is semiquantitative and can be extremely misleading.

These examples illustrate the danger in relying on heavily automated systems to perform the complex analyses that have, until recently, been considered the domain of research scientists. A properly designed and executed analysis requires a fundamental understanding of the strengths and limitations of the technique and the ability to tailor the method to the sample. These factors are lost when a computer replaces the chemist.

The solutions

At present there is no complete solution to the problem outlined above. The tremendous number of environmental samples requiring analysis demands increased reliance on automation, but the result is reduced accuracy. Some positive steps can be taken, however.

FIGURE 4
Background interference in a gas chromatogram



Scan no.	Computer library choices
341	3-bromo-1,1,1-trichloropropane
1103	docosane
1122	5-ethyl-5-proplyundecane
1142	5-ethyl-5-proplyundecane
1161	5-ethyl-5-proplyundecane

Reference Standards or Alternatives. Once the mass-spectrum has been analyzed and a tentative identification of a compound has been made, it is necessary to verify that the retention time of the compound matches that of the unknown in the sample. To do this, a known standard is prepared and analyzed. If both the retention times and the mass spectra match, the unknown has been identified.

For the priority pollutants, retention times are stored in the computer along with the mass spectra. Both retention time and mass-spectral matches are required for verification of the compound identification. Consequently, analyses for priority pollutants generally are reliable.

For the nonpriority pollutants the retention time is rarely verified. Frequently the matched spectrum is that of a rare compound and no known standard is available. There are few sources of standards for some nonpriority pollutants. But even if standards were available, this time-consuming process would severely limit the number of samples a laboratory could analyze completely.

For ongoing monitoring programs at sites where the major contaminants are nonpriority pollutants, however, the extra effort is warranted. It has been demonstrated that retention-time verification can significantly improve the quality of tentative identifications (*8*). Packages are already available to incorporate retention data into the library search algorithm, which could prove invaluable for site-specific libraries.

Without access to known retention times for these compounds, the analyst should use his or her knowledge of chemistry and the principles of gas chromatography to eliminate obvious errors. If a group of compounds in a homologous series (e.g., straight-chain hydrocarbons with the number of carbon atoms increasing sequentially or chlorinated aromatics with the number of chlorine atoms increasing sequentially) appears in a sample, the retention times should increase as the size or weight of the molecule increases.

If the tentative identification of peaks results in a homologous series that is out of sequence, it is obviously incorrect. Matches with inorganic compounds should be suspect. Most inorganic compounds are not very soluble in the organic solvents used to extract samples and would not elute from the gas chromatograph. Compounds that are known to be low-boiling should not

elute after compounds that are known to be high-boiling.

Unfortunately, glaring errors such as these abound in the lists of tentatively identified compounds produced by automated GC/MS. Once they are included in a final report they make their way into secondary reports and computerized data bases where they are safe from further scrutiny. Not only has important information been lost, but misinformation has been created.

Expanded Data Storage. One inherent weakness in many older computerized GC/MS systems that restricts their ability to produce credible results is the limited amount of fragmentation data stored for any particular compound. The fragmentation patterns for molecules contain much useful information about their structure, and the analyst can use them in a process similar to putting together a puzzle to reconstruct the original structure of the molecule. Certain fragments or patterns of fragments are strongly associated with heteroatoms or functional groups.

For example, doublet fragments two mass units apart and at a 3:1 ratio are associated with the two stable isotopes of chlorine. Some computers have limited storage space, however, and in an effort to maximize the number of compounds available in the library, only a set of the most abundant ions from each mass spectrum were stored.

Unfortunately, the missing pieces of the puzzle are often some of the most useful. The chlorine doublets for polychlorinated compounds are sometimes missing because one of the fragments is less abundant. The molecular ion, which would give the molecular weight of the compound, is often present at a very low intensity and is therefore not stored. Minor fragments that would yield a recognizable pattern are dropped. Data storage streamlining undermines the power of the technique in the automated mode.

Improvements in data systems have alleviated this problem in newer instruments, but data generated on older instruments are still subject to these flaws. The analyst can often detect structural clues in a mass spectrum that will lead to improved compound identification or at least rejection of an obviously incorrect identification.

Improved Human Scrutiny. Routine quality assurance procedures specify the use of proper internal standards, surrogates, blanks, and replicates and also define procedures for instrument tuning or calibration. When both spectral match and retention-time agreement are available for identification, these procedures ensure a high degree of reliability in the data. They do nothing, however, to solve any of the problems with tentative identifications of nonpriority pollutants. For unknown compounds, the skill and judgment of the analyst must be applied in reviewing the data.

A qualified analyst can find and eliminate obvious errors in compound identification and make the necessary procedure modifications to increase the number of good identifications. The analyst can detect patterns in the gas chromatograms from a set of related samples and focus on identifying those compounds that appear to be most abundant.

When library matching cannot identify a compound, the spectrum can be analyzed and interpreted by a spectroscopist. None of the procedures can be standardized; they require and rely on skill and judgment, yet they are absolutely essential in the proper use of the powerful analytical methods that we have at our disposal. Without them most tentative identifications are wasted efforts.

Improved Systems and Data Management. Improvements in hardware and software have increased the amount of information that can be stored in libraries. Today, the commercially available libraries in new data systems are derived from the EPA/NIH data base and contain over 42,000 compounds. These libraries are superior to those of a few years ago. However, thousands of compounds with little bearing on environmental issues are included. Inorganic compounds, noble gases, and highly reactive compounds such as arsine are often reported as tentatively identified compounds. At the same time many compounds are reported as unknowns, indicating that a matching spectrum was not found in the library.

Proper identification of the compounds found in environmental samples and inclusion of their spectra in the libraries would greatly enhance the reliability of automated compound identification. As the development of automated systems continues, attention must be paid to correcting the problems we have described. An increase in the quantity of data produced without an increase in the quality will benefit no one.

Improved Site-Monitoring Programs. The discovery of a contaminated site is typically followed by a sampling and analysis program designed to assess the nature and extent of the problem. General screening is always necessary in this phase, and standardized methods are invaluable. Once the preliminary data are collected, however, they should be used to develop analytical schemes tailored to the site.

By studying gas-chromatographic elution patterns, an analyst can determine the number and relative concentrations of the major recurring compounds in the samples. The relative contribution of priority pollutants and nonpriority pollutants to the contaminant load of the sample can be assessed, and the need for enhanced efforts to identify the nonpriority pollutants can be evaluated.

Analysis of the mass spectra for nonpriority pollutants, coupled with background information on the site, can often lead to proper compound identification even if the computer library matches are not accurate. Even without compound identification, spatially or temporally recurring mass spectra can be used to determine trends and patterns of transport and fate. Obvious errors in compound identification can be eliminated.

Follow-up analyses, after the initial screening, should focus on a specific set of compounds and the analytical procedures should be tailored to analyze for them accurately. These site-indicator compounds, the sample collection and preparation methods, and the analytical standards can be chosen based on knowledge of the chemical composition of the samples and their analytical behavior.

The number of samples and the breadth of analyses required to obtain needed information about a site, as well as the associated costs, will probably decrease as the useful information obtained from each sample increases. Although this is a departure from the trend toward more automation and standardization of methods, it recognizes the commonly observed individuality of each hazardous-waste site.

Looking ahead

The first step in solving a problem is to recognize it. The problems cited herein are not exceptional occurrences—they have arisen in almost every project where we have had the opportunity to review the raw chemical data. It might be argued that remedies to these problems are impractical and too costly. In the end, however, incorrect data always prove to be impractical and costly. Without some effort to correct these problems, the data explosion will supply us with unmanageable amounts of data—data of doubtful value—that will do little to help us solve the ever-increasing number of environmental problems.

Some solutions do exist, as shown in Table 1, but more thought must be given to this problem by analytical chemists, instrument manufacturers, and regulatory agencies. EPA is aware of these problems, and many procedures in EPA's contract laboratory pro-

GAIN
The Professional Edge
WITH MEMBERSHIP IN THE AMERICAN CHEMICAL SOCIETY

- Keep up-to-date with weekly copies of *CHEMICAL AND ENGINEERING NEWS*
- Enjoy substantial discounts on subscriptions to ACS's internationally respected, authoritative journals and publications
- Network with your fellow scientists at local, regional and national meetings
- Enhance your career opportunities with ACS employment services
- Save on insurance and retirement plans and tax deferred annuity programs
- Discover the latest advances in your discipline with a first-year-free Division membership

. . . and this is just the beginning.

Learn why 9 out of 10 ACS members renew year after year. Gain the Professional Edge: Join ACS now. For further information write or send the coupon below or call TOLL FREE 1-800-424-6747

American Chemical Society
1155 Sixteenth St., N.W.
Washington, DC 20036

YES! Please send information on the advantages of joining the ACS.

Name _____
Address _____
_____
_____
I am most interested in the following science(s): _____
_____

TABLE 1
Problems and Solutions

Problems	Solutions
Compounds incorrectly identified	Identify recurring elution patterns in sets of samples and concentrate effort on identification of major nonpriority pollutants Verify unknown retention times with known standards Increase human scrutiny—apply chemists' judgment to data review
Poor match of unknown spectrum with library spectrum	Improve environmental spectral libraries Interact with data system to produce better sample spectra before library matching
Sample complexity unsuited to standardized procedures	Use standardized methods mostly for screening, followed by more customized procedures to accommodate nonpriority pollutants

gram (CLP) are aimed at minimizing misinformation (*5*). However, data are lost because many compounds are reported as unknowns. The data user who relies solely on tabular, summarized data must beware.

Newer instruments have more complete spectral information in their files and improved data storage. Historical data and data generated on older instruments are much more likely to contain the errors described above.

It is imperative that all laboratories, whether participating in the CLP or not and regardless of the age of their instrumentation, make an effort to maximize the usefulness and accuracy of the data they produce. This will be accomplished with the proper use of a laboratory's analytical tools and abundant exercise of sound judgment by chemists.

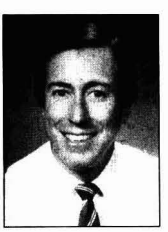
Acknowledgment

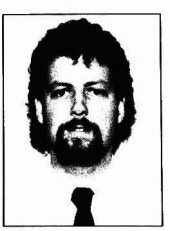
This article has been reviewed for suitability as an *ES&T* feature by Lawrence Keith, Radian Corp., Austin, Tex. 78766; and by Daniel L. Norwood, Analytical and Chemical Sciences, Research Triangle Park, N.C. 27709.

References

(1) *Fed. Regist.* **1979,** *44,* 69464–575.
(2) *Fed. Regist.* **1984,** *49,* 43234.
(3) *Test Methods for Evaluating Solid Waste: Physical/Chemical Methods;* Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency: Washington, D.C., 1980; EPA SW-846.
(4) *Test Methods for Evaluating Solid Waste: Physical/Chemical Methods,* 2nd ed.; Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency: Washington, D.C., 1984; NTIS PB85-10326/XAB EPA SW-864.
(5) U.S. EPA Contract Laboratory Program; "Statement of Work for Organics Analysis Multimedia Multi-Concentration"; U.S. Environmentat Protection Agency: Washington, D.C., 1986; IFB Series, WA-87J001 WA-87J002, WA-87J003.
(6) Donaldson, W. T. *Environ. Sci. Technol.* **1977,** *11,* 348–51.
(7) Shackelford, W. M.; Cline, D. M. *Environ. Sci. Technol.* **1986,** *20,* 652–57.
(8) Shackelford, W. M.; Cline, D. M. *Anal. Chim. Acta* **1983,** *146,* 15–27.
(9) Eichelberger, J. W.; Harris, L. E.; Budde, W. L. *Anal. Chem.* **1975,** *47,* 995–1000.

Kathleen C. Swallow *is an analytical chemist. She received her Ph.D. in analytical chemistry from MIT and her B.S. in chemistry from the University of Richmond. She was assistant professor of chemistry at Wellesley College and later set up and managed several private and industrial laboratories. She is a senior associate at Gradient Corporation, where she works on problems involving hazardous-waste chemistry and data evaluation.*





Neil S. Shifrin *(l) is an environmental engineer with a background in water quality and a cofounder of Gradient Corporation. He has performed numerous hazardous-waste site assessments involving the interpretation of site data and the development of monitoring programs. He received his Ph.D. from MIT and a B.S. in chemical engineering from the University of Pennsylvania.*

Philip J. Doherty *(r) is an anlytical chemist and senior scientist with Energy and Environmental Engineering, Inc. He previously worked as an independent consultant on the quality of environmental analyses and the interpretation of mass-spectra data. Doherty received his M.S. in analytical chemistry and his B.S. in chemistry from Tufts University.*

THE AMERICAN CHEMICAL SOCIETY ANNOUNCES A NEW JOURNAL PUBLISHED BIMONTHLY BEGINNING JANUARY/FEBRUARY 1988

CALL FOR PAPERS

Chemical Research in Toxicology

EDITED BY LAWRENCE J. MARNETT, WAYNE STATE UNIVERSITY
ASSOCIATE EDITOR, PAUL HOLLENBERG, WAYNE STATE UNIVERSITY

An all new international journal for scientists needing the most current chemical research in the highly active field of toxicology.

CHEMICAL RESEARCH IN TOXICOLOGY, the latest ACS journal, promises comprehensive reports in the field. A prestigious editorial advisory board, headed by Lawrence J. Marnett of Wayne State University, will assure expert coverage of all aspects of the molecular basis of toxicology.

Each bimonthly issue will publish full papers, rapid communications, and invited reviews on structural, mechanistic, and technological advances in research concerned with the toxicological effects of chemical agents.

SPECIFICALLY, *CHEMICAL RESEARCH IN TOXICOLOGY* WILL ADDRESS THESE IMPORTANT AREAS OF THE FIELD:

- Structure elucidation of novel toxic agents
- Chemical and physical studies on chemical agents that provide insight into their mode or mechanism of action
- Experimental and theoretical investigations of the interaction of toxic chemicals with biological macromolecules and other biological targets
- And much more!

CHEMICAL RESEARCH IN TOXICOLOGY will emphasize rigorous standards for characterization of compounds and the description of the methods used.

Toxic effects are broadly defined to include toxicity, mutagenicity, carcinogenicity, teratogenicity, neurotoxicity, immunotoxicity, and other related areas.

LOOK TO *CHEMICAL RESEARCH IN TOXICOLOGY* FOR RAPID PUBLICATION OF MANUSCRIPTS

The editors are working toward a timely turnaround from submission to publication. Contributors and subscribers will be at the forefront of developments in the field or toxicological research.

CHEMICAL RESEARCH IN TOXICOLOGY published bimonthly by American Chemical Society. One volume per year. Volume 1 (1988) ISSN 0893-228X

	U.S.	Canada and Mexico	Europe Air Service Included	All Other Countries Air Service Included
ACS Members				
One year	$ 46	$ 50	$ 54	$ 59
Two years	$ 82	$ 90	$ 98	$108
Nonmembers	$269	$273	$277	$282

Call TOLL FREE: (800) 277-5558 (U.S. only). In D.C. or outside the U.S. call (202) 872-4363, **or write:** American Chemical Society, Marketing Communications Department, 1155 Sixteenth Street, NW, Washington, DC 20036.

GUIDING *CHEMICAL RESEARCH IN TOXICOLOGY* IN ITS FIRST YEAR 1988 EDITORIAL ADVISORY BOARD

M.W. Anders, *University of Rochester*
Neal Castagnoli, Jr., *University of California, San Francisco*
John Essigmann, *Massachusetts Institute of Technology*
Doyle G. Graham, *Duke University Medical Center*
F. Peter Guengerich, *Vanderbilt University*
John E. Hearst, *University of California, Berkeley*
Sidney M. Hecht, *University of Virginia*
Stephen S. Hecht, *Naylor Dana Institute for Disease Prevention*
Richard Heikkila, *University of Medicine & Dentistry of New Jersey*
Sidney D. Nelson, *University of Washington*
Paul Ortiz de Montellano, *University of California, San Francisco*
Steven R. Tannenbaum, *Massachusetts Institute of Technology*
John A. Thompson, *University of Colorado*
Karen E. Wetterhahn, *Dartmouth College*

ES&T VIEWS

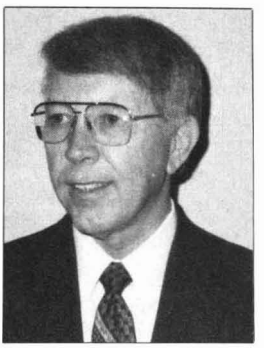
Health effects from radiation

By Robert E. Alexander

In the article "Nuclear Safety after Chernobyl," Christopher Flavin correctly observes that the Three Mile Island and Chernobyl nuclear accidents cast spotlights on unresolved safety problems (*ES&T,* Views, July 1987, pp. 624–25). However, the spotlights have brought little attention to a very important problem—the estimation of radiation health effects. The prevention of such effects is the basis for plant safety decisions and the primary reason for the costly design and operational complexities that Flavin writes about. The probabilistic risk assessment work he mentions has involved considerable research to estimate the probabilities of accidentally bringing the contents of a reactor core into the public domain. This probabilistic risk assessment also involved the estimation of early and delayed health effects.

Although delayed cancer and genetic effects are considered to be random, the risk coefficients used in their calculation are given as constants rather than as probability functions. This practice eliminates consideration of the probability of zero effects, a highly significant probability at low doses for which the coefficients are highly uncertain. The most significant problem highlighted by Three Mile Island and Chernobyl may be the very real possibility that important decisions to be made about nuclear electric power could have a speculative technical basis.

Consider the highly influential word "catastrophic" as used by Flavin in reference to Chernobyl. Thirty-one workers lost their lives at the plant, and to these workers and their families the accident was catastrophic indeed. However, these tragedies happened on-site, where radiation dose rates were very high, rather than in the public domain. The doses received were so large that



Robert E. Alexander

death intervened long before delayed effects had a chance to occur. Early effects (manifested within hours to months after doses exceeding about 100 rads) could happen to the public only if an accident much worse than Chernobyl were to occur.

Melting of the core in a U.S. light-water reactor takes time; redundant detection systems provide early warning when such accidents begin, and failure of a containment building is a low-probability event. If evacuation within a two-mile radius of a nuclear plant is completed prior to any failure in the containment building, it appears that off-site radiation doses high enough to cause early fatalities would be prevented.

This outcome would also be expected if containment failure were to occur during the evacuation procedure. Early containment failure is associated with rapid pressure rise caused by intense heating of the containment atmosphere. Under these conditions fission-product release would result during depressurization of the building. An explosion of great force, worse than at Chernobyl, with an immediate release of fission products is not considered to be a major concern.

Flavin refers to a hydrogen explosion that "almost resulted" at Three Mile Island. Although hydrogen combustion might be able to cause failure of a containment building, the failure would not be expected to occur sooner than about two hours after the start of core melt, thereby allowing considerable warning time for taking protective actions. Thus predictions of delayed deaths from radiation-induced cancer seem to me to be the most significant consequence of a reactor accident in terms of impressions left with decision-makers. I suspect that these predictions are more likely to prompt the word "catastrophic" and to alarm decision-makers around the world.

Most of the Chernobyl estimates involve many thousands of fatalities in the Northern Hemisphere; for example, a recent study sponsored by the U.S. Department of Energy published an estimate of 28,000 fatalities (*1*). This report repeatedly states that it is possible that no delayed deaths will occur. However, decision-makers are more likely to remember the 28,000 theoretical estimates than the 31 actual fatalities on-site. There are reasons to believe that the calculational results may be too clouded by uncertainty to be useful. For example, the risk coefficients used are based primarily on an epidemiology study involving 54,000 atomic bomb survivors. This sample size provides statistically sound information only for doses exceeding 10 rads. Average lifetime doses in the Northern Hemisphere are given below.

The DOE report makes it clear that the Chernobyl dose determinations are highly uncertain, that very low lifetime doses would likely produce no additional radiological risk, and that there are no direct data confirming that a few random ionizations in tissue will cause fatal cancers. In consideration of these facts, the authors of the report included the following footnote to each table pre-

0013-936X/88/0922-0144$01.50/0 © 1988 American Chemical Society

Emerging Developments in Environmental Science

ES&T

ENVIRONMENTAL SCIENCE & TECHNOLOGY

Enter your own monthly subscription to ES&T and be among the first to get the most authoritative technical and scientific information on environmental issues.

☐ **YES! I want my own one-year subscription to ENVIRONMENTAL SCIENCE & TECHNOLOGY at the rate checked below:**

1988 Published monthly	U.S.	Canada & Mexico	Europe	All Other Countries
ACS Member	☐ $ 30	☐ $ 38	☐ $ 48	☐ $ 54
Nonmembers—Personal	☐ $ 55	☐ $ 63	☐ $ 73	☐ $ 79
Nonmembers—Institutional	☐ $192	☐ $200	☐ $210	☐ $216

☐ Payment Enclosed (Payable to American Chemical Society)
☐ Bill Me ☐ Bill Company
Charge my ☐ VISA/MasterCard ☐ Access
☐ Diners Club/Carte Blanche ☐ Barclaycard

Card No. _____

Expires _____ Interbank No. _____ (M/C and Access)

Signature _____

Name _____

Title _____ Employer _____

Address ☐ Home
☐ Business _____

City, State, Zip _____

Employer's Business: ☐ Manufacturing ☐ Academic ☐ Government
☐ Other _____

Member rates are for personal use only.
Subscriptions outside the U.S., Canada, and Mexico are delivered via air service. Foreign payment must be made in U.S. currency by international money order, UNESCO coupons, U.S. bank draft, or order through your subscription agency. For nonmember rates in Japan, contact Maruzen Co., Ltd. Please allow 45 days for your first copy to be mailed. Redeem until December 31, 1988.

680 **MAIL THIS POSTAGE-PAID CARD TODAY!** 4354M

Emerging Developments in Environmental Science

ES&T

ENVIRONMENTAL SCIENCE & TECHNOLOGY

Enter your own monthly subscription to ES&T and be among the first to get the most authoritative technical and scientific information on environmental issues.

☐ **YES! I want my own one-year subscription to ENVIRONMENTAL SCIENCE & TECHNOLOGY at the rate checked below:**

1988 Published monthly	U.S.	Canada & Mexico	Europe	All Other Countries
ACS Member	☐ $ 30	☐ $ 38	☐ $ 48	☐ $ 54
Nonmembers—Personal	☐ $ 55	☐ $ 63	☐ $ 73	☐ $ 79
Nonmembers—Institutional	☐ $192	☐ $200	☐ $210	☐ $216

☐ Payment Enclosed (Payable to American Chemical Society)
☐ Bill Me ☐ Bill Company
Charge my ☐ VISA/MasterCard ☐ Access
☐ Diners Club/Carte Blanche ☐ Barclaycard

Card No. _____

Expires _____ Interbank No. _____ (M/C and Access)

Signature _____

Name _____

Title _____ Employer _____

Address ☐ Home
☐ Business _____

City, State, Zip _____

Employer's Business: ☐ Manufacturing ☐ Academic ☐ Government
☐ Other _____

Member rates are for personal use only.
Subscriptions outside the U.S., Canada, and Mexico are delivered via air service. Foreign payment must be made in U.S. currency by international money order, UNESCO coupons, U.S. bank draft, or order through your subscription agency. For nonmember rates in Japan, contact Maruzen Co., Ltd. Please allow 45 days for your first copy to be mailed. Redeem until December 31, 1988.

680 **MAIL THIS POSTAGE-PAID CARD TODAY!** 4354M

(800) 227-5558 (U.S. only)

NO POSTAGE
NECESSARY
IF MAILED
IN THE
UNITED STATES

BUSINESS REPLY MAIL

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

POSTAGE WILL BE PAID BY ADDRESSEE

American Chemical Society
Marketing Communications Department
1155 Sixteenth Street, N.W.
Washington, D.C. 20077-5768

(800) 227-5558 (U.S. only)

NO POSTAGE
NECESSARY
IF MAILED
IN THE
UNITED STATES

BUSINESS REPLY MAIL

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

POSTAGE WILL BE PAID BY ADDRESSEE

American Chemical Society
Marketing Communications Department
1155 Sixteenth Street, N.W.
Washington, D.C. 20077-5768

senting latent cancer estimates: "The possibility of zero health effects at very low doses and dose rates cannot be excluded." This careful, scientifically sound wording is typical of the radiobiology literature. Unfortunately, these statements usually do not reach decision-makers, and they almost never reach the general public.

Many health physicists are dismayed by the now-common practice of including extremely low doses in health effects estimations. When doses obtained in this manner are multiplied by risk coefficients valid at best for doses exceeding 10 rads and dose rates exceeding 1 rad/yr, the results can be alarming and misleading, and they may have a detrimental influence on decision-makers. If individual doses below 10 rads and dose rates below 1 rad/yr for a lifetime are excluded from the 28,000 estimated cancer deaths, only the evacuees are affected and the theoretical result is 410.

To my mind, the consequences predicted for the evacuees are technically questionable. I would characterize estimates of the type indicated for European U.S.S.R. (0.63 rad average) and Europe (0.15 rad average) as conjecture. I find any estimate of the type made for Asiatic U.S.S.R. (0.005 rad average) to be speculation. Estimates of the type made for Asia (0.001 rad average) and the United States (0.0005 rad average) I would classify as pseudoscientific speculation. Although these characterizations are given as one health physicist's opinion, I should think they would be comforting to millions of exposed people who are needlessly worried.

In my opinion there is a very limited place for conjecture and speculation in science. Even hypotheses must always be clearly identified as such, particularly when the results of hypothetical calculations can reach unsuspecting legislators and agency heads, influencing their decision-making process in a manner detrimental to the best interests of the nation.

Flavin has studied nuclear plant safety and concludes that "there must be greater preparation for the consequence of the inevitable failures" and that "important reforms must be introduced soon." Perhaps he is right. But surely it is true that the expenditure of resources for these preparations and reforms must be commensurate with our knowledge of the risks and that those who make the final decisions regarding these preparations and reforms must be well informed regarding these risks. There is a larger picture that should be considered. The catastrophe that I am worried about is that the competitive position of America may be damaged by those who fear that the sky is falling.

"The possibility of zero health effects at very low doses and dose rates cannot be excluded."

References

(1) *Health and Environmental Consequences of the Chernobyl Nuclear Power Plant Accident;* Acquisition No. DE 87013578, National Technical Information Service: Springfield, Va., 1987; DOE/ER-0332.

Robert E. Alexander is a scientist with the Office of Nuclear Regulatory Research at the U.S. Nuclear Regulatory Commission (Washington, D.C.) and is president of the Health Physics Society, McLean, Va.

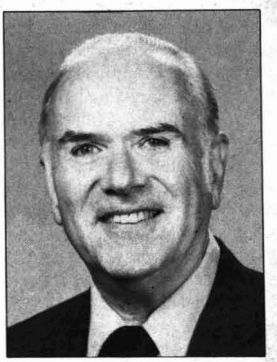
Numerical data for scientists

By Stephen R. Heller and Lewis H. Gevantman

The scientific community is currently undergoing phenomenal changes in the way it produces, compiles, and disseminates scientific information and data. Much of it can now be managed by computer. Similarly, bibliographic literature searching has become routine using a variety of on-line systems (see box).

A newer activity that is starting to make its presence felt in the scientific community is that of providing the scientist with access to numerical data through a variety of automated mechanisms. Several numerical data bases have emerged and are now being used.

Stephen R. Heller



Lewis H. Gevantman

0013-936X/88/0922-0145$01.50/0 © 1988 American Chemical Society

However, most of these data bases remain unique—some have search and retrieval capabilities, but for the most part they remain free-standing bodies of numerical data without connection to one another.

A decade ago the idea of combining related numerical data bases for the environmental science community (*1*) was activated first at the National Institutes of Health and subsequently by the EPA. Coordination with other government agencies led to a system of 22 data bases and software analysis programs entitled Chemical Information System (CIS). This system, which is under private operation, is available to the environmental scientist. However, some of the newer computer capabilities and improved data management designs are not available in the system.

A numerical data base is defined as a collection or compilation of numerical data that describes either singular or multiple physical parameters of a specified chemical substance. Generally, the number of parameters and substances are limited. The data base may have simply a listing of numbers or it may have search and retrieval software for extracting the desired data value. Some come with calculational capability for extrapolating or interpolating values based on theoretical or empirical grounds. Most of these data bases are free-standing and each may require the use of a unique approach for extraction of the information contained in the data base. This makes for the investment of considerable time and effort on the part of the user to learn and manipulate each data base. In addition, the data contained in such data bases are culled from the scientific literature and other sources with minimal attempt to evaluate the quality of the data. Also, some data bases are created with little or no regard for adding to or updating their capability. This tends to render the data less useful with the passage of time.

On-line dissemination

A better approach to on-line numerical data dissemination for environmental scientists has been initiated by Technical Database Services, Inc., (TDS, see box) in their Numerica system. In contrast to the individual free-standing bodies of data bases available to users, the Numerica system is one of a cluster of experimental data bases, each of which has been scrutinized and accepted by the data base developer for quality and timeliness. Although each data base comes from a different source, inconsistencies between data bases (primarily in the area of nomenclature) are resolved by the use of Chemical Abstracts Service (CAS) registry numbers. Furthermore, each part or data base is closely related to the other so that the data can be checked for consistency within all data bases. Programs are available to round out and compare calculational versus experimental values with further opportunity to extend the data into areas where no data exist. The search and retrieval strategies for accessing the data bases are also rendered in a consistent manner, so there is no need to learn how to use each data base. Consequently, the buildup of data bases clustered about a centralized theme such as environmental science presents a highly useful systems concept.

"The search and retrieval strategies for accessing the data bases are rendered in a consistent manner, so there is no need to learn how to use each data base."

Highlights of how the Numerica system searches for specific chemical properties data illustrate the system's utility in meeting the needs of the environmental scientist. For example, the chemical 1,1′-biphenyl (molecular formula $C_{12}H_{10}$) has been assigned CAS registry number 92-54-4. Access to the Numerica on-line system is achieved in the usual manner through a dial-up telephone network, in this case Telenet.

What data base to use

Before beginning a search of Numerica data bases, one must check to see which, if any, data base contains data on the chemical of interest. This can be done by using SYNDEX, which contains an index of CAS registry numbers, chemical names, synonyms, and TDS data base tags. This allows the user to save both time and money by avoiding systems that do not contain the needed data. The results of the search show that numerical data on 1,1′-biphenyl can be found in the Thermodynamic Research Center Database, the Carcinogenic Information Database for Environmental Substances (CIDES) (see box), the Environmental Fate Database (EFDB) (*2*), and the Log P and Related Parameters Database (*3*). Illustrative excerpts from three of these data bases are shown in Table 1. In performing a search for data and information on 1,1′-biphenyl, the first type of data to be searched is environmental fate data.

Yet another data base, CHEMEST, can be used to calculate many of the parameters described in Table 1. CHEMEST shows property relationships and fills in for missing data.

It is hoped that the searches and displays shown have conveyed the value of having high-quality data that are easily searched in an on-line system. Numerica is a simple system to use, and having the SYNDEX data base as a front end allows one to perform a quick and efficient search of available data before even going into a specific data base. Lastly, the ability or potential to compare experimental and calculated data (e.g., in the TRC Datafile) is a valuable resource.

Looking ahead

The future direction for Numerica is twofold. First, there is the need to bring other useful and important data bases

Sources of information on various data bases

Directory of Online Databases, Cuadra/Elsevier, 52 Vanderbilt Ave., New York, N.Y. 14305 (212-370-5520). The directory is published four times a year and is available on-line.

TDS, Technical Database Services, Inc., 10 Columbus Circle, Suite 2300, New York, N.Y. 10019 (212-245-0091).

CIDES, the Carcinogenic Information Database for Environmental Substances is currently being produced at TDS and will contain carcinogenic, mutagenic, physical, chemical, and environmental parameter data for over 1200 substances. For further information contact TDS above.

TRC, Thermodynamics Research Center. For information on activities and data bases contact TRC, Zachry Engineering Building, Room 58, The Texas A&M University System, College Station, Tex., 77843-3111 (409-485-5981). TRC publishes a yearly newsletter for those wishing to be kept informed of their activites.

into the present cluster. By integrating the new data with the present files, an ever-increasing numerical data capability is available to the user with a minimum investment of time and effort. Second, the cluster of environmental data permits the formation of other clusters of numerical data that may relate or be completely independent of the environmental data. The option to select the theme of the next cluster is obviously predicated upon the availability of data bases and the ability of such data bases to serve a need expressed by the user community.

For example, a new cluster aimed at chemical engineering, chemical manufacture, and data that embrace chemical and pharmaceutical concerns is a natural extension of the Numerica system. Obvious relationships to the Physical Properties Data System and other data bases would then promote the use of both data clusters because of the need to satisfy data requirements of a mutual nature. Similarly, a biologically oriented cluster would again have implications for relating the contents of the new set of data bases to the existing cluster. The flexibility and advantages described for constructing clustered data bases are believed to be clearly superior mechanisms for producing online systems in the future.

References

(1) Heller, S. R.; Milne, G.W.A. *Environ. Sci. Technol.* **1979** *13*, 798–803.
(2) Howard, P. H. et al. *J. Chem. Inf. Comp. Sci.* **1982** *22*, 38–44.
(3) Leo, A. J. *J. Chem. Soc.* Perkins Trans. II, **1983**, 825–38.

Stephen R. Heller is a research leader in the model and data base coordination laboratory of the Department of Agriculture, Beltsville, Md.

Lewis H. Gevantman is a guest researcher at the National Bureau of Standards in Gaithersburg, Md. He retired from federal service after 17 years as program manager in the NBS Office of Standard Reference Data.

TABLE 1
Typical printout information from 3 different data bases

A. TDS environmental fate data base menu

ID	BIPHENYL
CAS#	92)52)4 #5
Preferred Name:	BIPHENYL
9th Col Index:	1,1')BIPHENYL
Synonym:	BIPHENYL
Mol Weight:	154.21
Mol Formula:	C12H10
LOGP	BIPHENYL
CAS#	92)52)4 #14
Log O/W	Part.: 4.09 MEASURED
Remarks:	RECOMMENDED VALUE
Abbrev Ref:	HANSCH,C 7 LEO,AJ (1981)
SOIA	BIPHENYL
CAS#	92)52)4 #66
Soil Adsorp	Cns: .14E 04
Sum Comments:	CALCULATED
Abbrev Ref:	KENAGA,EE (1980)
UV	BIPHENYL
CAS#	92)52)4 #6
Absorption Coef:	.193E 05L/MOL)CM
Wavelength (NM):	246.5
Remarks:	NO ABS ABV 300 NM, IN MEOH
Abbrev Ref:	SADTLER (NA) @255 UV
VP	BIPHENYL
CAS#	92)52)4 #62
Vapor Pressure:	.975E 01 TORR MEASURED
Temperature (C):	25.
Remarks:	UNITS CONVERTED
Abbrev Ref:	WEAVER,WC ET AL. (1979) @2ND
WSOL	BIPHENYL
CAS#	92)52)4 #1
Water Solubil:	.71E 01 MG/L MEASURED
Temperature (C):	25.
Remarks:	UNITS CONVERTED BY SRC, AV, VALIDATED VALUE
Abbrev Ref:	PEARLMAN,RS ET AL. (1984)

B. TRC vapor pressure data file—calculated data

CAS Chemical Name: BIPHENYL
Molecular Formula: C12H10
CAS Registry No.: 92)52)4
Sources: SAV1; SAV2

T/K	P/kPa	Experimental Range	Rating	State	Date
TOP OF SET		—	—	—	
250.00		—	—	—	
260.00		—	—	—	
270.00		—	—	—	
280.00	1.7198E)04	E	C	C	1967
290.00	5.2600E)04	I	C	C	
300.00	1.5564E)03	I	C	C	
310.00	4.4616E)03	I	C	C	
320.00	1.2408E)02	I	C	C	
330.00	3.3520E)02	I	C	C	
340.00	8.8071E)02	I	C	C	

Legend: E is an extrapolated value; I is an interpolated value. In the "rating" column, data quality is rated from A to D; C is the value given to the above data. "State" refers to the physical state of the material—C for condensed, L for liquid, S for solid, G for gas.

C. Log P database—all solvents

Chemical Name: BIPHENYL
There are 18 entries related to your query:

Line No.	Name	Log P	Solvent No.
TOP OF FILE			
1	BIPHENYL	3.95	1
2	BIPHENYL	4.17	1
3	BIPHENYL	4.09*	1
4	BIPHENYL	3.16	1
5	BIPHENYL	4.04	1
6	BIPHENYL	4.04	1
7	BIPHENYL	3.79	1
8	BIPHENYL	3.89	1
9	BIPHENYL	3.76	1
10	BIPHENYL	3.77	1

*Recommended value.
Log P = octanol/water partition coefficient. The number ("No.") refers to the number of data points in the file. In the above example there is one data point for each of the 10 values of log P.

Causation in forest decline

By Richard M. Klein

Statistical and legal proof for the causes of contemporary forest decline and scientific demonstration of its nature, consequences, and sequelae have eluded the scientific community in spite of massive research efforts in Europe and North America. At the same time, the public and legislative bodies are attempting to make decisions of far-reaching social and economic importance. Woodman and Cowling (*1*) and others (*2–5*) have suggested that the causes of forest decline can be demonstrated by application of Koch's postulates, initially proposed to test the cause–effect relationship of diseases caused by microorganisms.

Since the postulates were first formulated by Robert Koch in 1876 (*6*), fairly precise rules have been developed for the evaluation of diseases caused by biotic agents (*7, 8*). These require that the presumed causal agent be isolated from affected hosts, that the agent be grown under controlled conditions, that the causal agent induce the same disease when introduced into a new host, and, finally, that the causal agent again be isolated and demonstrated to be identical to the first isolated agent.

But even in instances of microbial disease, Koch's postulates have not always worked. Viruses and obligatory pathogens may not be amenable to cultivation in vitro, and variations in host susceptibility, vigor, age, and other factors profoundly alter clear demonstrations of the postulates. As pointed out by Deumling (*9*), the postulates require controlled conditions, which are impossible to apply under field conditions, and modifications of the postulates for field studies (*10*) cannot provide definitive answers for causation. When there is good reason to suspect that causal factors are not primarily biotic agents, the utility of Koch's postulates is further diluted.

More to the point, the list of potential causal factors in forest decline is large and diverse (*11–13*). Natural causal factors, which may be acute or chronic, include stresses involving water, temperature, diseases, and insect infestations. Anthropogenic factors include precipitation acidity, the solubilization of indigenous and deposited metals, gaseous components, excess nitrogen,

Richard M. Klein

and other factors. Each of these factors varies in importance in time and space, and each is capable of synergistic interaction with both natural and anthropogenic factors. Many plant species are declining, and matters of plant age, site factors, and temporal considerations are involved. Hutterman (*3*) has suggested that a modified Koch's postulate formulation could be used to evaluate individual causal factors or stressing conditions under controlled conditions.

Koch's postulates, suitably modified, are primarily useful for demonstrating that the factor being tested is unlikely to be involved. Simulation experiments that do not test Koch's postulates have shown that many of the proposed stressing factors are capable of inducing responses consistent with the hypothesis that the factor is probably involved. It is, however, manifestly impossible to design and conduct a statistically sound multiple-factor test for Koch's postulates using mature trees under natural, but controlled, conditions—even with as few as 10 presumed causal factors, each presented in only three concentrations with analysis of many structural and functional criteria made over a 10-year period.

The medical profession, faced with similar problems and constraints, has developed methods of epidemiology for disease states involving multiple causal factors, the necessity of evaluating natural populations, and the time and space considerations that are analogous to the problems of forest decline. Our current understanding of lung cancer is based on such epidemiological concepts. Incitants include tobacco smoke; asbestos; radiation; viruses; a host of chemical substances in the environment; and matters of life style, age, vigor, sex, genetic factors, and race (*14*). The time period between initial exposure and disease development is also involved (*15*). Extrapolations from mice to human populations (as from tree seedlings to forest ecosystems) must be factored into the analysis. The result of such epidemiological evaluations is a probability statement that may be scientifically disappointing and certainly leads to different interpretations. Given the complexity of the problem, however, probability statements have proved to be adequate guidelines for the formulation of legislation and for the public.

"Many plant species are declining and matters of plant age, site factors, and temporal considerations are involved."

As pointed out by Weinberg (*16*), the questions being asked about cancer research far exceed the capabilities of science; so too for forest decline. The answers go beyond the realm of biological certainty, forcing us into the uncomfortable position of having to operate within a vague framework. Much the same point has been made by Deumling (*9*). However, epidemiological techniques can, as Koch's postulates cannot, provide involved people with well-

0013-936X/88/0922-0148$01.50/0 © 1988 American Chemical Society

documented and adequately supported probability estimates (*17, 18*). Although subject to modification as additional information becomes available, such probability estimates can be used as a base for critical decisions (*19–21*). Proposing that decisions be postponed until Koch's postulates are fulfilled is logically doomed to fail.

Acknowledgments

Preparation supported by the Vermont Agricultural Experiment Station, the R. K. Mellon Foundation, and the Robert and Marillyn Wilson Foundation. The advice of Deana Klein, Heiko Liedeker, Helen Myers, Timothy D. Perkins, and Hubert Vogelmann is acknowledged with thanks.

References

(1) Woodman, J. N.; Cowling, E.B. *Environ. Sci. Technol.* **1987,** *21,* 120–26.
(2) Adams, D. F. *J. Air Pollut. Control Assoc.* **1962,** *13,* 360–62.
(3) Hutterman, A. *Forstarchiv.* **1984,** *55,* 45–48.
(4) Last, F. T.; Fowlder, D.; Freer-Smoth, P. H. *Forstwiss. Centralbl.* **1984,** *193,* 20–48.
(5) Cowling, E. B. *J. Air Pollut. Control Assoc.* **1985,** *35,* 916–19.
(6) Koch, R. *Beitr. Biol. Pflanz.* **1876,** *2,* 277.
(7) Brock, T. D.; Smith, D. W.; Madigan, M. T. *Biology of Microorganisms,* 4th ed.; Prentice-Hall: Englewood Cliffs, N.J., 1984.
(8) Davis, B. D. et al. *Microbiology,* 3rd ed.; Harper & Row: New York, 1980.
(9) Deumling, D. *Environ. Sci. Technol.* **1987,** *21,* 612–13.
(10) Woodman, J. N. *Tree Physiology,* **1987,** *3, 1–5.*
(11) Schutt, P. *So Stirbt der Wald;* BLV-Verlag: Munich, 1983.
(12) *World resources: A Report by the Resources Institute for Environment and Development;* Mathews, J. T.; Hinricksen, D., Eds.; Basic Books: New York, 1986.
(13) Klein, R. M.; Perkins, T. D. *Ambio.* **1987,** *16,* 89–93.
(14) Doll, R.; Peto, R. *The Causes of Cancer;* Oxford University Press: New York, 1981.
(15) Farber, E. *Cancer Res.* **1984,** *44,* 5463–74.
(16) Weinberg, A. M. *Issues in Science and Technology* **1985,** *1,* 59–72.
(17) Lilienfeld, A. M.; Lilienfeld, D. E. *Foundations of Epidemiology;* Oxford University Press: New York, 1980.
(18) Miettinne, O. S. *Theoretical Epidemiology: Principles of Occurrence Research in Medicine;* Wiley: New York, 1985.
(19) Langbeim, L. I.; Lichtman, A. J. *Ecological Inference;* Sage: Beverly Hills, Calif., 1978.
(20) Ruckelshaus, W. D. *Science* **1983,** *221,* 1026–28.
(21) Ruckelshaus, W. D. *Issues in Science and Technology* **1985,** *1,* 19–38.

Richard M. Klein received his Ph.D. in botany and metabolic biochemistry from the University of Chicago. He was A. H. Caspary curator of plant physiology at the New York Botanical Garden before moving to the University of Vermont as a professor of botany. Klein is currently investigating aspects of physiological plant ecology with special reference to contemporary forest decline.

Just published . . . latest research results from leading scientists in the hot new area of superconductivity!

Chemistry of HIGH-TEMPERATURE SUPERCONDUCTORS

Looks at current progress and understanding from the point of view of solid-state chemistry . . .

Hot off the presses! This new book presents the most current information in developing technologies for commercial uses of high-temperature superconductivity. Although this area is multidisciplinary, chemistry plays a key role throughout . . . from materials preparation to processing for small- and large-scale operations. This book presents the chemistry necessary to further the research in this exciting area.

Information is presented in the following major areas:

• Theory • Materials Preparation and Characterization • Structure-Property Relationships • Surfaces and Interfaces • Processing and Fabrication • Applications • Research Needs and Opportunities

The editors are . . .

• David L. Nelson, Office of Naval Research • M. Stanley Whittingham, Schlumberger-Doll Research • Thomas F. George, State University of New York at Buffalo

Plus more than 100 contributors from major research groups worldwide!

ACS Symposium Series No. 351 Approx. 400 pages (28 chapters)
Clothbound (1987) **US & Canada $64.95, Export $77.95**

Order today . . . and put these critical new findings to work for you!

The ACS Guarantee: If you are not satisfied with your book for any reason, return it within 15 days for a full refund or charge card credit.

To charge your book by phone, call TOLL FREE (800) 227-5558.

ORDER FORM

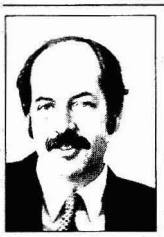
☐ Yes!
Please rush me *Chemistry of High-Temperature Superconductors!*
$64.95 US & Can. $77.95 Export
Qty: _____ Total: $_____
☐ Payment enclosed (make checks payable to American Chemical Society).
☐ Purchase order enclosed. P.O. # _____
Charge my ☐ MasterCard/VISA ☐ American Express
☐ Diners Club/Carte Blanche ☐ Access/Barclaycard
Account # _____ Expires _____
Interbank # _____ Name of Cardholder _____
Signature _____
Ship books to:
Name _____
Address _____
City, State, Zip _____

ORDERS FROM INDIVIDUALS MUST BE PREPAID. Prepaid and credit card orders receive free postage and handling. Prices subject to change without notice. Please allow 4–6 weeks for delivery. Foreign payment must be made in US currency by international money order, UNESCO coupons, or US bank draft. Order through your local bookseller or directly from ACS.

To charge your books by phone, CALL TOLL FREE (800) 227-5558. Mail this order form with your payment or purchase order to: American Chemical Society, Distribution Office Dept. 30, P.O. Box 57136, West End Station, Washington, DC 20037.

30

EPA's new pesticide-groundwater strategy



Richard M. Dowd

EPA is designing a strategy to address issues associated with pesticides in groundwater. A draft of the strategy was presented to interested parties last summer in anticipation of a formal proposal early this year.

The strategy responds to EPA's increased concern about reported detection of pesticides registered under FIFRA (the Federal Insecticide, Fungicide, and Rodenticide Act) in various groundwaters across the country. The strategic goal is to improve protection of groundwaters that are current or potential sources for public or private drinking-water supplies. The emphasis will be on measures to prevent contamination in excess of EPA standards rather than on cleaning up groundwaters that have already been contaminated.

EPA believes that the potential vulnerability of groundwater to pesticide contamination varies significantly from one locality to another. Accordingly, the agency intends to tailor preventive measures on a county level, where feasible, based on local groundwater vulnerability. For groundwater regimes that vary on a smaller geographical scale, criteria for the use of certain pesticides would be established and evaluation for applicability would be made by the user rather than by the regulatory agency. One result of this approach would be that some pesticides nationally registered under FIFRA may not meet local groundwater management criteria, and their use could be restricted in those places. EPA calls this provision a "differential approach."

Implementing the strategy will devolve responsibility on many more players than have previously had roles in FIFRA activities. New actors in the process include state groundwater managers as well as pesticide users. Registrants (e.g., manufacturers) of pesticides would play an increased role.

EPA's role remains central

EPA would first establish standards for allowable pesticide concentrations in groundwater. The agency has already chosen to adopt as standards the Maximum Contaminant Levels (MCLs), the enforceable pollutant limits under the Safe Drinking Water Act. Where no MCLs exist, EPA will establish interim levels. (Out of some 600 pesticide chemicals in use, only 6 MCLs have been set; 14 more are scheduled for proposal in 1988.)

EPA would also evaluate the chemicals' potentials for leaching to groundwater and is now seeking leaching data from registrants of 65 chemicals.

To implement the massive, complex task of assessing local groundwater and establishing localized preventive measures, EPA is looking for help from the states. The agency will encourage states to establish State Management Plans that would include assessments of local groundwater use and vulnerability. States would also develop and implement highly tailored prevention measures based on local groundwater differences. In some cases, this differential approach might lead to different prevention measures in different localities for individual chemicals. States with management plans approved by EPA would then take the lead in determining which preventive measures are appropriate.

For those states that do not adopt approved management plans, EPA will try to assess local groundwater and tailor preventive measures to state or county levels. Where this is not feasible, EPA will likely impose state- or county-wide pesticide registration cancellations if this is deemed necessary. States may well find it in their interests to develop their own plans to forestall federal controls that might be more stringent. In other words, the carrot for the states is the opportunity to adopt pesticide management measures that are more flexible and responsive to local conditions.

Pesticide registrants would also shoulder increased responsibilities. They would be required to conduct substantial groundwater monitoring for pesticides used in vulnerable areas. They must also educate users about "proper environmentally sound application" of their pesticides.

EPA indicates that the role of users is critical because they actually apply the pesticides. The strategy envisages requiring users to identify vulnerable groundwater in their fields to determine if special preventive measures are needed.

At this time EPA has not set a timetable for implementing the strategy—which is not surprising. Considering how long it normally takes the agency to make national registration decisions, which do not now include groundwater concerns, the amount of time it would take to complete this complex multilevel decision-making process for 600 pesticides in hundreds of counties is staggering. This lengthy time requirement and other daunting implementation and enforcement burdens are sure to stimulate lively discussion both during internal agency and administration review and during the formal public comment period between EPA's proposal and promulgation of a final strategy.

Richard M. Dowd, Ph.D., is president of R. M. Dowd & Company, environmental and science policy consultants in Washington, D.C.

0013-936X/88/0922-0150$01.50/0 © 1988 American Chemical Society

Toxic Air Pollution: A Comprehensive Study of Non-Criteria Air Pollutants. Paul J. Lioy and Joan M. Daisey, Eds. Lewis Publishers, 121 S. Main St., Chelsea, Mich. 48118. 1987. 294 pages. $49.95, cloth.

Reviewed by Julian B. Andelman, Graduate School of Public Health, University of Pittsburgh, Pittsburgh, Pa. 15261.

The Airborne Toxic Element and Organic Substances (ATEOS) project was funded by the state of New Jersey and conducted from 1981 to 1985. It involved measurements and assessments of a large number of potentially toxic, mostly noncriteria, ambient air contaminants at three urban sites and one rural site in New Jersey.

Toxic Air Pollution: A Comprehensive Study of Non-Criteria Air Pollutants, which describes this study, consists of eight chapters written by 11 of the 45 participants in the project. The participants represented three academic institutions, one research institute, and the Department of Environmental Protection of New Jersey.

The principal goals of the project were to obtain quantitative information on human exposures to outdoor ambient air carcinogens, assess biological activity levels for various fractions by short-term in vitro assays, evaluate time and location variables, and estimate possible sources and human health risks. The introductory chapter of the book describes the study design. The final chapter presents an overview that summarizes the study's important findings and considers their health and regulatory implications. Other chapters discuss and assess the composition and variability of the constituents studied, including inhalable particulate matter (IPM), volatile organic compounds (VOCs), and polynuclear aromatic hydrocarbons (PAHs). They also cover the mutagenicity of various IPM fractions, the nature of air pollution episodes, and models that assess pollution sources using the results of analyses obtained at various sites.

Particulate and vapor-phase samples were taken for 24 hours a day during four 39-day sampling periods from 1981 through 1983. Sampling was carried out during two winter and two summer periods. The chemical constituents analyzed included nine inorganic elements, sulfate, 16 PAHs extracted from various fractions of the IPM samples, and 25 volatile organics. These VOCs included a variety of chlorinated and nonchlorinated aromatic chemicals and 11 low-molecular-weight chlorinated organics. The Ames salmonella test was used to assess the mutagenicity of three extractable fractions of the IPM. Sampling and analytical methodologies are described in considerable detail.

Much of this large and complex study has been published in peer-reviewed journals and reports, which are listed in an appendix. Nonetheless, it is quite useful to have all of this information compiled in one book, together with the perspectives of the authors as well as background and expanded interpretations not normally found in a scientific journal. There is necessarily some repetition—such as when the chapters on Ames testing or source modeling discuss variations in IPM results with time or location—but the material generally is well organized.

To get a broad view of the study and its major findings, it may be useful first to read Chapter 1, on the study design, and then Chapter 8, an overview that discusses health and regulatory implications. Chapter 8 summarizes the principal findings of the other chapters and includes quantitative estimates of risk for several chemicals. The approach taken for the latter involves generally accepted risk assessment methodology. It does not provide insight into the risks likely from the whole range of ambient airborne chemicals to which residents of the study areas would be exposed because it considers only a few by example. One conclusion, however, is that the measured concentrations of benzo[*a*]pyrene and PAH "pose an unreasonable level of risk to the population" and that they "have the highest level of attributable risk of all the classes of material measured in the ATEOS project."

Many of the authors have considerable experience in their portion of the project, as shown by citations of their work in the reference lists. This adds to the authoritative nature of the study. The comparisons with studies elsewhere are particularly valuable in placing the results of this study in perspective. It has been concluded that the volatile organic chemical levels "are sufficiently low in New Jersey to disregard the notion that a statewide problem exists for this class of ambient air pollutants"; also, "levels of aromatic VOCs are consistent with those reported . . . for urban air." There is a brief reference to the EPA's Total Exposure Assessment Methodology (TEAM) study, which included measurements of indoor and outdoor concentrations of 20 VOCs in air at one of the cities included in the ATEOS study (the ATEOS and TEAM studies were conducted during approximately the same time periods).

It would have been more useful if the ATEOS results were compared with those of the TEAM study, especially since the latter found that indoor concentrations normally are much higher than those outdoors. In fact, it was assumed in the risk assessment for perchloroethylene that its indoor air concentrations are 80% of those outdoors, clearly at variance with the TEAM findings.

The ATEOS study also found that a number of VOCs that are human or animal carcinogens are ubiquitous at the study sites, but noted that their adverse health effects at these concentrations are essentially unknown. It was recommended that "ambient air monitoring should be designed to define the nature of mutagenic material in the extractable organic matter." It is clear that the aims of assessing likely exposures at the study sites have been achieved, but that the health risks from the totality of these ambient air exposures remain uncertain.

One can only admire the considerable effort and dedication required to bring this study to fruition—a sentiment that is reflected in this well-written and edited book. In spite of its somewhat skimpy index, *Toxic Air Pollution: A Comprehensive Study of Non-Criteria Air Pollutants* should prove valuable to those undertaking comprehensive air pollution studies, as well as to those in didactic courses considering the nature and complexity of toxic air pollution.

0013-936X/88/0922-0151$01.50/0 © 1988 American Chemical Society

professional consulting services directory

CenrefLabs
BRIGHTON, CO (303) 659-0497
LIBERAL, KS (316) 624-4292

ENVIRONMENTAL TESTING
Priority Pollutants • PCB's
RCRA Hazardous Waste Analyses
Drinking Water • Wastewater
Pesticides • Sludge
Engine Emission Monitoring

NEI
COMPLETE ANALYTICAL SERVICES GC/MS CAPABILITIES
☐ Screening & Analysis of Industrial & Hazardous Waste.
☐ Superfund & RCRA Requirements.
☐ Sampling to EPA Protocols.
☐ Toxicity Studies.
(516) 625-5500
60 SEAVIEW BLVD., PORT WASHINGTON, NY 11050
NYTEST ENVIRONMENTAL INC.

Gradient Corporation
44 Brattle Street
Cambridge, MA 02138
(617) 576-1555
- Exposure & Risk Assessment
- Chemical Fate & Transport
- Toxicity Analysis
- Chemical Data Bases

PRP Services – Toxic Torts – Resource Damages

CONSULTING GROUND-WATER GEOLOGISTS AND ENGINEERS
ROUX ASSOCIATES INC
ROUX
11 STEWART AVENUE
HUNTINGTON, NEW YORK 11743
516 673-7200
CHERRY HILL NEW JERSEY 609 424-3993
DANBURY CONNECTICUT 203 798-6969
WALNUT CREEK CALIFORNIA 415 945-1900

CLASSIFIED SECTION

HLA

Geochemists

Harding Lawson Associates, a professional services firm with offices in 13 major cities, currently has openings for Senior to mid level GEOCHEMISTS specializing in water quality in our Tustin, CA and Honolulu, HI offices.

Requires Water Quality Specialist experienced in project management to direct and supervise technical assignments including data analysis, preparation of reports, and support of the field team. Positions require BS/MS and 4-8 years' applicable experience and excellent communication skills.

Quality and dependability are HLA traditions. They will continue to be the foundation of our professional practice. We offer competitive compensation, benefits and a progressive, team oriented environment. Please send your resume to: HLA Staffing, Dept. ES, P.O. Box 578, Novato, CA 94948. EOE, M/F/H/V.

Harding Lawson Associates

Denver • Houston • Dallas • Phoenix • Anchorage • Honolulu • San Francisco Bay Area • Southern California • Sacramento

USE THE CLASSIFIED SECTION

Analytical Chemists/ Quality Assurance

We have 2 positions open in our San Antonio, Texas site office for highly qualified individuals to help us develop and monitor quality assurance activities in a major environmental sampling and analysis program. Individuals will be responsible for developing QA/QC requirements and evaluating commercial testing laboratories' performance in meeting those requirements. Evaluations will be based on a review of data and documentation and on-site inspections of laboratory operations. Both positions require expertise in analytical chemistry, a working knowledge of QA/QC principles and practices, and hands-on experience with the instrumentation and methods used in environmental testing (e.g., AA, ICP, GC, GC/MS). Experience with EPA test methods is highly desirable. The first position requires an advanced degree in Analytical Chemistry, 10 years of analytical laboratory or quality assurance experience, and at least one year of experience in environmental laboratory supervision. The second position requires a BS in Chemistry with emphasis on analytical procedures plus at least 5 years of experience in the quantitative analysis of environmental samples under a comprehensive QA/QC program. Individuals must be willing to travel 10 to 12 weeks a year.

For consideration, please submit your resume to J.V. Goudarzi, The MITRE Corporation, 7525 Colshire Drive, McLean, VA 22102. U.S. Citizenship required. An Equal Opportunity/Affirmative Action Employer.

MITRE

TENURE-TRACK FACULTY POSITIONS

Hazardous Waste and Water Quality Engineers—applicants are invited to apply for these two tenure-track positions. Salary and rank will be commensurate with qualifications and experience. Applicants should have the Ph.D. degree, a strong theoretical capability, be computer literate, and have excellent communication skills. Practical experience, registration as a Professional Engineer, and at least one degree in Civil Engineering are desirable attributes, but not absolute requirements. Duties will include undergraduate and graduate teaching, sponsored research, scholarly activities and professional service. Areas of expertise for the Hazardous Waste Engineering position include one or more aspects of toxic and hazardous waste including: aquatic chemistry; wastewater treatment technologies; disposal and destruction technologies; cleanup of HW landfills; reclamation of contaminated groundwater aquifers; and design/operation of hazardous waste control facilities. Areas of interest for the Water Quality Engineering position including the theory and modeling of one or more of the following: fate and transport of contaminants in natural aquatic systems, both surface and groundwaters; the hydrologic interaction between surface and groundwaters in karst geology; municipal water and wastewater; and hazardous waste treatment technologies. Send statement of qualifications, detailed resume and names of three or more references to: Dr. John S. Zogorski, Dean of Engineering, South Dakota School of Mines and Technology, Rapid City, South Dakota 57701-3995. An equal opportunity/affirmative action employer.

RESEARCH ASSOCIATE: Must have proven background in risk assessment of transporting hazardous materials, knowledge of techniques for assessing community vulnerability to hazards, computer mapping, statistical and probability analysis, and FORTRAN required. Responsible for development of computer programs for plotting alternative scenarios, conducting survey research, consulting with clients, preparing proposals with cost projections, and drafting reports. Strong educational background in urban planning and civil engineering essential. 40 hr week (8:00 a.m.–5:00 p.m.) salary $28,000 per year. Ph.D. in Geography Concentration, Risk, Risk Assessment. 2 yrs experience instructor-Civil Engineering. Qualified applicants send resume or application letter to: **AZ DES Job Service, Attn 732-A Re: Job #0802373, P.O. Box 6123, Phoenix, AZ 85005.** (Job location: Phoenix, Arizona.) Employer paid ad.

FACULTY POSITIONS

1. **Industrial Hygiene**
2. **Environmental Chemistry** — at Hebrew University Jerusalem, Israel. Tenure track, academic rank open. Ph.D. research and teaching experience required. Appointees will direct own research unit and develop teaching program at M.Sc. and Ph.D. level. Send resume, list of publications, names of three references to: **Prof. Hillel Shuval, School of Applied Science and Technology, Hebrew University, Jerusalem, Israel. (Telephone 972-2-233821.)**

CLASSIFIED ADVERTISING RATES

Rate based on number of insertions used within 12 months from date of first insertion and not on the number of inches used. Space in classified advertising cannot be combined for frequency with ROP advertising. Classified advertising accepted in inch multiples only.

Unit	1-T	3-T	6-T	12-T	24-T
1 inch	$100	$95	$90	$85	$80

For a healthier environment, we are the solution.

ENVIRONMENTAL TOXICOLOGISTS

International Technology Corporation, a leading environmental management company, offers challenging career opportunities to qualified professionals.

Our continued growth in Houston, Texas, has created opportunities for Environmental Scientist/Toxicologists to perform health risk assessments of CERCLA sites and risk evaluations associated with RCRA permitting activities. The high visibility positions provide opportunities to interface with our talented engineers and scientists, and to become involved in sales and marketing of environmental risk control services.

Ideal candidates will meet the following qualifications:

- Undergraduate degree in Environmental Engineering or Chemical Engineering; MS in Public Health preferred
- 5 years related work experience, including 3 years in the hazardous waste industry
- Experience in carcinogenic risk assessment, pathway exposure analysis and regulatory compliance

We offer a competitive salary program and attractive fringe benefit package. For immediate consideration, send your resume to: **Anthony J. Dury, PhD, Director, Corporate Staffing, International Technology Corporation, William Penn Plaza, 2790 Mosside Blvd., Monroeville, PA 15146-2790.** An Equal Opportunity Employer M/F/H/V.

IT INTERNATIONAL TECHNOLOGY CORPORATION

Creating a safer tomorrow.

ENVIRONMENTAL SPECIALIST
(Entry Level)

Merck Sharp & Dohme Research Laboratories, a world leader in pharmaceutical process development, has an outstanding ENTRY level opening for an environmental specialist in its Environmental Engineering Laboratory. Responsibilities will include:

- Developing and carrying out environmental bioassays, biomonitoring studies as well as physical-chemical analyses.
- Contributing to environmental impact studies related to new manufacturing processes and products.
- Carrying out experimental programs to resolve specific environmental problems.

Successful applicant must have BS/MS degree in Chemical Engineering, Chemistry, Biology, or a related field. Prior experience in conducting environmental toxicology studies and knowledge of environmental analytical chemistry and basic statistical methods is highly desirable. Must be able to clearly demonstrate well above average ability to learn new techniques quickly and to work independently. Must also have excellent communicative skills.

Merck Sharp & Dohme Research Laboratories are located in Rahway, New Jersey approximately 25 miles from New York City. Our salaries, benefits, and growth potential are excellent.

Interested candidates should submit their resume with the names of three references and salary requirements to: **Ms. Jacqueline A. Eiermann, Merck & Co., Inc., P.O. Box 2000, Rahway, NJ 07065.** Equal Opportunity Employer.

Merck & Co., Inc.

CLASSIFIED ADVERTISING RATES

Rate based on number of insertions used within 12 months from date of first insertion and not on the number of inches used. Space in classified advertising cannot be combined for frequency with ROP advertising. Classified advertising accepted in inch multiples only.

Unit	1-T	3-T	6-T	12-T	24-T
1 inch	$100	$95	$90	$85	$80

(Check Classified Advertising Department for rates if advertisement is larger than 10″.)

SHIPPING INSTRUCTIONS: Send all material to

Environmental Science & Technology
Classified Advertising Department
500 Post Road East
P.O. Box 231
Westport, CT 06881
(203) 226-7131

INDEX TO THE ADVERTISERS IN THIS ISSUE

ADVERTISERS **PAGE NO.**

Environ Corporation ..... **IFC**
Wise & Wrenn, Inc.

Kevex Corporation ..... **OBC**
J. Frasier Design Group

Advertising Management for the American Chemical Society Publications

CENTCOM, LTD.

President
Thomas N. J. Koerwer

Executive Vice President **James A. Byrne**
Senior Vice President **Benjamin W. Jones**
Clay S. Holden, *Vice President*
Robert L. Voepel, *Vice President*
Joseph P. Stenza, *Production Director*

500 Post Road East
P.O. Box 231
Westport, Connecticut 06880
(Area Code 203) 226-7131
Telex No. 643310

ADVERTISING SALES MANAGER
Bruce Poorman

ADVERTISING PRODUCTION MANAGER
Jay S. Francis

SALES REPRESENTATIVES

Philadelphia, Pa. . . . Patricia O'Donnell, CENTCOM, LTD., GSB Building, Suite 725, 1 Belmont Ave., Bala Cynwyd, Pa 19004 (Area Code 215) 667-9666

New York, N.Y. . . . Patricia O'Donnell, CENTCOM, LTD., 60 E. 42nd Street, New York 10165 (Area Code 212) 972-9660

Westport, Ct. . . . Edward M. Black, CENTCOM, LTD., 500 Post Road East, P.O. Box 231, Westport, Ct 06880 (Area Code 203) 226-7131

Cleveland, OH. . . . John Guyot, CENTCOM, LTD., 325 Front St., Berea, OH 44017 (Area Code 312) 234-1333

Chicago, Ill. . . . Michael J. Pak, CENTCOM, LTD., 540 Frontage Rd., Northfield, Ill 60093 (Area Code 312) 441-6383

Houston, Tx. . . . Michael J. Pak, CENTCOM, LTD., (Area Code 312) 441-6383

San Francisco, Ca. . . . Paul M. Butts, CENTCOM, LTD., Suite 1070, 2672 Bayshore Frontage Road, Mountainview, CA 94043. (Area Code 415) 969-4604

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

Boston, Ma. . . . Edward M. Black, CENTCOM, LTD., (Area Code 203) 226-7131

Atlanta, Ga. . . . Edward M. Black, CENTCOM, LTD., (Area Code 203) 226-7131

Denver, Co. . . . Paul M. Butts, CENTCOM, LTD., (Area Code 415) 969-4604

ES&T RESEARCH

Chemical and Physical Characteristics of Lakes in the Northeastern United States

David F. Brakke,*,† Dixon H. Landers,‡ and Joseph M. Eilers§

Institute for Watershed Studies, Western Washington University, Bellingham, Washington 98225, U.S. Environmental Protection Agency, 200 S.W. 35th Street, Corvallis, Oregon 97333, and Northrop Services, Inc., 200 S.W. 35th Street, Corvallis, Oregon 97333

■ The chemical status of 768 lakes in the northeastern United States was determined as part of the Eastern Lake Survey. The lakes were selected statistically, allowing for estimates of the chemical conditions in the northeastern lake population on the basis of 26 measured parameters. The objectives were to estimate the numbers of acidic [acid neutralizing capacity (ANC) ≤ 0] and low-ANC (≤50 μequiv/L) lakes in the Northeast and to describe associated chemical conditions in the lakes. The largest number of acidic lakes in the Northeast was estimated for the Adirondack area of New York, whereas the fewest acidic lakes were estimated to occur in Maine. Sulfate concentrations were lowest in Maine and highest in the Poconos/Catskills, corresponding to the pattern in sulfate deposition. Acidic lakes were associated with low levels of base cations (calcium and magnesium) and elevated sulfate levels. Clear water, acidic lakes also had elevated concentrations of aluminum. Acidic lakes were not uniformly distributed in the Northeast. The distribution of acidic lakes was influenced principally by concentrations of sulfate and base cations, among other factors such as lake type and hydrologic flow path. The data collected during the Eastern Lake Survey support the hypothesis that regional lake acidification has occurred in the northeastern United States.

Introduction

This paper represents an attempt to quantify the chemical status of lakes in the northeastern United States. The objective of the Eastern Lake Survey—Phase I (ELS-I) was to estimate characteristics of the lake population within the sampling region through extensive analysis of water samples collected from lakes selected as a statistical frame (*1*). The lakes were selected by a stratified design, with equal allocation of sample lakes to strata.

Lakes were sampled during the period of fall circulation; thus, the samples represent an index to the chemistry of the lakes in the target population. The target population was defined from 1:250 000-scale USGS topographic maps and was limited to lakes generally ≥4 ha in surface area. Detailed methods are provided in ref 1 and 2.

Table I. Subregional and Regional Summaries of Estimated Target Population Size ($\hat{N}$), Estimated Target Population Area ($\hat{A}$), and the Standard Errors (SE) of These Estimates for the Northeast, Eastern Lake Survey—Phase I

	lakes ≤2000 ha[a]				
subregion	n[b]	$\hat{N}_s$	SE($\hat{N}_s$)	$\hat{A}_s$	SE($\hat{A}_s$)
Adirondack Mountains (1A)	155	1290	47.6	118 777	22 186
Poconos/ Catskills (1B)	143	1479	92.9	26 872	2913
central New England (1C)	163	1483	57.5	72 412	12 013
southern New England (1D)	126	1318	93.7	36 403	4381
Maine (1E)	176	1526	66.0	173 400	25 725
Northeast	763	7096	165.3	427 865	36 414

[a] Subscript s denotes a subpopulation, in this case those lakes in the target population >4 ha and ≤2000 ha. [b] Number of lakes sampled.

A total of 26 chemical parameters was measured on each lakewater sample. In addition, information was collected on physical attributes such as elevation, lake and watershed area, lake type, and land use (*2*). This permits an extensive evaluation of the present chemical status of the lakes and presents the opportunity to examine relationships among physical and chemical variables that might influence the response of the lakes to acidic deposition or other perturbations. All data summarized in this paper are for population estimates of lake characteristics based on procedures detailed in (*2*).

Area and Lakes Sampled

The area selected for sampling in the northeastern United States is shown in Figure 1. It includes all of the New England states, plus parts of New York, Pennsylvania, and New Jersey. Lakes were selected systematically from an ordered list of all lakes appearing on 1:250 000-scale USGS topographic maps, which generally include only those lakes ≥4 ha. At least 50 lakes were selected for sampling from each of three alkalinity map classes (<100, 100–200, and >200 μequiv/L) in each of five subregions in the Northeast. Region 1A includes the Adirondack Mountains and surrounding areas, 1B includes the Catskills and Poconos, 1C is central New England, largely

† Institute for Watershed Studies.
‡ U.S. Environmental Protection Agency.
§ Northrop Services, Inc.

0013-936X/88/0922-0155$01.50/0 © 1988 American Chemical Society

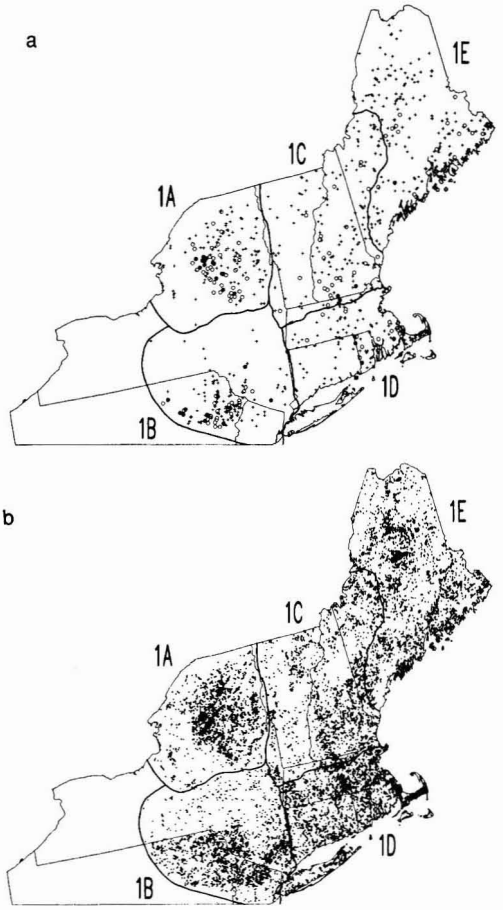


Figure 1. Locations of lakes sampled (a) in the Northeast as part of the Eastern Lake Survey. Lakes are coded by their measured ANC values (●) ≤ 0 (O) 0–50, (+) >50 μequiv/L. Lakes identified on 1:250 000-scale USGS maps (b) for the study area.

Vermont and New Hampshire, 1D is southern New England, and 1E contains most of Maine, except for the western mountains (Figure 1a). Seven hundred sixty-eight lakes were sampled in the Northeast (Table I). This represents a sampling intensity of 11% of the target population of lakes in the northeastern United States (Figure 1b).

Watersheds of lakes in the Northeast were generally larger than those in the upper Midwest (region 2) and Florida (3B) but smaller than those in the Southern Blue Ridge (3A) (*3*). Maine (1E) had the largest median watershed area in the Northeast, whereas the Poconos/Catskills (1B) had the smallest (Table II). Maine (1E) had the largest median lake area; the Adirondacks (1A) had the second largest. Lakes in the Poconos/Catskills (1B) were uniformly small. Site depths in the Poconos/Catskills (1B) and southern New England (1D) were among the shallowest of all subregions. Drainage lakes predominated in the Northeast (71% overall); however, in the Poconos/Catskills (1B), reservoirs were common (42%). Reservoirs were also common in southern New England, as were seepage lakes (Table III). Of the northeastern lakes, those in the Adirondacks (1A) and the Poconos/Catskills (1B) were at the highest elevations. The variations in lake

Table II. Median Physical Characteristics of Lakes in the Northeast

	median lake characteristics				
subregion	lake area, ha	watershed area, ha	watershed/lake ratio	depth, m[a]	residence time, yr[b]
Adirondack Mountains (1A)	20.9	265	12.7	5.6	0.23
Poconos/Catskills (1B)	12.7	169	11.6	3.2	0.25
central New England (1C)	14.3	353	16.7	4.5	0.17
southern New England (1D)	15.0	237	10.9	2.9	0.18
Maine (1E)	29.1	472	15.2	4.9	0.23
Northeast	16.7	271	13.0	4.2	0.20

[a] Site depth where the sample was collected. [b] Hydraulic residence time computed only for drainage lakes and reservoirs.

Table III. Estimated Percentage of Lakes by Hydrologic Types within the Northeast

	hydrologic lake type, %[a]			
subregion	drainage	seepage	closed	reservoir
Adirondack Mountains (1A)	77	8	7	8
Poconos/Catskills (1B)	54	4	0	42
central New England (1C)	81	7	7	5
southern New England (1D)	52	13	6	29
Maine (1E)	91	3	4	3
Northeast	71	7	5	17

[a] Determined on the basis of mapped information; see ref 2.

elevation were much greater than those observed in the upper Midwest or Florida. Roads and dwellings were the predominant watershed disturbances in all subregions, although logging was also commonly observed in Maine (1E).

Results

Northeast Regional Description. Using the statistical procedures described in ref 1, the Northeast was estimated to contain more low-pH (≤ 6.0) and low acid neutralizing capacity (ANC ≤ 50 μequiv/L) lakes than any other region and more acidic lakes (326 with ANC ≤ 0) than the Upper Midwest but not as many as Florida (*3*). The Northeast had the highest median sulfate concentration (115 μequiv/L) of all regions. The median calcium concentration (177 μequiv/L) was lower than that in the upper Midwest or Florida, and concentrations of magnesium in the Northeast were the lowest among the regions. However, only 5% of the lakes in the Northeast had calcium ≤ 50 μequiv/L, which was the lowest percentage of lakes below this reference value for all regions. Unlike those in other regions, acidic lakes in the Northeast were characterized by high levels of extractable aluminum (*1*). Acidic lakes in the Northeast also had higher concentrations of calcium, magnesium, and sulfate than did the acidic lakes in the upper Midwest or Florida.

Medians and the first and fourth quintile values are used in this analysis to compare the distributions of parameters among areas. Estimates of these values are given for several key variables in Figure 2. The interquintile difference ($Q_d = Q_4 - Q_1$) can be used as a measure of the

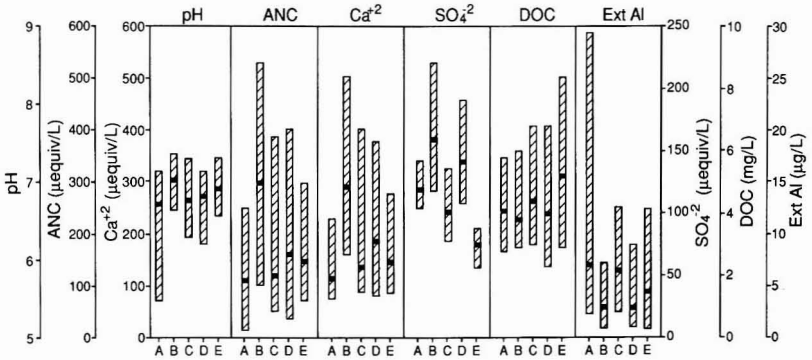


Figure 2. Population estimates (20th, 50th, and 80th percentiles) of pH, ANC, SO_4^{2-}, DOC, Ca^{2+}, and extractable aluminum for subregions in the Northeast: Adirondacks (A); Poconos/Catskills (B); central New England (C); southern New England (D); Maine (E).

variability in chemistry among lakes within subregions. As an example, for ANC, calcium, and sulfate, Maine (1E) showed less variability than the other subregions in the Northeast, whereas the Poconos/Catskills (1B) showed the greatest variability. The Adirondacks had the most acidic lakes (ANC $\leq$ 0) and the largest percentage of lakes with ANC $\leq$ 200 μequiv/L (Figure 2). The Poconos/Catskills had the greatest percentage of lakes with higher ANC (>200 μequiv/L). Concentrations of sodium and chloride increased toward the Atlantic coast due to contributions of sea salts; at distances of more than 50 km from the coast, concentrations were generally low (30 μequiv/L or less), with an increase within 20 km of the coast. Road salt contamination caused anomalously high values in many lakes in New England. These factors contribute to concentrations of sodium, potassium, and chloride that were higher in the Northeast than in the upper Midwest but lower than in Florida (*2–5*).

The Northeast was the only region in the eastern United States where most of the lakes were clear water (65% with true color $\leq$ 30 PCU). In addition, dissolved organic carbon (DOC) concentrations in dark water (>30 PCU) northeastern lakes were much lower than those in the dark water lakes in the upper Midwest or Florida and very low in many of the acidic lakes. Nearly half of the lakes with ANC $\leq$ 0 had DOC $\leq$ 2 mg/L (*6*). Dark water lakes were also shallower and smaller than clear water lakes, but their watershed areas were often larger.

Drainage lakes were by far the most common hydrologic type, followed by reservoirs. Seepage lakes were not common in the Northeast, representing only 7% of the lakes classified by hydrologic type (Table III). Seepage lakes, however, generally had the lowest values of ANC and pH of any hydrologic type in areas where they did occur. The median ANC for seepage lakes was 84 μequiv/L versus 145 μequiv/L for drainage lakes. In seepage lakes, the median estimated pH was 6.51 and in drainage lakes was 6.84. These observations of lower ANC and pH in seepage lakes compared with drainage lakes are consistent with the pattern described for northcentral Wisconsin and the Upper Peninsula of Michigan (*3,4*).

Nutrient concentrations were comparatively low for most of the lakes in the Northeast (Table IV). Median concentrations were estimated to be 0.4 μequiv/L (25 μg/L) nitrate, 1.4 μequiv/L (25 μg/L) ammonium, and 9 μg/L total phosphorus. True color values were similar among subregions, and turbidity was generally low. The median Secchi disk transparency was 2.3 m, and the estimated median value of dissolved inorganic carbon (DIC) was 2.1 mg/L.

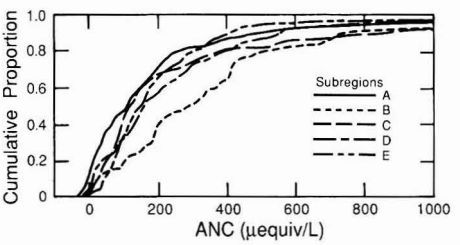


Figure 3. Cumulative frequency distributions [$F(x)$] for ANC in the Northeast: Adirondacks (A); Poconos/Catskills (B); central New England (C); southern New England (D); Maine (E).

Subregional Results. The chemistry of lakes in the Northeast is described in the following sections in three basic ways: (1) making comparisons on the basis of median and quintile values, (2) using population estimates of numbers or frequencies of lakes in relation to a reference value, e.g., the number of lakes with ANC $\leq$ 200 μequiv/L, and (3) describing the contributions of major cations and anions. The first two are calculated according to ref 1 and 2, whereas the curves for individual ions as a function of ANC are calculated from splines (*7*) appropriately weighted to produce statistical population estimates. All measured ions are shown as well as estimated organic anion concentrations from the model of Oliver et al. This model appears to overestimate the contribution of organic anions when compared to the anion deficit ($\sum$measured cations $-$ $\sum$measured anions) (Table IV). Aluminum is not shown, but it can contribute to cations especially in acidic lakes. These two factors explain the apparent deficit of cations relative to anions.

(1) Adirondacks (1A). The Adirondacks contained the highest percentage and number of acidic lakes of any subregion sampled, except Florida (3B) (*5*). A total of 138 lakes, representing 11% of the target population, was estimated to have ANC $\leq$ 0. Compared with other areas in the Northeast, the Adirondacks also had a higher percentage and number of lakes with ANC values $\leq$ 50 μequiv/L (36% or 459 lakes) (Figure 3). Because the Adirondacks contain many waters <4 ha in surface area, higher percentages of acidic lakes may have been found for smaller lakes than exist in the target population.

Clear water, low pH lakes in the Adirondacks often had high concentrations of extractable aluminum. Far more clear water lakes ($\hat{N}$ = 82) in this area had extractable aluminum concentrations $\geq$ 150 μg than in any other subregion sampled. By comparison, only 26 such lakes

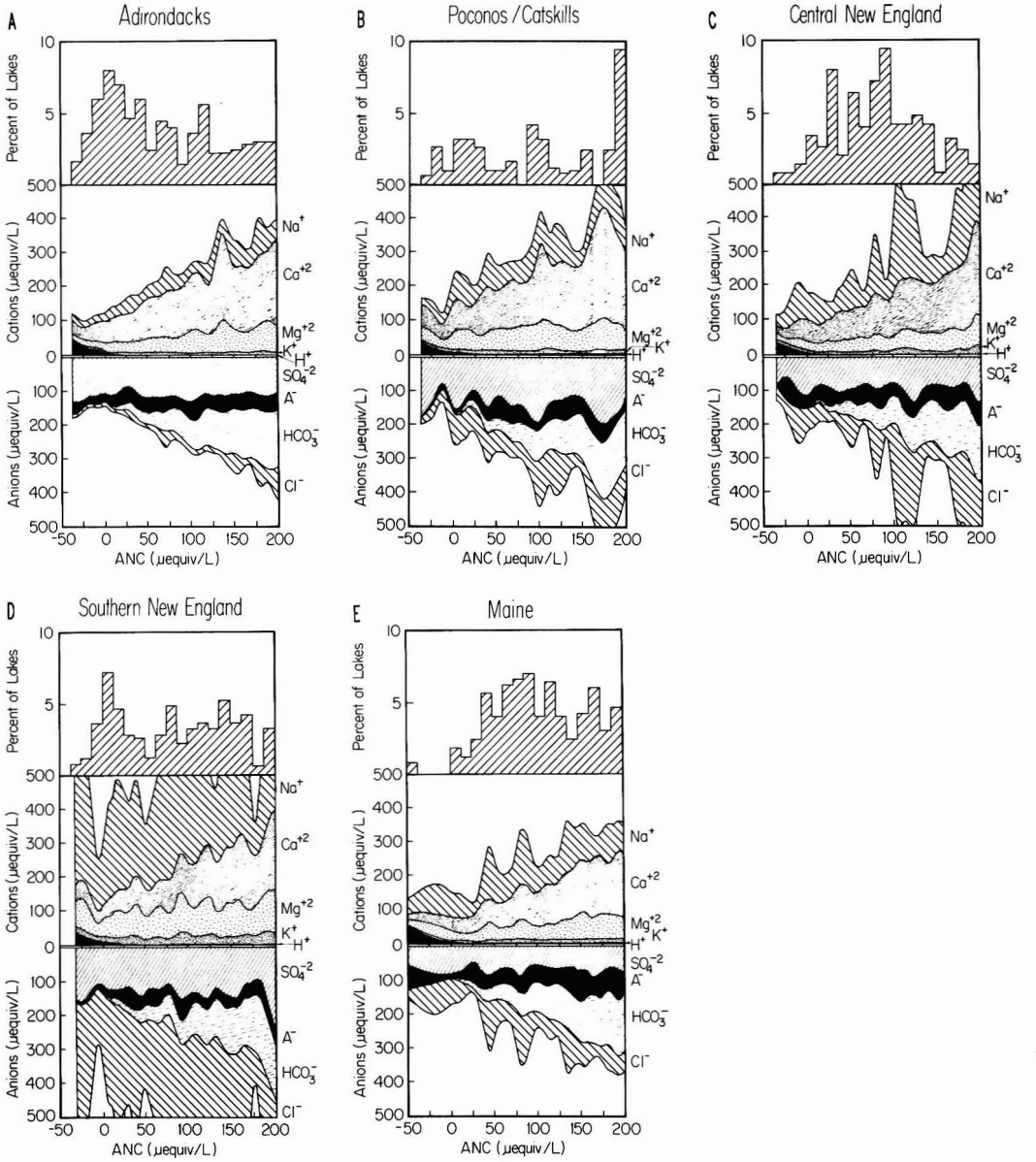


Figure 4. Major cations and anions for lakes with ANC ≤ 200 μequiv/L in the five subregions (A–E) in the Northeast. The method of smoothing for each ion was the IML function spline in SAS software with a smoothing parameter of 2 ($\sum wt_i$), where wt is the specific weight for stratum *i*. The percentages of lakes represented by ANC intervals are shown as histograms across the top of the spline plots.

occurred in all other subregions combined. Other studies have also found elevated aluminum associated with low pH in Adirondack lakes (*8–11*).

The median sulfate concentration in the Adirondacks was 119 μequiv/L. This value was lower than those observed in southern New England (1D) and the Poconos/Catskills (1B) but higher than those in central New England (1C) and Maine (1E). Thirteen percent of the lakes in the Adirondacks had sulfate concentrations > 150 μequiv/L compared to 56% in subregion 1B and 46% in 1D. These population estimates for sulfate are similar to results of a survey of 214 high elevation lakes in the Adirondacks done by Schofield (*9*) in 1975. The mean sulfate concentration for that survey was 133 μequiv/L.

In the Adirondacks, calcium was the dominant cation, and sulfate was the dominant anion for lakes with ANC ≤ 100 μequiv/L (Figure 4A). Sulfate concentrations were nearly constant across the range of ANC, as were estimated concentrations of organic anions. The concentrations of sulfate were 4–5 times higher than those of organic anions. Nitrate concentrations, even in the acidic lakes, were much lower than those of sulfate. The relative abundance of ions observed was consistent with other observations on individual lakes in the area (*10–12*). The equivalence of sulfate

Table IV. Median Chemical Characteristics of Lakes in the Northeast

variables	Adirondack Mountains (1A)	Poconos/ Catskills (1B)	central New England (1C)	southern New England (1D)	Maine (1E)	Northeast (1)
cations, μequiv/L						
calcium	145	291	137	187	147	177
magnesium	54	101	49	117	56	70
sodium	38	103	70	342	63	83
potassium	9	17	11	25	9	12
ammonium	1.5	2.2	1.3	1.4	1.2	1.4
anions, μequiv/L						
bicarbonate[a]	103	258	103	141	122	137
sulfate	119	159	101	141	75	115
organic[b]	24	13	25	0	42	22
organic[c]	37	37	43	38	52	41
chloride	11	110	43	382	33	60
nitrate	0.6	0.7	0.3	0.8	0.2	0.4
metals, μg/L						
iron	41	69	41	84	40	50
manganese	14	28	12	19	7	12
aluminum, total	67	36	58	48	56	50
aluminum, extractable	7	3	7	3	5	5
clarity						
true color, PCU	22	22	24	24	25	24
turbidity, NTU	0.5	1.4	0.7	0.9	0.6	0.7
Secchi disk, m[d]	2.8	1.8	2.6	1.6	2.6	2.3
DOC, mg/L	4.1	3.8	4.4	4.0	5.2	4.3
other						
conductance, μS/cm	30.7	63.7	34.9	81.5	33.0	43.3
silica, mg/L	2.3	1.0	1.9	2.1	1.9	1.9
total P, μg/L	4.7	21.9	7.4	14.0	5.7	9.0
DIC, mg/L	1.6	4.1	1.6	2.2	1.8	2.1

[a] Computed from open-system pH and dissolved inorganic carbon (*3*). [b] Defined as the anion deficit [$\sum$cations − $\sum$anions = $(Ca^{2+} + Mg^{2+} + K^+ + Na^+ + NH_4^+ + H^+) - (HCO_3^- + CO_3^{2-} + Cl^- + NO_3^- + SO_4^{2-} + F^- + OH^-)$]. [c] Computed with the model by Oliver et al. (*44*). [d] Shown only for lakes where Secchi disk depth < site depth.

exceeds that of bicarbonate in many individual lakes and is sometimes greater than that of base cations. In these cases, sulfate is balanced by hydrogen ion and aluminum. Sodium and chloride concentrations in the Adirondacks were the lowest in the Northeast (Figure 4A).

Specific subpopulations of lakes were analyzed for the eastern and western areas of the Adirondacks, using lakes located on either side of a meridian of 74°30′00″. These were identified because of suspected differences in precipitation and deposition. Whereas sulfate concentrations were similar on the western (windward) and eastern (leeward) areas of the Adirondack drainage divide, lake water pH, ANC, and calcium were estimated to be lower on the western side. Median ANC was 39 μequiv/L west of the divide and 167 μequiv/L east of the divide. Median calcium was 102 μequiv/L and pH was 6.15 on the west side as compared to 202 μequiv/L and 6.88, respectively, on the east side. The percentage of lakes with calcium ≤ 50 μequiv/L was 12.5% versus 4.0% on the west and east sides, respectively, whereas dissolved organic carbon concentrations were similar in both areas. Population estimates for lakes having ANC ≤ 0 were significantly higher on the west side (20%, $\hat{N}_s$ = 130) than on the east side (1.3%, $\hat{N}_s$ = 8), associated with the lower levels of base cations. Only 1.3% of the lakes on the east side were estimated to have extractable aluminum ≥ 50 μg/L, whereas 29% of the lakes on the west side had values ≥ 50 μg/L and 17% had values ≥ 150 μg/L, associated with the low pH lakes.

Both pH and ANC were strongly negatively correlated with elevation in the Adirondacks. This relationship was not observed to this degree in any other area in the Northeast. Likewise, Haines and Akielaszek (*13*) found only a weak relationship between elevation and ANC in clear water, headwater lakes in New England.

Most of the lakes in the Adirondacks were clear water. An equal percentage (34%) of dark water lakes occurred in lakes with pH ≤5.0 and in those with higher pH. Dissolved organic carbon concentrations in dark water lakes were relatively low compared to other areas, and only 39% of the dark water systems had DOC > 6 mg/L. Total phosphorus in the Adirondacks was the lowest in the Northeast. Together with low true color and DOC, this resulted in the highest Secchi disk transparencies in the Northeast (Figure 2).

Drainage lakes were the most common lake type in the Adirondacks, representing 77% of the population. Drainage lakes were characterized by having low ANC and pH values, as well as the highest extractable aluminum concentrations. Seepage lakes generally had lower concentrations of base cations and pH than did drainage lakes (*11*).

(2) Poconos/Catskills (1B). The Poconos/Catskills contained few acidic lakes; 78 lakes (5%) had ANC ≤ 0. This was the only part of the Northeast where less than half of the lakes had ANC values ≤ 200 μequiv/L, because median base cation (calcium and magnesium) concentrations in subregion 1B were very high relative to other areas in the Northeast (Table IV).

Lakes in the Poconos/Catskills were different in nearly all chemical aspects from other areas of the Northeast. Lake water sulfate concentrations in the Poconos/Catskills were very high (M = 159 μequiv/L), and very few lakes had sulfate concentrations ≤ 50 μequiv/L. Silica concentrations were low, but nutrients were the highest in the Northeast. There were also differences in physical characteristics. For example, reservoirs were common in this area, representing 42% of the total, but were much less frequent in other areas of the Northeast.

(3) Central New England (1C). Few acidic or low pH lakes were found in central New England. Only 35 lakes were estimated to have ANC ≤ 0, with the smaller lakes

generally being more acidic. No clear water lakes were estimated to have extractable aluminum concentrations ≥ 100 μequiv/L. Central New England had 262 lakes with ANC ≤ 50 μequiv/L and the second highest percentage of lakes with ANC ≤ 200 μequiv/L in the Northeast. This area had few (63) lakes with calcium concentrations ≤ 50 μequiv/L but had the lowest median calcium concentration (137 μequiv/L) in the Northeast.

Sulfate concentrations were lower than those in subregion 1A or 1B and showed more variance in the lower ANC lakes (Figure 4C). Organic anion concentrations were similar across the range in ANC, whereas sodium and chloride fluctuated greatly as a function primarily of proximity to the Atlantic coast.

Most of the lakes (68%) in central New England were clear water, with high Secchi disk transparencies. Unlike those in other northeastern subregions, dark water lakes in central New England had median and quintile pH and ANC values that were lower than those for clear water lakes. Central New England lakes were predominantly drainage lakes (81%), but the seepage lakes sampled generally had lower ANC and pH and higher extractable aluminum than drainage lakes, similar to observations in the upper Midwest (*3*, *4*).

Marked differences were noted between lakes in Vermont and in New Hampshire. No lakes in Vermont were estimated to have ANC ≤ 0, but 17 lakes in New Hampshire were estimated to have ANC ≤ 0. Also, many more lakes in New Hampshire (537) were estimated to have ANC ≤ 200 μequiv/L and lower concentrations of base cations than in Vermont (90). This is consistent with maps of bedrock geology (*14*, *15*), descriptions of geologic substrates (*16*), and previous mapping of lake alkalinities (*17*).

(4) Southern New England (1D). Five percent of the lakes in southern New England were acidic (66 lakes had ANC ≤ 0). Southern New England was estimated to have 284 lakes with ANC ≤ 50 μequiv/L and 755 with ANC ≤ 200 μequiv/L. Lakes with low ANC were not distributed uniformly within the subregion. Higher values of ANC were found in southern Connecticut and parts of Massachusetts; lakes with lower values of ANC were clustered mostly in eastern Massachusetts. Subregion 1D contained more lakes ($\hat{N}$ = 133) with calcium ≤ 50 μequiv/L than any other northeastern subregion.

Concentrations of sulfate were the second highest in the Northeast, with a median value of 141 μequiv/L. Median sodium and chloride concentrations in southern New England (1D) were the highest of any subregion due to proximity to the coast and also to road salt (Figure 4D). Median potassium and magnesium concentrations were the highest in the Northeast and contributed a greater fraction of cations for a given ANC. Sulfate concentrations increased and organic anion concentrations decreased in lakes at the lower range of ANC.

Most (62%) southern New England lakes were clear water. A much higher percentage (18%) of lakes with low DOC concentrations (≤2 mg/L) was found than in any other areas of the Northeast. Unlike other subregions of the Northeast, dark water lakes had much higher calcium concentrations than clear water lakes.

Drainage lakes were predominant (52%) in southern New England, although reservoirs were also common (29%). Seepage lakes generally had the lowest pH and ANC of any lake type, but they comprised only 13% of the lake population.

Silica concentrations in this subregion were relatively high for the Northeast (median = 2.1 mg/L) but variable (Q_d = 4.3). Phosphorus concentrations were also relatively high compared to those of central New England and Maine (median = 14.0 μg/L), similar to those reported by Deevey (*16*) for Connecticut.

(5) Maine (1E). Subregion 1E had the fewest acidic or low-pH lakes in the Northeast. Only 0.5% of the lakes had ANC ≤ 0, and 11% had ANC ≤ 50 μequiv/L. However, Maine had the most lakes with ANC ≤ 200 μequiv/L (1020 or 67%) in the Northeast; these lakes were found throughout Maine. ANC values > 200 μequiv/L were found in several areas but principally in the northern third of the state associated with lithologies containing free carbonates. The spatial distribution of lakes with high ANC was similar to that found by Mairs (*19*) and Haines and Akielaszek (*13*) and is related primarily to bedrock geology and the glacial marine limit. Maine lakes had calcium concentrations that were intermediate in the Northeast. None of the clear water lakes sampled in Maine had extractable aluminum ≥ 50 μg/L.

Maine had the lowest median sulfate in the Northeast (75 μequiv/L), and only 1% of the lakes had sulfate concentrations ≥ 150 μequiv/L. Other surveys have also found lower sulfate values than in other areas of the Northeast (*13*, *20*). Chloride concentrations declined sharply with distance from the coast, as other studies have shown (*13*, *20*, *21*). Concentrations of organic anions were higher in absolute concentration and in proportion to sulfate than in other areas of the Northeast (Figure 4E). In addition, in lakes with the lowest ANC, concentrations of organic anions increased while sulfate declined. This suggests organic anions have a greater role in contributing to lake acidity in Maine compared with other areas of the Northeast.

Maine contained the lowest percentage of clear water lakes (55%) and had a much higher percentage (42%) of lakes with DOC > 6 mg/L than any other northeastern subregion. Maine was unique in the Northeast in having dark water lakes with higher ANC concentrations than clear water lakes for the median and quintile values. As in the Adirondacks, dark water lakes in Maine generally were smaller but had larger watersheds than clear water lakes (median A_w:A_l was 23 for dark water lakes; 9 for clear water lakes). Dark water lakes in Maine also were shallower than clear water lakes. Both these factors contribute to lower estimated hydraulic residence times for dark water lakes compared to clear water lakes.

Maine had the highest percentage of drainage lakes in the Northeast (91%), the largest median lake area and watershed area, and some of the deepest lakes. Nutrient concentrations were low (estimated median total phosphorus = 5.7 μg/L) and Secchi disk transparency values relatively high (M = 2.6 m, Q_4 = 4.7 m), consistent with other investigations (*22–24*).

Discussion

The data collected during the Eastern Lake Survey have been used to estimate the current chemical status of lakes in the northeastern Unitd States, with particular reference to variables used to identify lake acidification. Changes in chemistry over time, which might be associated with acidic deposition or other influences, can only be inferred from these data. However, evaluation of present chemistry can suggest what changes might have occurred. For example, lakes impacted by road salt can be identified as outliers within a region or subregion because of high concentrations of sodium and chloride and high conductivity compared to other lakes with respect to distance from the coast (*25*, *26*). Similarly, an analysis of the ionic composition of lakes may also indicate whether acidification (as defined by the loss of alkalinity) has occurred and the

potential contribution of various ions to acidity.

Clear water lakes are usually dominated by calcium (and to a lesser extent magnesium) and bicarbonate, because in most watersheds these are the primary weathering products. Consequently, the sum of calcium and magnesium is normally related to alkalinity produced by weathering reactions (*27*). Concentrations of organic anions or other strong acid anions decrease ANC relative to calcium plus magnesium. One hypothesis of acidification (*28, 29*) states that increases in emissions of sulfur cause increases in sulfate deposition to watersheds. As sulfate concentrations increase in lakes and streams, cation concentrations also increase but do not completely compensate for the additional sulfate (*30*). In some sensitive hydrologic and geologic settings, as the concentrations of sulfate increase, bicarbonate (alkalinity) decreases and hydrogen and aluminum also increase. Thus, in areas of high deposition of sulfate, lakes with low concentrations of base cations would be expected to show replacement of bicarbonate by sulfate and decreases in lake water pH. If the supply of base cations is low relative to the external loading of strong acid anions, acidic lakes can result (*31*). Acidic lakes could also occur if the concentration of organic anions of low pK exceeded base cation concentrations.

Sulfate concentrations were highest in the Poconos/Catskills and lowest in Maine, conforming with the pattern of sulfate and pH in precipitation (*32, 33*). It is estimated that sulfate in precipitation in the northeastern United States has been enriched 8–12-fold above background values (*34*). In the Adirondacks, the median lake water value for sulfate was 119 μequiv/L, indicating that natural background sulfate might have been 10–15 μequiv/L, assuming the enrichment indicated by ref 34. In the Adirondacks, similar percentages of systems had ANC ≤ 0 (10.7%) and sulfate ≥ 150 μequiv/L (12.8%). Fewer acidic lakes were found in the Poconos/Catskills (5.3%), even though sulfate was higher than that in the Adirondacks. This is due to the higher levels of base cations, and hence higher original alkalinity, in the Poconos/Catskills compared with the Adirondacks.

Elevated sulfate in precipitation has led to elevated sulfate in lakes in the Northeast. This is consistent with current hypotheses of acidification (*28, 29*). However, no simple relationship between sulfate and lake water pH or ANC should be expected, and as shown in Figure 4, sulfate is approximately constant across a gradient of ANC. The response of different areas, as expressed in the frequency of acidic lakes, will vary depending on the supply of base cations and other factors, including hydrologic type and flow paths (*31*). Given the current and similar distribution of calcium in lakes among areas of the Northeast, increases in sulfate concentrations to new steady-state levels equivalent to those in the Adirondacks could be expected to result in a similar percentage of acidic lakes throughout New England (subregions 1C–1E) as is observed currently in the Adirondacks. Similarly, reductions in sulfate concentrations would be expected to result in the recovery of lakes. It should be noted that the apparent loadings of sulfur and lake water concentrations are higher in the Adirondacks than in some other areas where acidic lakes are known to occur (*31*). For example, higher percentages of acidic lakes have been found at much lower sulfate levels in southern Norway, because of a much lower base cation supply than that of the Adirondacks (*35*).

Ions other than sulfate, such as nitrate, chloride, and organic anions, also contribute to the acidity of lakes in the Northeast. Nitrate is found in precipitation (*33*), and additions of nitrate during periods of snowmelt runoff influence hydrogen ion concentrations (*36*). However, in the fall index sample taken by the Eastern Lake Survey, nitrate concentrations were very low. Some lakes, particularly the acidic lakes in the Adirondacks, had higher nitrate concentrations than the general population. Whereas 80% of the lakes in the Adirondacks had nitrate ≤ 3.7 μequiv/L, individual lakes, especially some of the special interest lakes (*2*), had concentrations of nitrate from 15 to 20 μequiv/L compared to a median sulfate concentration of 119 μequiv/L. Thus, nitrate may have contributed to the acidification of some lakes, especially in the Adirondacks, but it does not fully explain the long-term acidity status of those waters. Nitrate is likely to be most important during periods of high runoff, especially during snowmelt, and for relatively short periods of time.

Acidic lakes could also result from the exchange of sodium and hydrogen ions in soils related to precipitation events. This process, known as the salt effect (*37*), could produce acidic lakes, especially in coastal areas, and it was previously observed on Mount Desert Island, ME (*38*). Several acidic or low-alkalinity lakes were found by this study along the Atlantic coast in southern New England and Maine. However, few lakes had a ratio of Na:Cl less than that in seawater or coastal precipitation, and Sullivan et al. (*26*) concluded that there was little support for the neutral salt effect being a long-term acidifying process in northeastern lakes. The salt effect is a short-term process, which is difficult to observe from single samples in time and is restricted to coastal areas (*39*). A long-term acidification of lakes inland from the Atlantic coast, such as those in the Adirondacks, cannot be related to the salt effect.

Some dark water lakes in the Northeast are also acidic. Organic anions contribute to the acidity of the dark water lakes in many areas of the Northeast but do not explain all of the acidity, simply because atmospheric loadings of sulfate are so high. Many clear water, acidic lakes have very low DOC and estimated concentrations of organic anions that contribute to acidity (*40*). Across the upper Midwest and the Northeast, concentrations of DOC and organic anions are negatively correlated with sulfate and ANC (*41*). In addition, acidic, clear water lakes in the Northeast have hydraulic residence times similar to drainage lakes but 3 times slower than those in dark water lakes (*40*), suggesting hydrologic differences between acidic and dark water lakes. Because of regional differences in base cation supply (principally calcium and magnesium) (*31*), hydrologic flow path (*40, 42*), concentrations of DOC, and sulfate deposition (*31, 41*), there are differences among areas within the Northeast in the numbers of acidic lakes. Even though sulfate concentrations are very high in some areas, base cation concentrations may also be high, with the lakes retaining alkalinity. Within the subregions of the Northeast, sulfate concentrations were relatively uniform for lakes of the same hydrologic type. Acidic lakes (pH <5.0) had sulfate concentrations similar to those of lakes with higher pH but much lower concentrations of base cations (*6*).

Consistent differences in base cations, DOC, and sulfate were found between seepage lakes and drainage lakes (*40*). Seepage lakes had lower concentrations of base cations than did drainage lakes, but they also had lower concentrations of sulfate in all areas except southern New England (Figure 5). Where seepage lakes are clustered in certain areas, such as in eastern Maine (*25*), sulfate concentrations may be lower than those in drainage lakes, particularly those at higher elevations. Some higher elevation lakes may also be smaller than those covered by the

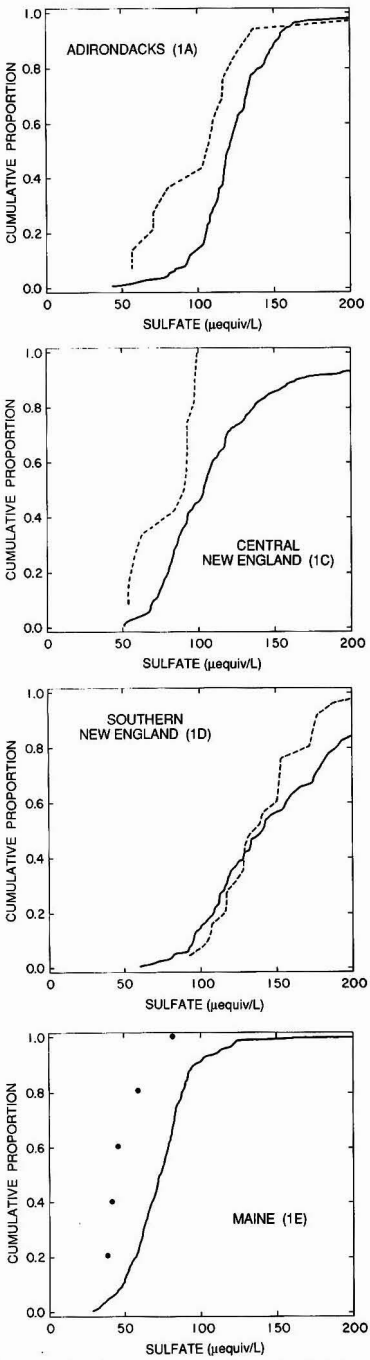


Figure 5. Cumulative frequency distributions of sulfate for seepage (--) and drainage (—) lakes in four of the five subregions of the Northeast. Individual seepage lakes are represented by dots for 1E.

ELS target population and have lower ANC and higher sulfate concentrations (*25*). Due to the many influences on lake water chemistry, it is important to identify carefully the subpopulations used in data analyses. Estimates of population characteristics for an entire subregion are not reflective in all cases of variations in chemistry, due to the distribution of terrigenous factors and lake hydrology.

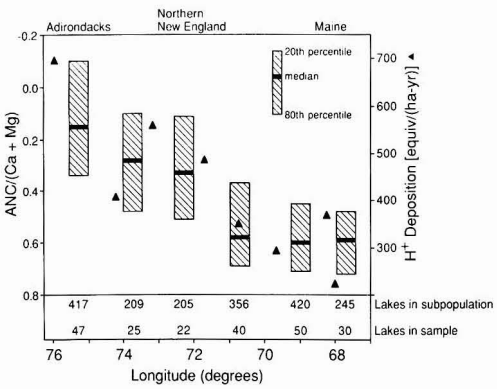


Figure 6. Population estimates (20th, 50th, and 80th percentiles) of the ratio ANC/[Ca + Mg] computed for subpopulations of lakes defined at intervals of 1°30′ longitude. Only lakes with specific conductance ≤ 30 μS/cm are included in these estimates. Hydrogen ion deposition data are derived from National Atmospheric Deposition Program stations for 1984 (*43*).

Several factors indicate that acidification of clear water lakes in the Northeast is largely associated with increased sulfate deposition. Other sources of acidity are less important, especially for clear water lakes in inland areas such as the Adirondacks. The distribution of acidic lakes in the Northeast and their ionic composition are consistent with the hypotheses of long-term acidification of surface waters due to increased sulfate deposition. This is indicated by the changing ratio of ANC:$[Ca^{2+} + Mg^{2+}]$ as a function of longitude across the Northeast. From the Adirondacks through Maine, the ratio increases as the deposition of $[H^+]$ declines (Figure 6). As sulfate concentrations in lakes decline from west to east along the northern portions of the Northeast, more HCO_3^- is present for given concentrations of $Ca^{2+} + Mg^{2+}$. This is evidence for long-term acidification. It appears that bicarbonate has been replaced by sulfate in areas receiving high deposition of acids, and lakes with low concentrations of base cations have become acidic in these areas. We can conclude on the basis of ionic contributions and other evidence that lake acidification in the northeastern United States has been due largely to atmospheric deposition of sulfate.

Acknowledgments

We acknowledge the many persons, especially Rick A. Linthurst, contributing to the Eastern Lake Survey. Stephen Norton, Richard Wright, and Spencer Peterson made many helpful comments on the manuscript; James Galloway and Edward Deevey provided suggestions on earlier analyses.

Registry No. C, 7440-44-0; Ca, 7440-70-2; Mg, 7439-95-4; Na, 7440-23-5; K, 7440-09-7; NH_4, 14798-03-9; Fe, 7439-89-6; Mn, 7439-96-5; Al, 7429-90-5; H^+, 12408-02-5.

Literature Cited

(1) Landers, D. H.; Overton, W. S.; Linthurst, R. A.; Brakke, D. F. *Environ. Sci. Technol.* **1988**, *22*, 128–135.
(2) Linthurst, R. A.; Landers, D. H.; Eilers, J. M.; Brakke, D. F.; Overton, W. S.; Meier, E. P.; Crowe, R. E. *Characteristics of Lakes in the Eastern United States;* U.S. EPA: Washington, DC, 1986; Vol. 1, pp 1–275; EPA/600/4-86/007a.

(3) Eilers, J. M.; Landers, D. H.; Brakke, D. F. *Environ. Sci. Technol.* **1988**, *22*, 172–177.
(4) Eilers, J. M.; Glass, G. E.; Webster, K. E.; Rogalla, J. A. *Can. J. Fish. Aquat. Sci.* **1983**, *40*, 1896–1904.
(5) Eilers, J. M.; Brakke, D. F.; Landers, D. H. *Environ. Sci. Technol.* **1988**, *22*, 164–172.
(6) Landers, D. H.; Eilers, J. M.; Brakke, D. F.; Kellar, P. E. *Verh. Int. Ver. Limnol.*, in press.
(7) Reinsch, C. H. *Numerische Mathematik* **1967**, *10*, 177–183.
(8) Driscoll, C. T.; Baker, J. P.; Bisogni, J. J.; Schofield, C. L. *Nature (London)* **1980**, *284*, 161–164.
(9) Schofield, C. L. *Ambio* **1976**, *5*, 228–230.
(10) Schofield, C. L. In *Acid Rain*; Haines, T. A., Johnson, R. E., Eds.; American Fisheries Society: Bethesda, MD, 1982.
(11) Driscoll, C. T.; Newton, R. M. *Environ. Sci. Technol.* **1985**, *19*, 1018–1024.
(12) Peters, N. E.; Schroeder, R. A.; Troutman, D. E. "Temporal Trends in the Acidity of Precipitation and Surface Waters of New York"; Water Supply Paper No. 2188; U.S. Geological Survey: Reston, VA, 1981.
(13) Haines, T. A.; Akielaszek, J. J. *A Regional Survey of the Chemistry of Headwater Lakes and Streams in New England: Vulnerability to Acidification*; U.S. Fish and Wildlife Service: Washington, DC, 1983; pp 1–141; FWS/OBS-80/40.15.
(14) Hendrey, G. R.; Galloway, J. N.; Norton, S. A.; Schofield, C. L.; Shaffer, P. W.; Burns, D. A. *Geological and Hydrochemical Sensitivity of the Eastern U.S. to Acid Precipitation;* U.S. EPA: Corvallis, OR, 1980; EPA-600/3-80/024.
(15) Norton, S. A. "Distribution of Surface Waters Sensitive to Acid Precipitation: A State Level Atlas"; NADP Technical Report No. 4; University of Maine: Orono, ME, 1982; pp 1–90.
(16) Brooks, J. L.; Deevey, E. S. In *Limnology in North America*; Frey, D. G., Ed.; University of Wisconsin Press: Madison, WI, 1963; Chapter 4, 117-162.
(17) Clarkson, B. *Vermont Acid Precipitation Program Winter Lake Surveys, 1980–1982*; Vermont Department of Water Resources and Engineering: Burlington, VT, 1982; pp 1–28.
(18) Deevey, E. S. *Am. J. Sci.* **1940**, *238*, 717–741.
(19) Mairs, D. F. *Limnol. Oceanogr.* **1966**, *11*, 68–72.
(20) Norton, S. A.; Davis, R.B.; Brakke, D. F. *Responses of Northern New England Lakes to Atmospheric Inputs of Acid and Heavy Metals*; Land and Water Resources Center, University of Maine: Orono, ME. 1981; pp 1–90.
(21) Mairs, D. F. *Water Resour. Res.* **1967**, *3*, 1090–1092.
(22) Davis, R. B.; Bailey, J. H.; Scott, M.; Hunt, G.; Norton, S. A. "Descriptive and Comparative Studies of Maine Lakes"; Technical Bulletin No. 88; University of Maine Life Sciences and Agriculture Experimental Station: Orono, ME, 1978; pp 1–337.
(23) Cooper, G. P. A. *Maine Dept. Inland Fish Game Fish Survey Rep. 1942*, *5*, 1–185.
(24) Bailey, J. H. *Proposed Trophic Classification of the Great Ponds of Maine*; Maine Department Environmental Protection: Augusta, ME, 1975.
(25) Norton, S. A.; Kahl, J. S.; Brakke, D. F.; Brewer, G. F.; Haines, T. A.; Nodvin, S. C. *Sci. Total Environ.*, in press.
(26) Sullivan, T. J.; Driscoll, C. T.; Eilers, J. M.; Landers, D. H. *Environ. Sci. Technol.* **1988**, *22*, 185–190.
(27) Henriksen, A. In *Proceedings of an International Conference on Acid Precipitation;* Drablos, D.; Tollan, T., Eds.; SNSF Project: Oslo, Norway, 1980; pp 68–74.
(28) Galloway, J. N.; Norton, S. A.; Church, M. R. *Environ. Sci. Technol.* **1983**, *17*, 541A–545A.
(29) National Academy of Science *Acid Deposition: Processes of Lake Acidification*; National Academy Press: Washington, DC, 1984; pp 1–11.
(30) Henriksen, A. *Verh. Int. Ver. Limnol.* **1984**, *22*, 692–698.
(31) Henriksen, A.; Brakke, D. F. *Environ. Sci. Technol.* **1988**, *22*, 8–14.
(32) Munger, J. W.; Eisenreich, S. J. *Environ. Sci. Technol.* **1983**, *17*, 32A–42A.
(33) Stensland, G. J.; Whelpdale, D. M.; Oehlert, G. In *Acid Deposition Long-Term Trends*; National Academy Press: Washington, DC, 1986; pp 128–199.
(34) Galloway, J. N.; Likens, G. E.; Keene, W. C.; Miller, J. M. *J. Geophys. Res.* **1982**, *87*, 8771–8776.
(35) Wright, R. F. *Environ. Sci. Technol.* **1988**, *22*, 178–182.
(36) Driscoll, C. T.; Schafran, G. C. *Nature (London)* **1984**, *310*, 308–310.
(37) Reuss, J. O.; Johnson, D. W. *J. Environ. Qual.* **1985**, *14*, 26–31.
(38) Kahl, J. S.; Anderson, J. L.; Norton, S. A. "Water Resource Baseline Data and Assessment of Impacts from Acidic Precipitation, Acadia National Park, Maine"; Technical Report No. 16; National Park Service, North Atlantic Region: Boston, MA, 1985; 123 p.
(39) Norton, S. A.; Henriksen, A.; Wright, R. F.; Brakke, D. F. In *Geochemistry and Monitoring in Representative Basins*; Moldan, B.; Paces, T., Eds.; Geological Survey: Prague, Czechoslovakia, 1987; pp 148–150.
(40) Brakke, D. F.; Eilers, J. M.; Landers, D. H. In *Acidification and Water Pathways*; Norwegian National Committee on Hydrology: Oslo, Norway, 1987; 281–290.
(41) Linthurst, R. A.; et al. *Water, Air, Soil Pollut.* **1986**, *31*, 577–591.
(42) Chen, C. W.; Cherini, S. A.; Peters, N. E.; Murdoch, P. S.; Newton, R. W.; Goldstein, R. A. *Water Resour. Res.* **1984**, *20*, 1875–1882.
(43) NADP/NTN *Precipitation Chemistry in the United States*, 1984; Natural Resource Ecology Laboratory, Colorado State University: Fort Collins, CO, 1986.
(44) Oliver, B. G.; Thurman, E. M.; Malcolm, R. L. *Geochim. Cosmochim. Acta* **1983**, *47*, 2031–2035.

Received for review February 9, 1987. Accepted October 26, 1987. The research described in this article has been funded as part of the National Acid Precipitation Assessment Program by the U.S. Environmental Protection Agency. This article was prepared at the EPA's Research Laboratory in Corvallis, OR, in part through Contract 68-03-3246 with Northrop Services and Cooperative Agreement CR812653 with Western Washington University. This is a contribution from the National Surface Water Survey of the EPA's Aquatic Effects Research Program. It has been subjected to the Agency's peer and administrative review and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Environ. Sci. Technol. 1988, 22, 164–172

Chemical and Physical Characteristics of Lakes in the Upper Midwest, United States

Joseph M. Eilers,*,† David F. Brakke,‡ and Dixon H. Landers§

Northrop Services, Inc., 200 S.W. 35th Street, Corvallis, Oregon 97333, Institute for Watershed Studies, Western Washington University, Bellingham, Washington 98225, and U.S. Environmental Protection Agency, 200 S.W. 35th Street, Corvallis, Oregon 97333

■ A statistical sampling of 592 lakes, representing an estimated 8575 lakes, was conducted in northern Minnesota, Wisconsin, and Michigan during Fall 1984 as part of the EPA's Eastern Lake Survey. The survey was designed to quantify the number of lakes with surface area greater than 4 ha that are acidic or that have low acid neutralizing capacity (ANC). The largest estimated number (102) and percentage (9.8%) of acidic lakes (ANC ≤ 0) in the upper Midwest were found in the upper peninsula of Michigan. There were an estimated 45 acidic lakes in northcentral Wisconsin, representing 3% of the target lakes, and the highest percentage (41.4%) of low ANC (≤50 μequiv/L) lakes was also observed in this area. No acidic lakes were sampled in the remaining portions of Minnesota, Wisconsin, or Michigan. Sulfate concentrations, relatively low compared to those in portions of the Northeast, were greatest in the upper peninsula of Michigan and were intermediate in northeastern Minnesota. Acidic lakes had low concentrations of major base cations and high sulfate concentrations and were most common in areas receiving greatest acidic deposition. The strong relationship of lake chemistry to the depositional gradient of hydrogen ions and the relatively modest concentrations of DOC in acidic lakes, coupled with the predominance of sulfate in these lakes, provide support for the hypothesis that some lakes in the upper Midwest have been acidified by acidic deposition.

Sample from the Upper Midwest

This paper presents the physical and chemical characteristics of lakes in the upper Midwest as determined from the EPA's Eastern Lake Survey (ELS). The approach was to sample a sufficient number of lakes within the region to estimate characteristics of the population of lakes defined by the statistical frame (*1*, *2*). Lakes were selected with a stratified design, with equal allocation of sample lakes to strata. The three stratification factors were region (e.g., upper Midwest), subregion (e.g., northeastern Minnesota), and alkalinity map class (e.g., suspected alkalinity < 100 μequiv/L). Sampling in the upper Midwest, as with other regions in the ELS, was limited to those areas where most lakes were believed to have alkalinity < 400 μequiv/L (Figure 1).

The target population was defined from 1:250 000-scale USGS topographic maps and consequently was limited to lakes generally >4 ha in surface area. The minimum size of lakes included on any given USGS topographic map varies, depending on the density of the lakes, their proximity to urban areas, the climatic conditions when the map was compiled, and the year the map was prepared. The field and analytical methods used in the upper Midwest were identical with those used in other regions (*1–4*)

The estimated number of lakes represented in each stratum (Table I) was computed by multiplying the number of lakes sampled by the inverse probability (*W*) of sampling a target lake within that stratum. Because the numbers of sample lakes in all strata were similar, strata with a large number of lakes in the target population necessarily had a correspondingly larger weighting factor (*W*) than strata where the sample size approached the size of the target population. Because of the influence of the very large lakes (>2000 ha) on the population estimates for lake area ($\hat{A}$), population estimates are presented here only for that portion of the target population ≤ 2000 ha.

Table I. Subregional and Regional Summaries of Estimated Target Population Size ($\hat{N}$), Estimated Target Population Area ($\hat{A}$), and the Standard Errors (SE) of These Estimates for the Upper Midwest, Eastern Lake Survey—Phase I

	lakes ≤2000 ha[a]				
subregion	n[b]	$\hat{N}_s$	SE($\hat{N}_s$)	$\hat{A}_s$	SE($\hat{A}_s$)
northeastern Minnesota (2A)	147	1457	74.3	142 979	37 582
upper peninsula of Michigan (2B)	146	1050	72.5	34 025	10 854
northcentral Wisconsin (2C)	153	1480	48.8	97 556	21 357
upper Great Lakes area (2D)	141	4515	293.9	226 896	58 202
upper Midwest (2)	587	8501	315.5	501 457	73 306

[a] Subscript s denotes a subpopulation, in this case those lakes in the target population >4 ha and ≤2000 ha. Five lakes with surface area > 2000 ha were sampled in the upper Midwest, but are excluded from the population estimates. [b] Number of lakes sampled.

The sampling intensity for the upper Midwest was the lowest among the three regions of the survey, with only 6.9% of the target population lakes being sampled. The estimated numbers of lakes >4 ha in the first three subregions (2A–2C) were similar (1050–1511), whereas 4515 lakes of this size were estimated in the upper Great Lakes area (2D). The relatively low sampling intensity in the upper Great Lakes area was reflected in the large standard error for $\hat{N}$.

Lakes in the upper Midwest were sampled from October 7 to November 13, 1984. Forty of the 57 target lakes not sampled were frozen. Poor weather conditions resulted in an additional 10 target lakes not being sampled and miscellaneous factors accounted for the balance of unsampled target lakes. The desired sample size of 50 lakes per stratum was not achieved in 7 of the 12 strata. However, only two strata (located in subregions 2B and 2D), where the actual sample sizes were 41 and 40, had substantially less than the desired number of sample lakes. For the purpose of this analysis, it was assumed that the nonsampled target lakes had properties similar to the sampled lakes, although the actual impact of this on the population estimates cannot be assessed at present.

Results: Regional Overview

Physical Characteristics of Lakes in the Upper Midwest. The lakes in the upper Midwest differed considerably among subregions in several physical characteristics (Table II). First, the lakes in the upper peninsula

† Northrup Services, Inc.
‡ Institute for Watershed Studies.
§ U.S. Environmental Protection Agency.

0013-936X/88/0922-0164$01.50/0 © 1988 American Chemical Society

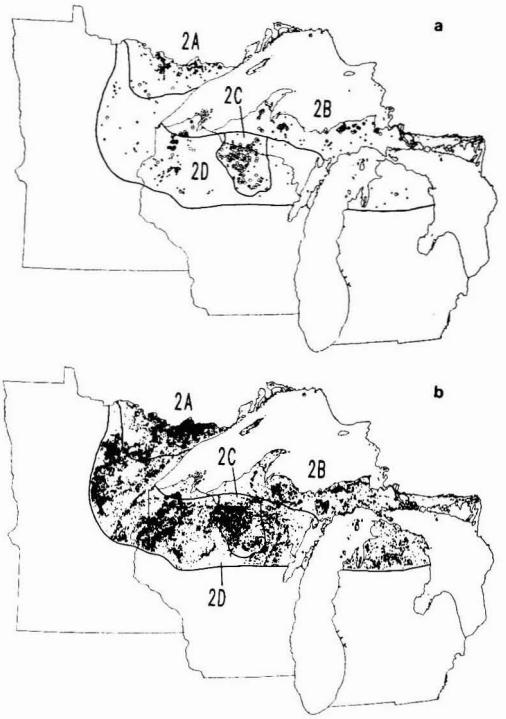


Figure 1. Locations of lakes sampled (a) in the upper Midwest as part of the Eastern Lakes Survey. Lakes are coded by their measured ANC values: (●) ≤0, (O) 0–50; and (+) >50 μequiv/L. Lakes identified on 1:250 000-scale USGS maps (b) for the study area.

Table II. Median Physical Characteristics of Lakes in the Upper Midwest

	median lake characteristics				
subregion	lake area, ha	watershed area, ha	watershed/lake ratio	depth, m[a]	residence time, yr[b]
northeastern Minnesota (2A)	17.0	201	9.7	5.3	0.65
upper peninsula of Michigan (2B)	11.1	115	10.2	2.9	0.25
northcentral Wisconsin (2C)	15.6	112	6.1	6.0	0.77
upper Great Lakes area (2D)	16.2	181	13.2	5.9	0.49
upper Midwest	14.8	177	10.3	5.6	0.48

[a] Site depth where the sample was collected. [b] Hydraulic residence time computed only for drainage lakes and reservoirs (2).

of Michigan (2B) were much smaller and shallower than lakes in the other subregions; the latter factor may cause these lakes to have shorter hydraulic residence times than lakes in other subregions with similar size watershed and surface areas. Lakes in the upper peninsula and in northcentral Wisconsin (2C) had much smaller watershed areas than those in the other two subregions. The lakes also showed considerable variety in hydrologic lake type, with 74% of the lakes in northeastern Minnesota (2A) defined as drainage lakes and 59% of the lakes in northcentral Wisconsin as seepage lakes (Table III).

The lakes in the upper Midwest were somewhat smaller than those observed in the Northeast and had smaller

Table III. Estimated Percentage of Lakes by Hydrologic Types within the Upper Midwest

	lake type, %[a]			
	drainage	seepage	closed	reservoir
northeastern Minnesota (2A)	74	16	8	2
upper peninsula of Michigan (2B)	51	38	6	5
northcentral Wisconsin (2C)	36	59	4	1
upper Great Lakes area (2D)	46	47	5	2
upper Midwest	50	43	5	2

[a] Determined on the basis of mapped information with the nomenclature of Wetzel (5).

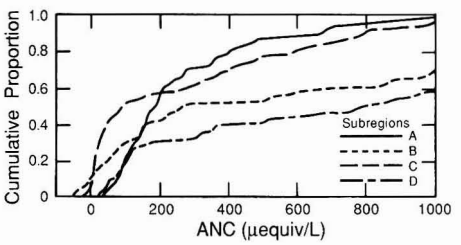


Figure 2. Cumulative frequency distributions [$F(x)$] for ANC in the upper Midwest: northeastern Minnesota (A); upper peninsula of Michigan (B); northcentral Wisconsin (C); upper Great Lakes area (D).

watershed areas, but were generally deeper than those in the Northeast. On the basis of interpolations from mapped sources of information, the hydraulic residence times for drainage lakes and reservoirs in the upper Midwest were approximately twice those of lakes in the Northeast. Finally, 43% of the lakes in the upper Midwest were seepage lakes (Table III), whereas only 7% were estimated to be seepage lakes in the Northeast (6). A high percentage of seepage lakes was also a feature of the Florida lakes (7).

Chemical Characteristics of Lakes in the Upper Midwest. The upper Midwest contained fewer ($\hat{N}$ = 148) acidic (ANC ≤ 0) lakes than the Northeast and the Southeast but contained almost as many low-ANC (ANC ≤ 50 μequiv/L) lakes ($\hat{N}$ = 1312) as the Northeast (1). All acidic lakes sampled in the upper Midwest were located in the upper peninsula of Michigan (2B) and northcentral Wisconsin (2C) (Figure 2). The greatest number [$\hat{N}$ = 102, upper confidence limit (UCL) = 157] and percentage (9.8%) of acidic lakes occurred in the upper peninsula of Michigan. The number and percentage of acidic lakes in this subregion were similar to those observed for the Adirondacks, where there were an estimated 138 acidic lakes representing 10.7% of the target population (6). The number and percentage of acidic lakes in northcentral Wisconsin were comparable to those observed in the Poconos/Catskills, central New England, and southern New England (6).

The distribution of low-ANC lakes (≤50 μequiv/L) in the upper Midwest was quite different from most other regions. Northcentral Wisconsin had the greatest percentage of low-ANC lakes in the ELS (41.4%) and the second greatest number of low-ANC lakes ($\hat{N}$ = 612), only exceeded by Florida with an estimated 742 low-ANC lakes. The 95% UCL for the number of low-ANC lakes in the upper Great Lakes area was similar to that for northcentral Wisconsin (UCL = 708 vs 705, respectively). The large confidence bound results from the low sampling intensity

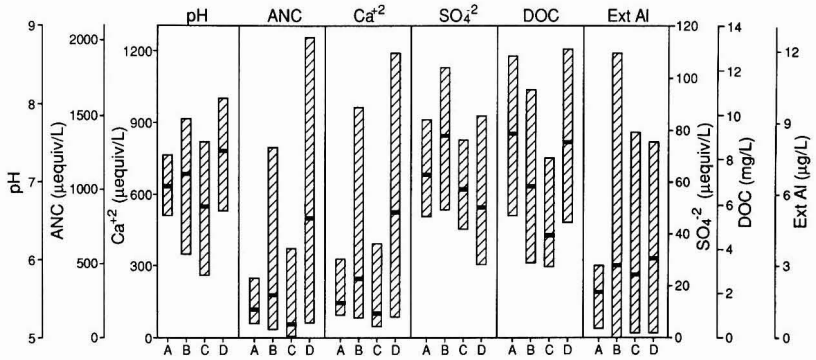


Figure 3. Population estimates (20th, 50th, and 80th percentiles) of pH, ANC, Ca^{2+}, SO_4^{2-}, DOC, and extractable aluminum for subregions in the upper Midwest: northeastern Minnesota (A); upper peninsula of Michigan (B); northcentral Wisconsin (C); upper Great Lakes area (D).

Table IV. Median Chemical Characteristics of Lakes in the Upper Midwest

variables	northeastern Minnesota (2A)	upper peninsula of Michigan (2B)	northcentral Wisconsin (2C)	upper Great Lakes area (2D)	upper Midwest
cations, μequiv/L					
calcium	143	246	101	522	238
magnesium	100	148	58	340	152
sodium	40	29	31	66	41
potassium	9	13	15	21	16
ammonium	1.5	0.6	2.2	2.1	1.6
anions, μequiv/L					
bicarbonate[a]	144	275	72	762	287
sulfate	62	78	57	50	57
organic[b]	78	55	34	81	73
organic[c]	89	67	46	82	73
chloride	9	10	11	22	17
nitrate	0.9	0.6	1.0	0.6	0.7
metals, μg/L					
iron	105	50	53	44	55
manganese	0	0	7	0	0
aluminum, total	40	31	21	20	23
aluminum, extractable	2	3	3	3	3
clarity					
true color, PCU	44	31	24	39	35
turbidity, NTU	1.1	0.9	0.8	1.0	0.9
Secchi disk, m[d]	1.6	1.5	2.3	1.9	1.9
DOC, mg/L	9.2	6.8	4.6	8.8	7.5
other					
conductance, μS/cm	30.4	47.2	22.5	91.6	44.3
silica, mg/L	2.6	2.3	0.6	2.4	2.3
total P, μg/L	13	13	14	19	17
DIC, mg/L	2.4	4.5	1.6	9.5	4.4

[a] Computed from open-system pH and dissolved inorganic carbon (*3*). [b] Defined as the anion deficit $[\sum(Ca^{2+} + Mg^{2+} + K^+ + Na^+ + NH_4^+ + H^+) - \sum(HCO_3^- + CO_3^{2-} + Cl^- + NO_3^- + SO_4^{2-} + F^-)]$. [c] Computed with the model by Oliver et al. (*8*). [d] Shown only for lakes where Secchi disk depth < site depth.

for subregion 2D, noted earlier. The regional pattern observed with ANC is repeated with pH, in that all lakes with pH ≤5.0 in the upper Midwest were found in Michigan and Wisconsin.

Population estimates of the 20th, 50th, and 80th percentiles are presented for several variables of major interest with respect to acidification for the subregions in the upper Midwest (Figure 3). The bar plots show that median pH values for these subregions are circumneutral; the vast majority of the lakes have current values above a level that might cause concern for aquatic biota (e.g., pH >6). The heterogeneity of lake chemistry within the upper Midwest is evident in the ANC and calcium concentrations for subregions 2B and 2D. Although the upper peninsula of Michigan has the highest percentage of acidic lakes in the upper Midwest, it also has a relatively large percentage of high-ANC lakes (>400 μequiv/L). Unlike ANC and calcium, the concentrations of sulfate among the subregions are much more uniform, with median values differing by less than 30 μequiv/L.

Lakes in the upper Midwest generally contained much higher concentrations of dissolved organic carbon (DOC) than lakes in the Northeast, with median values of 7.5 and 4.3 mg/L, respectively. However, in the subregions of the upper Midwest containing acidic lakes (2B and 2C), DOC concentrations were similar to those found in the Northeast. Aluminum concentrations in lakes of the upper Midwest were among the lowest in the East (*1*). Only in the upper peninsula of Michigan, where 9.8% of the lakes were acidic, were aluminum concentrations comparable to values observed in the Northeast (*6*).

Table IV provides population estimates for median concentrations of most chemical variables measured in the survey. Nitrate and ammonium concentrations were low in all subregions. Total phosphorus concentrations were similar among all subregions except the upper Great Lakes

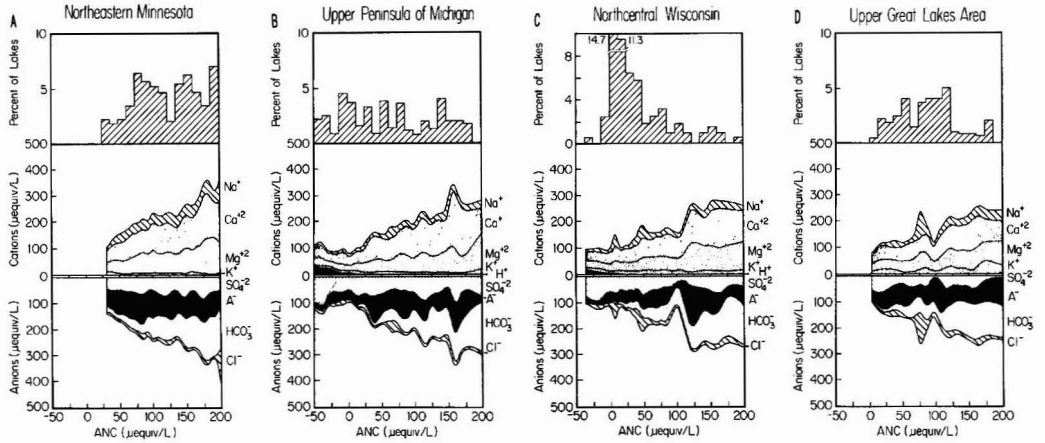


Figure 4. Major cations and anions for lakes with ANC ≤ 200 μequiv/L in the four subregions (A–D) in the upper Midwest. The method of smoothing for each ion was the IML function spline in SAS software (*8*) with a smoothing parameter of 2 ($\sum$ wt$_i$) where wt is the specific weight for stratum i. The percentages of lakes represented by ANC intervals are shown as histograms across the top of the spline plots. Contributions of cations such as AL^{n+}, Fe^{n+}, Mn^{n+}, and NH_4^+ and anions such as NO_3^- and F^-, which are important in some lakes, are excluded here to increase clarity of the presentation.

area, where they were approximately 30% greater than in the other subregions. The median percentage of agricultural land use in the watersheds (land use data derived from USGS topographic maps) of the upper Great Lakes area was 11.8%, whereas it was only 0.7%, 2.7%, and 4.4% for subregions 2A, 2B, and 2C, respectively. The higher total phosphorus values are consistent with a greater percentage of agricultural land use across this subregion relative to the other subregions; however, other factors, such as soil type or shoreline development, could also explain differences in phosphorus concentrations among subregions.

Color values in lakes of the upper Midwest were among the greatest observed in the East, exceeded only by those of Florida. This pattern is consistent with the relatively high DOC concentrations in this region (*7*). The low turbidity values show only slight differences among subregions. Secchi disk transparency values in the upper Midwest subregions were intermediate among other eastern subregions and were considerably less than those in the Adirondacks (*6*).

Manganese concentrations were very low in northeastern Minnesota and the upper Great Lakes area relative to the other midwestern subregions. Iron concentrations were relatively high throughout these midwestern lakes and were highest in northeastern Minnesota, where major deposits of iron ore are abundant.

Silica concentrations in northcentral Wisconsin were particularly low, and only lakes in Florida exhibited lower silica values. Both Florida and northcentral Wisconsin had the highest proportion of seepage lakes in the East. Northcentral Wisconsin was also noteworthy within the ELS for its dilute lakes, as indicated by the low conductance values for the subregion; 20% of the lakes had conductance values < 13.4 μS/cm. As noted earlier, the DOC concentrations in the upper Midwest were high, only exceeded by those in Florida (*7*). Within the upper Midwest, the highest DOC concentrations were associated with the two subregions (2A and 2D) for which acidic lakes were not sampled.

A general impression of the relative importance of major anions and cations among subregions can be gained by examining the median concentrations of the ions in Table IV. This impression, however, can be misleading if the proportion of ions shown for the median changes substantially at higher or lower concentrations. Alternatively, the concentrations of ions can be expressed for individual lakes as cation/anion bar charts. However, a strength of the survey is that it is a statistically selected sample that can be used to evaluate the chemistry of all lakes represented by the sample. To address these issues, the anions and cations for lakes with ANC ≤ 200 μequiv/L have been plotted against ANC (Figure 4). The curves for individual ions were computed with splines (*10*), appropriately weighted by the sample lakes.

The organic anion concentrations represented in Figure 4 were computed with the model of Oliver et al. (*8*). On the basis of ion balance considerations ($\sum$cations − [$\sum$measured anions + organic anions]), this model appears to overestimate the contribution of organic anions for lakes in the upper Midwest. However, even if this liberal estimate of organic anions is used, sulfate remains the dominant anion in the acidic lakes. Contributions from chloride are erratic, reflecting the occasional influence of road salt. Among the cations, calcium and magnesium are usually dominant. With the exception of some variation in subregion 2D, potassium concentrations are relatively low and constant in the upper Midwest (within the ANC range presented). Spikes in sodium concentration can be attributed to road salt contribution, but the base line concentrations of sodium are 2–3 times those of chloride on an equivalence basis. This disparity in sodium and chloride concentrations likely reflects increased sodium derived from weathering of silicate minerals (*11*), although chloride retention in wetlands may contribute somewhat to this disparity (*12*).

Results: Subregional Summaries

Northeastern Minnesota (2A). Most lakes in northeastern Minnesota had relatively high ANC and pH. No acidic lakes were sampled in subregion 2A, a finding consistent with the results of a sampling of 290 northeastern Minnesota lakes reported by Schnoor et al. (*13*). Only 1% of the lakes in the subregion was estimated to have pH ≤6.0. Calcium concentrations were also high; the 20th percentile value for this variable was the highest in the

upper Midwest. Sulfate concentrations were intermediate compared to other subregions in the upper Midwest.

Striking features of lakes in northeastern Minnesota were their high color (70% are considered dark water) and high DOC (76% of the lakes have DOC ≥ 6 mg/L) values. This is attributed, in part, to the extensive peatland (*14*) and the connected drainage lake networks (i.e., 74% of the lakes are drainage). The ratio of watershed area to lake area (A_w:A_l) for dark water lakes in northeastern Minnesota was 13.3, but comparison of this ratio with those from other subregions in the ELS shows that this variable alone is insufficient to explain the high color and high DOC in these lakes.

The lake chemistry in northeastern Minnesota showed relatively little heterogeneity. For example, the interquintile difference ($Q_d = Q_4 - Q_1$) for pH in subregion 2A was 0.77 pH unit compared to 1.75, 1.72, and 1.44 for subregions 2B, 2C, and 2D, respectively. A similar pattern was observed for ANC, where Q_d was 305 for subregion 2A and 1229, 585, and 1918 for subregions 2B, 2C, and 2D, respectively. Again, it is likely that the high degree of interconnected lakes contributes to the chemical homogeneity for this subregion.

The lakes in northeastern Minnesota had slightly larger lake surface and watershed areas than other lakes in the upper Midwest, but the A_w:A_l ratios were not substantially greater than those of other subregions. Consequently, the higher ANC concentrations in the northeastern Minnesota lakes may be attributed, in part, to the composition of surficial and bedrock geology. Other studies of lake chemistry and watershed factors in Minnesota (most of these studies extend beyond the boundaries of subregion 2A) show an association between surface water chemistry and soils (*15*), till (*16*), and bedrock geology (*14*). However, Winter (*17*) considered groundwater chemistry to be a better index of lake chemistry because it incorporates hydrology with the geology. The moderately high sulfate concentrations in northeastern Minnesota lakes (relative to the upper Midwest as a whole) were attributed to sulfide ores (*14*). The extractable aluminum concentrations in clear water lakes for subregion 2A were low, and none of the lakes sampled had values > 100 μg/L. Most of the lakes with moderately high aluminum values in northeastern Minnesota also had high DOC, and it is assumed that much of the extractable aluminum in these lakes is complexed with organic ligands (*18*).

Upper Peninsula of Michigan (2B). The upper peninsula of Michigan was estimated to have the highest percentage of acidic lakes (9.8%) in the upper Midwest. An estimated 9% of the lakes in this subregion had pH ≤5, also the highest percentage in the upper Midwest. However, because there is a relatively large population of high-ANC lakes in subregion 2B, median values for pH (7.10) and ANC (284 μequiv/L) are high relative to other subregions. The acidic lakes in subregion 2B were generally clear water (median color = 22 PCU). Thirty-eight percent of the lakes in subregion 2B were seepage lakes with very low concentrations of most ions (median Ca^{2+} = 111 μequiv/L; SO_4^{2-} = 67 μequiv/L). Sulfate concentrations were low (Q_4 = 104 μequiv/L) in subregion 2B compared to those in lakes in the Northeast, but they were approximately 20% greater than in other subregions of the upper Midwest. Silica concentrations were extremely low (Q_1 for silica in subregion 2B lakes was 0.3 mg/L). The extractable aluminum values were generally low (only 0.4% of the clear water lakes had values ≥ 100 μg/L), although the 80th percentile value of 12 μg/L was higher than elsewhere in the region.

Large interquintile differences for all primary variables, except sulfate, were observed. This heterogeneity of chemistry for lakes in subregion 2B can be explained by the contrasting composition of the bedrock types and the presence of high percentages of both seepage (38%) and drainage (51%) lakes (*13*). Subregion 2B also represents a large geographic area, extending over 600 km from east to west and exhibits a gradient in deposition chemistry (*19*). The greater number of low-ANC lakes observed in the eastern portion of the peninsula is consistent with the pattern observed by Schneider (*20*). The percentage of acidic lakes in the eastern portion of the upper peninsula of Michigan (east of longitude 87°) was estimated to be 18.2%, which also agrees with the estimate of 19% reported by Schnoor et al. (*13*) for a comparable area.

Northcentral Wisconsin (2C). Northcentral Wisconsin, although comprising the smallest land surface area of all subregions in the Eastern Lake Survey, had an estimated target population of 1480 lakes, excluding those > 2000 ha. Whereas only a small percentage of lakes (3%) were estimated to be acidic, 41% of the lakes were estimated to have ANC values ≤ 50 μequiv/L. These results agree with the findings of Eilers et al. (*21*) and Schnoor et al. (*13*) who reported 3% and 4% percent, respectively, of lakes in this area with ANC ≤ 0 and a high percentage of low-ANC lakes. The median ANC for lakes in northcentral Wisconsin (94 μequiv/L) was the lowest among all subregions in the East except Florida (84 μequiv/L).

The factors believed to contribute most to the low ionic concentrations of lakes in northcentral Wisconsin are hydrology (*21–24*), soils, and composition of the till (*25*). Seepage and drainage lakes exhibited chemistry markedly different from one another. The median A_w:A_l ratio for lakes in northcentral Wisconsin was lower than for other lakes in the upper Midwest and most other lakes in the ELS, with the exception of those in Florida. The modest influence of watershed factors for many of the seepage lakes results in low weathering rates reflected in low concentrations of silica and calcium (*13*).

Upper Great Lakes Area (2D). No acidic lakes were sampled in the upper Great Lakes area. The sampling intensity in the upper Great Lakes area was the lowest in the ELS (286 lakes sampled out of an estimated 4514). The subregion had a median ANC of 802 μequiv/L, by far the highest among all subregions. It also contained the largest number of lakes in the target population but the lowest percentage of lakes (31.3%) with ANC ≤ 200 μequiv/L of any subregion in the East. An estimated 20% of the lakes had pH values >8.07; only 4% of the lakes had pH values ≤6.0. The proportion of clear water and dark water lakes in subregion 2D was approximately equal. Lakes in subregion 2D contained high concentrations of many major ions, evident in Table III and Figure 4.

Most lakes sampled in subregion 2D with ANC ≤ 50 μequiv/L were in northwestern Wisconsin. This agrees with the expected pattern based on Omernik and Griffith (*26*) and a statewide survey of 1000 lakes by Lillie and Mason (*27*). However, lakes in northeastern Wisconsin are not well represented by the ELS (Figure 1), and data by Nichols and McRoberts (*28*) indicate that there may be a moderate proportion of acidic and low-ANC lakes in this area.

Subregion 2D contains at least three distinct geological provinces that result in distinct chemical differences among lakes in Minnesota, Wisconsin, and Michigan. The Minnesota portion of subregion 2D was described by Moyle (*16*) as a hard-water flora area, which he attributed, in part, to the presence of Paleozoic and Cretaceous sedimentary

rocks. Carbonate present in till (*29*) and in the soils (*15*) in this part of Minnesota may also contribute to high concentrations of calcium bicarbonate in these lakes. The lower peninsula of Michigan, also contained within subregion 2D, is underlain by Cretaceous sedimentary carbonate rocks (*30*); consequently, lakes in this area also had high values of ANC. High ANC values in lower Michigan are in agreement with the study by Schneider (*20*). In contrast, the Wisconsin portion of subregion 2D is underlain by sedimentary sandstones and igneous bedrock (*31*) and covered by 20–200 m of till containing a small percentage of carbonate (*32*).

Discussion

Lakes of the upper Midwest, especially those of Wisconsin and Michigan, had greater physical and chemical similarity to lakes of Florida (*7*) than to lakes of the Northeast (*6*). This similarity exists despite the major differences in climate and vegetation between the two areas. A high percentage of seepage lakes is common to both Florida and the upper Midwest, and both populations of seepage lakes generally have lower concentrations of base cations, sulfate, aluminum, and silica than lakes in the Northeast. Eighty percent of the acidic lakes in the upper Midwest and 84% of the acidic lakes in Florida are seepage lakes, in contrast to the Northeast where 78% of the acidic lakes are drainage lakes (*6*). However, the observation that seepage lakes represent a higher number of acidic lakes than expected, on the basis of their proportion of the populations in all regions, highlights the apparent sensitivity of these lakes to acidification.

The results of the Eastern Lake Survey have been presented according to the stratification factors (alkalinity class, subregion, region) used in the survey design. However, further use of these data need not be constrained by use of alkalinity class and subregions, although the restriction to the region study boundary cannot be altered. Where the need exists, the data can be subset into subpopulations that may be more appropriate for interpretation (*33*). Subpopulations can be defined on the basis of the chemical characteristics shown earlier in the description of acidic lakes (Table V). Likewise, the data can be subset on the basis of physical characteristics of the lakes, such as hydrologic type. Although hydrologic type is a coarse measure of lake and watershed interactions, it can be a useful classification tool. Hydrologic contributions to lakes from watersheds vary along a continuum. Seepage lakes appear to represent a minimum of watershed contributions, whereas drainage lakes represent a greater integration of terrestrial processes in the determination of lake water chemistry. The validity of this simplified concept of lake and watershed interactions is supported by empirical evidence showing that, within a given subregion, seepage lakes have lower ANC and base cations than drainage systems (*34*).

Applying this hydrologic classification approach to the evaluation of sulfate in lakes, we would expect seepage lakes to have lower sulfate concentrations than drainage lakes within the same geographic area. Internal lake processes such as sulfate reduction would be expected to have a greater effect on long-residence-time seepage lakes. Dry deposition of sulfate would be likely to have a greater influence on short-residence-time drainage lakes. When the cumulative distributions of sulfate in the seepage and drainage lakes are plotted by subregion (Figure 5), we observe the expected pattern in northeastern Minnesota and the upper peninsula of Michigan where the concentrations of sulfate are lower in seepage lakes compared to drainage lakes. However, in northcentral Wisconsin and

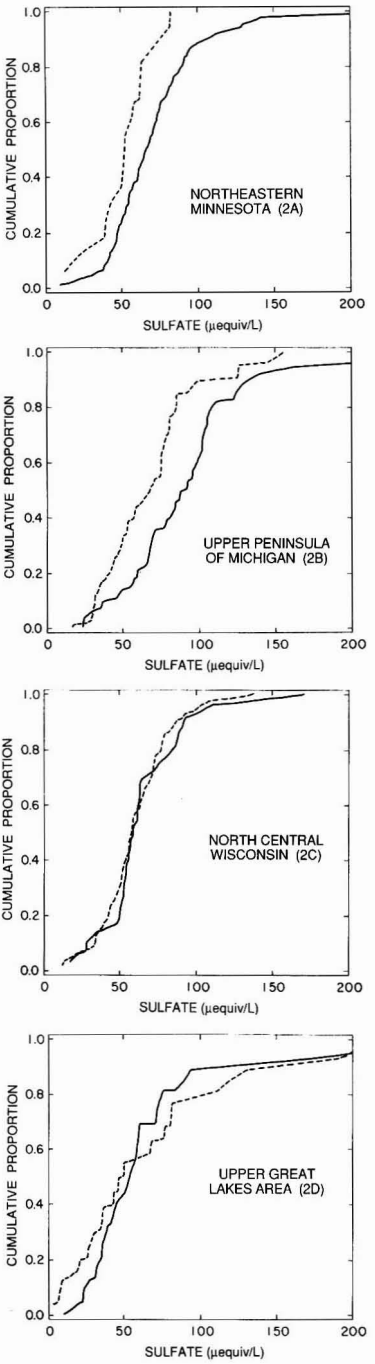


Figure 5. Cumulative frequency distributions of sulfate for seepage (– –) and drainage (—) lakes in the four subregions (A–D) in the upper Midwest.

the upper Great Lakes area (which includes much of the remainder of northern Wisconsin), there is little difference in sulfate concentration between the lake types. On the basis of the distributions observed in subregions 2A and 2B, the close agreement between the cumulative distri-

Table V. Population Estimates of Selected Variables for Acidic Lakes (ANC ≤ 0) in the Upper Midwest

variables	20th percentile	median	80th percentile
lake area, ha	4.7	6.6	12.5
watershed area, ha	24.4	48.1	129.4
site depth, m	1.0	3.6	7.5
sulfate, μequiv/L	48.5	61.3	79.4
calcium, μequiv/L	18.0	31.6	43.0
aluminum (ext), μg/L	9.2	21.8	46.7
DOC, mg/L	2.0	2.9	5.1
organic anion, μequiv/L[a]	0	14.8	33.3
organic anion, μequiv/L[b]	15.4	23.0	37.3
color	10.5	15.7	44.0

[a] Using organic anion deficit defined as ∑cations − ∑anions. [b] Computed with the model of Oliver et al. (*8*).

butions of sulfate, particularly in subregion 2C, does not appear to be caused by lower-than-expected concentrations in the drainage lakes. Possible explanations for the apparent depletion of sulfate in the Wisconsin drainage lakes include (a) greater hydraulic residence time (Table II), thus providing increased opportunity for in-lake reduction, (b) uptake of sulfur by the terrestrial vegetation, (c) sulfate reduction in the extensive wetlands in the area, and (d) sulfate adsorption in the soils. Without additional supporting data, it is not possible to further evaluate this question within the scope of this paper.

These data prompt the primary question: Can one use lake survey chemistry to infer a cause (acidic deposition) with an effect (the presence of acidic lakes)? Without adequate consideration of other potentially confounding factors, the answer must be "no". Factors that could differentially influence the chemistry of lakes across the upper Midwest include contribution of organic acids, watershed processes such as sulfate adsorption and weathering of sulfide sources, and in-lake processes such as sulfate reduction.

Given the relatively high concentrations of DOC observed in the upper Midwest, it is reasonable to expect that acidic lakes might be the result of organic acids. Population estimates of selected variables for acidic lakes (Table V) illustrate that these lakes have low to moderate DOC, and most could not be characterized as dystrophic lakes. These acidic lakes are primarily small, shallow seepage lakes with low base cations, low aluminum, and moderate sulfate concentrations. The organic acid concentrations were estimated both by use of anion deficit and by computation of organic acid with the empirical model by Oliver et al. (*8*); the results of both estimates indicate most of the acid anion in the acidic lakes is sulfate.

Because the net effect of in-lake processes, such as sulfate/nitrate reduction or cation exchange, is to promote alkalinity generation, they are very important in explaining the absence, but not the presence, of acidic lakes. However, watershed sources of sulfate, such as sulfide ores, are of potential concern in such an analysis. Thus, in defining the subpopulation of interest, we sought to restrict the analysis to lakes with minimal terrestrial watershed contributions.

The criterion used to select lakes that receive minimal watershed contributions (surface runoff or groundwater input) was conductance, an indirect measure of total ionic concentration. Hawkinson and Verry (*35*) used a criterion of 30 μS/cm to distinguish between "perched" and "nonperched" lakes in western Minnesota. Although the proportions of meteoric and watershed contributions in a lake of this conductance will vary, depending on the precipitation, evaporation, groundwater, and runoff, a water

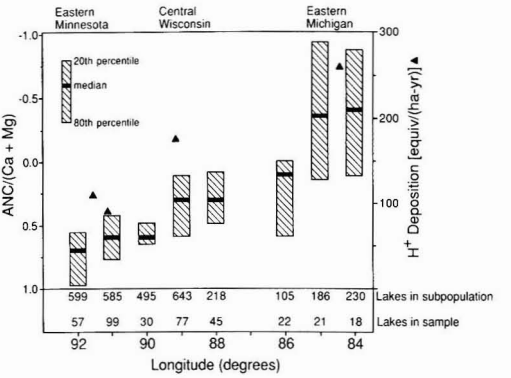


Figure 6. Population estimates (20th, 50th, and 80th percentiles) of the ratio ANC/[Ca + Mg] computed for subpopulations of lakes defined at intervals of 1° longitude. Only lakes with specific conductance ≤ 30 μS/cm are included in these estimates. Hydrogen ion deposition data are derived from National Atmospheric Deposition Program stations for December 1980 through November 1982 as reported by Glass and Loucks (*19*). Stations, from west to east, are Spooner, WI, Fernberg, MN, Trout Lake, WI, and Douglas Lake, MI.

budget for Vandercook Lake in northcentral Wisconsin (*24*) indicates that this lake, with conductance of 20 μS/cm, receives approximately 97% of its input from direct precipitation.

Of the four subregions in the upper Midwest delineated for the ELS, two subregions contain lake populations that show much greater homogeneity in chemistry than lakes in the other two subregions. Comparison of interquintile differences for many variables shows that northeastern Minnesota and northcentral Wisconsin have lakes that display a narrower range of chemical characteristics than do lakes in the upper peninsula of Michigan and the upper Great Lakes area. The upper peninsula of Michigan spans a distance of nearly 600 km, and the upper Great Lakes area spans the entire three-state region. Unlike northeastern Minnesota and northcentral Wisconsin, which are within well-defined geomorphic units, the other two subregions cross major physiographic provinces, evident in the substantial differences in glacial and bedrock geologic features. In addition, subregions 2B and 2D lie along the depositional gradient, making analyses of relationships with atmospheric deposition difficult to interpret. Thus, the results indicate that subregions 2B and 2D are too heterogeneous, and are unsatisfactory for analyses of spatial patterns in lake chemistry. Rogalla et al. (*36*) also found that high lake-to-lake variability in watershed/lake processes for the upper Midwest obscured possible patterns in estimated loss of ANC. The problem of relating lake chemistry to the depositional gradient in the upper Midwest is circumvented if estimates of the number and characteristics of the lakes are computed for subpopulations along this longitudinal transect.

If lake acidification is primarily a substitution (titration) of sulfate for bicarbonate and if the supply of base cations (represented by the dominant cations calcium and magnesium) is low relative to the strong acid inputs, we would expect to observe a loss of ANC along a gradient of acid deposition. Indeed, population estimates of the quantity ANC/[Ca + Mg] for low-conductivity lakes across the upper Midwest show close agreement with the hydrogen ion deposition (Figure 6). The decreasing value of the ratio from west to east for this subpopulation of low-conductivity lakes corresponding with an increase in hydrogen ion deposition suggests a substantial loss of ANC in the lakes

along the eastern portion of the depositional gradient. This pattern was previously observed by Glass and Loucks (*19*), Schnoor et al. (*13*), and Nichols and McRoberts (*28*). Low ratios of ANC/[Ca + Mg] also can be exhibited where organic acids represent a large proportion of the anions. However, DOC concentrations across the upper Midwest generally decrease from west to east. The median DOC value for lakes in extreme eastern Michigan is 6.5 mg/L, yet it is only 3.3 mg/L at longitude 85° (Michigan), and DOC increases to 10.2 mg/L at longitude 92° (Minnesota).

The results of the ELS illustrate that spatial patterns in lake chemistry in the upper Midwest are complex and that the use of current subregion boundaries, particularly for subregions 2B and 2D, is not optimal for relating deposition and lake chemistry. However, the flexible nature of the survey design makes it possible to poststratify the data into more meaningful subpopulations for further analyses.

Clearly, this analysis of the Eastern Lake Survey does not provide unequivocal evidence for anthropogenic acidification of lakes in the upper Midwest. For example, paleolimnological investigations of lakes in the upper Midwest and analyses of historical lake chemistry data from Wisconsin do not corroborate a recent trend in lake acidification (*37*). Preliminary paleolimnological results for 4 lakes in the upper Midwest (*38*) suggest little change in pH during the past 200 years. Krug et al. (*39*) have suggested that many freshwaters of the world are humic, implying that they are naturally acidic. With input of acidic deposition, sulfate could have replaced organics as the dominant anion, resulting in a chemical signature of the lakes similar to that of a lake that has lost bicarbonate (with no compensatory weathering of base cations). This explanation is not entirely satisfactory because we observe no acidic lakes in those areas of the upper Midwest where sulfate deposition is low (e.g., Minnesota). However, the results show that the *distribution* of acidic lakes cannot be attributed solely to organic anions. The results also show that the class of lakes that might be expected to acidify first, namely, the shallow, dilute lakes, exhibit chemical characteristics consistent with anthropogenic acidification. Thus, the distribution of acidic lakes in the upper Midwest is most consistent with acidification caused by atmospheric deposition.

Acknowledgments

We acknowledge the many persons, especially Rick A. Linthurst, who contributed to the Eastern Lake Survey. Paul Shaffer and Don Charles provided helpful comments on the draft manuscript. Statistical support was provided by Scott Overton, Jim Blick, Mark DeHaan, and Danny Kugler.

Registry No. C, 7440-44-0; Ca, 7440-70-2; Mg, 7439-95-4; Na, 7440-23-5; K, 7440-09-7; NH_4, 14798-03-9; Fe, 7439-89-6; Mn, 7439-96-5; Al, 7429-90-5; P, 7723-14-0; H^+, 12408-02-5.

Literature Cited

(1) Landers, D. H.; Overton, W. S.; Linthurst, R. A.; Brakke, D. F. *Environ. Sci. Technol.* **1988**, *22*, 128–135.
(2) Linthurst, R. A.; Landers, D. H.; Eilers, J. M.; Brakke, D. F.; Overton, W. S.; Meier, E. P.; Crowe, R. E. *Characteristics of Lakes in the Eastern United States*; U.S. EPA: Washington, DC, 1986; Vol. 1, pp 1–136; EPA/600/4-86-007a.
(3) Hillman, D. C. J.; Potter, J. F.; Simon, S. J. *National Surface Water Survey, Eastern Lake Survey—Phase I. Analytical Methods Manual*; U.S. EPA: Las Vegas, NV, 1986; EPA/600/4-86/009.
(4) Morris, F. A.; Peck, D. V.; Bonoff, M. B.; Cabble, K. J. *National Surface Water Survey, Eastern Lake Survey—Phase I. Field Operations Report*; U.S. EPA: Las Vegas, Nevada, 1986 EPA/600/4-86/010.
(5) Wetzel, R. G. *Limnology*, 2nd ed.; Saunders College Publishing: Philadelphia, 1983; 767 pp.
(6) Brakke, D. F.; Landers, D. H.; Eilers, J. M. *Environ. Sci. Technol.* **1988**, *22*, 155–163.
(7) Eilers, J. M.; Landers, D. H.; Brakke, D. F. *Environ. Sci. Technol.* **1988**, *22*, 172–177.
(8) Oliver, B. G.; Thurman, E. M.; Malcolm, R. L. *Geochim. Cosmochim. Acta* **1983**, *47*, 2031–2035.
(9) *SAS/IML Users Guide*; SAS Institute, Inc.: Cary, NC, 1985; Version 5.
(10) Reinsch, C. H. *Numerische Mathematik* **1967**, *10*, 177–183.
(11) Wentz, D. A.; Krohelski, J. T.; Rose, W. J.; Bockheim, J. G.; Garrison, P. J.; Knauer, D. R.; Goldstein, R. A. In *Acid Rain: Scientific and Technical Advances*; Perry, R., Harrison, R. M., Bell, J. N. B., Lester, J. N., Eds.; Selper Ltd.: London, 1987; pp 353–356.
(12) Bayley, S. E.; Schindler, D. W.; Turner, M. S. Presented at the American Society of Limnology and Oceanography Annual Meeting, Madison, WI, June 1987.
(13) Schnoor, J. L.; Nikolaidis, N. P.; Glass, G. E. *J.—Water Pollut. Control Fed.* **1986**, *58*, 139–148.
(14) Rapp, G., Jr.; Allert, J. D.; Liukkonen, B. W.; Ilse, J. A.; Loucks, O. L.; Glass, G. E. *Environ. Int.* **1985**, *11*, 425–440.
(15) Gorham, E.; Dean, W. E.; Sanger, J. E. *Limnol. Oceanogr.* **1983**, *28*, 287–301.
(16) Moyle, J. B. *J. Wildl. Manage.* **1956**, *20*, 303–320.
(17) Winter, T. C. *Water Resour. Res.* **1977**, *13*, 753–767.
(18) Driscoll, C. T.; Baker, J. P.; Bisogni, J. J.; Schofield, C. L. *Nature (London)* **1980**, *284*, 161–164.
(19) Glass, G. E.; Loucks, O. L. *Environ. Sci. Technol.* **1986**, *20*, 35–43.
(20) Schneider, J. C. *Mich. Acad.* **1975**, *8*, 59–84.
(21) Eilers, J. M.; Glass, G. E.; Webster, K. E.; Rogalla, J. A. *Can. J. Fish. Aquat. Sci.* **1983**, *40*, 1896–1904.
(22) Juday, C.; Birge, E. A.; Meloche, V. W. *Trans. Wis. Acad. Sci., Arts Lett.* **1935**, *29*, 1–82.
(23) Broughton, W. A *Trans. Wis. Acad. Sci., Arts Lett.* **1941**, *33*, 5–20.
(24) Lin, J. C.; Schnoor, J. L. *J. Environ. Eng. (N.Y.)* **1986**, *112*, 677–694.
(25) Simpkins, W. W.; McCartney, M. C.; Mickelson, D. M. "Glacial Geology of Forest County, Wisconsin"; Open File Report: Wisconsin Geological Natural History Survey: Madison, WI, 1978; pp 1–62.
(26) Omernik, J. M.; Griffith, G. E. *Total Alkalinity of Surface Waters: A Map of the Upper Midwest Region*; U.S. EPA: Corvallis, OR, 1985; pp 1–28; EPA/600/D-85-043.
(27) Lillie, R. A.; Mason, J. W. "Limnological Characteristics of Wisconsin Lakes"; Technical Bulletin No. 138, Wisconsin Department of Natural Resources: Madison, WI, 1983; pp 1–116.
(28) Nichols, D. S.; McRoberts, R. E. *Water, Air, Soil Pollut.* **1986**, *31*, 197–206.
(29) Brugam, R. B. *Hydrobiologia* **1981**, *80*, 47–62.
(30) Barr, K. M.S. Thesis, University of Minnesota, Minneapolis, MN, 1978, pp 1–293.
(31) Mudrey, M. G., Jr.; Brown, B. A.; Greenburg, J. K. *Bedrock Geologic Map of Wisconsin*; University of Wisconsin—Extension and Wisconsin Geological Natural History Survey: Madison, WI, 1982.
(32) Hadley, D. W.; Pelham, J. H. *Glacial Deposits of Wisconsin: Sand and Gravel Resource Potential, 1:500,000*; Wisconsin Geological Natural History Survey: Madison, WI, 1976; Map 10.
(33) Blick, D. J.; Overton, W. S.; Messer, J. J.; Landers, D. H. *Lake Reserv. Manage.* **1987**, *3*, 470–475.
(34) Brakke, D. F.; Eilers, J. M.; Landers, D. H. In *Proceedings of International Symposium on Acidification and Water Pathways*; Norwegian National Committee for Hydrology, Bolkesjø, Norway, 1987, pp 281–290.
(35) Hawkinson, C. F.; Verry, E. S. "Specific Conductance Identifies Perched and Groundwater Lakes"; USDA Forestry Service Research Paper NC-120; Central Forestry Experimental Station: St. Paul, MN, 1975; pp 1–5.

(36) Rogalla, J. A.; Brezonik, P. L.; Glass, G. E. *Water, Air, Soil Pollut.* **1986**, *31*, 95-100.
(37) Wiener, J. E.; Eilers, J. M. *Lake Reserv. Manage.* **1987**, *3*, 365-378.
(38) Charles, D. F.; et al. *Water, Air, Soil Pollut.* **1986**, *30* 355-365.
(39) Krug, E. C.; Isaacson, D. J.; Frink, C. R. *J. Air Pollut. Control Assoc.* **1985**, *35*, 109-114.

Received for review February 9, 1987. Accepted October 26, 1987. The research described in this article has been funded as part of the National Acid Precipitation Assessment Program by the U.S. Environmental Protection Agency. This article was prepared at the EPA's Research Laboratory in Corvallis, OR, in part, through Contract 68-03-3246 with Northrop Services and Cooperative Agreement CR812653 with Western Washington University. This is a contribution from the National Surface Water Survey of the EPA's Aquatic Effects Research Program. It has been subjected to the Agency's peer and administrative review and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Chemical and Physical Characteristics of Lakes in the Southeastern United States

Joseph M. Eilers,*,† Dixon H. Landers,‡ and David F. Brakke§

Northrop Services, Inc., 200 S.W. 35th Street, Corvallis, Oregon 97333, U.S. Environmental Protection Agency, 200 S.W. 35th Street, Corvallis, Oregon 97333, and Institute for Watershed Studies, Western Washington University, Bellingham, Washington 98225

■ A survey of the chemical status of 252 lakes, representing an estimated 2424 lakes, was conducted in the Southern Blue Ridge province and in Florida during Fall 1984. This survey was part of the Eastern Lake Survey designed to quantify the number of acidic lakes and lakes with low acid neutralizing capacity (ANC) with surface area greater than 4 ha. Of the 102 lakes sampled in the Southern Blue Ridge, none were acidic (ANC ≤ 0) and only 1.4% of the population of 258 lakes were estimated to have low ANC (≤50 μequiv/L). In contrast, an estimated 22% of the lakes in the Florida subregion were acidic, and 35.3% were estimated to have low ANC. Almost 90% of the lakes in the Southern Blue Ridge were reservoirs. These lakes generally had moderate ANC values (median = 250 μequiv/L) and had low concentrations of aluminum, dissolved organic carbon (DOC), and sulfate compared to those of Florida, the upper Midwest, and the Northeast. The lakes in the Southern Blue Ridge showed a high degree of chemical homogeneity relative to those of other regions in the East. In contrast, the chemistry of lakes in Florida exhibited a high degree of heterogeneity, indicating the presence of several distinct subpopulations. Florida had the highest proportion of acidic lakes in the East, some of which had moderately high concentrations of aluminum, DOC, and sulfate. Some of the Florida lakes are naturally acidic from organic acids. However, the many clear water, acidic lakes exhibit chemical characteristics that are not inconsistent with a hypothesis of acidification from deposition. The geographic separation of the Southern Blue Ridge from Florida and the strong contrasts in physical and chemical characteristics of the respective subregions require that they be treated as distinct regions.

Sample from the Southeast

This paper describes the physical and chemical status of lakes in the southeastern United States, on the basis of results of a survey by the U.S. Environmental Protection Agency. The purpose and approach are the same as those for the Northeast (*1*) and upper Midwest (*2*), and the methods are described elsewhere (*3*, *4*). The population of lakes represented here is limited to lakes generally ≥4 ha in surface area, and the chemical status from this Fall 1984 sampling represents an "index" but not a complete characterization of annual lake chemistry.

Table I. Subregional and Regional Summaries of Estimated Target Population Size ($\hat{N}$), Estimated Target Population Area ($\hat{A}$), and the Standard Errors (SE) of These Estimates, Eastern Lake Survey—Phase I

	lakes ≤2000 ha[a]				
subregion	n[b]	$\hat{N}_s$	SE($\hat{N}_s$)	$\hat{A}_s$	SE($\hat{A}_s$)
Southern Blue Ridge (3A)	94	258	20.5	24272	4797
Florida (3B)	148	2098	212.6	66169	10158

[a] Subscript s denotes a subpopulation, in this case those lakes in the target population ≤2000 ha. [b] Number of lakes sampled.

The two study areas from which the lakes were selected in the Southeast include most of the Southern Blue Ridge Province (3A) and much of Florida (3B) (Figure 1a). The Florida subregion also includes a portion of Georgia where 10 lakes were sampled within the Okefenokee Swamp. Sampling intensity differed substantially because there are few lakes present in the Southern Blue Ridge and a great number present in Florida (Figure 1b). Consequently, 36% of the lakes in subregion 3A were sampled compared to only 7% for subregion 3B (Table I). This difference in sampling intensity contributes to larger standard errors in population estimates for Florida compared to the Southern Blue Ridge. Population estimates are presented here only for the portion of the target population with surface area ≤ 2000 ha because several very large lakes have a disproportionate influence on the population estimates for lake area. This decision had no significant impact on the percentages of lakes as presented in this analysis.

Results

Unlike the Northeast (*1*) and upper Midwest (*2*) where the study areas were contiguous, the Southeast is represented by two disjunct subregions separated by approximately 300 km. The subregions have different climates and dissimilar physiographies that result in major distinctions in lake characteristics. Consequently, the subregional estimates for the Southern Blue Ridge (3A) and Florida (3B) are not combined into "regional" population estimates as was done for the Northeast and upper Midwest.

† Northrop Services, Inc.
‡ U.S. Environmental Protection Agency.
§ Institute for Watershed Studies.

0013-936X/88/0922-0172$01.50/0 © 1988 American Chemical Society

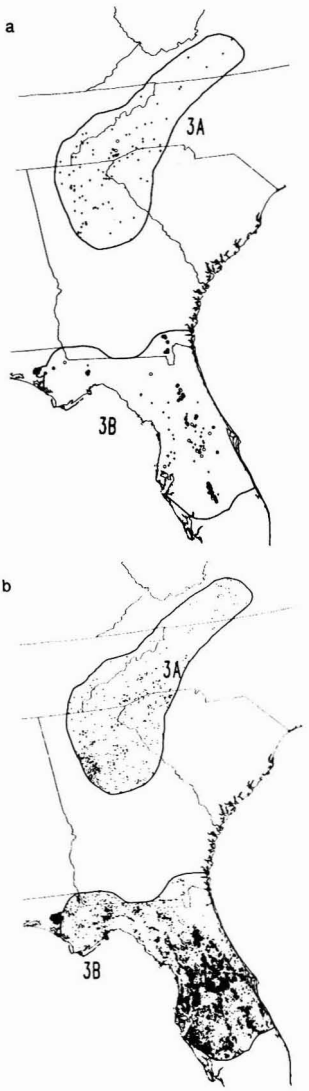


Figure 1. Locations of lakes sampled in the Southeast as part of the Eastern Lake Survey (a). Lakes are coded by their measured ANC values: (●) ≤0, (○) 0–50, and (+) >50 μequiv/L. Locations of all lakes present on 1:250 000-scale USGS maps (b).

Physical Characteristics. The lakes in the two southeastern subregions are very different in most physical respects (Table II). The lakes of the Southern Blue Ridge (3A) are located in the southern Applachian Mountains at a median elevation of 265 m; the lakes of Florida (3B) are part of the Southern Coastal Plain and have a median elevation of 21 m (*6*). The lakes in the Southern Blue Ridge are generally smaller than those in Florida, but the presence of several very large reservoirs causes the population estimate for total lake area to be high. Almost 90% of the lakes in subregion 3A are reservoirs, which is reflected in the high estimates for watershed area and watershed:lake area ratio, while hydraulic residence time is generally short. Most of the lakes in subregion 3B are seepage lakes, and no Florida reservoirs were sampled (it would be incorrect to infer from this that Florida does not have reservoirs). Hydraulic residence times were not computed for lakes in Florida because of considerable uncertainty in delineating watershed boundaries and because typical assumptions used in computing watershed runoff (i.e., that groundwater and surface watershed divides are defined by the same topographic boundaries) were violated.

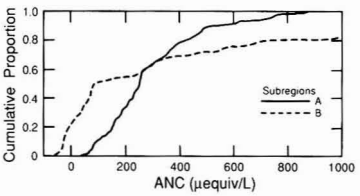


Figure 2. Cumulative frequency distributions [$F(x)$] for ANC in the Southeast: Southern Blue Ridge (A); Florida (B).

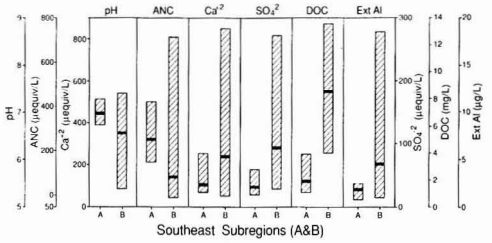


Figure 3. Population estimates (20th, 50th, and 80th percentiles) of pH, ANC, Ca^{2+}, $SO4^{2-}$, DOC, and extractable aluminum for subregions in the Southern Blue Ridge (A) and Florida (B).

Chemical Characteristics. No acidic (ANC ≤ 0) lakes were sampled in the Southern Blue Ridge, whereas Florida had the greatest number ($\hat{N}$ = 463) and highest percentage (22%) of acidic lakes of any subregion in the Eastern Lake Survey (*3*; Figure 2). The cumulative distributions show that over 35% of the lakes in Florida had ANC ≤ 50 μequiv/L compared to about 1% for the Southern Blue Ridge. The distribution for ANC in Florida shows a change in slope at approximately 80 μequiv/L, suggesting that at least two distinct groups of lakes are present. In contrast, the lakes in the Southern Blue Ridge appear to represent a continuum of ANC concentrations. A survey of 61 streams in the Southern Blue Ridge during Spring 1985 showed an ANC distribution similar to that observed for the lakes (*7*), and again, no acid waters were sampled.

Although it is helpful to examine the cumulative distributions for all variables, medians and quintiles generally provide an adequate basis for comparison. Population estimates of the 20th, 50th, and 80th percentiles are presented for several important variables relative to acid deposition effects (Figure 3). Figure 3 shows that, regardless of what variable is considered, the chemistry of lakes in the Southern Blue Ridge is far more homogeneous than that for Florida. The first quintile (Q_1 = 20th percentile) and median ANC values for Florida lakes were the lowest estimated from the survey, whereas the Q_1 ANC value for the Southern Blue Ridge was the highest estimated for any subregion in the East.

DOC concentrations in many Florida lakes were high, with a median value comparable to that observed in northeastern Minnesota (*2*). Unlike Minnesota, Florida possesses a moderate number of clear water lakes with DOC values as low as 0.3 mg/L. The lakes in the Southern Blue Ridge had the lowest DOC concentrations of any eastern subregion, generally 50% less than those in the Northeast (*4*).

Table II. Median Physical Characteristics of Lakes in the Southeast and Percentage of Lakes by Hydrologic Type

subregion	lake area, ha	watershed area, ha	watershed/ lake ratio	depth, m[a]	hydraulic residence time, yr[b]
Southern Blue Ridge (3A)	10.8	682	44.2	4.8	0.10
Florida (3B)	17.3	115	5.5	2.7	

	lake type[c]			
subregion	drainage	seepage	closed	reservoir
Southern Blue Ridge (3A)	7.0	0	2.7	89.9
Florida (3B)	21.5	65.8	12.6	0

[a] Site depth where the sample was taken. [b] Residence time computed only for drainage lakes and reservoirs in the Southern Blue Ridge. [c] Determined on the basis of mapped information with the nomenclature of Wetzel (5).

Table III. Median Chemical Characteristics of Lakes in the Southeast

variables	Southern Blue Ridge (3A)	Florida (3B)	variables	Southern Blue Ridge (3A)	Florida (3B)
cations, μequiv/L			metals, μg/L		
calcium	105	238	iron	83	19
magnesium	76	160	manganese	53	4
sodium	103	198	aluminum (total)	82	44
potassium	39	22	aluminum (ext)	2	4
ammonium	2.2	1.4	clarity		
anions, μequiv/L			true color, PCU	36	37
bicarbonate[a]	236	76	turbidity, NTU	3.9	0.9
sulfate	32	94	Secchi disk, m[d]	1.8	1.9
organic[b]	0	98	DOC, mg/L	1.9	8.6
organic[c]	20	78	other		
chloride	66	222	conductance, μS/cm	38.5	90.8
nitrate	3.1	1.0	silica, mg/L	9.0	0.3
fluoride	2.2	2.7	total P, μg/L	7	12
			DIC, mg/L	3.7	1.7

[a] Computed from open-system pH and dissolved inorganic carbon (8). [b] Defined as the anion deficit $[\sum(Ca^{2+} + Mg^{2+} + K^+ + Na^+ + NH_4^+ + H^+) - \sum(HCO_3^- + CO_3^{2-} + Cl^- + NO_3^- + SO_4^{2-} + F^- + OH^-)]$. [c] Computed with the model by Oliver et al. (9). [d] Calculated for only those lakes where Secchi disk depth < site depth.

Calcium concentrations were low in both subregion 3A and subregion 3B; only lakes in northcentral Wisconsin had lower concentrations in the East (2). Sulfate concentrations in the Southern Blue Ridge were the lowest observed in the East, whereas Florida had the highest sulfate estimates at the 80th percentile. Extractable aluminum concentrations (computed only for clear water lakes: color ≤ 30 PCU) were extremely low for the Southern Blue Ridge where no lakes exceeded 100 μg/L (4). Over 4% of the clear water lakes in Florida had extractable aluminum concentrations exceeding 100 μg/L, a proportion exceeded only by lakes in the Adirondacks (12.1%; 4).

One of the beneficial aspects of the Eastern Lake Survey is that samples were analyzed for a large number of parameters that are useful for a more complete evaluation of acid deposition impacts and for assessing the chemical status for a variety of environmental concerns. Median values for most variables measured in the survey show that lakes in Florida have greater ion concentrations than those in the Southern Blue Ridge (Table III). Notable exceptions are potassium, bicarbonate, and metals (Fe, Mn, total Al), where lakes in the Southern Blue Ridge have the greatest concentrations.

The color of the lakes in subregion 3A appears high, especially in relation to the low DOC values observed here. The high turbidity for subregion 3A suggests that the high color is, in part, related to particulates, probably derived from the clay soils of the area (10). Particulates are also likely to be responsible for the high total Al concentrations because extractable Al (largely monomeric Al) values were low, as were DOC concentrations. Although the survey was not conducted in a season optimal for evaluating nutrient concentrations, the results indicate that lakes in the Southern Blue Ridge have approximately 2–3 times greater nitrate and ammonium concentrations than most subregions in the East (4). In contrast, the total phosphorus concentrations in subregion 3A were among the lowest observed for the survey. The low phosphorus concentrations may be related to adsorption of the phosphorus on particulates. The concentrations of nitrate and ammonium for Florida lakes, and phosphorus estimates, which were high compared to those of the Southern Blue Ridge, were comparable to other subregions in the East (4). Another striking difference in lake chemistry between the two subregions is observed for silica, where the median concentration in the Southern Blue Ridge was 30 times greater than in Florida. Such a difference highlights the importance of weathering of clay soils in the Southern Blue Ridge, whereas little silica is released from the relatively unreactive sandy soils in Florida.

Magnesium concentrations were approximately 25–50% less than calcium concentrations in these two subregions. The interquintile differences ($Q_d = Q_4 - Q_1$), an indication of subregional heterogeneity, were low in subregion 3A relative to those in subregion 3B. Median concentrations of iron, manganese, and total aluminum in the Southern Blue Ridge were the highest observed in the eastern United States. The large watersheds of these lakes (watershed:lake area = 44:1) provide considerable opportunity for contribution of metals.

The median concentrations of major ions for the southeastern subregions shown in Table III provide a glimpse of the characteristics of these lakes but give no

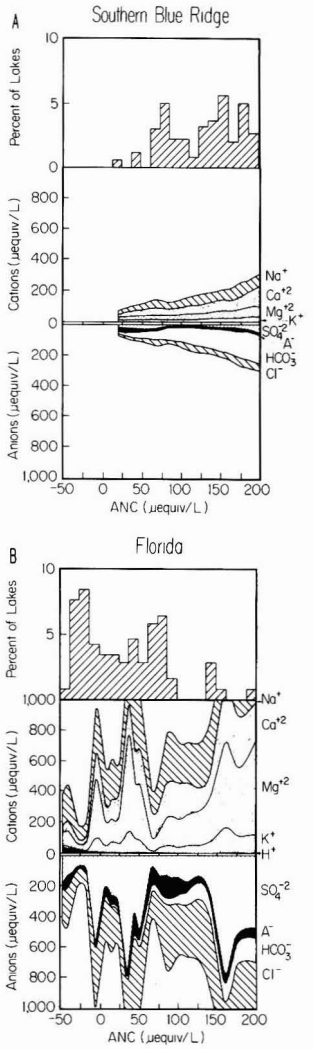


Figure 4. Major cations and anions for lakes with ANC ≤ 200 μequiv/L in the two subregions (A and B) in the Southeast. One reservoir, Lake Ocoee was removed from the data set for the Southern Blue Ridge because of abnormally high concentrations of calcium and sulfate (both > 700 μequiv/L; *11*). The method of smoothing for each ion was the IML function spline in SAS software (*12*) with a smoothing parameter of 2 ($\sum wt_i$), where wt is the specific weight for stratum *i*. The percentages of lakes represented by ANC intervals are shown as histograms across the top of the spline plots. Contributions of cations such as Al^{n+}, Fe^{n+}, Mn^{n+}, and NH_4^+ and anions such as NO_3^- and F^-, which are important in some lakes, are excluded here to increase the clarity of the presentation.

indication of the variability in lake chemistry. A more insightful examination of the lake chemistry can be obtained by simultaneously showing concentrations of anions and cations as is done here for lakes with ANC ≤ 200 μequiv/L (Figure 4). The spline plots (*13*) for the Southern Blue Ridge show that the lakes with ANC ≤ 200 μequiv/L have a remarkably stable ionic composition. Concentrations of most ions increase proportionally as a function of ANC concentration. Sodium and chloride concentrations are higher than expected given the distance from the coast, suggesting terrestrial sources. Although road salt is used

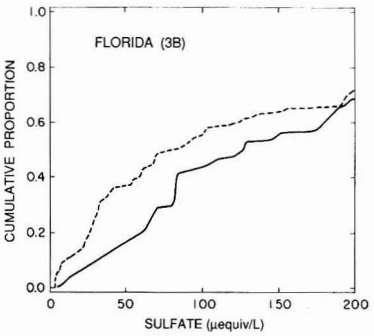


Figure 5. Cumulative frequency distributions of sulfate for seepage (– –) and drainage (—) lakes in Florida.

to some extent in this area (*14*), the relatively stable proportions of these two ions suggests that natural watershed sources are primarily responsible for the observed concentrations.

The ionic composition of the low ANC lakes in Florida (Figure 4B) is radically different from that observed in the Southern Blue Ridge. First, the total concentration of ions is considerably greater than that in the Southern Blue Ridge. Second, the relative abundance and actual concentrations of the major ions are highly variable in Florida lakes, providing additional support for the heterogeneity of the Florida lakes. The sodium and chloride ions, which are dominant throughout much of the ANC range, are derived from both deposition of marine aerosols and from weathering of ancient marine deposits. The major spikes in sulfate at ANC near −10, 30, and 170 μequiv/L are coincident with comparable spikes in magnesium, indicative of terrestrial weathering. Potassium is typically less than 25 μequiv/L in acidic lakes with minimal watershed disturbance.

Organic acid contributions in Florida lakes are relatively small for these low-ANC lakes, but concentrations of DOC are much greater in the higher ANC lakes as evidenced by the median DOC of 8.6 mg/L. Because the plot was scaled from −50 to 200 ANC, the ion composition of the 10 lakes sampled in the Okefenokee Swamp is not displayed. The ANC values for these lakes ranged from −63 to −209 μequiv/L with pH values from 4.33 to 3.81. The extremely acidic conditions result from the presence of strong organic acids (DOC ranged from 25.9 to 48.2 mg/L), whereas sulfate did not exceed 13 μequiv/L.

Hydrologic characterization has played an important role in distinguishing chemical differences in lakes. In the Northeast (*1*) and the upper Midwest (*2*), seepage lakes were generally found to have lower concentrations of sulfate than drainage lakes. Differences in concentrations of ANC and DOC were also observed between the two lake classes. In the Southern Blue Ridge, only 10% of the lakes within the study frame are natural; the remaining ones are reservoirs. Thus, there is little to be gained by further evaluating hydrologic classes of lakes in subregion 3A. In Florida, most of the lakes originate from sinkhole activity, but the hydrogeologic setting of these lakes is such that it is uncertain what the drainage lake classification represents. The topographic relief in Florida is very low; consequently, the watersheds contributing to drainage lakes are poorly defined and changeable, depending on variations in annual precipitation. Nevertheless, when sulfate concentrations are compared between the lake types in Florida, seepage lakes are found to have lower concentrations than drainage lakes (Figure 5). This pat-

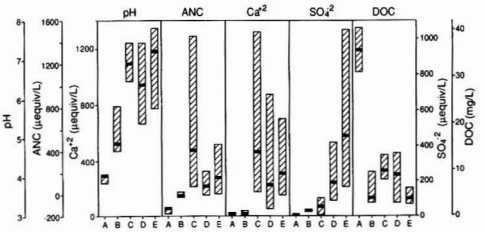


Figure 6. Population estimates (20th, 50th, and 80th percentiles) of pH, ANC, Ca^{2+}, SO_4^{2-}, and DOC computed for subpopulations of lakes defined as the Okefenokee Swamp (A), the Florida panhandle (B), Gulf Coast (C), northcentral peninsula (D), and the southcentral peninsula (E). The estimated number of lakes represented within each of these subpopulations is 10, 260, 581, 963, and 51.

tern is evident up to 200 μequiv/L, above which point there is no longer an indication of a difference in sulfate concentrations.

Discussion

The results of the survey illustrate that the lakes of the Southern Blue Ridge and Florida have major physical and chemical differences that preclude presenting the results in a southeastern regional summary. Population estimates for a group of lakes are most meaningful if there are geographic or chemical features in common. The contrasts in chemistry and physical characteristics are greater between these two subregions than those observed both among and within other regions in the East. Whereas the lakes in the Southern Blue Ridge have a distinct and uniform chemical signature, lakes in Florida are highly diverse and are difficult to characterize as a single population.

With respect to deposition, the Southern Blue Ridge receives somewhat higher loadings of sulfate than Florida (*15*), yet the proportions of acidic lakes in these two subregions differ greatly (0 and 22%, respectively). A hypothesis proposed to explain the absence of acidic lakes in the Southern Blue Ridge is that soils are adsorbing sulfate with a concomitant weathering of bicarbonate (*16*). This hypothesis is supported by data on watershed input/output budgets, which show a net accumulation of sulfur in the watersheds (*17*, *18*). Presumably, as the sulfate adsorption capacity of the soils is exhausted, sulfate will become mobilized with a corresponding loss of bicarbonate in the surface waters (*16*). Because the bicarbonate concentrations in the Southern Blue Ridge lakes are relatively high, only a small proportion of the lakes likely would be at risk to complete loss of ANC.

For Florida, the results are more enigmatic. Twenty-two percent of the lakes are acidic despite a sulfate deposition loading substantially less than that observed in the Adirondacks (*15*), a subregion with only half as many acidic lakes. The first step in understanding this apparent inconsistency in subregion 3B is to recognize that Florida consists of several distinct subpopulations of lakes, as delineated in Linthurst et al. (*4*). Population estimates for the five subpopulations recognized in these data indicate major differences among the geographic areas (Figure 6). The most distinctive group of lakes is the Okefenokee Swamp, which is characterized by extremes of organic acids (median DOC = 35.7 mg/L) and sulfate (median sulfate = 5 μequiv/L). However, the 10 lakes in the Okefenokee Swamp represent a small minority of the estimated 2098 lakes in the Florida subregion. The acidic lakes in the Okefenokee Swamp contained very high DOC concentrations, and any possible relationship to acid deposition in these lakes can be discounted. The lakes in the panhandle of Florida were also low-calcium, acidic lakes but had low to moderate DOC values. These are seepage lakes located in highly weathered ancient dunes and are believed to act as groundwater discharge systems (*19*). The lakes in the panhandle exhibit chemical characteristics that generate the greatest interest with respect to possible impact from acidic deposition. Base cation and DOC concentrations are low, and an estimated 80% of the 260 lakes are acidic. The lakes in the Gulf Coast area (western Florida peninsula) were generally high ANC systems and merit little attention with respect to acidification. Lakes in the northcentral and southcentral peninsula of Florida had DOC concentrations similar to each other, but lakes in the southcentral peninsula contained higher concentrations of most major ions.

Most of the acidic lakes in Florida are seepage lakes and presumably they receive much of their water directly from meteoric sources. However, a small volume of groundwater input can provide substantial ANC to these lakes. Potassium concentrations exceeding 25 μequiv/L may offer a chemical signature for identifying those lakes receiving groundwater influx sufficient to maintain positive ANC in the lake.

Superimposed on this complex geographic variability, low relief, and large number of seepage lakes is a high incidence of anthropogenic disturbance in the watersheds. Of the 159 total lakes sampled in Florida, all but 37 were judged to have substantial shoreline or watershed disturbances. The landuse disturbance appeared greatest in the southcentral peninsula where orange groves commonly were cultivated to the lakeshore. Application of fertilizers or irrigation with water drawn from underlying aquifers, in part, may explain the high sulfate concentrations of lakes in this area. In addition, natural breaches in the Floridan aquifer may also contribute to elevated sulfate by influx of groundwater to the lakes.

Excluding chloride and assuming that anion deficit is a reasonable surrogate for unmeasured organic acids, approximately half of the acidic lakes in Florida have organic acids as the dominant anion. The remaining acidic lakes in Florida are generally clear water seepage lakes with sulfate as the dominant acid anion. Chloride is found in concentrations proportional to those of sodium, and there appears to be little basis for acidification by neutral salts in these lakes (*20*, *21*). Assuming chloride is a conservative ion and that groundwater contributions to the acidic lakes are minimal, the acidic status of these Florida lakes can be explained by evaporative concentration of relatively low rates of acidic deposition. For undeveloped lakes in the panhandle and the northcentral peninsula, Baker et al. (*21*) found that lake chemistry is consistent with acidification by atmospheric deposition, which also is in agreement with the observations from an earlier study (*20*). However, it is unlikely that the mechanism(s) of acidification of clear water lakes in Florida and the linkage to atmospheric deposition will be satisfactorily understood until the hydrologic pathways are better known. It appears that slight differences in groundwater flowpaths can have large influences on lake chemistry. In view of the large declines in the potentiometric surface of the Floridan aquifer (*19*), the influence of human activities in modifying these groundwater flowpaths may be particularly important in the Florida lakes.

Acknowledgments

We acknowledge the many persons, especially Rick A. Linthurst, who contributed to the Eastern Lake Survey.

We thank Barry Rochelle for helpful comments on an earlier draft. Statistical support for these analyses was provided by Scott Overton, James Blick, Mark DeHaan, and Dan Kugler.

Registry No. C, 7440-44-0; Ca, 7440-70-2; Mg, 7439-95-4; Na, 7440-23-5; K, 7440-09-7; NH_4, 14798-03-9; Fe, 7439-89-6; Mn, 7439-96-5; Al, 7429-90-5; P, 7723-14-0; H^+, 12408-02-5.

Literature Cited

(1) Brakke, D. F.; Landers, D. H.; Eilers, J. M. *Environ. Sci. Technol.* **1988**, *22*, 155–163.
(2) Eilers, J. M.; Brakke, D. F.; Landers, D. H. *Environ. Sci. Technol.* **1988**, *22*, 164–172.
(3) Landers, D. H.; Overton, W. S.; Linthurst, R. A.; Brakke, D. F. *Environ. Sci. Technol.* **1988**, *22*, 128–135.
(4) Linthurst, R. S.; Landers, D. H.; Eilers, J. M.; Brakke, D. F.; Overton, W. S.; Meier, E. P.; Crowe, R. E. *Characteristics of Lakes in the Eastern United States*; U.S. EPA: Washington, DC, 1986; Vol. I, pp 1–136; EPA/600/4-86/007a.
(5) Wetzel, R. G. *Limnmology*, 2nd ed; Saunders College Publishing: Philadelphia, 1983; 767 pp.
(6) Overton, W. S.; Kanciruk, P.; Hook, L. A.; Eilers, J. M.; Landers, D. H.; Brakke, D. F.; Blick, D. J., Jr.; Linthurst, R. A.; DeHaan, M. S.; Omernik, J. M. *Characteristics of Lakes in the Eastern United States*; U.S. EPA: Washington, DC, 1986; Vol. II, pp 1–374; EPA/600/5-86/007b.
(7) Eshleman, K. N.; Blick, D. J.; Kaufmann, P. R.; Mitch, M. E.; Stambaugh, S. M.; Messer, J. J. *Lake Reserv. Manage.* **1987**, *3*, 476–481.
(8) Hillman, D. C. J.; Potter, J. F.; Simon, S. J. *National Surface Water Survey, Eastern Lake Survey—Phase I. Analytical Methods Manual*; U.S. EPA: Las Vegas, NV, 1986; EPA/600/4-86/009.
(9) Oliver, B. G.; Thurman, E. M.; Malcolm, R. L. *Geochim. Cosmochim. Acta* **1983**, *47*, 2031–2035.
(10) Thornton, K. W.; Kennedy, R. H.; Carroll, J. H.; Walker, W. W.; Gunkel, R. C.; Ashby, S. In *Symposium on Surface Water Impoundments*; Stefan, H., Ed.; ASCE: New York, 1980; Volume 1, pp 654–661.
(11) Kanciruk, P.; Eilers, J. M.; McCord, R. A.; Landers, D. H.; Brakke, D. F.; Linthurst, R. A. *Characteristics of Lakes in the Eastern United States*; U.S. EPA: Washington, DC 1986; Vol. III, pp 1–439; EPA/600/4-86/007c.
(12) *SAS/IML User's Guide*; SAS Institute, Inc.: Cary, NC, 1985; Version 5.
(13) Reinsch, C. H. *Numerische Mathematik* **1967**, *10*, 177–183.
(14) Salt Institute *Survey of Salt, Calcium Chloride, and Abrasives Use in the United States and Canada for 81/82 and 82/83*; Salt Institute: Alexandria, VA, 1985; pp 1–18.
(15) Stensland, G. J.; Whelpdale, D. J.; Oehlert, E. In *National Academy of Sciences. Acid Deposition: Long-Term Trends.* National Academy Press: Washington, DC, 1986; pp 128–199.
(16) Galloway, J. S.; Norton, S. A.; Church, M. R. *Environ. Sci. Technol.* **1983**, *17*, 541a–545a.
(17) Rochelle, B. P.; Church, M. R.; David, M .B. *Water, Air, Soil Pollut.* **1987**, *33*, 73–83.
(18) Rochelle, B. P.; Church, M. R. *Water, Air, Soil Pollut.*, in press.
(19) *Water Resources Atlas of Florida*; Fernald, E. A., Patton, D. G., Eds.; Florida State University: Tallahassee, FL, 1984.
(20) Hendry, C. D.; Brezonik, P. L. *Water Resour. Bull.* **1984**, *20*, 75–86.
(21) Baker, L. A.; Pollman, C. D.; Eilers, J. M., submitted for publication in *Water Resour. Res.*

Received for review February 9, 1987. Accepted November 10, 1987. The research described in this article has been funded as part of the National Acid Precipitation Assessment Program by the U.S. Environmental Protection Agency. This article was prepared at the EPA's Research Laboratory in Corvallis, OR, in part, through Contract 68-03-3246 with Northrop Services and Cooperative Agreement CR812653 with Western Washington University. This is a contribution from the National Surface Water Survey of the EPA's Aquatic Effects Research Program. It has been subjected to the Agency's peer and administrative review and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Environ. Sci. Technol. 1988, 22, 178–182

Acidification of Lakes in the Eastern United States and Southern Norway: A Comparison†

Richard F. Wright

Norwegian Institute for Water Research, Box 33, 0313 Oslo, Norway

■ Synoptic surveys of lake chemistry in the eastern United States and in Norway span comparable gradients in acid deposition. Sulfate levels in lakes of both areas (less natural background) reflect inputs of sulfate from the atmosphere. Lake acidification and acid lakes occur in both regions. Levels of nonmarine Ca plus Mg provide a better measure of lake sensitivity than alkalinity. Alkalinity may be low due to high sensitivity or as a result of acidification. Lakes become acidic (alkalinity <0; pH <5.3) when nonmarine sulfate levels (less natural background) are greater than nonmarine Ca plus Mg. Nitrate levels are highest in lakes receiving the highest acid deposition, but NO_3 generally accounts for <10% of strong acid anions. A much higher percentage of lakes in southern Norway are acidic compared to the eastern United States because a larger fraction of the Norwegian lakes are inherently more sensitive.

Introduction

The 1984 synoptic survey of water chemistry of 1615 lakes in the eastern United States (*1*) provides data similar to those obtained from synoptic surveys conducted in the mid-1970s in Norway (*2*, *3*). These regions span similar gradients in acid deposition.

In the eastern United States wet deposition of sulfate ranges from <10 kg of SO_4 ha^{-1} yr^{-1} in northwestern Minnesota to >30 kg of SO_4 ha^{-1} yr^{-1} in the Adirondack Mountains of New York (*4*). This range is comparable to that in southern Norway where wet deposition is <10 kg of SO_4 ha^{-1} yr^{-1} inland and exceeds 30 kg of SO_4 ha^{-1} yr^{-1} along the south coast (*5*). Dry deposition, of course, comes in addition.

Major-ion chemistry relationships observed in Norwegian lakes led to the development of several general concepts regarding sensitivity and acidification of softwater lakes (*6–8*). Here I apply these concepts to lakes in the eastern United States and compare the major-ion chemistry and acidification of lakes in the eastern United States and southern Norway. I confine my analysis to lakes in glaciated regions of the United States, as these are most comparable to those of Norway.

The Data

Linthurst et al. (*1*) describe the lake selection, sampling, analysis, and quality control procedures of the 1984 Eastern Lake Survey. Of the 1615 lakes sampled, 1360 lie in glaciated regions. Some of these lakes exhibit chemical characteristics indicative of significant inputs of pollutants from within the catchment. Such inputs confound the evaluation of atmospheric deposition. Inputs of domestic sewage are indicated by high levels of phosphorus; lakes with total P levels >30 μg of P/L were thus excluded. Inputs of road-deicing salts are indicated by high levels of chloride. Lakes excluded were those in the upper midwest (region 2) with Cl levels >50 μequiv/L, in the Adirondacks and central New England (regions 1A and 1C) with Cl levels >100 μequiv/L, in the Catskills and Poconos and in Maine (regions 1B and 1D) with Cl levels >300 μequiv/L, and in southern New England (region 1D) with Cl levels >500 μequiv/L. These limits for both P and Cl were set by inspection of the data (Table I). Many of these excluded lakes are also "outliers" with respect to other parameters such as alkalinity, base cations, SO_4, and NO_3.

The Norwegian data used for comparison come from the 1974–1975 survey of 716 lakes in southernmost Norway (*3*). Lakes in seven townships along a transect from Bykle 200 km in the interior to Mandal on the coast span a gradient in acid deposition similar to that in the United States from Minnesota to New York. The Norwegian data were grouped by township to give a data set comparable to the U.S. data grouped by subregion (Table II).

I define alkalinity here as the difference between the sum of charges of strong base cations ($\sum$[BC]) minus the sum of charges of strong acid anions ($\sum$[AA]) (*9*):

$$\begin{aligned} \text{alk} &= \sum[\text{BC}] - \sum[\text{AA}] \\ &= ([\text{Na}^+] + [\text{K}^+] + [\text{Ca}^{2+}] + [\text{Mg}^{2+}] + [\text{NH}_4^+]) - \\ &\qquad ([\text{SO}_4^{2-}] + [\text{NO}_3^-] + [\text{Cl}^-]) \end{aligned}$$

From the ionic balance it can be shown that alkalinity defined in this manner is identical with

$$\text{alk} = [\text{CO}_3^{2-}] + [\text{OH}^-] + [\text{HCO}_3^-] + [\text{organic anions}] - [\text{H}^+] - \sum[\text{Al}^+]$$

where $\sum[\text{Al}^+]$ is the sum of positively charged aluminum species and units are again μequiv/L. Softwater lakes have negligible $[\text{CO}_3^{2-}]$ and $[\text{OH}^-]$. Clearwater lakes have negligible concentrations of organic anions. In such lakes alkalinity reduces to

$$\text{alk} = [\text{HCO}_3^-] - [\text{H}^+] - \sum[\text{Al}^+]$$

Results and Discussion

Sea Salts. In both the United States and Norway, concentrations of Na in lakes are highly correlated to concentrations of Cl (Tables I and II), and the concentrations of both ions are generally highest in coastal lakes. Exceptions are lakes receiving inputs from road-deicing salts. Linear regressions of Na on Cl for lakes in the northeastern United States (subregions 1A–1E) yield slopes of 0.8–0.9 (*1*), which is close to the ratio in seawater of 0.86. For the entire set of 700 Norwegian lakes the slope is 0.85 (*3*).

This points to atmospheric inputs of seawater salts as a major source of Na and Cl. Weathering and ion exchange comprise a second source of Na to these lakes. The magnitude of this second source appears independent of distance from the coast as Na* + K* concentrations are similar in all subregions in the United States and townships in Norway (Tables I and II).

To examine lake acidification and to compare inland with coastal lakes, it is necessary to subtract out the seasalt component. This can be done by assuming that all Cl comes from seasalts and that the ionic ratios of other major ions are as in seawater. The concentrations in excess of the seasalt contribution are denoted here by asterisks.

Base Cations. Softwater lakes in areas not receiving significant acid deposition are commonly [Ca*]–[Mg*]–

†This research is a contribution from the National Surface Water Survey of the Aquatic Effects Research Program.

 0013-936X/88/0922-0178$01.50/0 © 1988 American Chemical Society

Table I. Numbers and Chemical Characteristics of Lakes Grouped by Region and Subregion in the 1984 Eastern Lake Survey[a]

region and subregion	no. of lakes: target population	no. of lakes: sampled	no. of lakes: less outliers	mean ± SD, μequiv/L: Ca* + Mg*	mean ± SD, μequiv/L: Na* + K*	mean ± SD, μequiv/L: SO_4*	mean ± SD, μequiv/L: NO_3*
region 1: Northeast							
(1A) Adirondacks	1290	155	131	241 ± 168	34 ± 22	116 ± 25	2 ± 4
(1B) Catskills + Poconos	1506	144	102	327 ± 52	27 ± 22	146 ± 49	2 ± 5
(1C) central New England	1494	164	108	282 ± 261	44 ± 15	94 ± 27	1 ± 1
(1D) southern New England	1325	127	76	200 ± 54	43 ± 26	108 ± 44	2 ± 4
(1E) Maine	1542	178	170	261 ± 67	44 ± 15	69 ± 24	1 ± 1
region 2: Upper Midwest							
(2A) northeastern Minnesota	1499	150	136	323 ± 149	44 ± 12	66 ± 27	2 ± 2
(2B) upper Michigan	1050	146	132	672 ± 543	32 ± 19	79 ± 35	1 ± 2
(2C) north-central Wisconsin	1510	155	128	284 ± 250	30 ± 17	62 ± 22	1 ± 2
(2D) upper Great Lakes area	4514	141	100	879 ± 894	51 ± 37	58 ± 46	1 ± 2

[a] Lakes with total P levels >30 equiv of P/L were excluded as were lakes with high Cl levels (>50 equiv/L in Region 2; >100 equiv/L in subregions A1 and 1C; >300 equiv/L in subregions 1B and 1E; >500 equiv/L in subregion 1D). The data are weighted by alkalinity class in the original sample. See ref 1 for details.

Table II. Numbers and Chemical Characteristics of Lakes by Township Sampled in the 1974–1975 Survey in Southernmost Norway (*3*)

township	code	no. of lakes (165 total)	mean ± SD, μequiv/L: Ca* + Mg*	mean ± SD, μequiv/L: Na* + K*	mean ± SD, μequiv/L: SO_4*	mean ± SD, μequiv/L: NO_3*
Mandal	Ma	11	106 ± 51	16 ± 5	121 ± 16	16 ± 5
Audnedal	Au	10	72 ± 39	12 ± 8	90 ± 12	4 ± 3
Åseral	Ås	45	24 ± 9	14 ± 5	39 ± 10	7 ± 4
Bygland	Bg	39	28 ± 15	15 ± 9	50 ± 18	5 ± 5
Valle	Va	32	30 ± 9	9 ± 3	33 ± 9	8 ± 3
Bykle	Bk	28	22 ± 11	14 ± 8	23 ± 7	4 ± 2

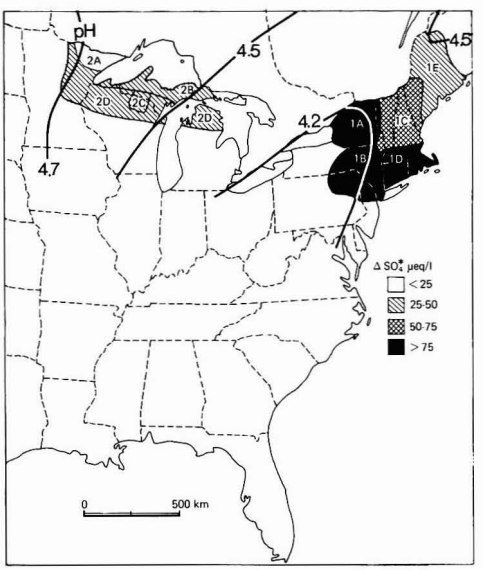


Figure 1. Map of eastern United States showing regions and subregions included in this analysis of the 1984 Eastern Lake Survey (data from ref 1). Shading indicates mean nonmarine sulfate concentrations above background level of 30 μequiv/L (northeastern Minnesota, 40 μequiv/L). Also shown are volume-weighted annual mean H^+ concentrations in precipitation (expressed as pH) in 1980 (from ref 13). The data are weighted by alkalinity class in the original sample (*12*).

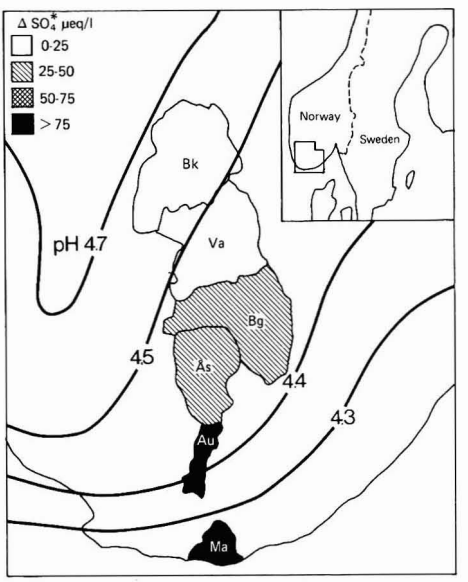


Figure 2. Map of southernmost Norway showing six townships included in this comparison (data from ref 3). Shading indicates mean nonmarine sulfate concentrations above background level of 10 μequiv/L. Also shown are volume-weighted annual mean H^+ concentrations in precipitation (expressed as pH) from 1974 to 1975 (from ref 2).

$[HCO_3]$ waters (*10*). Na* and K* concentrations are generally minor relative to Ca* and Mg* concentrations (*8*).

These generalizations also hold for the 1984 U.S. lake survey. In northeastern Minnesota (subregion 2A) alkalinity is highly correlated to [Ca*] + [Mg*] (*1*). In all subregions [Na*] + [K*] levels average about 30–40 μequiv/L, only 10% or less of average [Ca*] + [Mg*], and are not significantly correlated to alkalinity.

Acidification. Inputs of sulfur from the atmosphere are generally reflected in elevated sulfate concentrations in surface waters (*2, 8, 11*). Lakes in the 1984 Eastern Lake

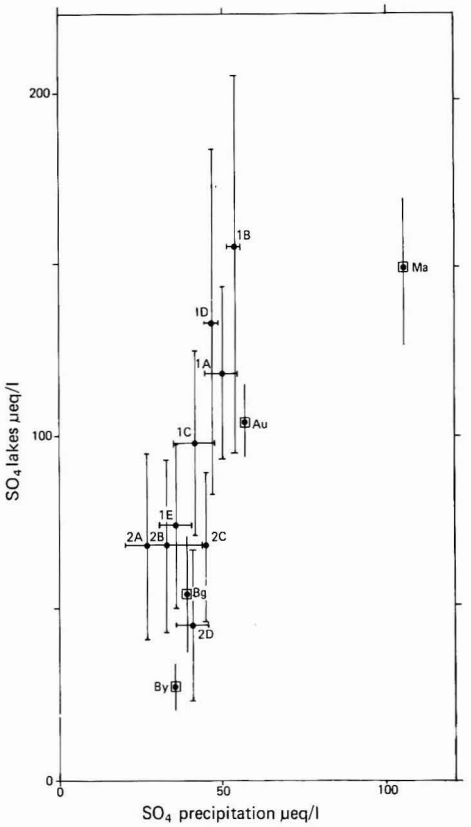


Figure 3. Mean and standard deviation of sulfate concentrations by subregion (United States) or township (Norway) in precipitation and lakes. See Tables I and II for codes (data from ref 1 and 3). The U.S. data are weighted by alkalinity class.

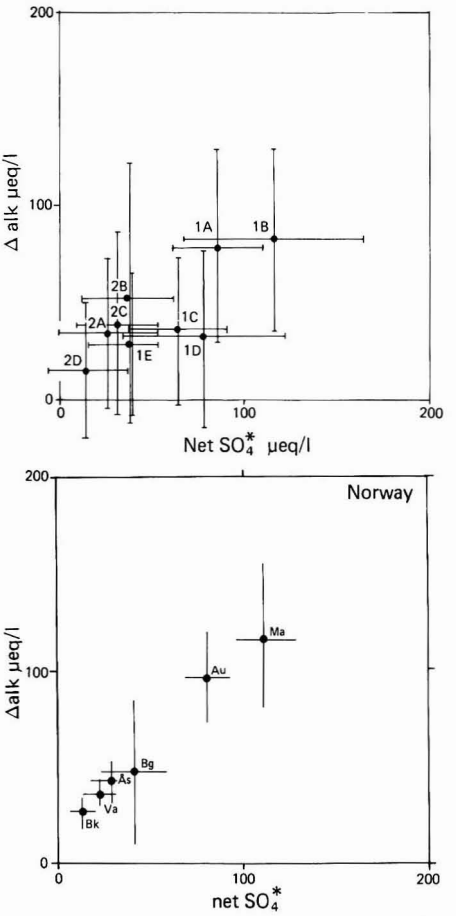


Figure 4. Acidification estimated by Δalkalinity and net $[SO_4^*]$ (μequiv/L) in lakes grouped by subregion (United States) (top panel) or township (Norway) (bottom panel). Δalkalinity is defined as $[Ca^*] + [Mg^*]$ – alkalinity. Net $[SO_4^*]$ is defined as nonmarine $[SO_4]$ above estimated background. For subregions 2B, 2C, and 2D, lakes in alkalinity class 3 are excluded here. Means and standard deviations are shown.

Survey as well as in the 1974–1975 Norwegian survey exhibit this relationship (Figures 1–3). Sulfate concentrations in lakes are generally higher than those in wet precipitation because of additional sulfur inputs from dry deposition of gases and aerosols and the concentrating effect due to evapotranspiration. The slope of this relationship is about 2.

Atmospheric inputs of sulfate of anthropogenic origin come in addition to a natural background level of $[SO_4^*]$. Background $[SO_4^*]$ may be of atmospheric source or from weathering within the catchment. Background levels are generally low and of regional character (*8*). Here I use as background $[SO_4^*]$ of 30 μequiv/L for lakes in the United States (40 μequiv/L for northeastern Minnesota) and 10 μequiv/L for Norway. These levels are estimated from lake chemistry data from regions not receiving significant acid deposition. Background $[SO_4^*]$ in Minnesota is apparently higher due to inputs of terrestrial dusts (*12*). Sulfate concentrations (above background) increase along the gradient from Minnesota to New York and similarly from central Norway to the south coast (Figures 1 and 2).

Increases in lakewater sulfate due to acid deposition must necessarily be accompanied by an equivalent decrease in another anion or an increase in one or more cations. Empirical lake data from Europe and North America indicate that acidification involves the loss of alkalinity and an increase in Ca* + Mg* concentrations (*6*, *8*). Other major ions such as Na*, K*, NH_4, NO_3, and organic anions do not play a major role. Exceptions to this general pattern include some very highly colored lakes in which organic anions are significant and some lakes in regions receiving high deposition of nitrogen compounds. Neither the Eastern Lake Survey nor the Norwegian survey includes an appreciable number of such lakes.

Nitrate levels in lakes in the U.S. survey as well as Norway seldom exceed 10% of SO_4 levels on an equivalent basis. There is some indication that atmospheric deposition results in elevated nitrate levels in these lakes, however, for lakes in regions receiving high deposition (example: Adirondacks in the United States and Mandal in Norway) also exhibit higher NO_3 concentrations.

Lake acidification involves $[SO_4^*]$ on the one hand and alkalinity ($[HCO_3] - [H^+] - \sum[Al^+]$) and $[Ca^*] + [Mg^*]$ on the other. The acidification equation

$$([Ca^*] + [Mg^*] - \text{alkalinity}) = ([SO_4^*] - \text{background } [SO_4^*])$$

thus provides two quantitative measures of acidification. This equation is simply a consequence of the ionic balance

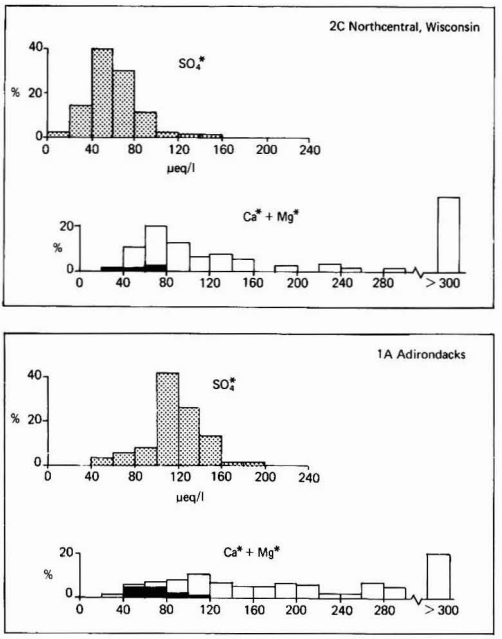


Figure 5. Frequency histograms of nonmarine SO_4 and nonmarine Ca + Mg concentrations in lakes of subregions 2C (north-central Wisconsin) and 1A (Adirondacks). The gradient in sulfur deposition across the northern United States is reflected in sulfate concentrations in lakes with the highest mean levels in the mid-Atlantic states. Acid lakes (alkalinity <0; pH <5.3) are indicated by solid shading. These are sensitive lakes (low Ca* + Mg* levels) at which the SO_4* level exceeds the threshold level of Ca* + Mg*. The data are weighted by alkalinity class (*1*).

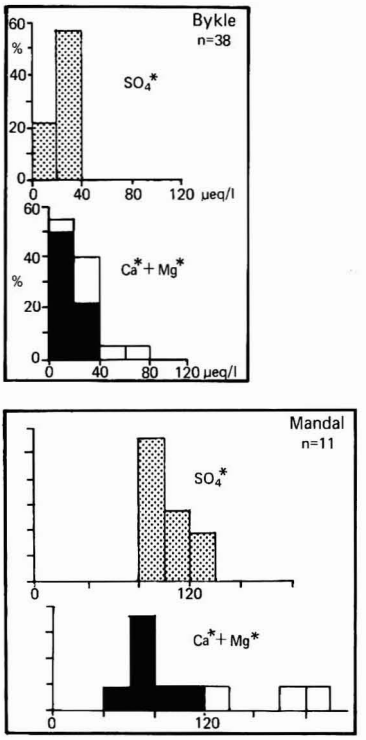


Figure 6. Frequency histograms of nonmarine SO_4 and nonmarine Ca + Mg concentrations in Bykle and Mandal townships in Norway. The gradient in acid deposition from low levels inland (Bykle) to high levels at the coast (Mandal) is reflected in SO_4* concentrations in the lakes. Acid lakes are indicated by solid shading.

in which the sea-salt component is removed and minor ions are neglected (*8*). The left-hand side is termed "Δalk" and right-hand side "net [SO_4*]" (*6*, *8*).

The acidification equation links the chemical parameters [Ca*] + [Mg*], alkalinity, and [SO_4*]. Alkalinity will be negative (pH <5.3), if net [SO_4*] > [Ca*] + [Mg*].

Grouped by subregion or township, both the U.S. data and Norwegian data fit the acidification equation (Figure 4). As sulfate levels (less background) increase so does the difference ([Ca*] + [Mg*]) – alkalinity. The latter may reflect an increase in [Ca*] + [Mg*] or a decrease in alkalinity; these synoptic data provide no direct information as to changes over time. The close relationship between net [SO_4*] and Δalk for lakes in both the United States and Norway indicates that sea-salt correction and neglect of minor ions can be made when evaluating acidification.

Ca* + Mg* levels provide a better estimate of original lake sensitivity than alkalinity. Alkalinity can be low because of high sensitivity, as is the case in relatively unimpacted lakes in inland Norway (Bykle). Alkalinity can also be low in the case of moderately sensitive lakes that have been acidified by acid deposition, as is the case for lakes on the south coast (Mandal). Although Ca* + Mg* levels increase as a result of acid deposition, this increase is probably smallest in low Ca* + Mg* level lakes (i.e., sensitive lakes) and thus does not greatly affect the sensitivity classification of such lakes.

When the net SO_4* level is greater than the Ca* + Mg* level, a threshold is exceeded at which the lake becomes acid. As acid deposition increases over the west-to-east gradient from Minnesota to New York, lakes with higher and higher Ca* + Mg* levels become acid (pH <5.3) (Figure 5). In northeastern Minnesota where net SO_4* levels averages about 25 μequiv/L, no lake sampled had a Ca* + Mg* level below 25 μequiv/L, and thus no acid lakes were found. Farther east in north-central Wisconsin, net SO_4* levels average about 30 μequiv/L and exceed the threshold in the most sensitive lakes; these thus have negative alkalinity.

The same situation holds for Norway. When the net SO_4* level exceeds the Ca* + Mg* level, lakes are acid with pH <5.3 (Figure 6). A larger fraction of the Norwegian lakes are acid because they are inherently more sensitive than the U.S. lakes.

The major-ion chemistry of lakes in eastern United States and southern Norway indicates that acidification of lakes entails similar chemical changes in both regions. Sulfate concentrations in lakes closely reflect sulfur deposition from the atmosphere. The gradient in lakewater sulfate from Minnesota to New York is similar to that in Norway from 200 km inland to the south coast. This sulfate gradient is accompanied by a gradient in lake acidification as defined as [Ca*] + [Mg*] less alkalinity. Other ions are of minor importance or do not exhibit significant regional distributions.

In areas of Norway that receive acid deposition similar to areas in the United States, such as Mandal on the south coast and the Adirondack Mountains of New York, the degree of acidification is similar. In both areas lakes with Ca* + Mg* levels below about 100 μequiv/L are acidified to pH <5.3.

Acidification of softwater lakes entails characteristic changes in major-ion chemistry. In glaciated regions the

key factors are sulfate deposition, sea-salt inputs, and lake sensitivity. These simplified chemical relationships allow comparison of lake acidification between widely-separated regions and provide a starting point for empirical predictive models of lake acidification.

Acknowledgments

I thank D. Brakke, J. Eilers, D. Landers, S. Norton, and T. Sullivan for constructive criticism.

Registry No. Ca, 7440-70-2; Mg, 7439-95-4.

Literature Cited

(1) Linthurst, R. A.; Landers, D. H.; Eilers, J. M.; Brakke, D. F.; Overton, W. S.; Meier, E. P.; Crowe, R. W. *Characteristics of Lakes in the Eastern United States*; U.S. Environmental Protection Agency: Washington, DC, 1986; Vol. I; EPA-600/4-86-0071.
(2) Wright, R. F.; Henriksen, A. *Limnol. Oceanogr.* **1978**, *23*, 487–498.
(3) Wright, R. F.; Snekvik, E. *Verh.—Int. Ver. Theor. Angew. Limnol.* **1978**, *20*, 765–775.
(4) Munger, J. W.; Eisenreich, S. J. *Environ. Sci. Technol.* **1983**, *17*, 32A–42A.
(5) Dovland, H.; Joranger, E.; Semb, A. In *Impact of Acid Deposition on Forest and Freshwater Ecosystems in Norway*; Braekke, F., Ed.; SNSF Project: 1432 Ås, Norway, 1976; pp 14–35.
(6) Henriksen, A. In *Ecological Impact of Acid Deposition*; Drabløs, D., Tollan, A., Eds.; SNSF Project: 1432 Ås, Norway, 1980; pp 68–74.
(7) Wright, R. F.; Henriksen, A. *Nature (London)* **1983**, *305*, 422–424.
(8) Wright, R. F. *Predicting Acidification of North American Lakes*; Acid Rain Research Report 4/83; Norwegian Institute for Water Research: Oslo, Norway, 1983.
(9) Kramer, J. R.; Davies, S. S. *Environ. Sci. Technol.* **1988**, *22*, 182–185.
(10) Wright, R. F.; Gjessing, E. T. *Ambio* **1976**, *5*, 219–223.
(11) Kramer, J. R.; Andren, A. W.; Smith, R. A.; Johnson, A. H.; Alexander, R. B.; Oehlert, G. In *Acid Deposition Long-Term Trends*; National Academy Press: Washington, DC, **1986**; pp 231–299.
(12) Munger, J. W. *Atmos. Environ.* **1982**, *16*, 1633–1645.
(13) Barrie, L. A.; Hales, J. M. *Tellus, Ser. B* **1984**, *36B*, 333–335.

Received for review February 9, 1987. Accepted September 4, 1987. Although the research described in this article has been funded as part of the National Acid Precipitation Assessment Program by the U.S. Environmental Protection Agency through Purchase Order 8606LT0449 with Northrop Services Inc., it has not been subjected to the Agency's review and therefore does not necessarily reflect the views of the Agency, and no official endorsement should be inferred.

Estimation of Non-Carbonato Protolytes for Selected Lakes in the Eastern Lakes Survey

James R. Kramer* and Steven S. Davies

Department of Geology, McMaster University, Hamilton, Ontario L8S 4M1, Canada

■ U.S. Environmental Protection Agency Eastern Lakes Survey titration data are used to obtain concentration–pK_a distributions for high-quality data. Acid and base titration data for waters with dissolved organic carbon (DOC) greater than 3 mg of C/L are assessed with a multivariable regression technique. The resulting averages normalized to DOC are used to define an average organic cocktail. This mixture can reduce the pH below 5 for carbonato systems of alkalinity equal to 200 μequiv/L when the DOC is greater than 7 mg of C/L or for alkalinities equal to 50–100 μequiv/L for a DOC of 4 mg of C/L. Alkalinities of 2000 μequiv/L are barely affected by 10 mg of C/L DOC levels.

Introduction

The role of organic acids in dilute surface waters is a topic of considerable interest, especially with respect to their possible role in surface water acidification (*1–5*). Some studies consider naturally occurring organic acids as simple mixtures with discrete dissociation constants (pK_a) (*6*, *7*), whereas Perdue and Lytle (*8*) proposed a model of normally distributed pK_a values. In the past few years, various spectral affinity techniques have been used to produce concentration–pK curves, assuming that the system can be modeled by a summation of monoprotic reactions (*9*, *10*). For example, Leuenberger and Schindler (*11*) recently applied a least-squares integral spectrometry analysis to characterize the concentration–pK_a distribution of fulvic acid.

The U.S. EPA National Surface Water Survey (NSWS) carried out acid and base titrations of a large number of lakes in their Eastern Lakes survey (ELS) (*12*). In addition, dissolved inorganic carbon (DIC) and pH were analyzed so that carbonate alkalinity might be estimated, and dissolved organic carbon (DOC) was also analyzed, allowing distinction of high-organic waters. Quite rigid quality assurance checks on protolyte parameters were used to isolate and further assess high-quality data (*13*).

The principal objective of this paper is to characterize the non-carbonato protolytes in waters relatively rich in organic matter, with data from the ELS. These waters are defined as having >3 mg of C/L DOC, the level where color is usually apparent (*14*).

Theory

The ion balance expression can be written for an aqueous system consisting of carbonato and other monoprotic ($[Ot]_i$) species as

$$\sum[M] - \sum[A] = ANC = Alk + \sum[Ot]_i \quad (1)$$

where $\sum[M]$ and $\sum[A]$ are the sums of charges of strong base cations and acidic anions and ANC is the acid neutralizing capacity. Alk = alkalinity = $[HCO_3] + 2[CO_3] + [OH] - [H]$; for the ith other species, $HOt_i = H^+ + Ot^-_i$, with $C_i = [HOt]_i + [Ot]_i$ and $K_i = [H^+][Ot^-]_i/[HOt]_i$. The concentrations all are relative to the initial solution concentration V_s.

Equation 1 can be modified for acid or base titration by addition of the strong acid anion and strong base cation concentration terms. Thus

$$(\sum[M] - \sum[A])V_s + T_bv_b = V_s\sum[Ot]_i + V_s(Alk) + T_av_a \quad (2)$$

0013-936X/88/0922-0182$01.50/0 © 1988 American Chemical Society

where T_a and T_b are acid and base titrant concentrations (equiv/L) and v_a and v_b are cumulative acid and base titrant volumes (L). Rearranging eq 2 to solve for $\sum[Ot]_i$ and substituting eq 1 into eq 2 results in

$$\sum[Ot]_{ij} = ANC - (Alk)_j + T_b v_{bj}/V_s - T_a v_{aj}/V_s \quad (3)$$

Equation 3 is valid at any titrant condition j.

Equation 3 is solved for each titrant condition by substituting in the value for ANC obtained either by the difference in analytical data for strong base cations ([Na] + [K] + [Ca] + [Mg] + [NH_4]) minus strong base anions ([SO_4] + [NO_3] + [Cl]) or from a Gran analysis for ANC, the value for alkalinity obtained by DIC–pH_j data, the titrant concentrations (T) and volumes (v), and the sample volume, V_s. Equation 4 gives the value for $(Alk)_j$, where

$$(Alk)_j = \frac{DIC([H]_j K_1 + 2K_1K_2)}{12010([H]_j^2 + [H]_j K_1 + K_1K_2)} + \frac{K_w}{[H]_j} - [H]_j \quad (4)$$

DIC is dissolved inorganic carbon (mg of C/L), K_1, K_2, and K_w are the first and second dissociation constants for carbonic acid and the dissociation constant for water, respectively, for the temperature and ionic strength condition.

Thus for each titrant point a value of $\sum[Ot]_{ij}$ can be obtained by substituting eq 4 into eq 3. $\sum[Ot]_{ij}$ can be expanded as

$$\sum[Ot]_{ij} = \frac{C_1K_1}{[H]_j + K_1} + \frac{C_2K_2}{[H]_j + K_2} + \ldots + \frac{C_mK_m}{[H]_j + K_m} \quad (5)$$

Choosing values of K_1, K_m, and discrete intervals (ΔpK), eq 5 can be written as a multivariable linear equation (zero intercept), which can be solved by regression techniques:

$$\sum[Ot]_j = C_1X_1 + C_2X_2 + \ldots + C_mX_m \quad (6)$$

where

$$X_k = K_k/([H] + K_k)$$

Thus values of C_1 to C_m are solved for corresponding values of K_1 to K_m (pK_1 to pK_m).

Alternatively the carbonato contribution can be determined as one of the $[Ot]_{ij}$ terms of eq 3. Thus, eq 3 becomes

$$\sum[Ot]_{ij} = ANC + (T_b v_b - T_a v_a)/V_s \quad (7)$$

Equation 7 is solved for C_i–K_i values with eq 6. In this case, a concentration value corresponding to a p$K \simeq 6.3$ should result, reflecting the first dissociation of carbonic acid. Alk can be determined from this concentration value and the initial solution pH (eq 4), which in turn can be compared to the alkalinity obtained from the DIC–pH pairs.

Methods and Materials

Selected data from the NSWS ELS were used in a compilation of C_i–pK_i statistics. Approximately 650 data sets, representing high-quality data with DOC concentration greater than 3 mg of C/L, were chosen. The data were considered high quality if three consistent alkalinities were obtained from three DIC–pH measurements and were less than or equal to two consistent ANC estimates. ANC was determined from a Gran analysis of the acid titration data and from the difference of ([NH_4] + [Na] + [K] + [Ca] + [Mg]) – ([SO_4] + [Cl] + [NO_3]). Consistency was considered achieved if a relative standard deviation of 10% or 10 μequiv/L for values less than 200 μequiv/L was obtained. The ANC value determined by Gran analysis was used in the calculations.

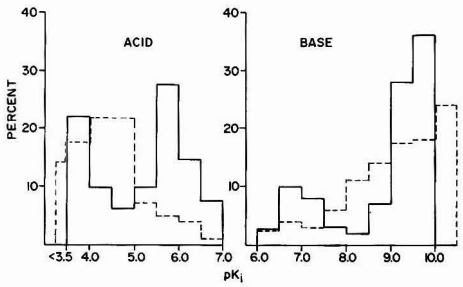


Figure 1. Percent distribution of pK_i values determined for the ELS. Acid and base titrations are shown and independently are summed to 100%. The dashed line shows the suggested distribution of pK's for simple carboxylic acids (*15*).

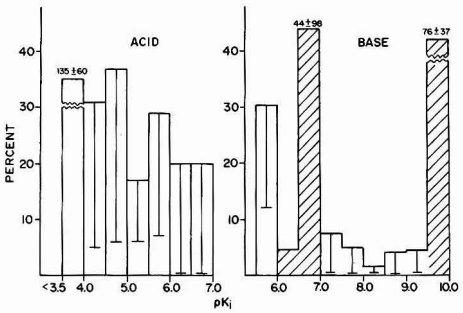


Figure 2. Concentration distributions for pK intervals determined for the ELS. The vertical lines represent the relative standard deviation. The shaded areas reflect regions where carbonato contribution would be significant and hence normalization to DOC would not apply.

The final C_i–pK_i array was obtained by an iterative procedure. Initially an array is obtained for a pK interval of 0.5 in the range of 0.5 pK unit beyond the pH bounds. Then four iterative fitting steps, each consisting of elimination of concentrations less than zero (zero was defined as $<2 \times 10^{-6}$ M) and addition of pK's at the pH values for the two largest absolute deviations of measured and fitted functions, were carried out. A standardized matrix inversion procedure (*16*) was used to obtain the requisite accuracy. The final summary was made for those results showing only a multiple linear regression coefficient of >0.95 and with no negative C_i's. Approximately half of the data were usable for the final assessment.

Results

Both total titration data and titration data with the carbonato contribution removed were assessed. Data with carbonato contribution removed gave poor results, however, probably due to the loss of CO_2 during titration. Therefore, only results for all protolytes are presented.

Results are tabulated as a frequency distribution of pK_i values (Figure 1) and as a C_i/DOC versus pK_i distribution (Figure 2). Both acid and base titration data were used to calculate the summaries. The pK_i distribution of carboxylic acids (*15*) is also given in Figure 1 for comparison. The pK_i distribution for the ELS and that for measured carboxylic acids would probably be similar if the carbonato component at pK_i of about 6 and 10 could be removed. It does appear, however, that the maximum acidic pK_i es-

Table I. An Average Organic Acid Cocktail for the ELS

pK median	concn/DOC, μmol/mg of C	pK median	concn/DOC, μmol/mg of C
3.25	7.9	4.75	2.2
3.75	13.5	5.25	5.0
4.25	6.7	5.75	0.4

timation for ELS is 0.5 lower than the distribution of simple carboxylic acids. This analysis, however, agrees quite well with the assessment of Perdue et al. (*8*), who found a mean pK of 3.7 for analysis of southeastern Georgia aquatic humic matter. Thus naturally occurring aquatic humic matter can be quite acidic.

The acidic C_i/DOC distribution for the ELS has an average of about 20 μequiv/mg, being near the upper end of other estimates (*17*, *18*). On the other hand, the basic C_i/DOC ratios, ignoring the carbonato regions, average about 4. The average value of 135, determined for the pK_i interval of 3.5–4.0, is quite high, but this value represents only a small fraction of the protolytes in any given sample.

An average organic acid cocktail for the ELS is calculated with the results of Figure 1 to weigh the concentration data in Figure 2. Table I gives the C_i/DOC values for the acidic pK_i range of <6.0. This limit was imposed in order to suppress the effect of the carbonato protolytes. The final weighted concentration/DOC values can be construed to give a one-value estimate similar to that suggested by Oliver et al. (*18*). Thus, DOC is used as a surrogate for the total organic acid concentration with a fixed pK_i–C_i distribution.

Titration of a Carbonato System with Organic Acids

A "back of the envelope" calculation is made for the pH effect of mixing various hypothetical carbonato systems with an organic protolyte. For this calculation, one assumes an initial carbonato system (pH, alkalinity) and mixes with various amounts of average ELS organic acid (Table I). The total concentration of organic acid is represented by DOC. The resultant pH is determined from this mixture as a function of DOC. Ion balance considerations are used to obtain the resulting H ion concentration for pHs less than 7 and relative to initial alkalinity:

$$\text{Alk} \simeq C_t \frac{K_1}{[\text{H}] + K_1} + \sum C_d \frac{(\text{DOC})K_d}{[\text{H}] + K_i} \qquad (8)$$

where C_t and K_1 are the carbonato concentration and the first dissociation constant and C_d and K_d are the DOC normalized organic acid concentrations and constants given in Table I. The calculation proceeds as follows. From an initial pH and alkalinity, C_t and P_{CO_2} are calculated. [H] is determined by trial and error solution of eq 8, assuming either a closed system (C_t is constant) or a fixed P_{CO_2}. Figure 3a shows the results of this calculation for a constant C_t, and Figure 3b shows the results for a constant P_{CO_2}.

The calculations show that the pH values of low-alkalinity waters (<100 μequiv/L) are reduced below a pH of 5 for <4 mg of C/L DOC acid equivalent. This conclusion implies that slightly colored low-alkalinity waters can be acidified by organic acids. Higher alkalinity waters would be influenced by higher DOC concentrations (>7 mg of C/L), and "hard" waters (~2000 μequiv/L alkalinity) are not affected. The pH suppression is less sensitive to low DOC additions for a constant P_{CO_2} assumption as would be expected.

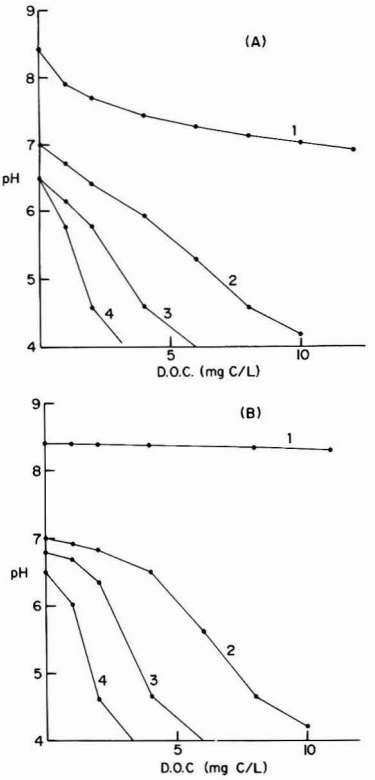


Figure 3. pH decreases as a function of added average ELS "organic acid" (Table I), expressed as DOC for an assumption of (a) constant carbonate concentration and (b) constant P_{CO_2}. Initial carbonato assumptions for which calculations are made are as follows: (1) pH 8.4, Alk = 2000 μequiv/L, C_t = 2020 μM, $P_{CO_2} = 10^{-3.3}$ atm; (2) pH 7, Alk = 200 μequiv/L; C_t = 244 μM, $P_{CO_2} = 10^{-2.9}$ atm; (3) pH 6.5, Alk = 100 μequiv/L, C_t = 170 μM, $P_{CO_2} = 10^{-2.6}$ atm; (4) pH 6.5, Alk = 50 μequiv/L, C_t = 85 μM, $P_{CO_2} = 10^{-3.0}$ atm.

Registry No. C, 7440-44-0.

Literature Cited

(1) Hemond, H. F. *Ecol. Monogr.* **1980**, *50*, 507–526.
(2) McKnight, D.; Thurman, E. M.; Wershaw, R. L. *Ecology* **1985**, *66*, 1339–1352.
(3) Ephraim, J.; Alegret, S.; Malthuthu, A.; Bicking, M.; Malcolm, R. L.; Marinsky, J. A. *Environ. Sci. Technol.* **1986**, *20*, 354–366.
(4) Krug, E. C.; Frink, C. R. *Science (Washington, D.C.)* **1983**, *221*, 520–525.
(5) Rosenqvist, I. Th. *Sci. Total Environ.* **1978**, *10*, 39–49.
(6) Cronan, C. S.; Aiken, G. R. *Geochim. Cosmochim. Acta* **1985**, *49*, 1697–1705.
(7) Eshleman, K. N.; Hemond, H. F. *Water Resour. Res.* **1985**, *21*, 1503–1510.
(8) Perdue, E. M.; Lytle, C. R. *Geochim. Cosmochim. Acta* **1984**, *48*, 1257–1263.
(9) Shuman, M. S.; Collins, B. J.; Fitzgerald, P. J.; Olson, D. L. In *Aquatic and Terrestrial Humic Materials*; Christman, R. F., Gjessing, E. T., Eds.; Ann Arbor Science: Ann Arbor, MI, 1983; pp 349–370.
(10) Tobler, H. J.; Engel, G. *N. S. Arch. Pharmacol.* **1983**, *322*, 183–192.
(11) Leuenberger, B.; Schindler, P. W. *Anal. Chem.* **1986**, *58*, 1471–1474.
(12) Linthurst, R. A.; Landers, D. H.; Eilers, J. M.; Brakke, D. F.; Overton, W. S.; Meier, E. P.; Crowe, R. E. *Characteristics*

of Lakes in the Eastern United States; EPA/600/4-86/007a; U.S. Environmental Protection Agency: Washington, DC, 1986; Vol. 1, 136 pp.
(13) Hillman, D. C.; Fountain, J.; Simon, S. J.; Kramer, J. R.; Meier, E. P. *Quality Assurance and Quality Control in the EPA National Surface Water Survey. Application of Chemical Equilibria to the Evaluation of pH, DIC, ANC and BNC Data*; LEMSCO Management Services: Las Vegas, NV, 1986; 41 pp.
(14) Malcolm, R. L. In *Humic Substances in Soil, Sediment and Water*; Aiken, G. R., McKnight, D. M., Wershaw, R. L., MacCarthy, P., Eds.; Wiley-Interscience: New York, 1986; pp 181–210.
(15) Perdue, E. M. In *Humic Substances in Soil, Sediment and Water*; Aiken, G. R., McKnight, D. M., Wershaw, R. L., MacCarthy, P., Eds.; Wiley-Interscience: New York, 1986; pp 493–526.
(16) Davis, J. C. *Statistics and Data Analysis in Geology*; Wiley: New York, 1973; pp 420ff.
(17) Dempsey, D. A.; O'Melia, C. R. In *Aquatic and Terrestrial Humic Materials*; Christman, R. F., Gjessing, E. T., Eds.; Ann Arbor Science: Ann Arbor, MI, 1983; pp 239–274.
(18) Oliver, B. G.; Thurman, E. M.; Malcolm, R. J. *Geochim. Cosmochim. Acta* **1983**, *47*, 2031–2035.

Received for review February 9, 1987. Accepted August 17, 1987.

Evaluation of the Role of Sea Salt Inputs in the Long-Term Acidification of Coastal New England Lakes†

Timothy J. Sullivan,*,‡ Charles T. Driscoll,§ Joseph M. Eilers,‡ and Dixon H. Landers∥

Northrop Services, Inc., 200 S.W. 35th Street, Corvallis, Oregon 97333, Department of Civil Engineering, Syracuse University, Syracuse, New York 13244, and U.S. EPA Environmental Research Laboratory, 200 S.W. 35th Street, Corvallis, Oregon 97333

■ Input of neutral salt (NaCl) from sea spray, followed by Na^+–H^+ exchange within the soil exchange complex, has been proposed as an important factor in surface water acidification of coastal areas. This hypothesis was tested on a regional basis by comparing the Na:Cl ratio of lake water with that of precipitation for the coastal lakes included in the U.S. Environmental Protection Agency Eastern Lake Survey-I in New England. The precipitation Na:Cl ratio closely approximated that of seawater at monitoring stations located within approximately 20 km of the coast. Few lakes in this coastal region exhibited a Na:Cl ratio less than that observed in precipitation. Those lakes that were acidic (ANC ≤ 0) showed no tendency toward a lowered Na:Cl ratio. Sodium contribution from, rather than retention by, watershed soils was suggested by the data from these lakes. Although episodic acidification of runoff due to NaCl deposition may occur, there is little support for the neutral salt effect being an important long-term acidifying process in Northeastern lakes.

Introduction

The neutral salt effect is a well-known soil phenomenon whereby the pH of an electrolytic solution is altered as it percolates through a soil column. The effect is due to ion exchange on soil surfaces and can lead to either a retention or a release of H^+ depending on soil pH, bonding energy of the salt cation or anion, and the salt content of both the soil and added electrolytic solution (*1*, *3*). This process is potentially relevant to surface water acidification, since a decrease in leachate pH may occur from very acidic soils. On neutral soils this effect is small due to increasing bonding energy of H^+, with subsequent reduction in ion exchange (*1*). Wiklander (*1*) suggested that several reactions are important in acidification of leachate:

$$R\text{–}H + Na^+ + Cl^- \rightleftharpoons R\text{–}Na + H^+ + Cl^- \quad (1)$$

$$R\text{–}Al(OH)_2 + Na^+ + Cl^- \rightleftharpoons R\text{–}Na + Al(OH)_2^+ + Cl^- \quad (2)$$

$$Al(OH)_2^+ + Cl^- + H_2O \rightleftharpoons Al(OH)_3 + H^+ + Cl^- \quad (3)$$

$$Al(OH)_2^+ + H^+ \rightleftharpoons Al(OH)^{2+} + H_2O \quad (4)$$

where R indicates a negatively charged functional group within the soil exchange complex. Inputs of neutral salt result in acidification of leachate draining acidic soils (eq 1 and 3), but base saturation and soil pH are increased. Equation 4, which consumes H^+, is more significant in circumneutral soils.

Several researchers have speculated that the neutral salt effect could be an important factor contributing to the acidification of surface waters in parts of Scandanavia and North America (*2*, *4*). Krug et al. (*4*) argued that many areas experiencing acidification are coastal and that electrolyte concentrations in precipitation are more important than acidity (pH) in the acidification of surface waters. Further interest in this phenomenon has been stimulated by recent results in Acadia National Park, Maine, where Kahl et al. (*5*) have presented evidence for NaCl acidification of stream water in a coastal catchment on an event basis.

Episodic acidification of stream water had previously been linked with NaCl inputs in the Breidvikdalen catchment of coastal western Norway (*6*). Particularly during sea salt enriched autumn rainstorms, water draining acidic soils within this catchment was acidified coincident with Na^+ retention. Soil retention of Na^+, however, was evidently a short-term phenomenon since there was close agreement between atmospheric input and drainage water output budgets of Na^+ on an annual basis. Seip (*7*) examined these studies and others in the Norwegian SNSF Project. He concluded that, on the basis of input/output budgets, correlations between Na^+ and Cl^- in runoff, and laboratory studies, Na^+ is readily transported through soil compared to Ca^{2+} and Mg^{2+}, and the acidification of drainage waters due to retention of Na^+ from sea salt should be small in most cases.

The relative importance of natural and anthropogenic causes of surface water acidification has been the focus of intense debate in recent years. A strong positive correlation has been established between precipitation chemistry and surface water chemistry in many areas, although it is difficult to prove a causal relationship (*7*). Contributions

†This research is a contribution from the National Surface Water Survey of the EPA Aquatic Effects Research Program.
‡Northrop Services, Inc.
§Syracuse University.
∥U.S. EPA Environmental Research Laboratory.

0013-936X/88/0922-0185$01.50/0 © 1988 American Chemical Society

to surface water acidification from natural sources, such as marine salt deposition, are therefore relevant. Issues of natural sources of acidification are particularly important in view of recent efforts throughout the northern hemisphere to curb emissions of acidifying sulfur compounds.

In order to evaluate the possible regional importance of watershed Na^+ retention leading to H^+ enrichment, it is first necessary to obtain an index of Na^+ input. The Na:Cl ratio of precipitation provides such an index for coastal areas, where Na:Cl in precipitation very closely approximates that of seawater (0.86) (*6*, *8*, *9*). Variability in this relationship increases further inland. The predominant source of Cl^- in coastal precipitation is sea spray. A small amount may originate from anthropogenic emissions, but this quantity is apparently negligible compared to background coastal levels (*10*, *11*). Watershed sources of Cl^- are also generally negligible (*12*). Thus, because the input ratios are reasonably well established, the Na:Cl ratio of surface waters provides a means to evaluate NaCl-induced acidification of coastal sites.

An extensive data base has recently been developed by the U.S. Environmental Protection Agency in those regions of the eastern U.S. which are expected to contain significant numbers of lakes with low acid-neutralizing capacity (ANC) (*13*). Phase I of the Eastern Lake Survey (ELS-I), conducted in autumn 1984, employed a statistical (probability) sampling design such that regional extrapolations with known uncertainty could be performed to estimate the number of acidic and low ANC lakes. The statistical sampling design and large data base provide a unique opportunity to evaluate the regional influence of NaCl on lake acidification, as well as other related issues. The survey determined that there were a number of acidic lakes (ANC $\leq$ 0 μequiv L^{-1}) in coastal areas and that concentrations of sodium and chloride decreased rapidly with distance from the coast (*14*). These observations suggest the potential for the acidification of low-alkalinity lakes in coastal areas. The purpose of this paper is to estimate, with ELS-I data, the number of coastal lakes in the northeastern U.S. that have become acidic because of Na^+ retention and to evaluate the role of NaCl in lake acidification processes. We examined NaCl acidification in the context of chronic effects on water chemistry using data from the autumn index sample. These data are not, however, suitable for investigating potential episodic effects of NaCl deposition from sea spray.

Methods

Scope. Coastal precipitation chemistry data were made available through existing precipitation monitoring networks, NADP/NTN and MAP3S (*15*, *16*). Data were used from 21 monitoring stations located within 100 km of the east coast in order to establish Na:Cl wet input ratios as a function of distance from coast.

Phase I of the Eastern Lake Survey (ELS-I) provided the lake chemistry data used in this study (*13*). In ELS-I, three regions were sampled which had been identified as having significant numbers of low ANC lakes by use of the map developed by Omernik and Powers: the Northeast (1), Upper Midwest (2), and Southeast (3) (*17*). Each region was further subdivided into two or more subregions on the basis of geographic homogeneity and physiography.

Evaluation of potential sea salt acidification was necessarily restricted to coastal lakes where (1) NaCl deposition is significant and (2) the Na:Cl ratio in precipitation is reasonably constant (*6*, *8*, *9*). On the basis of our examination of coastal precipitation chemistry data (see, e.g., Figure 2), the pattern of concentrations of Na^+ and Cl^- in

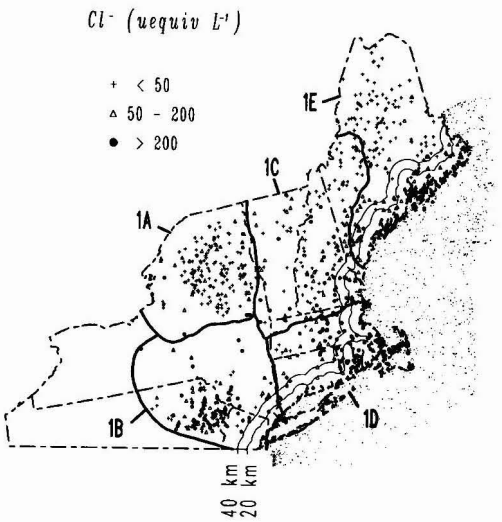


Figure 1. Map of ELS-I region 1 showing locations of the 144 lakes included in the analysis of potential neutral salt acidification of lake water.

lakes (*14*), and these earlier studies, we limited this investigation to lakes within 20 km of the coast. In this coastal strip, Na:Cl precipitation ratios should approximate that of seawater ($\pm$ analytical error) and watersheds experience the highest loading of sea salt. If evidence of surface water acidification by Na^+ retention cannot be demonstrated for acid-sensitive coastal lakes, it is unlikely to be meaningful further inland as a regional phenomenon.

Portions of two ELS-I regions coincided with the 20-km zone selected for investigation: coastal New England (in region 1) and Florida/southeast Georgia (in region 3). The Florida subregion (3B) contained the largest number of acidic lakes of any subregion. Lakes in this subregion, however, were generally farther from the coast; only 21 of the 150 lakes sampled were located within 20 km of the coast. Furthermore, lakes in subregion 3B exhibited a positive relationship between $[Na^+]$ and distance to seawater (*13*, *18*). This suggests a substantial Na^+ contribution from the watersheds, more specifically from shallow groundwater sources (*18*). Therefore, subregion 3B was excluded from our investigation, and further analyses were limited to coastal areas of region 1 (the Northeast) of the Eastern Lake Survey.

Lake Selection. Subregions were stratified by alkalinity map classes according to a preliminary version of the regional surface water alkalinity map prepared by Omernik and Kinney (*19*). The designated alkalinity strata were <100 μequiv L^{-1}, 100–200 μequiv L^{-1}, and >200 μequiv L^{-1}. Approximately 50 lakes were randomly selected from each of the three map classes in each subregion and assigned a weighting factor on the basis of the frame population of each map class (universe of lakes considered for study in ELS-I, essentially including all lakes $\geq$4 ha, with specific conductance $\leq$1500 μS cm^{-1}, and not locally influenced by intense anthropogenic activities). A total of 768 lakes were sampled in the Northeast, of which 144 were within 20 km of the coast (Figure 1).

Sampling. Northeastern lakes were sampled by helicopter between 10 October and 18 November 1984 at a depth of 1.5 m in the deepest part of the lake. In most cases, sampling coincided with the period of complete mixing following fall turnover. Preliminary processing of

samples for water chemistry, including pH, was accomplished at a nearby mobile field laboratory. Subsequent analyses at an analytical laboratory included ANC (acidimetric titration with modified Gran analysis), Cl^- (ion chromatography), and Na^+ (flame atomic adsorption spectroscopy). Details on sampling, analytical methodologies, statistical design, and QA/QC protocols were provided by Linthurst et al. (*13*), Best et al. (*20*), and Hillman et al. (*21*) and summarized in Landers et al. (*22*).

Data Treatment. Precipitation chemistry data from NADP/NTN and MAP3S networks were analyzed by analysis of variance and linear regression of the Na:Cl ratio in precipitation as a function of distance from coast. Results of these analyses were used in delineating the coastal zone in which Na:Cl input ratios could be characterized and evaluating wet input ratios relative to lake ratios in the selected coastal zone.

The lake water Na:Cl ratio was determined for all lakes in region 1 within 20 km of the coast. The relationship between potential Na^+ retention and lake acidity was evaluated by linear regression of both ANC and pH as a function of the ratio of Na^+ to Cl^- in lake water. Analyses were performed for the following subgroups of ELS-I lakes in region 1: 0–5, 0–10, 6–10, and 11–20 km from the coast. A key assumption in this analysis was that chloride is conservative in the coastal watersheds under investigation. The assumption of conservative Cl^- behavior has been shown to be valid on the basis of soil column studies (*23*), sediment microcosm studies (*24*), and ion budgets (*25–27*). Bayley et al. (*28*) recently concluded that Cl^- retention is significant in some soils and wetlands in the Experimental Lakes Area (ELA) in Ontario. However, Cl^- deposition is very low at ELA, yielding typical lake Cl^- concentrations $\sim$ 15 μequiv L^{-1}, more than an order of magnitude less than that of the typical lakes included in this study. Retention of a small amount of Cl^- or minor analytical error would thus greatly influence ELA budget calculations. Implicit in this analysis were the additional assumptions that (1) the precipitation input Na:Cl ratio could be well established for coastal Northeast lakes and (2) Na^+ retention in watershed soils (leading to H^+ release and consequent leachate acidification) would be reflected in a decreased Na:Cl ratio of coastal lake water as compared to established precipitation input ratios.

Road salt is a potential complicating factor in the interpretation of the sea salt effect, because lakes with high sodium and chloride were found at considerable distance inland from the coast (*13*). A subset of coastal lakes was therefore selected which were determined to be without paved roads in their watersheds on the basis of examination of U.S.G.S. topographic maps (1:250 000). Analyses were repeated for this subset of lakes.

We used the following relationship to quantify the extent of acidification by retention of Na^+ from sea salt inputs:

$$\text{sea salt acidification} = [Cl^-](0.86) - [Na^+] \quad (5)$$

This expression compares the theoretical Na^+ concentration calculated from measured Cl^- (assuming conservative behavior and the Na:Cl of seawater [0.86]) with measured Na^+ values. The difference between theoretical Na^+ (on the basis of measured Cl^-) and measured Na^+ is an estimate of drainage water acidification due to Na^+ retention, if the input ratio equals that of sea water. We compared sea salt acidification to ANC by linear regression analysis.

Results and Discussion

Data from coastal precipitation stations indicated that the ionic composition of coastal precipitation closely approximated that of seawater. Weighted annual means of the Na:Cl ratio of precipitation for all NADP/NTN and MAP3S monitoring stations within 100 km of the east coast are presented in Figure 2 for the period 1979–1984. The Na:Cl ratio of precipitation closely approximated that of seawater only for stations in close proximity to the coast. Further inland, the Na:Cl ratio in precipitation becomes more uncertain due to contributions of excess Na^+ from the soil (*29*), enhanced inland transport of Cl^- relative to Na^+ [possibly due to loss of Cl^- from NaCl particles by volatilization (*30*)], and local anthropogenic sources of Cl^- (e.g., combustion of leaded gasoline). These factors become significant only as coastal NaCl loads diminish (*31*, *11*). Salt deposition as a function of coastal proximity is confounded by road salt in New England, but the minimum Na^+ concentration in ELS-I lakes declined abruptly between 20 and 40 km from the coast, approaching a background concentration of 30 μequiv L^{-1} (Figure 3; *13*). This trend agrees with the observations of Ogden (*8*) that 80% of the marine aerosol in Nova Scotia was deposited within 20 km of the coast. Chloride patterns tend to be similar to those for Na^+ (*13*), although background concentrations are not reached until 75–100 km inland (*32*). The data in Figure 2 include 8 precipitation monitoring stations located within 20 km of the coast with a total of 28 annual mean measurements during 1979–1984. Mean and standard deviation for this subset were 0.83 and 0.04, respectively. Analysis of variance for this subset revealed a significant ($P < 0.05$) trend of decreasing Na:Cl with coastal distance (slope = –0.003, intercept = 0.85, $R^2 = 0.20$). However, the slope of this relationship is relatively small, yielding minor variations in estimates for precipitation Na:Cl based on distance from the coast for stations within the 20-km coastal zone (95% CI = 0.75–0.86).

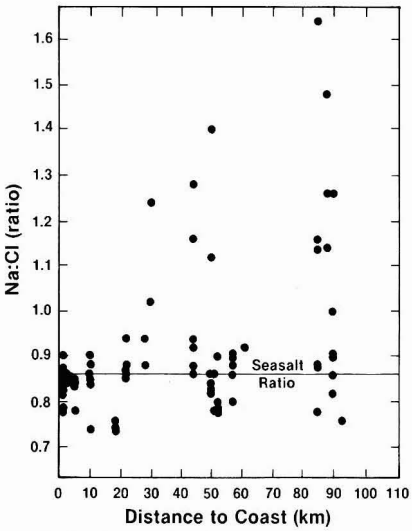


Figure 2. Na:Cl ratio in precipitation as a function of distance to the seacoast. Data are from the 21 NADP/NTN and MAP3S precipitation monitoring stations for the period 1979–1984. The seawater ratio Na:Cl = 0.86 is provided as a reference.

Few lakes in coastal New England had Na:Cl ratios less than those measured by coastal precipitation monitoring stations (12% had Na:Cl < 0.86, Figures 4 and 5). Rather, most lakes contained proportionately higher sodium concentrations than were observed in precipitation, due to weathering reactions in the watersheds. For those lakes that did exhibit low Na:Cl ratios (although still within the

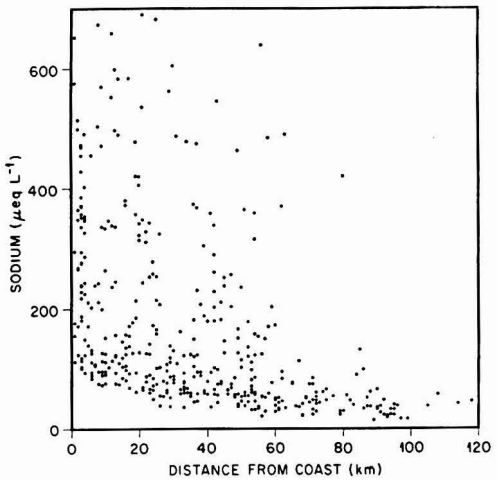


Figure 3. Lake water sodium concentration (μequiv L^{-1}) versus lake distance (km) from coast for region 1, Eastern Lake Survey-Phase I [from Linthurst et al. (*13*)].

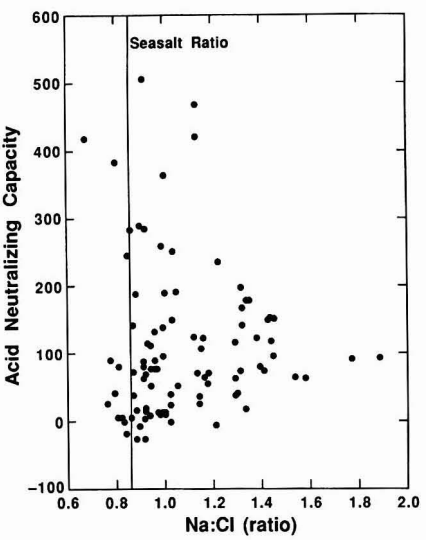


Figure 4. Acid neutralizing capacity (ANC) (μequiv L^{-1}) as a function of the Na:Cl molar ratio in ELS-I region 1 lakes 0–10 km from the seacoast. One outlier was deleted at Na:Cl = 7. Five lakes with ANC > 600 μequiv L^{-1} are not depicted.

range expected on the basis of wet input), there was no clear pattern of concomitant low ANC or pH (Figures 4, 5).

Results of regression analyses are presented in Table I. ANC and pH as a function of the Na:Cl ratio for lakes ≤10 km from the coast are graphically depicted in Figures 4 and 5, respectively. Only one regression was significant at $p < 0.05$, that of pH = $a + b$(Na:Cl) for lakes within 10 km (Table I, Figure 5). Examination of Figure 5, however, reveals that the significance is derived from the right side of the graph (Na:Cl > 1.1), suggesting excess Na^+ inputs in many lakes with pH over 6.0. In the event of neutral salt acidification, we would observe a decreased Na:Cl (below the input ratio) for low-pH lakes. Such a relationship is not evident in Figure 5. Also, the pH as a

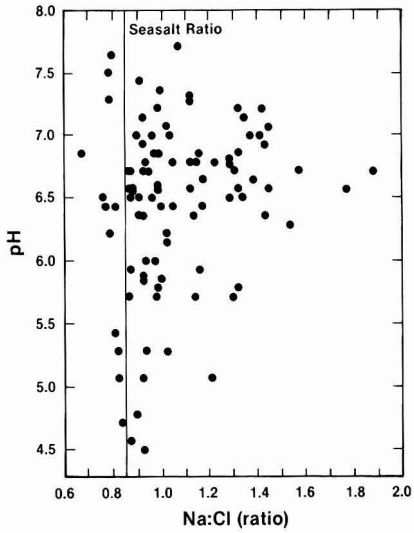


Figure 5. pH as a function of the Na:Cl molar ratio in ELS-I region 1 lakes 0–10 km from the seacoast. One outlier was deleted at Na:Cl = 7.

Table I. Results of Regression Analyses for Acidity as a Function of the Molar Na:Cl Ratio for Coastal New England Lakes

model	coastal distance, km	d.f.	F	$P > F$
ANC = $a + b$ (Na:Cl)	0–5	60	0.159	0.6917
	6–10	33	2.151	0.1523
	0–10	94	1.284	0.2600
	11–20	51	3.052	0.0868
pH = $a + b$ (Na:Cl)	0–5	60	1.453	0.2329
	6–10	33	0.939	0.3399
	0–10	94	4.338	0.0400[a]
	11–20	51	0.252	0.6181

[a] Significant at $P \leq 0.05$.

function of Na:Cl ratio was not significant for lakes in closer proximity to the coast (≤5 km), further suggesting watershed sources of Na^+ due to weathering rather than retention. Results similar to those presented in Table I were obtained when analyses were restricted to drainage lakes only or to lakes without paved roads in their watersheds (presumably no road salt). Similar results were also obtained when analyses were performed within individual alkalinity map strata. Those relationships that were significant derived their significance from high pH/ANC waters with Na:Cl > 1.1.

The lack of a significant relationship between ANC and Na:Cl ratio does not by itself, however, demonstrate that Na^+ retention has not occurred in the drainages of some lakes. Because lakes vary in their acid/base characteristics, a decrease in ANC due to Na^+ retention would be independent of initial lake water ANC. But if Na^+ retention was a significant regional process, causing lakes to become acidic (ANC ≤ 0 μequiv L^{-1}), we should find a cluster of acidic lakes with Na:Cl ratios less than the observed input ratio. None of the acidic lakes in coastal New England showed an Na:Cl ratio less than the observed ratio in precipitation ± one standard deviation (0.83 ± 0.04) (Figures 4 and 5). An analagous situation exists between SO_4^{2-} and ANC. Although lake SO_4^{2-} concentration was not found to be negatively correlated with ANC for the

full data set of Northeastern lakes, almost all low ANC lakes in the Northeast had SO_4^{2-} as the major anion (*13*, *14*). This is taken as strong circumstantial evidence for SO_4^{2-}-induced acidification.

For the 18 lakes within 20 km of the coast that exhibited Na:Cl less than 0.86, the magnitude of sea salt acidification (eq 5) showed a mean ± standard deviation of 28 ± 34 μequiv L^{-1}. Of these lakes potentially acidified by sea salt influence, the mean ANC was 240 ± 246 μequiv L^{-1}. Half of these lakes had ANC values greater than 150 μequiv L^{-1} and therefore only nine of the low Na:Cl lakes could be significantly acidified by sea salt contribution. Linear regression analysis of the low Na:Cl lakes demonstrated a weak positive correlation between ANC and sea salt acidification [ANC = 131 μequiv L^{-1} + 2.8(sea salt acidification); n = 18; R^2 = 0.15], indicating that the extent of acidification by Na^+ retention was generally greatest in high ANC lakes. In the low ANC lakes (≤50 μequiv L^{-1}), the potential effect was small in magnitude, but of some significance, showing a mean potential sea salt acidification of 25 μequiv L^{-1}. These calculations should be viewed as approximations because small errors in the analytical determination of Na^+ or Cl^- result in large uncertainty in estimating possible sea salt acidification. Furthermore, the mean observed Na:Cl ratio of coastal precipitation (0.83) was somewhat less than the marine ratio of 0.86 (Figure 2).

Sodium ions are, in general, weakly bound in soils (*33*, *1*) and have been reported to move readily through coastal catchments (*25*). It seems reasonable to assume that soils in coastal watersheds of the Northeast would be approximately at steady state with respect to long-term patterns of NaCl deposition. Long-term acidification due to cation exchange involving marine sources of Na^+ therefore seems unlikely in the absence of major climatic changes affecting NaCl deposition. Similar conclusions were reached by Overrein et al. (*25*) in Norway. Seip (*34*) also emphasized that long-term accumulation of sodium will not occur in a stable terrestrial system.

Mg:Cl ratios were also evaluated because Mg^{2+} may have a higher retention on acidic soils than does Na^+ (*33*), although the Mg^{2+} concentration in seawater is only 23% of the Na^+ concentration on an equivalent basis. We did not find evidence of Mg^{2+} retention in watershed soils of drainage lakes. Three lakes within 20 km of the coast had a Mg^{2+} deficit > 100 μequiv L^{-1}, calculated as

$$Mg^{2+} \text{ deficit} = [Cl^-](0.196) - [Mg^{2+}] \qquad (6)$$

where concentrations are in μequiv L^{-1}. All three of these lakes were of the seepage (no outlet, no inlet) or spring (outlet, no inlet) type. Six coastal lakes had a Mg:Cl equivalent ratio less than that of seawater (0.196) and ANC ≤ 50 μequiv L^{-1}. Only three of these were drainage lakes, and they all had a Mg^{2+} deficit less than 24 μequiv L^{-1}. Thus, we find no evidence supporting chronic Mg^{2+} retention in Northeastern coastal drainage systems.

We emphasize that samples were collected for this study during fall mixing and should be interpreted as an index of water chemistry on an annual basis only. These results, therefore, only apply for long-term evaluation of water chemistry. Episodic pH depressions caused by high inputs of sea salts can be a significant short-term acidifying phenomenon, as suggested by the research of Skartveit (*6*) and Kahl et al. (*5*) on stream systems. Sutcliffe et al. (*35*) demonstrated that sea salt deposition may show marked seasonal trends, and Skartveit (*6*) showed that as much as 30% of the annual wet Cl^- deposition can occur on just five to six episode days. Repeated neutral salt episodes would not, however, lead to long-term acidification. Once a coastal terrestrial system has reached steady state with respect to long-term Na^+ deposition, leachate would actually be less acidic than in an otherwise similar noncoastal site because the soil has become less acidic in response to higher Na^+ saturation. Further research is needed to evaluate the potential effects of episodic sea salt inputs on low-alkalinity coastal surface waters. There is no evidence to suggest, however, that the group of low-alkalinity, low-pH lakes identified in coastal areas of region 1 by the ELS-I fall survey (*13*) have become acidic as a result of the neutral salt phenomenon. Na^+ deposition declines sharply inland of 20 km, as do lake water concentrations of Na^+ and Cl^- (*13*, *14*). Therefore, there is little support for the neutral salt effect having caused a significant increase in the number of acidic Northeastern lakes.

Acknowledgments

We gratefully acknowledge the assistance of M. T. Dana and J. Gibson in providing precipitation chemistry data. Valuable criticisms were received from D. F. Brakke, M. R. Church, E. Krug, R. A. Linthurst, S. Norton, and H. M. Seip.

Registry No. NaCl, 7647-14-5; Na, 7440-23-5.

Literature Cited

(1) Wiklander, L. *Geoderma* **1975**, *14*, 93.
(2) Rosenqvist, I. Th. *Sci. Total Environ.* **1978**, *10*, 271.
(3) Seip, H. M.; Tollan, A. *Sci. Total Environ.* **1978**, *10*, 253.
(4) Krug, E. C.; Isaacson, P. J.; Frink, C. R. *J. Air Pollut. Control Assoc.* **1985**, *35*, 109.
(5) Kahl, J. S.; Anderson, J. L.; Norton, S. A. "Water Resource Baseline Data and Assessment of Impacts from Acidic Precipitation". Acadia National Park, Maine; Technical Report 16; National Park Service, North Atlantic Region: Boston, MA, 1985; 123 pp.
(6) Skartveit, A. *Nord. Hydrol.* **1981**, *12*, 65.
(7) Seip, H. M. In *Ecological Impact of Acid Precipitation*; Drablos, D., A. Tollan, Eds.; SNSF Project; SNSF: Oslo, Norway, 1980.
(8) Ogden, J. G. *Water, Air, Soil Pollut.* **1982**, *17*, 119.
(9) Lebowitz, L. G.; de Pena, R. G. *J. Geophys. Res., D: Atmos.* **1985**, *90*, 8149.
(10) Granat, L. *Tellus* **1972**, *24*, 550.
(11) Kennedy, V. C.; Zellweger, G.; Avanzino, R. *Water Resour. Res.* **1979**, *15*, 687.
(12) Gorham, E. *Philos. Trans. R. Soc. London, B* **1958**, *241*, 147.
(13) Linthurst, R. A.; Landers, D. H.; Eilers, J. M.; Brakke, D. F.; Overton, W. S.; Meier, E. P.; Crowe, R. E. *Characteristics of Lakes in the Eastern United States*; Population Descriptions and Physico-Chemical Relationships. U.S. Environmental Protection Agency: Washington, DC, 1986; EPA-600/4-86-007A; Vol. 1.
(14) Brakke, D. F.; Landers, D. H.; Eilers, J. M. *Environ. Sci. Technol.* **1988**, *22*, 155–163.
(15) MAP3S *Atmos. Environ.* **1982**, *16*, 1603.
(16) Watson, C. R.; Olsen, A. R. *Acid Deposition System (ADS) for Statistical Reporting: System Design and User's Code Manual*; U.S. Environmental Protection Agency: Washington, DC, 1974; EPA-600/8-84-023.
(17) Omernik, J. M.; Powers, C. F. *Ann. Assoc. Am. Geogr.* **1983**, *73*, 133.
(18) Eilers, J. M.; Landers, D. H.; Brakke, D. F. *Environ. Sci. Technol.* **1988**, *22*, 172–177.
(19) Omernik, J. M.; Kinney, A. J. *Total Alkalinity of Surface Waters: A Map of the New England and New York Region*; U.S. Environmental Protection Agency: Corvallis, OR, 1985; EPA-600/D-84-216.
(20) Best, M. D.; Drouse, S. K.; Creelman, L. W.; Chaloud, D. J. *National Surface Water Survey, Eastern Lake Survey—Phase I, Quality Assurance Report*; U.S. Environmental Protection Agency: Las Vegas, NV, 1986; EPA-600/4-86/011.

(21) Hillman, D. C. J.; Potter, J. F.; Simon, S. J. *National Surface Water Survey, Eastern Lake Survey—Phase I, Analytical Methods Manual*; U.S. Environmental Protection Agency: Las Vegas, NV, 1986; EPA-600/4-86/009.
(22) Landers, D. H.; Overton, W. S.; Brakke, D. F.; Linthurst, R. A.; Eilers, J. M. *Environ. Sci. Technol.* **1988**, *22*, 128–135.
(23) Mansell, R. S.; Elseftawy, A.; Hunt, P. G. *Soil Sci.* **1972**, *15*, 113.
(24) Baker, L. A.; Brezonik, P. L.; Edgerton, E. S.; Ogburn, R. W., III *Water, Air, Soil Pollut.* **1985**, *25*, 215.
(25) Overrein, L. N.; Seip, H. M.; Tollan, A. "Acid Precipitation—Effects on Forests and Fish"; final report; SNSF Project; SNSF: Oslo, Norway, 1980.
(26) Christophersen, N.; Seip, H. M.; Wright, R. F. *Water Resour. Res.* **1982**, *18*, 977.
(27) Baker, L. A.; Pollman, C. D.; Brezonik, P. L. "Development of Interpretive Models for Lake Acidification in Florida"; Florida Acid Deposition Study, Phase IV; Environmental Engineering and Sciences, Inc.: Gainsville, FL, 1985; ESE 83-152-0602-0120.
(28) Bayley, S. E.; Schindler, D. W.; Turner, M. A. Presented at the American Society of Limnology and Oceanography Annual Meeting, Madison, WI, June 1987.
(29) Junge, C. E.; Werby, R. T. *J. Meterol.* **1958**, *15*, 417.
(30) Erickson, E. *Tellus* **1960**, *12*, 63.
(31) Delmas, R.; Servant, J. *J. Rech. Atmos.* **1974**, *8*, 861.
(32) Mairs, D. F. *Water Resour. Res.* **1967**, *3*, 1090.
(33) Lag, J. *Acta Agric. Scand.* **1968**, *18*, 148.
(34) Seip, H. M. *Nature (London)* **1986**, *322*, 118.
(35) Sutcliffe, D. W.; Carrick, T. R.; Heron, J.; Rigg, E.; Talling, J. F.; Woof, C.; Lund, J. W. G. *Freshwater Biol.* **1982**, *12*, 451.

Received for review February 9, 1987. Accepted September 14, 1987. The research described in this article has been funded as part of the National Acid Precipitation Assessment Program by the U.S. Environmental Protection Agency (EPA). It has been subjected to the Agency's peer and administrative review, and it has been approved for publication.

Reactions That Modify Chemistry in Lakes of the National Surface Water Survey

Sijin Lee and Jerald L. Schnoor*

Department of Civil and Environmental Engineering, University of Iowa, Iowa City, Iowa 52242

■ A simple mass balance equation was used to determine the important reactions that occur in selected lake watersheds of the Adirondack Park, the Southern Blue Ridge Province of the Appalachian Mountains, and a portion of northern Florida. The mass balance requires only three input parameters: precipitation ion concentration, lake ion concentration, and an evapoconcentration factor appliable to the watershed. It was determined that the most important alkalizing reaction in all three study areas was the production of base cations (Ca^{2+}, Mg^{2+}, and Na^{+}) by ion exchange and chemical weathering, followed by sulfate adsorption in the Southern Blue Ridge watersheds and nitrate assimilation/reduction in the Adirondack Park. Dry deposition of sulfate was important to the sulfate balance in the Adirondack watersheds and was of the same order of magnitude as wet precipitation inputs. Chloride ion could not be used to provide an independent check on the mass balance methodology because unmeasured sources such as dry deposition and mineral dissolution appeared to be significant, especially in the Southern Blue Ridge Province and Florida watersheds.

Introduction

The chemistry of lake water in dilute or headwater ecosystems is an admixture of precipitation solutes, dry deposition, and biogeochemical reaction products of the land and water (*1*). Precipitation water is modified as it passes through the canopy by leaching of vegetation and dissolution of dry deposited materials (*2*). Throughfall water is further affected by decomposition and mineralization products of leaf litter and organic soil (*3*). In the upper soil horizons, ion-exchange reactions, ammonia assimilation by vegetation, and microbially mediated nitrification reactions are likely to occur (*4*). As the water percolates into the lower soil horizons, it becomes progressively more neutralized (less acidic) by sulfate exchange reactions and chemical weathering (dissolution) of minerals in the glacial till and bedrock (*5–7*). Lake chemistry represents a mixture of precipitation, runoff water, interflow, and groundwater chemistry. Within the lake, further reactions modify the chemistry, including nitrate and ammonium assimilation by plants and reactions at the sediment–water interface (e.g., cation exchange and sulfate reduction; ref 8–10).

Lakes that have been acidified by acid deposition are those lacking carbonate minerals and characterized by sensitive hydrological settings (*1*). Schnoor and Stumm (*1*) presented various reactions that modify the H^+ balance in waters. Table I shows the stoichiometry of some of these processes. The overall change in alkalinity (or acid neutralizing capacity, ANC) of a lake can be calculated from the stoichiometry of the weathering reactions, ion exchange, redox reactions, and biological production and respiration. In some instances, acidic deposition may be sufficient to disturb an existing H^+ balance and cause the acidification of a lake. A quantitative example is provided by the hydrogen ion budget in the Hubbard Brook Ecosystem by Driscoll and Likens (*11*).

The purpose of this study was to assess (on a large-scale regional basis) which reactions are most important in controlling the acid–base chemistry of lakes, on the basis of a mass balance approach for major ions. There are two data sets that were used for the study. In 1984, the Eastern Lakes Survey of the National Surface Water Survey (NSWS) was begun by the U.S. EPA (*12*, *13*) in order to assess the present acidity status of surface waters and to establish a base line for temporal variability associated with these surface waters. The second data base, of the Acid Deposition System (ADS) for Statistical Reporting, is a collection of precipitation chemistry data to monitor atmospheric deposition trends in the U.S. (*14*). The ADS data base was used to determine the chemistry of wet deposition to lakes of the NSWS in the eastern U.S. Lake chemistry was determined from the NSWS in order to estimate the net reaction or change of major cation and anion concentrations (Ca^{2+}, Mg^{2+}, K^+, Na^+, NH_4^+, NO_3^-, Cl^-, SO_4^{2-}). A simple mass balance equation was then used to calculate the magnitude of important processes that

 0013-936X/88/0922-0190$01.50/0 © 1988 American Chemical Society

Table I. Typical Processes Which Modify the Alkalinity Balance in Surface Waters

	changes in alkalinity, equiv/mol reacted
typical weathering reactions	
calcite: $CaCO_3(s) + H^+ \leftrightarrow Ca^{2+} HCO_3^-$	+2
anorthite: $CaAl_2Si_2O_8(s) + 2H^+ + H_2O \leftrightarrow Ca^{2+} + Al_2Si_2O_5(OH)_4(s)$	+2
potassium feldspar: $KAlSi_3O_8(s) + H^+ + 4^1/_2H_2O \leftrightarrow K^+ + 2H_4SiO_4 + {}^1/_2Al_2Si_2O_5(OH)_4(s)$	+1
olivine: $MgFeSiO_4(s) + 4H^+ \leftrightarrow Mg^{2+} + Fe^{2+} + H_4SiO_4$	+4
albite: $2NaAlSi_3O_8(s) + 2H^+ + 9H_2O \leftrightarrow 2\,Na^+ + 4H_4SiO_4 + Al_2Si_2O_5(OH)_4(s)$	+2
ion exchange/sorption	
sulfate sorption: $2ROH + SO_4^{2-} \leftrightarrow R_2SO_4 + 2OH^-$	+2
Na exchange: $NaR + H^+ \leftrightarrow HR + Na^+$	+1
Ca exchange: $CaR_2 + 2H^+ \leftrightarrow 2HR + Ca^{2+}$	+2
redox processes (microbial mediation)	
nitrification: $NH_4^+ + 2O_2 \leftrightarrow NO_3^- + H_2O + 2H^+$	−2
denitrification: $5CH_2O + 4NO_3^- + 4H^+ \leftrightarrow 5CO_2 + 2N_2 + 7H_2O$	+1
SO_4^{2-} reduction: $SO_4^{2-} + 2CH_2O + 2H^+ \leftrightarrow 2CO_2 + H_2S + H_2O$	+2
ammonia assimilation: $NH_4^+ + 4CO_2 + HCO_3^- + H_2O$ (sun) $\rightarrow C_5H_7NO_2 + 5O_2$	−1
nitrate assimilation: $NO_3^- + 5CO_2 + 4H_2O$ (sun) $\rightarrow C_5H_7NO_2 + 7O_2 + OH^-$	+1

modify chemistry for each lake, and these are summarized on a regional basis.

National Surface Water Survey (NSWS)

The National Surface Water Survey was begun in the fall of 1984 with the Eastern Lakes Survey (phase I). Fall was chosen because thermal stratification is small at that time and chemical variations between the surface water and bottom water of a lake are reduced. Water chemistry variables in the survey included acidity, acid neutralizing capacity (ANC), extractable aluminm, total aluminum, dissolved ammonium, dissolved inorganic carbon, dissolved organic carbon, dissolved calcium, dissolved chloride, true color, total dissolved fluoride, dissolved iron, dissolved magnesium, dissolved manganese, dissolved nitrate, pH, total phosphorus, dissolved potassium, secchi disk transparency, dissolved silica, dissolved sodium, dissolved sulfate, specific conductance, and turbidity. A description of the analytical techniques and procedures is provided by the U.S. Environmental Protection Agency (*12*, *13*). Quality assurance and quality control procedures on sampling and analytical techniques were quite rigorous (*12*, *13*).

Selection of the final target population of lakes for inclusion within the Eastern Lake Survey—Phase I was a stepwise process. First, a population of lakes represented on 1:250 000 U.S. Geological Survey (USGS) maps was identified. USGS maps of this scale generally include only those lakes greater than approximately 4 ha (hectares) in area. Therefore, lakes smaller than 4 ha were not included in the survey. Some lakes were subsequently identified as "nonlakes", such as wetlands or flowing water, and were eliminated from consideration.

The remaining lakes defined the preliminary target population for the Eastern Lake Survey—Phase I. These lakes were identified within subregions. Subregions were delineated on the basis of similarities in surrounding physical geography, land-use characteristics, and available water quality information. The initial target population of lakes was further reduced to a final target population after ELS—Phase I field work began. An effort was made to eliminate lakes that were obviously impacted by anthropogenic factors (agriculture, urban development, sewage treatment discharges, or mine tailings) and those that had appeared on maps but which were found to be no longer in existence. Also eliminated from sampling were inaccessible lakes: lakes on which it was impossible to land a helicopter, lakes to which access permission was denied, or lakes which were found to be frozen.

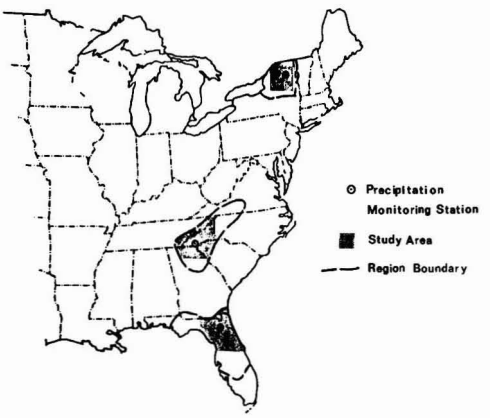


Figure 1. Location of study area.

The sampling protocol was designed to sample only lakes greater than 1.5-m depth which were mixed during fall turnover. However, a few shallow lakes (less than 1.5 m in depth) were sampled if a sample free of sediment could be obtained. Likewise, thermally stratified lakes were sampled and identified if turnover had not yet occurred. A few lakes were dropped with specific conductance values greater than 1500 μS/cm.

Methodology

Study Area Selection. As shown in Figure 1, three study areas were selected from the NSWS subregions: the Adirondack Park of New York, the southern Blue Ridge Province, and the northern portion of Florida and extreme southern Georgia. The Adirondack Park of New York includes some lakes which have been affected by acidic deposition (*15*, *16*), and the Southern Blue Ridge Province has soils which are reported to adsorb/exchange sulfate and thereby to neutralize acid deposition (*18*). The third study area in contrast is Florida with a distinct marine influence and proximity. These areas were selected because they are quite different geologically and hydrologically and have decreasing acid deposition from north to south.

All NSWS lakes were selected which were within a 100-mile radius from a National Atmospheric Deposition Program (NADP) monitoring station. It was assumed that precipitation chemistry was roughly similar within each area (Adirondack Park, Southern Blue Ridge) or within

Table II. Mean Concentrations of Major Ions and Their Standard Deviations for Lakes in Each Study Area

study area	major ions, μequiv/L							
	Ca^{2+}	Mg^{2+}	K^+	Na^+	NH_4^+	SO_4^{2-}	NO_3^-	Cl^-
Adirondack Park (n = 147)	195 ± 194	67 ± 70	8.8 ± 6.3	62 ± 97	2.1 ± 1.9	119 ± 26	2.3 ± 3.7	44 ± 122
Southern Blue Ridge (n = 73)	133 ± 236	60 ± 47	28 ± 20	127 ± 322	3.2 ± 4.2	53 ± 123	6.9 ± 19	86 ± 326
Florida (n = 61)	576 ± 803	403 ± 630	91 ± 143	494 ± 1790	4.8 ± 13	342 ± 558	4.8 ± 9.1	623 ± 2190

a 100-mile radius (Florida). This assumption restricts the area and number of lakes selected in each subregion. Since there is only one precipitation monitoring station (Huntington, NY) in the Adirondack Park, it was assumed that all of the lakes (located between 43°07′40″ N < latitude < 44°50′00″ N and 73°22′30″ W < longitude < 75°15′30″ W) receive a uniform precipitation chemistry. It is known that the actual chemistry and pH of precipitation follows a gradient from southwest or northeast through the Adirondacks, but the NADP precipitation monitoring station is near the center of the area and was taken to be an acceptable average. (The volume-weighted pH of precipitation at the NADP station in Huntington, NY, is 4.43, while that in the southwest is pH ~4.2 and in the northeast pH ~4.5.) The number of lakes selected in the Adirondack Park was 147. In the case of the Southern Blue Ridge Province, there were two available precipitation monitoring stations. Seventy-three lakes were selected in the Southern Blue Ridge (73 out of 112 in the NSWS data set) which were between 34°10′00″ N < latitude < 37°10′00″ N and 82°30′00″ W < longitude < 85°30′00″ W. This area includes northeastern Georgia, western North Carolina, northwestern South Carolina, and eastern Tennessee. The state of Florida has one NADP precipitation station at Bradford Forest. The study area was restricted between 28°28′30″ N < latitude < 31°28′30″ N and 80°42′00″ W < longitude < 83°40′00″ W on the basis of 100-mile radius selection criterion. The number of lakes selected in this region was 61 out of 141 in the NSWS data set.

Variables in the Data Base. The NSWS data set contains four watershed descriptors (lake surface area, lake watershed area, lake elevation, and lake depth) and 43 water chemistry parameters, with 1619 observations in 18 states. The NSWS deposition and land-use data set contains three wet deposition parameter values (H^+, SO_4^{2+}, and NO_3^-), annual precipitation, annual runoff data from map contour, and 11 land-use variables with 769 observations in nine states. The ADS 1984 annual data summary contains nine precipitation chemistry parameters (Ca^{2+}, Mg^{2+}, K^+, Na^+, NH_4^+, NO_3^-, Cl^-, SO_4^{2-}, H^+, and pH) with 65 measuring stations in 30 states. Since both data sets contain the major eight ions (Ca^{2+}, Mg^{2+}, K^+, Na^+, NH_4^+, NO_3^-, Cl^-, and SO_4^{2-}), the NSWS data set was utilized for lake chemistry, while the NADP data set was used for wet precipitation chemistry.

Major ion concentrations of precipitation for the Adirondack Park and the state of Florida were precipitation volume-weighted mean values from 1984. In the case of the Southern Blue Ridge, the volume-weighted mean of two stations (1984 volume-weighted mean precipitation chemistry values) was used.

Steady-State Mass Balance. The basic mass balance equation around a control volume (the watershed) for various ion species can be written as

$$\text{accumulation} = \text{inputs} - \text{outputs} \pm \text{reactions} \quad (1)$$

where the positive sign (+) on the reaction term indicates production of the ion and the negative sign (−) indicates consumption or uptake of the ion in the watershed. The left-hand side of eq 1 will be equal to zero at steady state. After rearrangement of the equation, it can be expressed as

$$\pm\text{reactions} = \text{outputs} - \text{inputs} \quad (2)$$

or for a watershed that contains a lake discharge as

$$\text{reactions} = QC_{\text{lake}} - IC_{\text{precip}} \quad (3)$$

where Q = annual runoff (cm/yr), I = annual precipitation (cm/yr), C_{lake} = ion concentration of the lake (μequiv/L), and C_{precip} = ion concentration of the precipitation (μequiv/L).

Dividing eq 3 by Q yields

$$\text{RXN} = \frac{\text{reactions}}{Q} = C_{\text{lake}} - FC_{\text{precip}} \quad (4)$$

where F = evapoconcentration factor = I/Q and RXN = net reaction (μequiv/L). In this formulation, it was assumed that the watershed basin is "tight" hydrologically (i.e., that all outflow goes out through the lake). Groundwater export or import to the watershed is assumed negligible. Equation 4 indicates the quantitative relationship between precipitation ion concentration and surface water ion concentration. Each major cation (Ca^{2+}, Mg^{2+}, K^+, Na^+, NH_4^+) and anion (SO_4^{2-}, NO_3^-, Cl^-) was evaluated with eq 4 to quantify production or consumption of the ions. If the RXN term was close to zero, it meant that the ion was almost conservative. If the RXN term was positive, it meant that the watershed produced the ion by some process, and if it was negative, the ion was consumed by some process or processes, either in the terrestrial or aquatic portion of the watershed.

Three variables in eq 4 were obtained from the data bases. Ion concentrations in the lakes (C_{lake}) were taken from the NSWS data base. Precipitation chemistry for each ion (C_{precip}) was obtained from the ADS data base as volume-weighted average in 1984 at the NADP precipitation stations. The evapoconcentration factor for the watershed (F) was estimated from the annual average estimated precipitation and potential runoff data in the NSWS land-use data base (*12*). Evapoconcentration factors were variable from lake to lake and from region to region. In the Adirondack Park, the evapoconcentration factor was 1.7 ± 0.5 (n = 147); in the Southern Blue Ridge Province, it was 2.2 ± 0.6 (n = 73); in the Florida watersheds, it was 9.4 ± 6.1 (n = 61). The Florida lakes included many seepage lakes with very small surface water discharges (Q) and quite large evapoconcentration factors. In these cases, the assumptions of the model (eq 4) could be violated, and the results contain a large uncertainty.

Results and Discussion

The mean lake chemistry for each of the study areas is presented in Table II. The sum of the cation concentrations does not equal the sum of the anion concentrations (electroneutrality) due to the statistical procedure (using mean values). In addition, some lakes show a deficiency of anions due to the influence of organic anions in solution which are not measured directly. In all three study areas, calcium is the largest cation concentration. Calcium is generated by canopy leaching, ion exchange, mineralization

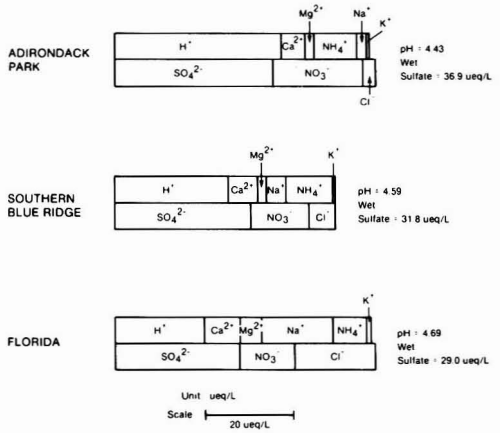


Figure 2. Precipitation chemistry (volume-weighted mean value of 1984). Bar diagrams for study area from acid deposition system (ADS) data base (*14*).

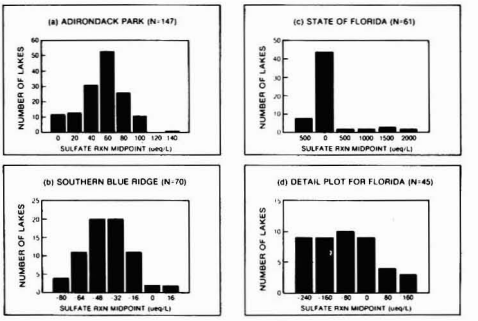


Figure 3. Sulfate reaction histogram using eq 4 for each study area. A positive reaction term indicates production of the ion in the watershed. A negative reaction term indicates consumption. Numbers on abscissa refer to the midpoint of equal-spaced reaction intervals.

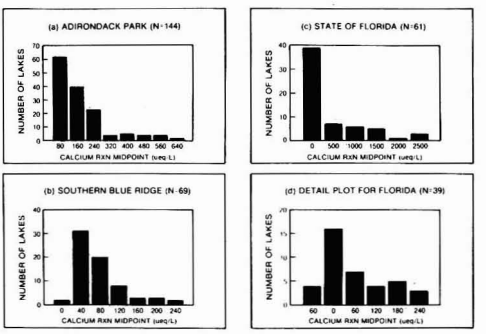


Figure 4. Calcium reaction histogram using eq 4 for each study area.

of organic material in the soil and litter, and chemical weathering. Chemical weathering of rock-forming minerals is the ultimate source of calcium, in addition to atmospheric transport of wet and dry deposition. The other major cations (Mg^{2+}, Na^+, K^+) have similar sources as calcium, although Na^+ is especially prevalent in some samples from Florida and the Southern Blue Ridge Province. Sulfate is the predominant anion in the Adirondack Park, while chloride is predominant in the Southern Blue Ridge and Florida. Nitrate and ammonium concentrations are remarkably low in most lakes, presumably because of the assimilatory uptake of these nutrients by terrestrial vegetation and aquatic algae.

Figure 2 is a bar diagram representation of the annual volume-weighted average ion concentrations in precipitation for each study area. The concentration of sulfate in precipitation was greatest in the Adirondack Park (37 μequiv/L) in 1984, compared to the Southern Blue Ridge Province (32 μequiv/L) and Florida (29 μequiv/L). Likewise, hydrogen ion concentrations were greatest in the Adirondack Park (38 μequiv/L), compared to the Southern Blue Ridge Province (25 μequiv/L) and Florida (21 μequiv/L). There were significantly greater ammonium and nitrate concentrations in the Adirondack Park than in the other study areas. Sodium and chloride ions were greatest in the Florida lakes due to the marine influence on precipitation and aerosol deposition.

Frequency histograms for the results of the mass balance eq 4 are shown in Figure 3 for the three study areas. In Figure 3a, it can be seen that there are a large number of lakes which have a positive RXN term for eq 4. The most frequently occurring sulfate RXN term had a magnitude of 50–70 μequiv/L with a midpoint at 60 μequiv/L. This result supports one of two hypotheses: either (1) dry deposition of sulfur and sulfate (which is unaccounted in eq 4) has contributed to the measured sulfate concentrations in these lakes, or (2) there exists a large sulfate-generating mechanism in the watershed such as sulfide mineral oxidation. Since sulfide minerals are a relatively small proportion of the total in the Adirondack Park and contact deposits are not prevalent in the study area, it is likely that the first hypothesis is the source of the sulfate. The result indicates that dry deposition of sulfate in the Adirondack Park is of the same magnitude as wet deposition, in accordance with measurements in literature references (*17*). If dry deposition had been measured accurately and included in eq 4, the distribution of reaction terms (RXN) in Figure 3 would have been shifted to the left.

In contrast to the unmeasured sulfate source in the Adirondack Park, the Southern Blue Ridge Province (SBR) had a sulfate loss (RXN term) of −24 to −54 μequiv/L as the most frequently occurring result (Figure 3b). This is caused by the sorption of sulfate anions (and subsequent generation of equivalent alkalinity, Table I) in the soils of the SBR watersheds (*18–21*). Forty-two lake watersheds in the Florida study area also showed a loss of sulfate (Figure 3c,d), but the magnitude of the reaction was greater due to a larger input of marine sulfate precipitation. Florida lakes are anomalous in that there were also several lakes which showed a large generation of sulfate in the watershed, probably due to the exchange and leaching of sulfate ions from sedimentary deposits with high sulfate contents.

Figure 4 gives the results for Ca^{2+} of the RXN term (eq 4) via a frequency histogram of lakes in each study area. In the Adirondacks of Figure 4a, the distribution shows that all lakes produce calcium within the watershed by the processes previously discussed (ion exchange, leaching, mineralization, weathering). The greatest number of lakes produced 40–120 μequiv/L calcium. Nineteen lakes produced more than 300 μequiv/L calcium, probably indicating the presence of some carbonate minerals or readily weatherable Ca-rich plagioclase, such as anorthosite bedrock, in the watershed. Slightly less calcium was produced in the SBR lakes, with most lakes producing 20–100 μequiv/L (Figure 4b). Florida had 22 lakes out of 61 (36%) which produced a large amount of calcium in the watershed, indicating carbonate geology (Figure 4c). The production of calcium and alkalinity by chemical weath-

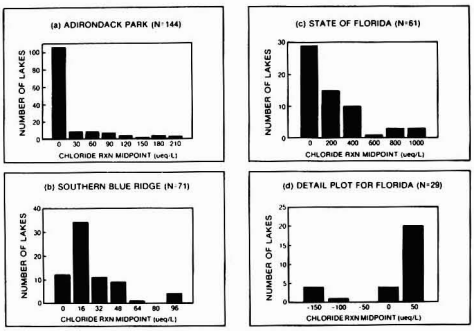


Figure 5. Chloride reaction histogram using eq 4 for each study area.

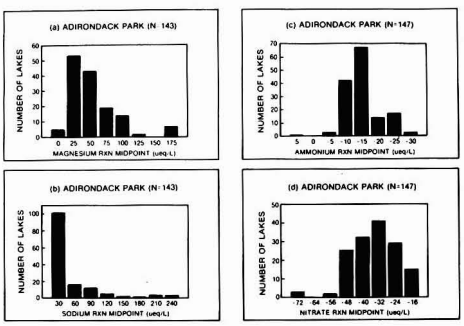


Figure 6. Ion reaction histogram for Adirondack Park, NY, using eq 4.

ering is a major reaction controlling the acid/base balance in dilute surface waters (*22*).

Chloride ions are a good means to check the methodology and evapoconcentration factors which were calculated from the NSWS land-use data base. Chloride should serve as a conservative tracer in watersheds without marine deposits or chloride inputs. Figure 5a shows that the methodology seems to work quite well on watersheds in the Adirondack Park—106 lakes out of 144 were centered around 0 μequiv/L as the reaction midpoint. However, the remaining 38 lakes seem to have some source of chloride. If the evapoconcentration factor were substantially underestimated, this would cause an apparent source of chlorides. A small amount of chloride is deposited by dry processes (ca. 12–27 μequiv/L), but significant inputs of road salt, septic tank discharges, or mineral weathering would be necessary to account for chloride RXN terms from 45 to 210 μequiv/L. In the Southern Blue Ridge Province, it is likely that dry deposition accounts for most of the RXN term between 8 and 24 μequiv/L. However, highly weathered soils of this nonglaciated region contain some chloride-exchanging clays (Figure 5b). Further evidence of marine influence in watersheds of the Florida study area is shown in Figure 5c, where some very significant sources of chlorides were evident from dry deposition (50–100 μequiv/L) and, especially, dissolution of ancient marine deposits in the watershed.

The reactions of other major ions (Mg^{2+}, Na^+, NH_4^+, and NO_3^-) in watersheds of the Adirondack Park are shown in Figure 6. The most frequently occurring RXN term of eq 4 for magnesium ions was 13–37 μequiv/L and for sodium ions was 15–45 μequiv/L. Magnesium ions are produced in the watersheds by ion exchange and chemical weathering of mafic minerals, particularly pyroxenes and amphiboles. Sodium ions come from sodium plagioclase

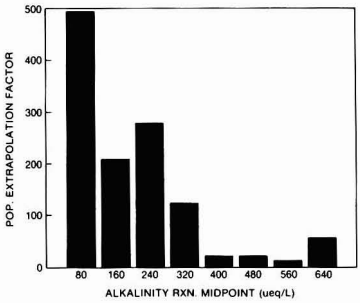


Figure 7. Alkalinity reaction histogram for Adirondack Park, NY.

minerals and, to a lesser extent, dry deposition.

Ammonium oxidation or assimilation is an acidifying influence in the watersheds. Conversely, nitrate reduction or assimilation is alkalizing. Both ions are consumed in the watersheds of the Adirondack Park, but since nitrate is of a higher concentration in precipitation than ammonium (21 μequiv/L compared to 10 μequiv/L), the consumption of nitrate is approximately 20–52 μequiv/L, while ammonia is only 8–27 μequiv/L. Thus, the net effect of the nitrogen cycle in the Adirondack watersheds is alkalizing, given the precipitation inputs.

The summation of all the alkalizing reactions minus the summation of all acidifying reactions in the watershed can be determined with eq 4. In eq 4, C_{lake} is the Gran alkalinity concentration in the lake, while C_{precip} is negative alkalinity, i.e., H^+ – acidity of precipitation from pH measurements. Results are shown in Figure 7. Weighting factors were assigned for each lake on the basis of alkalinity-derived map units. This allows the Adirondacks study area to be scaled up to represent all the lakes in the NSWS subregion. Most watersheds (1120 out of 1230) have the capacity to supply more than 50 μequiv/L alkalinity, equivalent to precipitation with pH 4.6 and an evapoconcentration factor (F) of 2.0. However, there are some extremely sensitive watersheds (110 out of 1230) that do not have the capability to neutralize precipitation which is more acidic than pH 4.6. Thus, all of these lakes are presently acidic (ANC less than zero).

Error Analysis

There are three input parameters in eq 4: C_{lake}, C_{precip}, and F. Among these three parameters, the evapoconcentration factor (F) is the most sensitive parameter. However, C_{precip} could be as important as the evapoconcentration factor if dry deposition of the ions, especially sulfate ion, and the uncertainty of measuring the deposition concentration of the ions are considered. On the basis of available data, the uncertainty in the evapoconcentration factor was ±0.5 for the Adirondack Park and ±0.6 for SBR; for the precipitation concentration, it would be approximately ±50% of the mean; and for the lake concentration it would be about ±10% analytical error. The error analysis was performed only for the evapoconcentration factor, the most sensitive parameter. Florida lakes were excluded from the analysis because they include many seepage lakes and are influenced by marine aerosol deposition.

For the lakes in the Adirondack Park, the summation of all the alkalizing reactions minus the summation of all acidifying reactions in the watershed was utilized with the regional standard deviation (0.5) of the evapoconcentration factor. If the evapoconcentration factor were increased 0.5 for each of the lakes in the region, 1210 lakes out of 1230

had the capacity to supply more than 50 μequiv/L alkalinity. On the other hand, if the evapoconcentration factor was decreased 0.5 for each of the lakes in the region, still 85% of the lakes (1055 out of 1230) had the capacity to produce more than 50 μequiv/L alkalinity. This result indicates that the regional error due to the variation in the evapoconcentration factors of each of the lakes in the region would not significantly change the results of the regional summation of the reactions.

For the lakes in the SBR, the sulfate sorption RXN, which is the most important reaction in the region, was tested with the regional standard deviation (0.6) of the evapoconcentration factor to appreciate the importance of the variation of the evapoconcentration factor in the SBR. When each of the lakes in the region used the mean evapoconcentration factor, as shown in Figure 3b, the most frequently occurring sulfate RXN was −40 μequiv/L. If the evapoconcentration factor were increased 0.6 for each of the lakes in the region, −64 μequiv/L was the most frequent sulfate RXN, and 94% of the lakes (69 out of 73) adsorbed the sulfate anion in the soils of the SBR watershed. On the other hand, if the evapoconcentration factor were decreased 0.6 for each of the lakes in the region, the most frequently occurring sulfate RXN was −16 μequiv/L, and 14 out of 73 lakes produced sulfate instead of sorbing sulfate in the watershed. This result indicates that the uncertainty of the evapoconcentration factor of each of the lakes in the region might alter the regional conclusion of the study, that sulfate is sorbed in most watersheds of the Southern Blue Ridge at a level of 38.5 ± 29.7 μequiv/L.

Conclusions

A number of reactions are important to the alkalinity balance in watersheds of the National Surface Water Survey. Specific conclusions of this research follow:

(1) The mass balance methodology (eq 4) works well for determining the various reactions for each ion in lake watersheds. However, the interpretation of results is complicated by dry deposition when only wet precipitation inputs are used in the model equation.

(2) Dry deposition of sulfate amounts to 10–70 μequiv/L of inputs to the Adirondack Park watersheds, which is of the same magnitude as wet precipitation inputs.

(3) Calcium production (mostly by chemical weathering and ion exchange) is by far the largest source of neutralization of acid deposition in the majority of the watersheds in the Adirondack Park, Southern Blue Ridge Province, and Florida. Other base cations are produced (Mg^{2+}, Na^{+}) and are also important to the acid/base budgets.

(4) Chloride ion is essentially conservative in the Adirondack Park (except for a few lakes with other distinct sources). Dry deposition of chloride and perhaps ion exchange/dissolution are sources in the Southern Blue Ridge and Florida lakes.

(5) Since nitrate and ammonium ion inputs in these watersheds are largely assimilated by terrestrial and aquatic plants, the net effect on the acid/base balance depends on the relative deposition of each ion in the watershed. In the Adirondack Park, nitrate assimilation and reduction exceed ammonium assimilation and oxidation such that the net effect is alkalizing to the watersheds.

Acknowledgments

We thank Dixon Landers, Robbins Church, and Joe Eilers of the U.S. EPA and Tony Olson of Battelle-Pacific Northwest Laboratory for their valuable discussions and correspondence of data.

Registry No. Ca, 7440-70-2; Mg, 7439-95-4; Na, 7440-23-5; NH_4, 14798-03-9.

Literature Cited

(1) Schnoor, J. L.; Stumm, W. In *Chemical Processes in Lakes*; Stumm, W., Ed.; Wiley-Interscience: New York, 1985; pp 311–338.
(2) Lindberg, S. E.; Lovett, G. M.; Richter, D. D.; Johnson, D. W. *Science (Washington, D.C.)* **1986**, *231*, 141–145.
(3) Johnson, D. W.; Richter, D. D.; Lovett, G. M.; Lindberg, S. E. *Can. J. For. Res.* **1985**, *15*, 773–782.
(4) Reuss, J. O.; Johnson, D. W. *J. Environ. Qual.* **1985**, *14*, 26–31.
(5) Velbel, M. A. *Am. J. Sci.* **1985**, *285*, 904–930.
(6) Schnoor, J. L.; Stumm, W. *Schweiz. Z. Hydrol.* **1986**, *48*(2), 171–195.
(7) Cosby, B. J.; Hornberger, G. M.; Galloway, J. N.; Wright, R. F. *Environ. Sci. Technol.* **1985**, *19*, 1144–1149.
(8) Schindler, D. W.; Turner, M. A.; Stainton, M. P.; Linsey, G. A. *Science (Washington, D.C.)* **1986**, *232*, 844–847.
(9) Baker, L. A.; Brezonik, P. L.; Edgerton, E. S., Ogburn, R. W., III *Water, Air, Soil Pollut.* **1985**, *25*, 215–230.
(10) Cook, R. B.; Kelly, C. A.; Schindler, D. W.; Turner, M. A. *Limnol. Oceanogr.* **1986**, *31*, 134–143.
(11) Driscoll, C. T.; Likens, G. E. *Tellus* **1982**, *34*, 283.
(12) Linthurst, R. A.; Landers, D. H.; Eilers, J. M.; Brakke, D. F.; Overton, W. S.; Meier, E. P.; Crowe, R. E. *Characteristics of Lakes in the Eastern United States*; U.S. Environmental Protection Agency: Washington, DC, 1986; Vol. 1; EPA/600/4-86/007A.
(13) Linthurst, R. A.; Landers, D. H.; Eilers, J. M.; Kellar, P. E.; Brakke, D. F.; Overton, W. S.; Crowe, R.; Meier, E. P.; Kanciruk, P.; Jeffries, D. S. *Water, Air, Soil Pollut.* **1986**, *31*, 577–592.
(14) Watson, C. R.; Olsen, A. R. *Acid Deposition System (ADS) for Statistical Reporting: System Design and User's Code Manual*; U. S. Environmental Protection Agency: Research Triangle Park, NC, 1984; EPA 600/8-84-023.
(15) Schofield, C. L. *Ambio* **1976**, *5*, 228–230.
(16) Likens, G. E.; Wright, R. F.; Galloway, J. N.; Butler, I. J. *Sci. Am.* **1979**, *241*, 43–51.
(17) Summers, P. W.; Bowersox, V. C.; Stensland, G. J. *Water, Air, Soil Pollut.* **1986**, *31*, 523–525.
(18) Reuss, J. O.; Johnson, D. W. *Acid Deposition and the Acidification of Soils and Waters*; Springer-Verlag: New York, 1986; pp 7–53.
(19) Johnson, D. W.; Todd, D. E. *Soil Sci. Soc. Am. J.* **1983**, *47*, 792–800.
(20) Johnson, D. W.; Reuss, J. O. *Philos. Trans. R. Soc. London, B* **1984**, *305*, 383–392.
(21) Galloway, J. N.; Norton, S. A.; Church, M. R. *Environ. Sci. Technol.* **1983**, *17*, 541–545.
(22) Schnoor, J. L.; Nikolaidis, N. P.; Glass, G. E. *J.—Water Pollut. Control Fed.* **1986**, *48*, 139–148.

Received for review February 9, 1987. Revised manuscript received September 16, 1987. Accepted October 13, 1987. This research was supported by a cooperative agreement with the Corvallis Environmental Research Laboratory Agency. It has not been subjected to the Agency's peer and policy review, and no official endorsement should be inferred.

Environ. Sci. Technol. 1988, 22, 196–204

Parametric Distributions of Regional Lake Chemistry: Fitted and Derived

Mitchell J. Small,* Michael C. Sutton, and Mark W. Milke

Civil Engineering and Engineering and Public Policy, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213

■ Parametric probability distribution functions are determined for regional lake chemistry in four subregions of the Eastern Lake Survey (ELS) of the U.S. EPA National Surface Water Survey. The subregions are the Adirondacks, northeastern Minnesota, northcentral Wisconsin, and the Southern Blue Ridge Province. ANC data are fit with a three-parameter lognormal distribution, and the distributions of pH and total base cations are derived from physically based relationships estimated for each region. The parametric distribution functions provide very good representations of observed data in each area, with the exception of northcentral Wisconsin, where bimodal ANC and base cation distributions are observed, suggesting the need for a mixture of distributions. The derived distributions of pH allow for interregional comparison, with unimodal pH distributions in unacidified areas and bimodal pH distributions in regions impacted by acid deposition. Future research of regional variations in water chemistry is proposed in the context of the correlation structure of large-scale spatial variations of soil and geologic properties.

Introduction

The value of analyzing regional distributions of lake chemistry is demonstrated in the accompanying papers of Landers et al. (*1*), Brakke et al. (*2*), and Eilers et al. (*3*, *4*). The accompanying papers present cumulative frequency distributions of physical and chemical parameters of lakes in regions of the Eastern Lake Survey (ELS) of the National Surface Water Survey (NSWS), providing insight into the underlying geo- and biochemical processes affecting water quality in each region. This paper extends the analysis of regional distributions by providing methods for fitting parametric probability models to the observed frequency distributions. A consistent set of probability distribution functions is fitted and derived from regional data for acid neutralizing capacity (ANC), pH, and total base cations.

Cumulative frequency distributions provide a complete numerical and graphical description of the observed distributions of chemical and physical characteristics of lakes in a region. Why then the need for parametric distribution functions? As indicated by Mackay and Patterson (5) in their discussion of spatial concentration distributions, "It is useful and instructive to fit equations to these distributions so that changes with time or space can be ascertained rigorously." This rigor is realized here in three particular ways. First, mathematical distribution functions provide a compact, albeit approximate, representation of the chemical distributions. Second, the form of the equations and the values of associated parameters provide insight into important chemical processes in a region, including the extent of acidification and major buffering relationships. This insight is amplified when common functional forms are found to provide good representations in a number of regions, suggesting a commonality of processes. Finally, the fitted distributions can be used as input to acidification models which directly predict shifts in regional distributions of lake chemistry resulting from changes in the level of acid deposition. A direct distribution model of this type is demonstrated by Small and Sutton (*6*).

Small and Sutton (*6*) utilize a three-parameter lognormal distribution to represent the regional distribution of ANC. Shifts in the distribution resulting from changes in acid deposition are predicted by applying empirical weathering models to the moments of the ANC distribution. The resulting pH distribution is derived with a semiempirical pH–ANC relationship. Application of the method is demonstrated by Small and Sutton (*6*) with a sample of lakes in the Adirondack Park region of New York State; however, it is not known how representative these lakes are of the overall population in the region.

In this paper the methods for fitting chemical distributions presented by Small and Sutton (*6*) are extended by (i) incorporating population weighting factors in parameter estimation (now possible with the stratified ELS data sets), (ii) developing a method for including residuals of the pH–ANC relationship in the pH distribution function, and (iii) deriving a three-parameter lognormal distribution for base cations based on a simple relationship with ANC.

Application of the methods is illustrated for four subregions in the ELS: the Adirondacks (1A), northeastern Minnesota (2A), northcentral Wisconsin (2C), and the Southern Blue Ridge Province (3A). The regions were selected because they are relatively small and thus somewhat homogeneous in terms of the level of deposition within a region. The presence of a relatively uniform level of deposition is one of the criteria for aquatic receptor regions in the methodology of Small and Sutton (*6*). While intraregional gradients in deposition do exist in the selected subregions (e.g., from southwest to northeast in the Adirondacks), they are not as large as in other ELS subregions which extend over larger geographic areas. The four subregions together span a wide range of deposition magnitudes and geological and soil characteristics. As such they provide an appropriate basis for demonstrating and comparing fitted and derived distribution functions.

ANC Distribution

The regional distribution of ANC is represented by a three-parameter lognormal function. The probability density function (pdf) is given by (*7*)

$$f_{\mathrm{ANC}}(\mathrm{anc}) = \frac{1}{(\mathrm{anc}-\theta)\phi\sqrt{2\pi}} \exp\left\{\frac{-[\ln(\mathrm{anc}-\theta)-\xi]^2}{2\phi^2}\right\} \quad \mathrm{anc} \geq \theta$$
$$= 0 \quad \mathrm{anc} < \theta \tag{1}$$

where anc denotes a particular value of the random variable ANC and θ, ξ, and ϕ are the parameters of the distribution. The cumulative distribution function (cdf) is given by

$$F_{\mathrm{ANC}}(\mathrm{anc}) = \mathrm{Prob}[\mathrm{ANC} \leq \mathrm{anc}] \tag{2}$$

and is computed numerically or from tables by noting that $\ln(\mathrm{anc}-\theta)$ is normally distributed with mean ξ and standard deviation ϕ.

Parameter estimation follows the method given in Small and Sutton (*6*) with modifications to account for the stratified design of the sample and the resulting availability of a population weighting factor, w_i, for each lake in the

0013-936X/88/0922-0196$01.50/0 © 1988 American Chemical Society

Table I. Fitted Parameters for Regional Data Sets

	subregion			
	(1A) Adirondacks	(2A) NE Minn	(2C) NC Wisc	(3A) S Blue Ridge
(A) sample size, n	155	150	155	102
(B) ANC lognormal parameters				
θ, μequiv/L	−41.0	23.0	−50.0	−18.0
ξ	4.96	5.13	5.30	5.62
ϕ	1.07	0.97	1.08	0.63
(C) pH–ANC relationship				
a	5.24	6.02	5.4	5.22
c, μequiv/L	9.37	49.27	12.77	9.96
d, μequiv/L	11.02	29.81	7.58	7.35
σ_ϵ	0.29	0.31[a]	0.41	0.40
(D) BC–ANC relationship				
reduced sample size	144	144	145	94
α, μequiv/L	131	120	99.3	24.1
β	1.22	1.01	1.02	1.34
R^2	0.93	0.96	0.98	0.79

[a] Computed with the NC Wisconsin pH–ANC relationship.

region. The lognormal distribution is thus fitted to be representative of the overall population.

The parameter θ is first estimated according to the method of Stedinger (*8*):

$$\hat{\theta} = \frac{\text{anc}_{(1)}\text{anc}_{(n)} - \text{anc}_{0.5}^2}{\text{anc}_{(1)} + \text{anc}_{(n)} - 2\text{anc}_{0.5}} \quad (3)$$

where $\text{anc}_{(1)}$ is the minimum, $\text{anc}_{(n)}$ is the maximum, and $\text{anc}_{0.5}$ is the median of n regional observations. The median is computed as the value of anc where the observed cumulative frequency distribution is equal to 0.5. The observed cumulative frequency distribution is calculated as

$$\tilde{F}(\text{anc}) = \frac{\sum_{i^*(\text{ANC}\le\text{anc})}^{i} w_{i^*}}{\sum_{i=1}^{n} w_i + w_{\min}} \quad (4)$$

where i^* denotes all lakes in the region with ANC ≤ anc and $w_{\min}$ is the minimum population weighting factor in the survey. The inclusion of $w_{\min}$ in the denominator is a minor adjustment to provide for an appropriate plotting position. The estimates of ξ and ϕ are computed from the weighted mean and variance of ln (anc − $\hat{\theta}$):

$$\hat{\xi} = \frac{\sum_{i=1}^{n} w_i \ln(\text{anc}_i - \hat{\theta})}{\sum_{i=1}^{n} w_i} \quad (5)$$

$$\hat{\phi}^2 = \frac{\sum_{i=1}^{n} w_i[\ln(\text{anc}_i - \hat{\theta}) - \hat{\xi}]^2}{\sum_{i=1}^{n} w_i} \quad (6)$$

Results. The estimated lognormal parameters for the four regions are summarized in Table I, and the fitted and observed cdf's are compared in Figure 1 for three of the regions: the Adirondacks, Southern Blue Ridge Province, and northeastern Minnesota. In these and all subsequent figures each lake is represented by a square with an area proportional to its population weighting factor, w_i. Very good agreement between the fitted and observed distributions is indicated for these regions. As a quantitative measure of fit, the Kolmogorov–Smirnov statistic—the maximum expected difference between the observed and fitted cumulative probabilities—has a value ranging from 0.13 to 0.11 for sample sizes ranging from n = 102 to n = 155 (significance level 0.05). The maximum differences between observed and fitted distributions are less than these values for the three regions. While the overall fits are good, there is a clustering of lakes in the ANC range 200–250 μequiv/L in each of the three regions shown in Figure 1, resulting in a distinct discontinuity in the observed cdf's relative to the fitted distributions. This clustering can result from the increased buffer capacity provided by the carbonic acid system over this ANC range (e.g., ref 9).

Table II. Parameters of Mixture Distribution for Northcentral Wisconsin ANC

subpopulation	fraction of population	parameters
no-inlet lakes	0.748	lognormal θ = −36 μequiv/L ξ = 4.8 ϕ = 1.11
inlet lakes	0.252	uniform m = 588 μequiv/L h = 617 μequiv/L

In the remaining region, northcentral Wisconsin, the fitted lognormal deviates significantly from the observed distribution. The latter exhibits a distinct bimodality and a heavy upper tail. To attempt to identify a more representative parametric distribution, the use of a mixture of distributions is explored. Mixtures of distributions arise when data are sampled from two or more distinct subpopulations. For a mixture of two distributions of ANC, the overall pdf is expressed as

$$f_{\text{ANC}}(\text{anc}) = p_1 f_{1,\text{ANC}}(\text{anc}) + (1 - p_1) f_{2,\text{ANC}}(\text{anc}) \quad (7)$$

where p_1 is the fraction of the population in the first subpopulation with pdf $f_{1,\text{ANC}}(\text{anc})$ and $1 - p_1$ is the fraction in the second subpopulation with pdf $f_{2,\text{ANC}}(\text{anc})$. A parallel expression describes the overall cdf.

The approach taken to identifying subpopulations in the northcentral Wisconsin data set utilizes classications by hydrologic lake type. Hydrologic lake type classifications are based on the presence of inlets and outlets to the lake: drainage lakes include outlets, closed lakes have no outlet, and seepage lakes have neither inlets nor outlets. While the hydrologic lake type is known to play an important role in aquatic acidification in general (e.g., ref 10), its importance in northern Wisconsin has been particularly noted because of the flat topography (*11*).

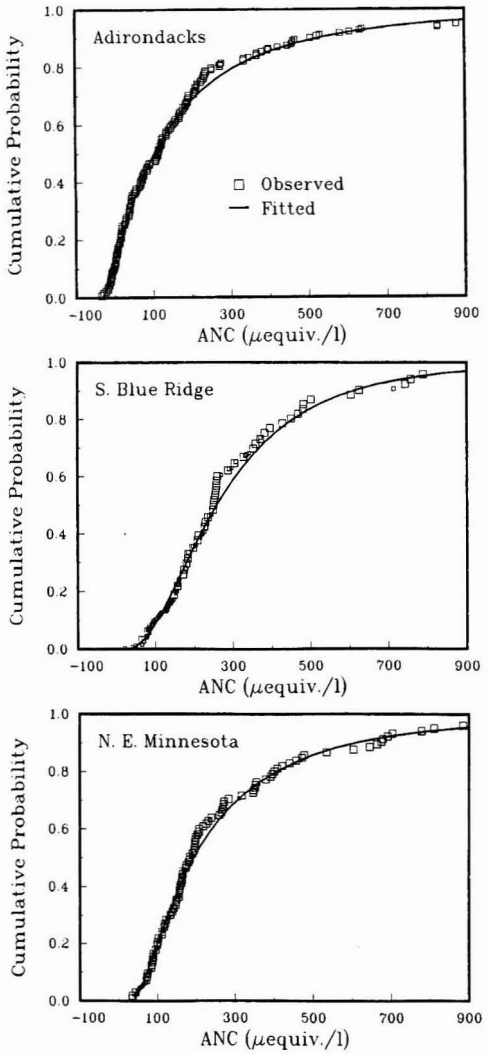


Figure 1. Comparison of fitted three-parameter lognormal and observed cumulative distributions of ANC. (In this and all figures, size of square proportional to population weighting factor.)

Identification of distinct subpopulations in northcentral Wisconsin was found to be most effective by separating lakes with no inlets from those with inlets. As indicated in Table II, the sample includes 123 lakes with no inlets representing 75% of the population weight in the survey and 32 lakes with inlets representing 25% of the population weight. The ANC distribution for lakes without inlets was fit with a three-parameter lognormal in the method previously described, while the ANC for inlet lakes was fit with a uniform distribution with midpoint m and half-range h by use of the maximum likelihood procedure presented in Johnson and Kotz (*12*).

The estimated parameters of the ANC mixture distribution for northcentral Wisconsin are summarized in Table II. The fitted and observed distributions are compared in Figure 2 for each of the subpopulations and the overall distribution. Also shown is the single lognormal distribution determined from the parameters in Table I. Note that in contrast to the other three regions, the observed

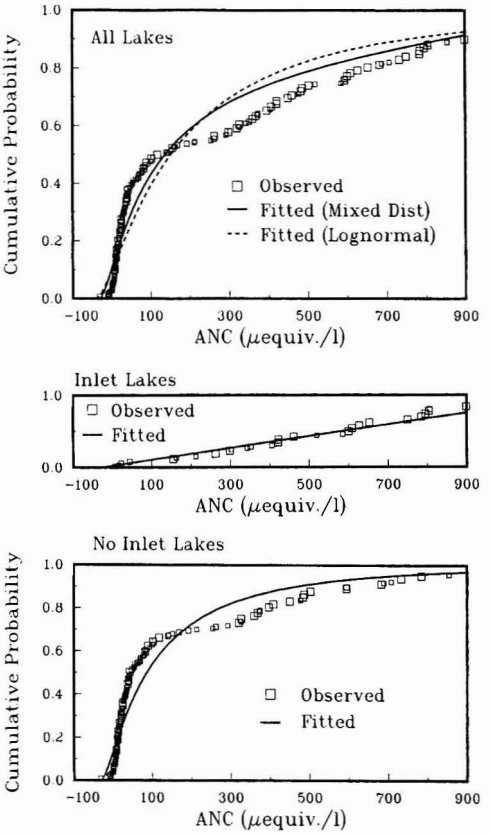


Figure 2. Comparison of fitted and observed cumulative distributions of ANC in northcentral Wisconsin for component distributions and total mixture distribution.

data indicate a distinct absence of lakes in the ANC range 200–250 μequiv/L.

The mixture distribution shown in Figure 2 provides an improved overall fit to the data relative to the single lognormal; however, significant differences remain. The use of more advanced statistical procedures for mixture classification and estimation (*13*) can lead to further improvements in the fit of the observed distribution, and these techniques should be pursued for the northcentral Wisconsin region. Given this, it must be recalled that the ELS lakes are sampled from finite populations. While the sample sizes are generally small relative to the parent populations so that the confidence levels of estimators are unaffected, the reality of finite populations modifies our thinking about the nature of the underlying distributions. The particular geochemical features of a region lead to a particular, finite set of lakes, and it is these lakes with which we are concerned. In certain areas, such as northcentral Wisconsin, the geologic features are distinct, and the resulting distribution of lake chemistry may not be readily captured by a simple probability model.

pH Distribution

The ANC distribution provides a useful characterization of the acidification status of lakes in a region. However, for certain evaluations, such as the determination of fishery status, pH may be a preferred indicator. It is thus useful to develop a parametric form for the regional pH distri-

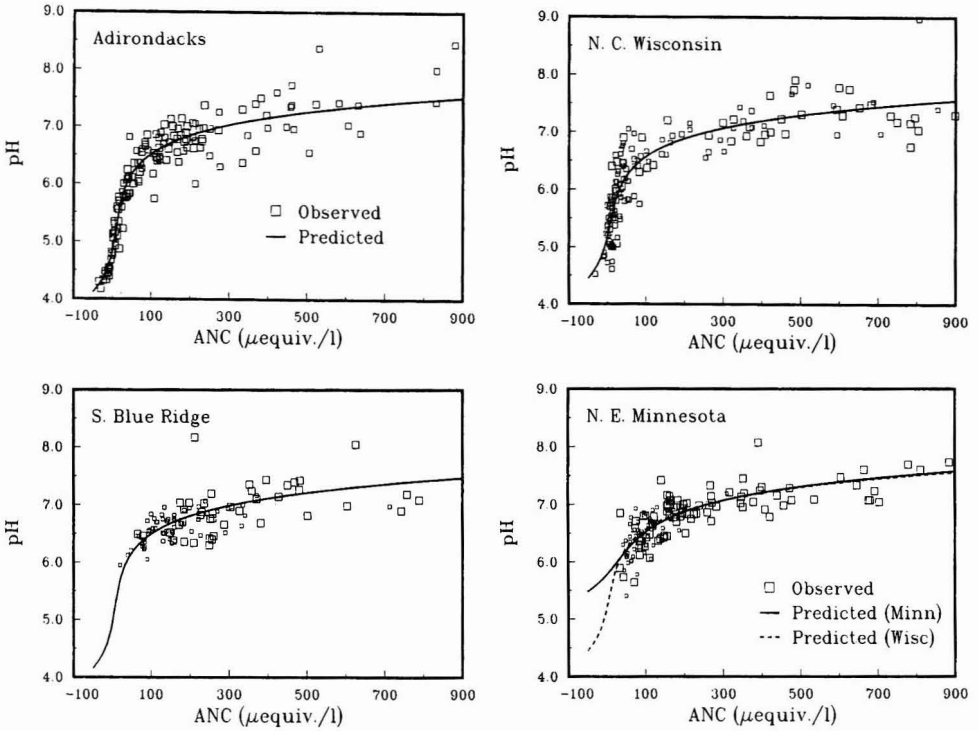


Figure 3. Observed and fitted pH–ANC relationship.

bution, especially one that takes advantage of the known chemical relationship between ANC and pH. This is particularly important when applying regional acidification models that utilize ANC as the predictive variable (e.g., ref 14–19). The availability of such a relationship allows predicted shifts in the regional ANC distribution to be translated into corresponding shifts in the regional pH.

This section presents the framework for a parametric regional pH distribution derived from the regional ANC distribution. The parameters of the pH distribution include the parameters of the pH–ANC relationship as well as the parameters of the ANC distribution. Two forms of the derived pH distribution are presented. The first is a mathematically straightforward solution utilizing the predicted pH–ANC relationship directly. The second is a more complex form incorporating the deviation of predicted and observed pH in the pH–ANC relationship, requiring an additional parameter.

The regional pH–ANC relationship is given by

$$\mathrm{pH} = a + b \operatorname{arcsinh}\left(\frac{\mathrm{ANC} - d}{c}\right) \qquad (8)$$

where arcsinh( ) denotes the inverse hyperbolic sine function (*20*) and a, b, c, and d are parameters of the relationship. Small and Sutton (*21*) demonstrate that eq 8 can be derived from fundamental chemical principles, though approximations are required to account for the effect of weak acids. They also discuss interpretation of the parameters as approximations for regionally representative dissolved CO_2 saturation relative to atmospheric CO_2 and concentrations of weak acid anions. To estimate eq 8, the parameter b is fixed at 0.4343 (1/ln 10) and a, c, and d are estimated by weighted, nonlinear least-squares regression (*22*). The regression weights are the population weighting factors from the ELS survey.

Results. The estimated parameters for the four ELS subregions are given in Table I, section C. Also shown is the standard error of the predicted pH, given by σ_ϵ. The fitted functions are compared to the observed pH–ANC data in Figure 3.

The results in Table I and Figure 3 indicate a consistent and effective set of estimated relationships, with one exception. The parameters estimated for northeastern Minnesota are very different from those estimated for the other subregions. Furthermore, although the predicted pH matches the observed data over the range of observed pH and ANC, the relationship outside this range, at low ANC, predicts values of pH which are too high given our physical understanding and experience with the pH–ANC relationship. It would be inappropriate to use this relationship to predict the downward shift in the regional distribution of pH should increased acidification in the area occur.

To address this problem, the fitted relationship for northcentral Wisconsin is also plotted with the northeastern Minnesota data in Figure 3. The relationships are virtually identical over the range of observed pH and ANC, but the Wisconsin relationship follows the expected trajectory at lower ANC. The northcentral Wisconsin pH–ANC relationship is thus used for all subsequent analyses of the northeastern Minnesota data set. Because the estimation problem results from the lack of data at low ANC and pH, caution may also be appropriate in the use of the Southern Blue Ridge Province relationship, which is based on a data set similarly limited, though a more effective set of parameter values appears to have been estimated for this region.

Direct Derivation of pH Distribution. Because the pH–ANC relationship in eq 8 is monotonically increasing,

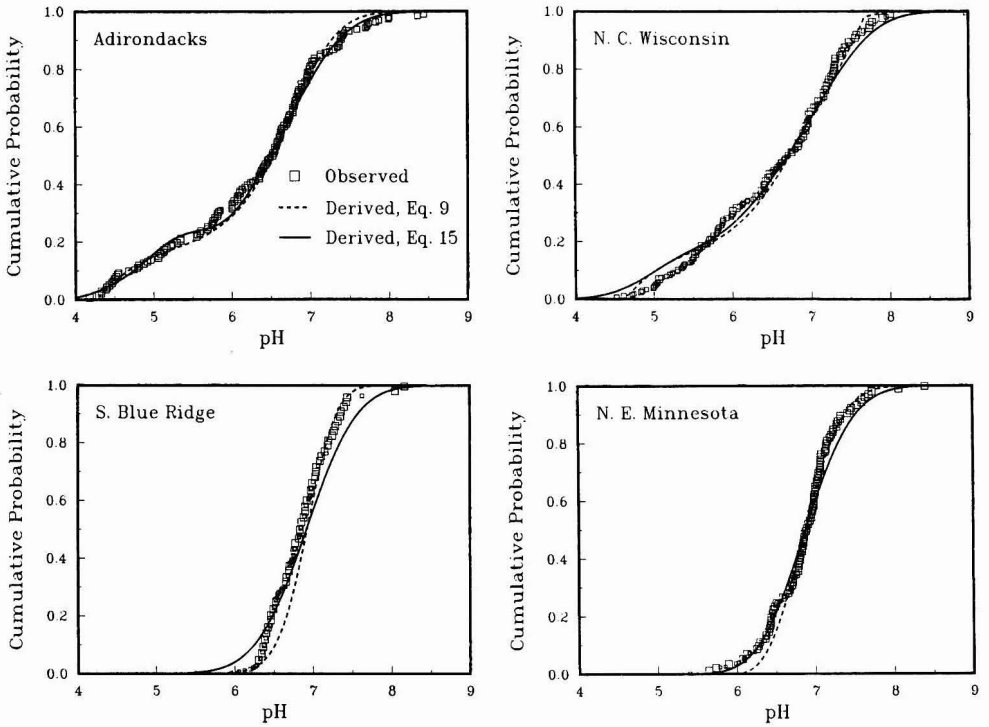


Figure 4. Observed and derived cumulative distribution functions of pH.

the cdf of regional pH can be computed directly from the cdf of ANC:

$$F_{pH}(pH) = F_{ANC}[anc(pH)] \quad (9)$$

where anc(pH) is calculated from the inverse of eq 8:

$$ANC = d + c \sinh\left(\frac{pH - a}{b}\right) \quad (10)$$

This ignores the effect of pH–ANC residuals, which are addressed in the following section, but allows for a direct and simple computation of the pH distribution.

Application of eq 9 to the four ELS subregions is demonstrated in Figure 4, indicated by the dashed lines. Generally good fits are obtained. Further discussion of the derived cdf's is deferred until after the formulation and application of the model incorporating residual deviation from the pH–ANC relationship.

Derivation of pH Distribution with pH–ANC Residuals. To account for the inexact nature of the pH prediction in eq 8, the relationship can be expressed as

$$pH = p\hat{H} + \epsilon \quad (11)$$

where pH is the observed value and $p\hat{H}$ is the value predicted by the estimated equation for each region:

$$p\hat{H} = \hat{a} + \hat{b} \operatorname{arcsinh}\left(\frac{ANC - \hat{d}}{\hat{c}}\right) \quad (12)$$

The residuals, ϵ, for each region are plotted as a function of ANC in Figure 5. In each case the residuals are well represented by a normal distribution with a mean zero and standard deviation σ_ϵ, given in Table I. Furthermore, the distribution of ϵ appears to be relatively constant as a function of ANC, although some small variations are apparent, such as the wider range of residuals indicated at lower ANC values for northcentral Wisconsin and possibly the northeastern Minnesota data set.

Given the above characterization of pH residuals, the pH distribution can be determined as the conditional distribution of $p\hat{H} + \epsilon$ integrated over possible values of ANC. Assuming the normal distribution for ϵ, this is given by

$$F_{pH}(pH) = \int_{anc=\theta}^{\infty} \Phi\left[\frac{pH - p\hat{H}(anc)}{\sigma_\epsilon}\right] f_{ANC}(anc)\, d\, anc \quad (13)$$

where $\Phi[\,]$ is the cdf of the standardized normal variate and $p\hat{H}(anc)$ is determined from eq 12. To obtain an expression suitable for numerical integration, the variable substitution

$$x = \frac{\ln(anc - \theta) - \xi}{\sqrt{2\phi}} \quad (14)$$

is made. Substituting eq 1 and 14 into eq 13

$$F_{pH}(pH) = \frac{1}{\sqrt{\pi}} \int_{x=-\infty}^{\infty} \Phi\left[\frac{pH - p\hat{H}[anc(x)]}{\sigma_\epsilon}\right] \exp(-x^2)\, dx \quad (15)$$

where

$$anc(x) = \theta + \exp(\sqrt{2}x\phi + \xi) \quad (16)$$

Equation 15 is solved by Hermite quadrature integration (*20*, p 924). While the cdf of eq 15 is expressed in a com-

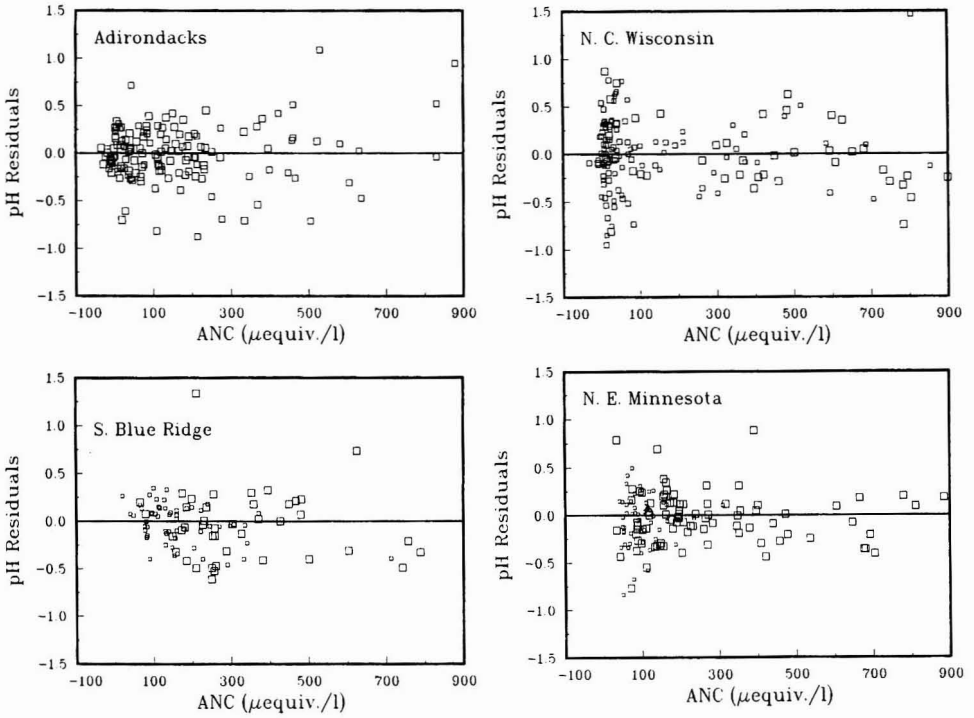


Figure 5. Residuals of fitted pH–ANC relationship.

plicated mathematical form, it includes, like eq 9, the three lognormal parameters of the ANC distribution and the four parameters of the pH–ANC relationship. An additional parameter, σ_ϵ, is required.

Comparison of Derived Distributions. The derived distributions of pH determined from eq 15 are shown in Figure 4, indicated by the solid lines. Comparing these results to those obtained with eq 9 demonstrates that the inclusion of the residual effect spreads the distribution downward and upward at the respective lower and upper tails. This is as expected. Relative to the observed data, both eq 9 and eq 15 provide good representations, but the latter is not consistently superior to the former despite the presence of an additional parameter. In the Adirondacks, both eq 9 and 15 provide an excellent representation of the data throughout the pH distribution. In the Southern Blue Ridge Province the simple model (eq 9) is superior at high pH while neither model is very accurate at low pH. Equation 9 underestimates the probability of low pH in the Southern Blue Ridge Province while eq 15 overestimates the probability of low pH. In northeastern Minnesota eq 9 provides a better fit at high pH while eq 15 is better at low pH. In northcentral Wisconsin, both provide a generally good prediction, though not quite as good as in the case of the Adirondacks. Given the significant increase in mathematical complexity required to implement eq 15 relative to eq 9 and the comparable predictive success of the two approaches, the use of the simpler model ignoring the effect of pH–ANC residuals appears justified.

Interregional Comparison of pH Distributions. To examine the extent of acidification in different regions, it is useful to compare the probability density functions of pH. The pdf can be calculated as the numerical derivative of eq 9 or eq 15, for the simple or complex formulations,

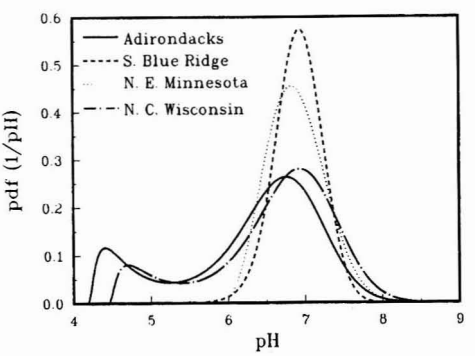


Figure 6. Comparison of derived probability density functions of pH (eq 17).

respectively. For the simple formulation a closed-form expression also exists for the pdf (*6*):

$$f_{pH}(pH) = \frac{c}{b}\cosh\left(\frac{pH-a}{b}\right)\times$$

$$\exp\left\{\frac{-\left[\ln\left(d-\theta+c\sinh\left(\frac{pH-a}{b}\right)\right)-\epsilon\right]^2}{2\phi^2}\right\}\Bigg/$$

$$\left[d-\theta+c\sinh\left(\frac{pH-a}{b}\right)\right]\phi\sqrt{2\pi} \quad (17)$$

The pdf's resulting from application of eq 17 are presented in Figure 6. The shapes of the distributions are

particularly interesting, with bimodal pH distributions in the Adirondacks and northcentral Wisconsin where significant acidification has occurred and unimodal pH distributions in the largely unacidified regions of northeastern Minnesota and the Southern Blue Ridge Province. Comparing the acidified and unacidified regions, the results suggest that in areas impacted by high acid deposition there is a subgroup of lakes with a pH that is significantly reduced, while another, larger group is for the most part unaffected.

Base Cation Distribution

It is widely recognized that base cation concentrations, especially calcium, play an important role in fish viability and response to acidification (e.g., ref 23–25). It is thus useful to consider parametric forms of regional base cation distributions and their relationship with other chemical variables.

The concentration of base cations and ANC in a lake are closely linked (*26–28*). Prior to the onset of acidic deposition, electroneutrality requires that the sum of the base cations ($Ca^{2+} + Mg^{2+} + Na^{+} + K^{+}$) be very nearly equal to the predominant anion: bicarbonate ion, the major source of ANC. Small differences in the sum of the base cation and ANC concentration can be due to background sulfate, other low-level ions, or sea-salt effects. As acidification proceeds, the ANC of a lake is reduced. The reduction of ANC is buffered in the watershed by neutralization processes including chemical weathering, cation exchange, and oxidation–reduction, which result in the generation of base cations (*29*). Effective neutralization of acidic deposition can occur due to in-lake processes including exchange of H^+ and Ca^{2+} in lake sediments and biological reduction of sulfate or nitrate in the water column and sediments to form ANC (*30, 31*). While cation exchange in sediments results in a net increase of base cations, biological reduction does not.

The implications of the processes discussed above for the base cation–ANC relationship are as follows. Prior to acidification a plot of base cations vs ANC should yield a fairly straight line with a slope near 1 and an intercept near 0, depending on background sulfate and particular geological features of the region. As acidification occurs, lake ANC is reduced while base cations are generated. The magnitudes of the respective shifts depend upon the relative importance of chemical weathering, biological reduction, etc. As such, increased deposition should increase the intercept of the base cation–ANC relationship and may modify the slope as well. As the lakes of a region may not all be in equilibrium with the deposition input at any given time, deviations from the linear relationship may occur. However, assuming that these deviations are small so that a straight-line relationship is maintained, the relationship within a region for a given time can be represented by the linear regression equation

$$\mathrm{BC} = \alpha + \beta \mathrm{ANC} + \epsilon_1 \tag{18}$$

where BC is the sum of the base cations (μequiv/L), α is the intercept, β is the slope, and ϵ_1 is the residual error of the linear regression. In a manner analogous to pH, the distribution of BC can be derived directly from ANC if the effect of the residual (ϵ_1) is ignored. In particular, if ANC has a three-parameter lognormal distribution with parameters θ, ξ, and ϕ, then BC given by eq 18 has a three-parameter lognormal distribution with parameters

$$\theta_1 = \alpha + \beta\theta \qquad \xi_1 = \xi + \ln \beta \qquad \phi_1 = \phi \tag{19}$$

For the inlet lakes of northcentral Wisconsin where a uniform ANC distribution is assumed, the derived base cation distribution is uniform with parameters

$$m_1 = \alpha + \beta m \qquad h_1 = \beta h \tag{20}$$

Results. Base cation distribution parameters were derived for each of the four ELS subregions with regression techniques. While the desired relationship between base cations and ANC is linear, the highly skewed (i.e., lognormal) nature of the variables violates the statistical assumptions of classical linear regression. To partially address this problem and to provide a more faithful representation of the predominant linear relationship, an initial, weighted linear regression was performed for each region. Observations identified by the Minitab statistical package (*32*) as outliers due to high residuals or large influence on the estimated relationship were removed for a second regression analysis. Removed observations generally had very high ANC and/or high base cation concentrations.

The results of the second weighted linear regression analysis are summarized in Table I, section D. The estimated values of α and β are within expected ranges with α greater than 0 and β near 1 or greater. The highest value of α is obtained for the Adirondacks where the level of acid deposition is the greatest, though the value of α for northcentral Wisconsin is not higher than that for northeast Minnesota, suggesting region-specific differences in geochemistry. The value of α for the Southern Blue Ridge Province is much smaller than that in the other regions. This may be indicative of the importance of sulfate adsorption for controlling acidification in this region, as opposed to base cation exchange and weathering which predominate in the other regions. Note that because the distributions of ANC and BC values in the reduced sample sets still deviate significantly from normality, the values of R^2 in Table I should be interpreted with caution.

The derived lognormal distributions (and mixed distribution in the case of northcentral Wisconsin) for base cations are compared to the observed distributions in Figure 7. A very good agreement is indicated. The lower extent of the base cation distribution in the Adirondacks and northeastern Minnesota would be better represented if the effect of BC–ANC residuals were incorporated in the model; however, this improvement would probably be too small to justify the added mathematical complexity. Note that the northcentral Wisconsin base cation distribution has a shape similar to that of ANC and is not accurately represented by the derived mixture distribution.

In applying the method for derived base cation distributions it is important to remember that α and β are not fixed, independent of deposition. This is important to recognize when predicted changes in ANC distributions derived from regional lake acidification models are used to infer changes in base cation distributions. Similarly, if acidification results in a modification of the activity of weak organic acids, then the values of the parameters of the pH–ANC relationship (eq 8) may also change as acidification or recovery occurs. In analyses performed to date (*6*), the parameters in eq 8 have been assumed to be constant; however, a complete regional lake acidification model must incorporate possible changes in their values, as well as changes in the BC–ANC relationship reflected in the values of α and β.

Discussion

The results presented in this paper indicate that a consistent set of fitted and derived distribution functions can be used to represent empiricially observed variations

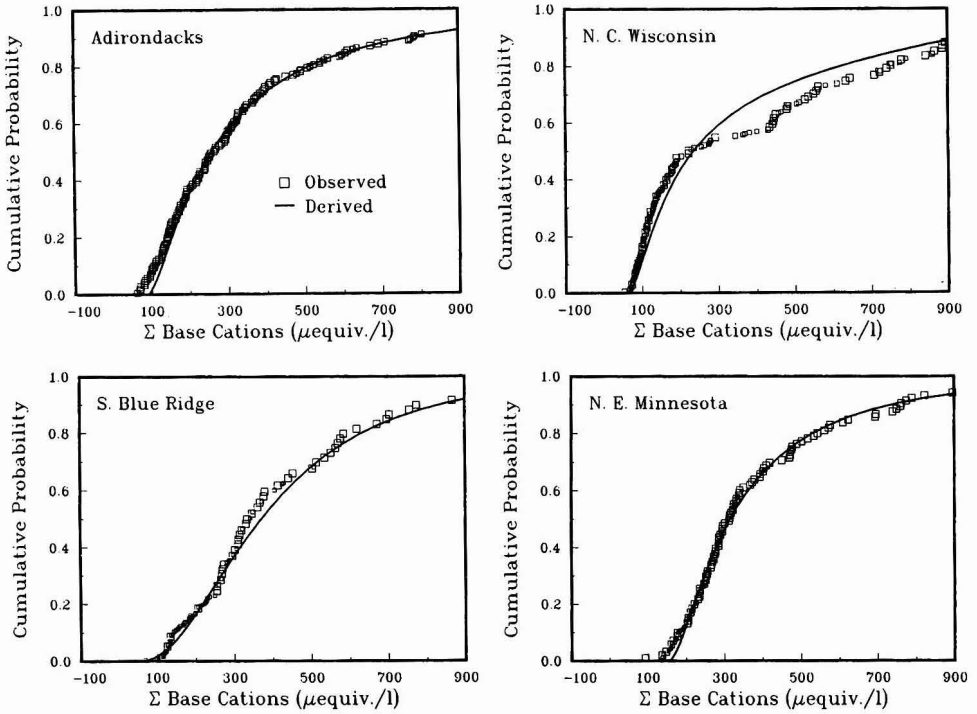


Figure 7. Observed and derived cumulative distribution functions of total base cations ($Ca^{2+} + Mg^{2+} + Na^{+} + K^{+}$).

in lake water chemistry in ELS regions. With the notable exception of northcentral Wisconsin, regional ANC's are well described by a three-parameter lognormal distribution. Simple relationships between pH and ANC and between base cations and ANC can then be used to derive accurate regional distributions of pH and base cations. The probability models are effective in that they provide a compact, yet accurate representation of the observed empirical distributions and can be used to provide input for both Monte Carlo analysis and direct distribution models of regional acidification. The question arises, however, is there more to the underlying equations than a purely empirical fit? In the words of Mackay and Paterson (*5*), can "the equation(s) be based on an understanding of the fundamental causes of the variation". To address this issue, attention can be largely focused on the joint lognormal equations for ANC and base cations, since the distribution of pH is derived from ANC with relationships based, at least in part, on physical principles.

The lognormal distribution is commonly found to represent the variation of chemical concentrations in surface waters (e.g., ref 33) and soil conditions, including hydraulic and chemical properties (34–37). Of particular relevance to the generation of base cations and ANC are spatial variations in soil depth and the chemical composition of soils (e.g., ref 38), including variations in the partial pressure of carbon dioxide in soil gas (*39*, *40*). These variations occur across regions with certain random and periodic patterns. Individual watersheds and their lakes integrate these variations over subareas of a region, resulting in a particular chemical profile for each lake. It should thus be possible to relate the variations in lake chemistry to a more fundamental description of the spatial correlation structure of geochemical factors across a region. This is an appropriate area for continued basic research into the nature and causes of regional-scale variability of lake water chemistry.

Conclusions

A consistent and effective set of parametric probability functions are fitted to regional distributions of ANC, pH, and total base cations in four of the ELS subregions. Population weighting factors from the ELS are used in parameter estimation to provide population-based equations. A three-parameter lognormal distribution provides an excellent representation of ANC in three of the regions, the Adirondacks, Southern Blue Ridge Province, and northeastern Minnesota, but cannot account for ANC bimodality in northcentral Wisconsin. A preliminary attempt to identify a mixture of distributions for ANC in northcentral Wisconsin on the basis of hydrologic lake type (inlet vs no inlet lakes) improved the fit to only a small extent, and further study of this region is needed.

Distributions of pH derived directly with a fitted pH–ANC relationship provide very good representations of observed pH. Little improvement in agreement between derived and observed pH distributions is obtained from a mathematically more sophisticated formulation incorporating residuals of the pH–ANC relationship, and as such, use of the simpler equation appears to be justified. Distributions of base cations derived from a linear base cation–ANC relationship provide good regional representation, but it must be remembered that the parameters of this relationship are expected to change with changing levels of acid deposition. The parameter values of the pH–ANC relationship may also change in response to varying levels of acid deposition, although the full extent and implications of this change are not well understood.

The shape and form of the chemical distributions provide much insight into regional acidification and buffering

processes. As an example, the derived distributions of pH in unacidified regions are unimodal while the derived pH distributions in acidified areas are bimodal, suggesting that a subset of lakes in the latter are impacted while the remaining lakes are largely unaffected in terms of pH. Further study of the characteristics of the ANC, pH, and base cation distributions is suggested in the broader context of the large-scale correlation structure of soil and geologic properties.

Acknowledgments

The work benefitted from suggestions by James Blick, Joe Eilers, Robert Fuller, Charles Minns, Kenneth Reckhow, and Edward Rubin. Comments from an anonymous reviewer provided a number of significant insights in the paper.

Literature Cited

(1) Landers, D. H.; Overton, W. S.; Linthurst, R. A.; Brakke, D. F. *Environ. Sci. Technol.* **1988**, *22*, 128–135.
(2) Brakke, D. F.; Landers, D. H.; Eilers, J. M. *Environ. Sci. Technol.* **1988**, *22*, 155–163.
(3) Eilers, J. M.; Brakke, D. F.; Landers, D. H. *Environ. Sci. Technol.* **1988**, *22*, 164–172.
(4) Eilers, J. M.; Landers, D. H.; Brakke, D. F. *Environ. Sci. Technol.* **1988**, *22*, 172–177.
(5) Mackay, D.; Paterson, S. *Environ. Sci. Technol.*, **1984**, *18*, 207A–214A.
(6) Small, M. J.; Sutton, M. C. *Water Resour. Res.* **1986**, *22*, 1749–1758.
(7) Johnson, N. L.; Kotz, S. *Continuous Univariate Distributions—1*; Houghton Mifflin: Boston, 1970; p 113.
(8) Stedinger, J. R. *Water Resour. Res.* **1980**, *16*, 481–491.
(9) Stumm, W.; Morgan, J. J. *Aquatic Chemistry*, 2nd ed.; Wiley: New York, 1981; p 176.
(10) Driscoll, C. T.; Newton, R. M. *Environ. Sci. Technol.* **1985**, *19*, 1018–1024.
(11) Eilers, J. M.; Glass, G. E.; Webster, K. E.; Rogalla, J. A. *Can. J. Fish. Aquat. Sci.* **1983**, *40*, 1896–1904.
(12) Johnson, N. L.; Kotz, S. *Continuous Univariate Distributions*—2; Houghton Mifflin: Boston, 1970; p 60.
(13) Titterington, D. M.; Smith, A. F. M.; Makov, U. E. *Statistical Analysis of Finite Mixture Distributions*; Wiley: Chichester, England, 1985.
(14) Schnoor, J. L.; Palmer, W. D.; Glass, G. E. In *Modeling of Total Acid Precipitation Impacts*; Schnoor, J. L.; Butterworth: Boston, 1984; pp 155–174.
(15) Schnoor, J. L.; Nikolaidis, N. P.; Glass, G. E. *J.—Water Pollut. Control Fed.* **1986**, *58*, 139–148.
(16) Thompson, M. E. *Water, Air, Soil Pollut.* **1982**, *18*, 215–226.
(17) Wright, R. F.; Henriksen, A. *Nature (London)* **1983**, *305*, 422–424.
(18) Wright, R. F. "Predicting Acidification of North American Lakes"; Acid Rain Research Report No. 3; Norwegian Institute for Water Research: Oslo, Norway, 1983.
(19) Jones, M. L.; Marmorek, D. R.; Cunningham, G. *Predicting Extent of Damage to Fisheries in Inland Lakes of Eastern Canada due to Acidic Precipitation*; ESSA Ltd. for the Canadian Department of Fisheries and Oceans: Sault Ste Marie, Ontario, Canada, 1984.
(20) Abramowitz, M.; Stegun, I. A. *Handbook of Mathematical Functions*, 9th ed.; Dover: New York, 1972; pp 86–89.
(21) Small, M. J.; Sutton, M. C. *Water Res.* **1986**, *20*, 335–343.
(22) Dixon, W. J. *BMDP Statistical Software*; University of California Press: Los Angeles, 1981.
(23) Fromm, P. O. *Environ. Biol. Fishes* **1980**, *5*, 79–93.
(24) Wright, R. F.; Snekvik, E. *Verh. Int. Ver. Limnol.* **1978**, *20*, 765–775.
(25) Brown, D. J. A. *Water, Air, Soil Pollut.* **1982**, *18*, 343–351.
(26) Henriksen, A. *Nature (London)* **1979**, *278*, 542–545.
(27) Kramer, J.; Tessier, A. *Environ. Sci. Technol.* **1982**, *16*, 606A–615A.
(28) Galloway, J. N.; Norton, S. A.; Church, M. R. *Environ. Sci. Technol.* **1983**, *17*, 541A–545A.
(29) Schnoor, J. L.; Stumm, W. In *Chemical Processes in Lakes*; Stumm, W., Ed.; Wiley-Interscience: New York, 1985; pp 311–338.
(30) Cook, R. B.; Kelly, C. A.; Schindler, D. W.; Turner, M. A. *Limnol. Oceanogr.* **1986**, *31*, 134–148.
(31) Schindler, D. W.; Turner, M. A.; Stainton, M. P.; Linsey, G. A. *Science (Washington, D.C.)* **1986**, *232*, 844–847.
(32) Ryan, B. F.; Joiner, B. L.; Ryan, T. A., Jr. *Minitab Handbook*, 2nd ed.; Duxbury: Boston, 1985.
(33) Di Toro, D. M. *J. Environ. Eng. Div. (Am. Soc. Civ. Eng.)* **1984**, *110*, 607–628.
(34) Freeze, R. A. *Water Resour. Res.* **1975**, *11*, 725–741.
(35) Biggar, J. W.; Nielsen, D. R. *Water Resour. Res.* **1976**, *12*, 78–84.
(36) Baker, F. G. *Water Resour. Res.* **1978**, *14*, 103–108.
(37) Yates, S. R.; Warrick, A. W.; Myers, D. E. *Water Resour. Res.* **1986**, *22*, 623–630.
(38) Ahrens, L. H. *Geochim. Cosmochim. Acta* **1957**, *11*, 205–212.
(39) Trainer, F. W.; Heath, R. C. *J. Hydrol.* **1976**, *31*, 37–55.
(40) Drake, J. J. *J. Hydrol.* **1983**, *61*, 223–236.

Received for review February 9, 1987. Accepted October 26, 1987. Support for this study was provided in part by the U.S. Environmental Protection Agency (EPA) through the National Acid Precipitation Assessment Program (NAPAP) and by the Claude Worthington Benedum Foundation and the National Science Foundation (PYI, ECE-8552772). However, it has not been subjected to EPA or NAPAP peer review, and no official endorsement should be inferred.

Environ. Sci. Technol. 1988, 22, 205–211

Long-Term Fate of Organic Micropollutants in Sewage-Contaminated Groundwater

Larry B. Barber, II,* E. Michael Thurman, and Michael P. Schroeder

Water Resources Division, U.S. Geological Survey, Denver Federal Center, Lakewood, Colorado 80225

Denis R. LeBlanc

Water Resources Division, U.S. Geological Survey, Boston, Massachusetts 02114

■ Disposal of secondary sewage effluent by rapid infiltration has produced a plume of contaminated groundwater over 3500 m long near Falmouth, MA. Approximately 50 volatile organic compounds were detected and identified in the plume, at concentrations ranging from 10 ng/L to 500 μg/L, by closed-loop stripping and purge-and-trap in conjuction with gas chromatography–mass spectrometry. The dominant contaminants were di-, tri- and tetrachloroethene, *o*- and *p*-dichlorobenzene, C_1 to C_6 alkylbenzenes, 2,6-di-*tert*-butylbenzoquinone, and several isomers of *p*-nonylphenol. The chloroethenes and chlorobenzenes had the same general distribution as chloride and boron and appear to be transported with little retardation. Less soluble compounds, such as nonylphenol and di-*tert*-butylbenzoquinone, appear to be retarded during subsurface transport by sorption processes. Although biodegradation of labile organic compounds occurs near the infiltration beds, many trace compounds, including chlorinated benzenes, alkylbenzenes, and aliphatic hydrocarbons, have persisted for more than 30 years in the aquifer.

Introduction

Rapid infiltration of waste water into the subsurface is frequently used for disposal of treated sewage. This practice depends on direct passage of large quantities of water through the unsaturated zone for renovation. Organic compounds not removed during treatment and percolation are introduced directly into groundwater where additional attenuation may occur through chemical, physical, and biological mechanisms (*1–4*). Biological degradation and sorption are the dominant processes controlling the fate of organic compounds during infiltration and subsurface transport (*5–10*). Rapid infiltration requires high-permeability sediments (*11*), a hydrologic property that makes an aquifer susceptible to contamination. Sewage effluents disposed of by rapid infiltration generally have undergone pretreatment and contain only trace levels of volatile, nonpolar organic chemicals (*6–9, 12, 13*). However, because of the recalcitrant nature of compounds that persist through treatment and infiltration, attenuation within the aquifer where biological and chemical activity is diminished may be negligible.

To evaluate the long-term impact of rapid infiltration waste water disposal, we investigated the occurrence of volatile organic compounds in a well-characterized plume of sewage-contaminated groundwater. Volatile compounds were selected for study because of their environmental relevance and potential impact on human health, as well as their relative ease of detection and identification. Because of potentially low concentrations and the diversity of compounds present, closed-loop stripping (CLS) in conjunction with gas chromatography–mass spectrometry (GC–MS) was used for qualitative screening. Purge-and-trap (PT) GC–MS was used for quantification of volatile compounds at concentrations >1.0 μg/L.

Site Description

The study site is located at Otis Air Base, approximately 100 km southeast of Boston, MA (Figure 1). An extensive plume of contaminated groundwater has resulted from continuous disposal of secondary treated sewage effluent into a shallow unconfined aquifer since 1936 (*14*). The treated sewage, which has a trace organic composition typical of municipal and domestic effluents (*6–9, 12, 13*), is discharged to sand beds where it percolates 6.5 m to the water table. The aquifer consists of 30–40 m of stratified sand and gravel with an average hydraulic conductivity of about 1.3×10^{-3} m/s and a porosity of about 35% (*14*). The water table slopes to the south-southwest at 1.5 m/km (Figure 1), and the groundwater flow velocity ranges from 0.3 to 1.0 m/day (*14, 15*).

Experimental Section

Sampling. The locations of wells (3.2–5.1-cm i.d. PVC screened over 0.3–1.0-m intervals) and well clusters sampled in this study are shown in Figure 1. Samples were collected by stainless steel submersible or peristaltic pumps fitted with Teflon tubing. To minimize contact time with casing material and to provide a native-water flush for the pumps, at least 3 well volumes of water were evacuated prior to sampling. During well evacuation, specific conductance was monitored, and samples were collected after values stabilized. Samples for organic analysis were collected without headspace in precleaned glass bottles with Teflon-lined caps and stored at 4 °C. Samples for inorganic analysis were filtered (0.45 μm) and stored in plastic bottles. Sediment samples for organic carbon analysis were collected by split-spoon core and frozen.

Analytical Methods. The sediment samples were freeze-dried, passed through a 125-μm sieve, and analyzed for organic carbon (*16*). In the water samples, boron was determined by directly coupled plasma emission spectroscopy (*17*), chloride was determined by ion chromatography (*17*), dissolved organic carbon (DOC) was determined by high-temperature oxidation with coulometric detection (*16*), and detergents were determined by methylene blue active substance (MBAS) assay (*18*).

Volatile organic compounds were determined by PT (*18*) and CLS (*19–21*) in conjunction with GC–MS. The CLS apparatus was set up on site, and samples were processed immediately after collection. Samples for PT were analyzed within 30 days of collection. In both methods, tentative compound identification was based on computer matching of sample mass spectra with those in the National Bureau of Standards Library. Identification of target compounds was confirmed with authentic standards. Surrogate standards (to monitor sample behavior) were added at time of collection, and internal standards (for quantitation) were added prior to GC–MS analysis. In the

Not subject to U.S. Copyright. Published 1988 by the American Chemical Society

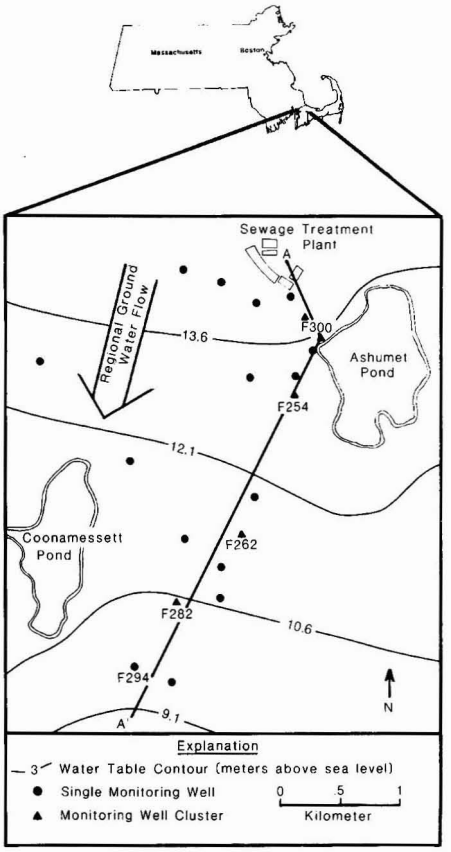


Figure 1. Map of study area showing water table configuration, direction of groundwater flow, and location of wells sampled during this study.

CLS method, concentrations were calculated against the internal standard (1-chlorooctane) by using total ion peak areas and assuming a relative response factor of 1. For PT analysis, quantitation was based on extracted ion current data with response factors determined from analysis of standards.

Results and Discussion

Boron and Dissolved Organic Carbon. The extent of groundwater contamination emanating from the sewage disposal beds was determined by mapping the distribution of boron. Boron was a good indicator of contamination because (1) it was unique to the sewage source, (2) there was a well-defined concentration gradient between contaminated and uncontaminated groundwater, and (3) it had the same distribution characteristics as the "conservative" solute chloride (*14*, *20*). Under the pH conditions of the aquifer (pH 5–7), dissolved boron occurs as the neutral undissociated orthoboric acid species (22, 23), which should be transported with little sorption. Also, boron does not undergo significant biochemical alteration (*23*). The boron plume was approximately 3500 m long, 1100 m wide, and 30 m thick during the 1985 sampling period (Figure 2).

Dissolved organic carbon had a similar distribution as boron (Figure 2), indicating transport at the same relative velocity. Two zones of elevated DOC were present: (1)

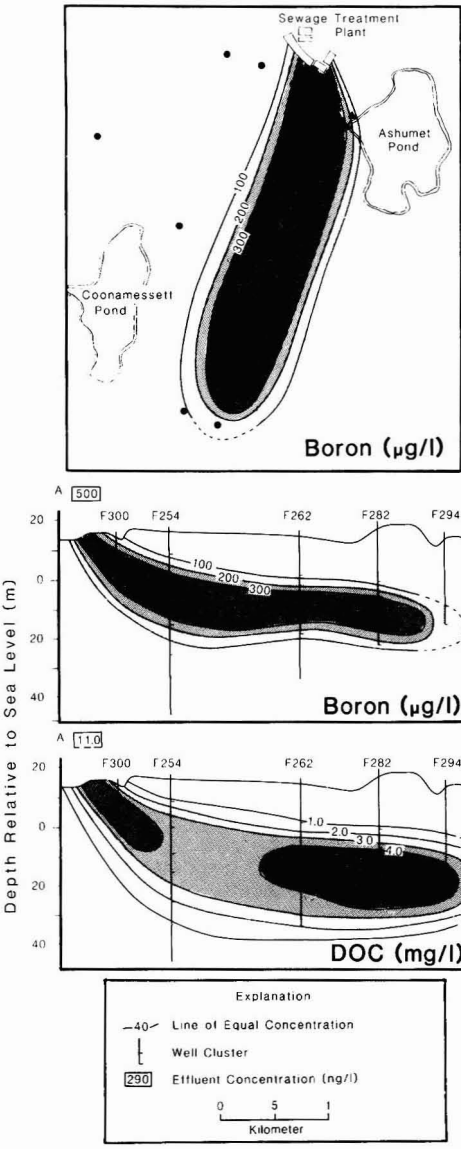


Figure 2. Distribution of boron and dissolved organic carbon (DOC). Figures based on data complied from samples collected July 1983 and July 1985. Cross-section location shown in Figure 1. Vertical exaggeration = 25×.

a zone near the infiltration beds, and (2) a zone centered between wells F262 and F294. The high DOC concentrations near the beds represent labile organic substances that are further degraded within the aquifer, as indicated by the concentration decrease from 11 mg/L in the infiltration ponds to 3 mg/L after 400 m of travel. Approximately 2000 m downgradient, DOC concentrations increase to 4 mg/L in a zone that coincides with elevated MBAS concentrations (*24*). The zone of high MBAS consists of relatively nonbiodegradable branched-chain alkylbenzenesulfonic acid (ABS) anionic surfactants that were introduced into the aquifer between approximately 1950 and 1965 (*24*, *25*). In 1965, more readily degradable lin-

ear-chain alkylbenzenesulfonic acid (LAS) replaced ABS. Surfactants that are biologically resistant under in situ conditions (as indicated by their persistence in the aquifer) account for 50% of the DOC in the downgradient portion of the plume (*20*, *24*, *25*). Maximum DOC concentrations in the contaminated groundwater were approximately 4.0 mg/L, whereas concentrations in the uncontaminated groundwater were around 0.4 mg/L. Such low DOC levels (only 10 times above background) are characteristic of groundwater contamination at rapid infiltration sites (*6*, *9*).

Occurrence and Distribution of Volatile Organic Compounds. Over 100 chromatographic peaks were observed in many CLS samples collected from the plume. Approximately 50 compounds occur with considerable frequency and have been tentatively identified (Table I), including alkyl and halogenated aliphatic hydrocarbons (saturated and unsaturated), alkyl and halogenated aromatic hydrocarbons, alkylphenols, and a variety of oxygen-, nitrogen- and sulfur-containing substances. Many compounds listed in Table I have been reported at other rapid infiltration sites (*6–9*, *13*).

Dichloroethene (DCE), trichloroethene (TCE), and tetrachloroethene (PCE) were the dominant volatile contaminants in the groundwater and occurred at concentrations orders of magnitude greater than the other volatile compounds. However, the present-day effluent has extremely low concentrations of DCE, TCE, and PCE. The only other volatile compounds with concentrations approaching 1 μg/L in the groundwater were the dichlorobenzene isomers (DCB), nonylphenol isomers (NP), 2,6-di-*tert*-butylbenzoquinone (DTBB), and several phthalate esters, all of which are present at significant concentrations in the recent effluent. The total amount of volatile compounds recovered ranged from 1 to 50 μg/L for CLS and from 1 to 1000 μg/L for PT. Although the volatile carbon compounds account for only a minor fraction of the total carbon pool, the high levels of DCE, TCE, and PCE pose a potential health risk.

Five target compounds (TCE, PCE, DCB, NP, and DTBB) were selected to characterize the groundwater contamination on the basis of (1) their pervasiveness in sewage effluents, (2) their wide range of physicochemical properties, and (3) their frequency of occurrence in the plume. The probable source of TCE and PCE is their use as degreasing solvents (*26*). Dichlorobenzene isomers are components of toilet-bowl cleaners and other household and industrial products (*26*). Although all three DCB isomers (ortho, meta, para) were detected, *o*- and *p*-DCB were dominant. The source of NP (which occurs as a mixture of approximately 15 isomers) is probably the aerobic–anaerobic degradation of alkylphenol–polyethoxylate nonionic surfactants (*27*). The compound DTBB results from the oxidation of 2,6-di-*tert*-butyphenol, a widely used antioxidant (*28*).

Data for target compounds from well cluster F254 and the sewage effluent are summarized in Table II. The CLS method was used for broad-spectrum qualitative screening, because of its capability to determine a wide range of compounds at concentrations below 1 μg/L. However, because of limitations inherent in the internal standard quantitation scheme (i.e., assuming a relative response factor of 1 for all compounds detected), the concentrations are semiquantitative. Likewise, the effect of variable recoveries for the range of compounds determined, and the effect on recoveries of having concentration differences of 5 orders of magnitude between low- and high-level compounds (Tables I and II), confuses interpretation of the concentration data. Because recoveries are less than 100%, the data represent minimum concentrations in the aquifer. The chlorinated ethenes were the only volatile compounds detected by PT. However, the PT method provided more accurate results for these compounds than CLS at concentrations greater than 1–10 μg/L (Table II), due to

Table I. Volatile Organic Compounds Identified by CLS and PT GC–MS Analysis of Contaminated Groundwater, 1984

compound	max concn,[a] ng/L	identity
Aromatic Hydrocarbons		
alkyl compounds		
benzene	100	*b*
C_1 to C_6 benzene[d]	1160	*b*
naphthalene	10	*c*
tetrahydronaphthalene[d]	10	*c*
decahydronaphthalene[d]	20	*c*
methylnaphthalene[d]	10	*c*
C_1 to C_2 tetrahydronaphthalene[d]	20	*c*
dihydro-1*H*-indene	20	*c*
C_1 to C_2 dihydro-*H*-indene[d]	110	*c*
C_2 phenylmethylbenzene	100	*c*
halogenated compounds		
chlorobenzene	20	*b*
chloromethylbenzene	50	*c*
m-dichlorobenzene	30	*b*
p-dichlorobenzene	600	*b*
o-dichlorobenzene	670	*b*
trichlorobenzene	10	*c*
iodobenzene	80	*c*
bromobenzene	10	*c*
Aliphatic Hydrocarbons		
alkyl compounds		
trimethylpentane[d]	530	*c*
trimethylpentene[d]	160	*c*
C_1 to C_4 cyclohexane[d]	360	*c*
C_{12} alkene[d]	100	*c*
limonene	70	*c*
adamantane	30	*b*
halogenated compounds		
dichloroethene[e]	2.8×10^5	*b*
trichloroethene[e]	9.5×10^4	*b*
tetrachloroethene[e]	1.0×10^6	*b*
bromoadamantane	30	*c*
Oxygen-Containing Compounds		
dimethylethylphenol	20	*c*
octylphenol	360	*c*
p-nonylphenol[d]	790	*b*
nonanal	20	*b*
decanal	20	*c*
undecanal	20	*c*
dodecanal	10	*c*
2,6-di-*tert*-butyl-*p*-benzoquinone	390	*b*
dimethylbutanol	70	*c*
methylhexanol	30	*c*
alkyl ester butanoic acid	150	*c*
dibutyl phthalate	450	*b*
alkyl ester propanoic acid	90	*c*
benzeneacetaldehyde	10	*c*
Nitrogen-Containing Compounds		
methylquinoline	40	*c*
quinolinol	20	*c*
C_4 hexanamide	80	*c*
C_2 methanamine	10	*c*
C_4 quinolinone	40	*c*
methyltriazole	30	*c*
Sulfur-Containing Compounds		
dimethyltrisulfide	10	*c*
C_5 tetrahydrothiophene	20	*c*

[a] Maximum concentration for all samples. [b] Based on matching spectra and retention time with standard. [c] Based on NBS library match. [d] Mixture of several isomers. [e] Determined by PT analysis.

Table II. Summary of Closed-Loop Stripping (CLS) and Purge-and-Trap (PT) Data for Sewage Effluent and Well F254[a]

well no.	sampling date	CLS					PT	
		TCE	PCE	DCB	DTBB	NP	TCE	PCE
effluent	1983	nd	nd	70	310	920	nd	nd
F254-8	1983	nd	nd	nd	nd	nd	nd	nd
	1984	30	100	nd	10	nd	nd	nd
F254-16	1983	160	1450	20	100	nd	nd	2600
	1984	80	200	50	150	40	nd	500
F254-22	1983	1500	1500	30	100	150	2600	6800
	1984	1250	25320	160	560	1210	69800	981900
F254-32	1983	nd	390	120	20	30	16000	11100
	1984	3590	5400	340	70	30	32300	32800
F254-42	1983	1150	20	nd	70	nd	5300	1600
	1984	1200	170	nd	30	nd	5200	500
F254-51	1983	nd	70	nd	10	nd	nd	nd
	1984	nd	nd	nd	10	nd	2700	500
F254-64	1983	nd	nd	nd	30	nd	nd	nd
	1984	nd	nd	nd	50	nd	nd	nd

[a] TCE = trichloroethene; PCE = tetrachloroethene; DCB = sum of total dichlorobenzene isomers; DTBB = di-*tert*-butylbenzoquinone; NP = sum of total nonylphenol isomers; nd = not detected. Concentrations are averages from replicate analysis in ng/L.

Table III. Summary of Data of Time-Series Closed-Loop Stripping Analysis at Well F254-72 (1984)[a]

compound[b]	concentrations					
	1	2	3	mean	SD	coeff var
trichloroethene	220	1100	540	620	445	0.72
2,3-dimethyl-2-butanol	10	70	50	43	30	0.70
trimethylpentane isomers	410	530	310	416	110	0.26
2-methyl-2-hexanol	10	30	20	20	10	0.50
tetrachloroethene	9320	16560	13640	13173	3642	0.28
C_3 cyclohexane isomers	50	50	30	43	11	0.26
1-chlorohexane[c]	40	70	20	43	25	0.58
C_2 benzene isomers	20	30	10	20	10	0.50
C_3 benzene isomers	100	70	40	70	30	0.43
1,4-dichlorobenzene	100	80	70	83	15	0.18
1,2-dichlorobenzene	80	70	60	70	10	0.14
C_4 benzene isomers	120	90	60	90	30	0.33
2,3-dihydro-1,3-dimethyl-1*H*-indene	70	40	40	50	17	0.34
2-methylquinoline	40	30	40	36	5	0.14
1-chlorododecane[c]	70	80	10	53	37	0.70
2,6-di-*tert*-butyl-*p*-benzoquinone	310	150	390	283	122	0.43
methylpropylquinolinone	40	20	40	33	11	0.33
4-(1,1,3,3-tetramethylbutyl)phenol	360	80	120	186	151	0.81
nonylphenol isomers	1080	240	480	600	437	0.72

[a] Sample 1 collected 7/24; sample 2 collected 7/26; sample 3 collected 7/31. Samples 1 and 2 were stripped within 6 h of collection; sample 3 was stripped after 60 days. [b] Compounds listed in elution order; concentrations in ng/L. [c] Surrogate standards.

saturation of the CLS charcoal trap. Because of the wide range of compounds and concentrations encountered, both CLS and PT were necessary to evaluate the occurrence of volatile organics.

In addition to analytical variability, recovery of compounds from the aquifer was also influenced by well pumping and sample collection procedures. Evaluation of sampling devices used in this study showed that recovery of TCE and PCE using the peristaltic pump was only 70% that of the submersible pump (*29*). Both CLS and PT data showed variability within the aquifer with time to be a significant factor controlling compound concentrations (*20*, *29*). Although similar concentrations were observed in many wells sampled at 1-year intervals, some wells (i.e., F254-22, Table II) showed considerable changes, illustrating the dynamic nature of the plume.

Time-series CLS replicates were collected at several sites to evaluate combined field and analytical variability. Replicate data for well F254-22 are presented in Table III. Overall precision for field samples was similar to that obtained in laboratory studies. For the data in Table III, 60 days elapsed until sample 3 was stripped, whereas samples 1 and 2 were stripped within 6 h of collection. A notable effect of storage was the loss of the surrogate standards, although most contaminants were present at concentrations within the range of variability determined in replicate analysis without storage.

Evaluation of the sample and blank processing sequence showed no memory effects between analyses of contaminated samples, blanks, and uncontaminated samples. Introduction of compounds during sample collection was evaluated with groundwater from control wells, which was similar to distilled water blanks. Samples from control wells collected immediately after sampling contaminated wells showed that carry-over from collection equipment was negligible. Control wells also indicated no significant leaching of contaminants from casing material.

Small-scale vertical variability in the occurrence and concentrations of volatile compounds was complex, and patterns varied considerably over distances of a few meters (Table II). However, on a larger horizontal scale (100–1000 m), rather uniform zones of contamination were identified (Figure 3). The maximum extent of TCE, PCE, DCB, and DTBB occurrence was similar (3500 m), and each compound was detected in the farthest downgradient well (F294) showing contamination by inorganic and bulk or-

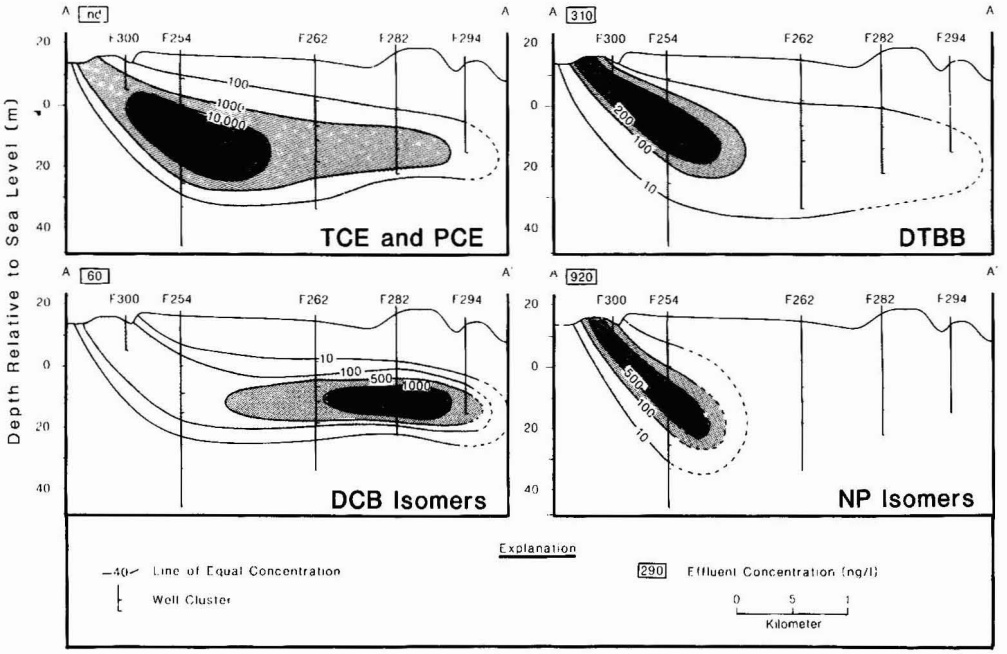


Figure 3. Distribution of volatile organic target compounds. Concentrations in ng/L. Cross-section location shown in Figure 1. Vertical exaggeration = 25×.

ganic tracers. Although elevated TCE and PCE concentrations extend over 3500 m from the infiltration beds, the center of mass for these compounds is located near well F254, 2000 m upgradient from the front. The distribution of combined DCB isomers shows a zone of maximum concentration at well F282 (3200 m from the beds) that coincides with the distribution of boron and DOC maxima (Figure 2), as well as surfactant highs (*24*). The extent of elevated DTBB (Figure 3) was slightly less than DCB, TCE, and PCE, and maximum concentrations were confined to the upgradient portion of the plume coincident with the TCE and PCE maxima. Nonylphenol was restricted to the area near the infiltration beds and was not detected beyond well F254 (1200 m). The zone of NP approximately coincides with the region of maximum DTBB, TCE, and PCE.

Subsurface Behavior. The observed distribution of target compounds could result from (1) variations in source composition reflecting changing trends in chemical usage, (2) variations in bed loading, (3) sorptive interactions with aquifer solids, (4) biological transformations, and (5) hydrogeologic factors such as dispersion and changing flow conditions. Dilution by mixing with uncontaminated groundwater beneath the infiltration beds appears to be minor, as indicated by similar concentrations of boron in the effluent and the groundwater directly downgradient from the beds.

The maximum extent of boron, DOC, MBAS, TCE, PCE, and DCB contamination is consistent with estimated distances of transport (assuming no retardation and an average flow velocity of 0.3 m/day) if the compounds were introduced in the early 1950s, which roughly coincides with the proliferation in organic chemical use. The similar distribution of the DCB, DOC, MBAS, and boron maxima indicate simultaneous introduction into the aquifer and transport at approximately the same velocity. The apparent separation of the centers of mass for TCE and PCE from DCB (Figure 3) suggests that DCB may be moving at a faster rate, provided the compounds were introduced into the system at the same time. Conversely, the compounds may be moving at the same rate but were introduced at different times. If DTBB and NP were introduced at the same time as these other compounds, their limited distribution suggests that transport is being retarded.

Sorption. Separation of organic mixtures can result from differential rates of movement within the aquifer, as a function of the compounds' solubility characteristics and the amount of organic carbon on the sediments (*1–4*). By treating transport through the aquifer as a one-dimensional process with constant flow in a homogeneous porous medium (*1*), an estimate of the retention behavior of an organic compound can be obtained from the relation between K_{ow} (octanol/water partition coefficient) and percent organic carbon on the sediments (*30–32*). Assuming that the <125-μm fraction of the aquifer material is most important for sorption and that sorption follows a linear isotherm, an average retardation factor (R_{fz}) for a given solute (z) can be calculated by the equation of Schwarzenbach et al. (*10*):

$$R_{fz} = r_z/r_w = 1 + 3.2ff_{oc}(K_{owz})^{0.72}\rho(1 - \epsilon)/\epsilon$$

where r_w = water residence time, r_z = solute z residence time, f = fraction of material <125 μm, f_{oc} = fraction organic carbon on <125-μm material, ρ = grain density (g/cm^3), and ϵ = total porosity. This equation is valid for sediments with f_{oc} greater than 0.001 and assumes chemical equilibrium conditions.

The f_{oc} of the <125-μm sediment fraction varied spatially with highest values (f_{oc} = 0.0075) generally occurring near the beds. Sediments from control sites and the downgradient part of the plume had f_{oc} values ranging from 0.0001 to 0.0025. The f_{oc} for sediments >125 μm was <0.0001. The higher values near the beds reflect steady-

state development of organic coatings on the sediments over time, as a result of carbon loading from the secondary effluent; thus, compounds in the downgradient portion of the plume may have encountered lower levels of organic carbon on the sediments near the beds and as a result may not have been retained as strongly as recently introduced compounds.

Retardation factors were calculated for the target compounds using the following aquifer properties: $f = 0.05$, $f_{oc} = 0.001$, $\rho = 2.60$ g/cm^3, and $\epsilon = 0.30$. log K_{ow} values from the literature (*33*) were used for TCE (2.29), PCE (2.88), and *p*-DCB (3.39), and values for DTBB (4.42) and NP (4.70) were measured in our laboratory by methods given in Chiou et al. (*30*). The predicted values were 1.0 for TCE, 1.1 for PCE, 1.3 for *p*-DCB, 2.5 for DTBB, and 3.4 for NP. Observed R_f values based on the maximum distance of measurable concentrations of the target compounds normalized against the distribution of boron and chloride were 1.0 for TCE, PCE, and *p*-DCB, 1.1 for DTBB, and 2.4 for NP. Observed R_f values for the leading edge of the zones of maximum concentrations were 2.4 for TCE and PCE, 1.1 for *p*-DCB, 2.6 for DTBB, and 3.3 for NP.

The predicted R_f values indicate that TCE and PCE should move approximately 20% faster than *p*-DCB, which is inconsistent with field observations that show the core of TCE and PCE contamination to be upgradient from the DCB maxima. These calculations support the hypothesis that separation of the cores results from introduction of TCE and PCE later than DCB rather than sorption processes. The restricted occurrence of NP could be due to source or geochemical factors. Although the magnitude of transport is consistent with introduction in the mid-1960s at the change from ABS to LAS surfactants (assuming no retardation and an average flow velocity of 0.3 m/day, NP would have been transported approximately 2000 m since 1966), early detergent literature indicates that alkylphenol–polyethoxylate surfactants have been in use since the 1940s (34). On the basis of NP's predicted R_f, it should have been transported approximately 1300 m if introduced in 1945, which is consistent with observations and suggests that NP distribution is controlled by sorption processes. DTBB has a predicted R_f intermediate between TCE and NP, which also matches observed distributions. Despite retarding interactions, NP and DTBB have been transported considerable distances. It is possible that the transport of nonionic organic compounds is enhanced by the presence of surfactants, especially in the downgradient portion of the plume where their concentrations are greatest.

Biological Processes. Several features of the trace organic data indicate the influence of biological processes. Many compounds such as DTBB, which is highly branched, and NP, which is an end product of biological treatment, would be expected to be resistant to biological degradation under aquifer conditions. However, many other compounds such as alkylbenzenes and nonhalogenated aliphatic hydrocarbons are not as persistent and should be capable of degradation within the aquifer.

When trace organic contaminants are introduced into groundwater, which has a limited microbial population with respect to the secondary treatment environment, biological degradation rates are slow, particularly if suitable nutrient substrates are not available (*5*). Although maximum DOC values in the contaminated groundwater were around 4 mg/L, much of the carbon consists of biologically resistant surfactants (*24*, *25*). Microbial activity in the groundwater has been shown to be carbon limited in laboratory studies (*35*), although it is possible that oxygen is also a limiting nutrient.

Tetrachloroethene can undergo microbially mediated reductive dehalogenation in strongly reducing groundwater to form TCE and DCE (*36*) but tends to persist under aerobic to denitrifying conditions (*10*, *37–39*). Although di-, tri-, and tetrachloroethene were present in the plume, insufficient data exist to evaluate whether they result from biological processes or whether the homologues are due to other factors such as mixed solvents. However, the presence of oxygen (0.1–5.0 mg/L) throughout much of the plume makes reductive dechlorination unlikely.

Concentrations of DCB, NP, and DTBB in the effluent and contaminated groundwater near the beds were similar, indicating little degradation during infiltration. In the downgradient portion of the plume, concentrations of many compounds (chlorinated aromatics, alkyl aromatics, alkyl aliphatics) were equal to or greater than in the present-day effluent. The persistence of potentially degradable substances such as DCB during 30 years of subsurface transport (as indicated by association with ABS surfactants and by consideration of flow velocities and travel distances) contrasts with the findings of several investigators, who report biological removal of *p*-DCB during infiltration under oxygenated conditions (*7*, *8*, *10*, *37*). However, others have shown no microbial utilization of *p*-DCB under denitrifying conditions (*37*, *39*), such as occur near the infiltration beds (*35*).

The long-term persistence of DCB and other potentially degradable compounds (i.e., aromatic and aliphatic hydrocarbons) present in the downgradient zone can be explained by considering the dynamics of the groundwater system. In the zone of denitrification near the infiltration beds where DCB is persistent, readily utilizable DOC is consumed. In the downgradient portion of the plume where microaerophilic to aerobic conditions exist (dissolved oxygen at well F282 ranged from 5.0 mg/L at the most shallow depth to 0.2 mg/L in the zone of maximum DCB) and DCB has the potential of being degraded, biologically labile DOC has been depleted, and the system is carbon limited. Thus, because of nutrient limitations, significant degradation of trace levels of refractory organic compounds has not occurred. The population of free-living bacteria also decreases with distance from the beds, providing further evidence that the system is nutrient limited (*40*).

Conclusions

A complex plume of over 50 volatile organic compounds was identified in the groundwater at Otis Air Base by use of CLS and PT in conjuction with GC–MS analysis. The compounds DCB, DTBB, TCE, and PCE proved to be good indicators of sewage contamination because they were (1) relatively unique to the sewage source, (2) mobile in the low organic carbon sediments, and (3) not readily biodegradable. Distribution patterns in the aquifer show that, once refractory compounds reach the saturated zone, many are transported at approximately the same rate as groundwater flow. There appears to be retardation due to sorption for poorly soluble compounds such as NP and DTBB but not for TCE, PCE, and DCB. Sorption is limited by the low organic carbon content of the sediments. Many trace organic compounds have persisted for over 30 years as the result of their recalcitrant nature and nutrient limitations within the aquifer.

Persistent organic compounds not removed by secondary treatment have the potential to contaminate large quantities of groundwater when effluents are disposed of by rapid infiltration into low-carbon, permeable aquifers. The resulting contamination will present future problems be-

cause chemical and biological processes in the aquifer are not capable of attenuating the pollutants under ambient conditions.

Acknowledgments

We thank J. L. Leenheer, R. W. Harvey, S. P. Garabedian, and D. Caine for reviewing the manuscript and D. Caine for field and laboratory assistance. The determinations of K_{ow} were made by T. I. Brinton, and the figures were drafted by E. C. Barber.

Registry No. *m*-DCB, 541-73-1; *p*-DCB, 106-46-7; *o*-DCB, 95-50-1; TCE, 79-01-6; PCE, 127-18-4; benzene, 71-43-2; naphthalene, 91-20-3; tetrahydronaphthalene, 119-64-2; decahydronaphthalene, 91-17-8; methylnaphthalene, 1321-94-4; chlorobenzene, 108-90-7; chloromethylbenzene, 100-44-7; trichlorobenzene, 12002-48-1; iodobenzene, 591-50-4; bromobenzene, 108-86-1; trimethylpentane, 29222-48-8; limonene, 138-86-3; adamantane, 281-23-2; dichloroethene, 25323-30-2; bromoadamantane, 102938-79-4; dimethylphenol, 1300-71-6; octylphenol, 27193-28-8; *p*-nonylphenol, 104-40-5; nonanal, 124-19-6; decanal, 112-31-2; undecanal, 112-44-7; dodecanal, 112-54-9; 2,6-di-*tert*-butyl-*p*-benzoquinone, 719-22-2; dimethylbutanol, 79956-98-2; methylhexanol, 61949-26-6; dibutyl phthalate, 84-74-2; benzeneacetaldehyde, 122-78-1; methylbenzeneacetaldehyde, 69380-02-5; methylquinoline, 27601-00-9; quinolinol, 1321-40-0; methyltriazole, 6086-21-1; dimethyl trisulfide, 3658-80-8; tetrahydrothiophene, 110-01-0; 2,3-dimethyl-2-butanol, 594-60-5; 2-methyl-2-hexanol, 625-23-0; 1-chlorohexane, 544-10-5; 2,3-dihydro-1,3-dimethyl-1*H*-indene, 4175-53-5; 2-methylquinoline, 91-63-4; 1-chlorododecane, 112-52-7; methylpropylquinolinone, 95618-09-0; 4-(1,1,3,3-tetramethylbutyl)phenol, 140-66-9; boron, 7440-42-8.

Literature Cited

(1) Cherry, J. A.; Gillham, R. W.; Barker, J. F. *Groundwater Contamination: Studies in Geophysics*; National Academy Press: Washington, DC, 1984; p 46.
(2) Mackay, D. M.; Roberts, P. V.; Cherry, J. A. *Environ. Sci. Technol.* **1985**, *19*, 384.
(3) McCarty, P. L.; Reinhard, M.; Rittmann, B. E. *Environ. Sci. Technol.* **1981**, *15*, 40.
(4) Roberts, P. V.; McCarty, P. L.; Reinhard, M.; Schreiner, J. *J.—Water Pollut. Control Fed.* **1980**, *52*, 161.
(5) Bouwer, E. J.; McCarty, P. L. *Ground Water* **1984**, *22*, 433.
(6) Bouwer, E. J.; McCarty, P. L.; Bouwer, H.; Rice, R. C. *Water Res.* **1984**, *18*, 463.
(7) Bouwer, E. J.; McCarty, P. L.; Lance, J. C. *Water Res.* **1981**, *15*, 151.
(8) Hutchins, S. R.; Tomson, M. B.; Wilson, J. T.; Ward, C. H. *Water Res.* **1984**, *18*, 1025.
(9) Hutchins, S. R.; Tomson, M. B.; Ward, C. H. *Environ. Toxicol. Chem.* **1983**, *2*, 195.
(10) Schwarzenbach, R. P.; Giger, W.; Hoehn, E.; Schneider, J. K. *Environ. Sci. Technol.* **1983**, *17*, 472.
(11) Bouwer, H.; Lance, J. C.; Riggs, M. S. *J.—Water Pollut. Control Fed.* **1974**, *46*, 834.
(12) McCarty, P. L.; Reinhard, M. *J.—Water Pollut. Control Fed.* **1980**, *52*, 1907.
(13) Tomson, M. B.; Dauchy, J.; Hutchins, S.; Curran, C.; Cook, C. J.; Ward, C. H. *Water Res.* **1981**, *15*, 1109.
(14) LeBlanc, D. R. *U.S. Geol. Sur. Water-Supply Pap.* **1984**, *No. 2218*, 28 p.
(15) LeBlanc, D. R.; Garabedian, S. P.; Quadri, R. D.; Morin, R. H.; Teasdale, W. E.; Paillet, F. L. *Open-File Rep.—U.S. Geol. Surv.* **1987**, *No. 86-481*.
(16) *Annual Book of ASTM Standards*; American Society for Testing Materials: Philadephia, PA, 1983; Section 11, Vol. 11.02, Method D4129-82 and D513-82, pp 98–105.
(17) *Techniques of Water Resources Investigations*; Fishman, M. J.; Friedman, L. C., Eds.; U.S. Geological Survey: Reston, VA, 1984; Book 5, Chapter A1 (in review).
(18) *Techniques of Water Resources Investigations*; Wershaw, R. L.; Fishman, M. J.; Grabbe, R. R.; Lowe, L. E. Eds.; U.S. Geological Survey: Reston, VA, 1983; Book 5, Chapter A3, 173 p.
(19) Grob, K.; Zurcher, F. *J. Chromatogr.* **1976**, *117*, 285.
(20) Barber, L. B., II Masters Thesis, University of Colorado, Boulder, 1985, 162 p.
(21) Barber, L. B., II; Thurman, E. M.; Schroeder, M. P. *Open-File Rep.—U.S. Geol. Surv.* **1984**, *No. 84-475*, 89.
(22) Choi, W. W.; Chen, K. Y. *Environ. Sci. Technol.* **1979**, *13*, 189.
(23) Waggott, A. *Water Res* **1969**, *3*, 749.
(24) Thurman, E. M.; Barber, L. B., II; LeBlanc, D. L. *J. Contam. Hydrol.* **1986**, *1*, 143.
(25) Thurman, E. M.; Willoughby, T.; Barber, L. B., II; Thorn, K. A. *Anal. Chem.* **1987**, *59*, 1798.
(26) Moore, J. W.; Ramamoorthy, S. *Organic Chemicals in Natural Waters, Applied Monitoring and Impact Assessment*; Springer-Verlag: New York, 1984, 289 p.
(27) Giger, W.; Brunner, P. H.; Schaffner, C. *Science (Washington, D.C.)* **1984**, *225*, 623.
(28) Lopez-Avila, V.; Hites, R. A. *Environ. Sci. Technol.* **1981**, *15*, 1386.
(29) Thurman, E. M.; Brooks, M. G.; Barber, L. B. *Open-File Rep.—U.S. Geol. Surv.* **1986**, *No. 86-481*.
(30) Chiou, C. T.; Porter, P. E.; Schmedding, D. W. *Environ. Sci. Technol.* **1983**, *17*, 227.
(31) Karickhoff, S. W.; Brown, D. S.; Scott, T. A. *Water Res.* **1979**, *13*, 241.
(32) Schwarzenbach, R. P.; Westall, J. *Environ. Sci. Technol.* **1981**, *15*, 1360.
(33) Callahan, M. A.; Slimak, M. W.; Gabel, N. W.; May, I. P.; Fowler, C. F.; Freed, J. R.; Jennings, P.; Durfee, R. L.; Whitmore, F. C.; Maestri, B.; Mabey, W. R.; Holt, B. R.; Gould, C. Report No. EPA-440/4-79-029b; Office of Water and Waste Management, U.S. Environmental Protection Agency: Washington, DC, 1979.
(34) Schwartz, A. M.; Perry, J. W. *Surface Active Agents: Their Chemistry and Technology*; Interscience: New York, **1949**; 579 p.
(35) Smith, R. L.; Duff, J. H. *Open-File Rep.—U.S. Geol. Surv.* **1984**, *No. 84-475*, 153.
(36) Parsons, F.; Lage, G. B. *J.—Am. Water Works Assoc.* **1985**, *77*, 52.
(37) Kuhn, E. P.; Colberg, P. J.; Schnoor, J. L.; Wanner, O.; Zehnder, A. J. B.; Schwarzenbach, R. P. *Environ. Sci. Technol.* **1985**, *19*, 961.
(38) Bouwer, E. J.; Rittmann, B. E.; McCarty, P. L. *Environ. Sci. Technol.* **1981**, *15*, 596.
(39) Bouwer, E. J.; McCarty, P. L. *Appl. Environ. Microbiol.* **1983**, *45*, 1295.
(40) Harvey, R. W.; Smith, R. L.; George, L. *Appl. Environ. Microbiol.* **1984**, *48*, 1197.

Received for review January 5, 1987. Accepted August 25, 1987.

Environ. Sci. Technol. 1988, 22, 212–216

Source Resolution of the Fine Carbonaceous Aerosol by Principal Component–Stepwise Regression Analysis

Sotiris E. Pratsinis*

Department of Chemical and Nuclear Engineering, Center for Aerosol Processes, University of Cincinnati, Cincinnati, Ohio 45221-0171

Melvin D. Zeldin and Elizabeth C. Ellis

Southern California Edison Company, Rosemead, California 94270

■ The sources of the fine ($d_p < 3.5$ μm) total and carbonaceous aerosol mass at Duarte (near Los Angeles) were resolved by principal component–stepwise regression analysis of aerosol (elemental and ion) and gas concentration data that were randomly collected throughout 1983. Major contributions to the fine aerosol mass were made by motor vehicles (48%) and atmospheric (sulfate and ozone chemistry) conversion processes (30%), and minor contributions were made by soil dust (13%) and marine aerosols (9%). Motor vehicles dominated (65%) the fine carbonaceous aerosol mass followed by atmospheric processes (20%), soil dust (13%), and fuel oil fly ash (2%). Secondary nitrogen-containing compounds were found to be closely related to automobile emissions.

Introduction

Carbonaceous compounds constitute the largest fraction of the ambient fine aerosol in large cities (Los Angeles, New York, Denver, Albuquerque, Portland) (*1–4*). They contain several toxic substances of major concern to human health (*5*). Reactive hydrocarbons play a key role in various atmospheric chemistry processes (for example, in formation of nitrates and to a lesser extent in formation of sulfates) (*6, 7*). Carbonaceous compounds in the aerosol are responsible for a major part of the visibility degradation observed in urban airsheds since they include light-absorbing species (soot) and are often in the visibility-reducing particle size range [$0.1 < d_p < 1$ μm (8)].

The development of reliable methods for source resolution of carbonaceous compounds will assist the development of rational strategies for the control of the emissions of carbonaceous compounds. A receptor modeling procedure for source resolution of these compounds begins with separation of the primary from the secondary components, and then the source contributions in each component are calculated. Particulates released from sources constitute the primary aerosol component while particulates formed in the atmosphere by gas-to-particle conversion constitute the secondary aerosol component. The primary/secondary separation has been estimated by various means, including staged temperature combustion (*9, 10*), sequential solvent extractions (*11, 12*), or liquid chromatography (*13*). The latter two methods give a more detailed breakdown of carbonaceous compounds into two, three, or more groups according to their degree of polarity. The major difficulty in the source resolution of individual carbonaceous compounds is that only a small fraction of them (usually about 5–10% by mass) can be identified as individual chemical species (*13, 14*). At present, the division into primary and secondary fractions, organic and black carbon, and the nonpolar (hydrocarbon), polynuclear aromatic hydrocarbons (PAH), moderately polar, and polar organic groups provides the most useful information.

With these types of classification, source apportionment has been carried out by carbon balances (*4, 15, 16*) and multiple linear regression (*4, 17*). Carbon balances use source ratios of tracers to carbon and primary carbon emission inventories (*18*) to determine primary source contributions at a receptor site. Secondary contributions are determined either by difference (total minus primary carbon) (*15*) or by scaling source thermograms to receptor thermograms (*10*). Primary carbon source contributions are also determined by multiple linear regression (MLR) of a large number of carbonaceous group concentrations to the ambient concentrations of known source tracers. Secondary carbon contributions can be determined either by difference or by regression on secondary aerosol precursor concentrations (O_3, HNO_3) at the receptor (*17*). At present, the results from these methods are accompanied by high uncertainties in the predicted source contributions (*16, 17*), limiting the application of these methods in the development of air pollution control strategies.

The purpose of this paper is to quantitatively determine the source contributions to the carbonaceous aerosol at a Los Angeles site by principal component–stepwise regression analysis (*19, 20*). This method preserves all the advantages of MLR and relaxes its requirement for unique source tracers. Varimax-rotated principal component analysis is applied to a set of gas and aerosol data to unravel the sources of variance of the data set. By examination of the extent of correlations between principal components and original aerosol variables, the nature (primary sources or secondary atmospheric conversion processes) of each component is determined. The validity of the method is investigated by apportioning the fine aerosol mass to the sample absolute scores of the principal components (sources). Next, the method is used to apportion the thermally defined fractions of the carbonaceous aerosol to these components.

Experimental Methods

All aerosol samples were collected at Duarte, CA, a suburban residential site located about 35 miles inland to the east and downwind of metropolitan Los Angeles. Two high-volume (Hi-vol) samplers were operated to collect fine ($d_p < 3.5$-μm) aerosols on 8 × 10 in. acid-washed prefired quartz filters for organic thermographic analysis, total fine aerosol mass, NO_3^-, SO_4^{2-}, and NH_4^+ analysis. A combination of a cyclone with 7.2- and 3.5-μm impactor plates was used for collection of the fine aerosol. The impactor plates were lightly greased with Vaseline to prevent particle bounce off. A Sierra Model 244 dichotomous sampler with a single impaction stage with cut point $d_p < 3.5$ μm was used to collect fine aerosol for elemental inorganic analysis by PIXE (proton induced X-ray emission spectroscopy). All samplers were operated for 8 h (noon to 8 p.m.). The airflow rates through the Hi-vol and dichotomous samplers were 1133 and 16.7 L/min, respectively.

Thirty-five samples were collected on randomly selected days throughout 1983. The carbonaceous aerosol component was determined by thermal analysis (*21*): volatile

 0013-936X/88/0922-0212$01.50/0 © 1988 American Chemical Society

Table I. Average Concentration of Fine ($d_p < 3.5$ μm) Aerosol Components and Gases in Duarte, CA, in 1983

aerosol component	concn[a] $x \pm \sigma$, ng/m^3	no. of samples detected[b]
volatile C (VC)	3901 ± 2290	35
organic C (OC)	7242 ± 5101	35
black C (BC)	4350 ± 3308	35
Na	783 ± 334	35
Al	215 ± 167	26
Si	615 ± 372	34
P	205 ± 131	27
S	3907 ± 2479	35
K	175 ± 119	35
Ca	212 ± 112	35
Ti	58 ± 34	34
Mn	12 ± 9	30
Fe	404 ± 195	35
Ni	8 ± 6	34
Cu	14 ± 9	34
Zn	116 ± 72	35
Br	90 ± 45	35
Sr	49 ± 33	32
Pb	558 ± 300	35
NH_4^+	4518 ± 4193	35
NO_3^-	5311 ± 8038	35
SO_4^{2-}	10061 ± 7656	35
mass	60129 ± 30892	35
O_3 (in pphm)	7 ± 4.4	35
NO_2 (in pphm)	6 ± 2.3	35
NO (in pphm)	0.8 ± 0.9	29
CO (in ppm)	1.4 ± 0.7	34

[a] Arithmetic average concentrations and corresponding standard deviations. [b] Daily aerosol samples were collected over an 8-h period, and gas concentrations are the corresponding 8-h averages.

carbon (VC) (carbon volatilized below 250 °C), organic carbon (OC) (carbon volatilized between 250 and 450 °C), and black carbon (BC) (carbon volatilized above 450 °C). All elemental concentrations in aerosol samples and blank filters were analyzed by PIXE, except Na, which was determined by atomic absorption. The aerosol mass was determined gravimetrically as the average of the duplicate measurements on the quartz filters. Sulfate and nitrate were analyzed by ion chromatography and NH_4^+ by indophenol blue colorimetry. No estimates of sampling artifacts for nitrate or organic aerosols were made.

Mean gas concentrations were obtained from the nearby air quality monitoring station at Azusa of the South Coast Air Quality Management District (3 km away) by averaging the reported hourly average gas concentrations over the 8-h sampling period (Table I). Elemental aerosol concentrations were obtained after subtracting the average of 38 Teflon blank filter contributions from every sample (Table I).

Statistical Methods

Principal component analysis followed by stepwise regression on the absolute principal component scores was used to apportion fine aerosol mass and carbon-containing aerosol components to their sources. Thurston and Spengler (*19*) first employed this method to resolve the sources of ambient fine ($d_p < 2.5$ μm) and coarse ($2.5 < d_p < 15$ μm) aerosols in metropolitan Boston. According to this procedure, the variance of a large set of *intercorrelated* variables (for example, ambient gas and aerosol component concentrations) is explained by a smaller set of *independent* variables (principal components). These components are linear combinations of the original variables of the data set. The extent of correlations [$0.70 < r^2 < 0.99$ (*22*)] between principal components and original data variables is used to assign source identity to each one of the principal components. To facilitate this task, the principal components are transformed by varimax rotation prior to their source assignment. Although, in principle, an equal number of principal components to the number of data variables is obtained, only a few principal components are retained [eigenvalues larger than unity after rotation (*23*)] for subsequent data analysis.

Once the sources explaining most of the variance of the data have been determined, quantitative estimates of the source contributions to the ambient concentrations of any other air quality variable (not included in the data that were used to generate the principal components) were obtained by regressing it on the sample absolute scores of the principal components. This procedure was used to apportion fine particulate mass, volatile carbon, organic carbon, and black carbon to their sources. The dependent variable variance explained by each principal component was also calculated as the percent of R^2 of the stepwise regression model. The numerical computations were carried out according to the procedures FACTOR and STEPWISE of the SAS statistical package (*24*).

Results and Discussion

The arithmetic mean concentrations and standard deviations of the aerosol and gas variables in 35 randomly collected 8-h samples in 1983 along with their frequency of detection at Duarte, CA, are shown in Table I. Elements with mean aerosol concentrations lower than the standard deviations of their concentrations in the average blank filter were excluded from subsequent analysis (Sr, P). Air quality variables with low detection frequency (Al, Mn, NO) were excluded from statistical analysis. Copper was not included in the data since its concentration was affected by abrasion of the copper motor brushes from the collocated Hi-vol samplers (*25*, *26*).

A preliminary investigation of the sources of variance of the data was made by examining the correlations between the various air quality variables. High correlations ($r^2 > 0.90$) were found between Pb and Br, between VC and OC, and between S and SO_4^{2-}. Good correlations ($r^2 > 0.80$) were found among VC, OC, BC, Br, Pb, CO, and NO_2, among Pb, NH_4^+, and NO_3^-, among S, SO_4^{2-}, and NH_4^+, and among Si, Ca, and Fe. These results indicate the importance of motor vehicle emissions and resuspension of soil and secondary aerosol on determining the variance of the data set.

Principal Component Analysis. Principal component analysis revealed six principal components, explaining 92% of the variance (Table II). The first component correlates well with Pb, Br, and CO, and it is attributed to cars using gasoline and diesel fuels as well as other areawide sources (tire tread, brake lining) with a spatial distribution similar to that of motor vehicles (*26*). Interestingly enough, this component also correlates quite well with nitrates and nitrogen dioxide. As a result, this component could have been assigned as a nitrate component. However, as it is shown later in this paper, this component is responsible for a major fraction of carbonaceous aerosol and especially black carbon. Consequently, this component accounts for primary particulate emissions from motor vehicles and secondary nitrate aerosols. This indicates that ambient nitrate concentrations are probably mostly influenced by motor vehicle emissions. Our sampling site is located downwind of the primary sources in Los Angeles and receives a considerable amount of secondary aerosols. It is possible that particles and nitrogen oxides released from automobiles in the western and central part of the Los Angeles basin reach our sampling site after a significant

Table II. Loadings of Rotated Principal Components at Duarte, CA, 1983

	motor vehicles	soil dust	sulfate chemistry	ozone chemistry	marine aerosol	fuel oil fly ash
Na	−0.13	0.07	0.08	0.07	0.98[a]	0.05
Si	0.15	0.94	0.06	0.09	−0.12	0.02
S	0.19	0.08	0.94	0.20	0.09	0.07
K	0.19	0.58	0.06	0.23	0.16	0.14
Ca	0.07	0.92	−0.05	0.09	0.20	0.08
Ti	0.20	0.63	0.03	0.00	0.03	0.03
Fe	0.46	0.78	0.08	0.17	0.03	0.09
Ni	0.47	0.13	0.11	0.00	0.07	0.86
Zn	0.65	0.29	0.32	0.14	0.06	0.11
Br	0.80	0.28	0.31	0.23	−0.17	0.17
Pb	0.90	0.21	0.29	0.09	−0.12	0.14
CO	0.75	0.21	0.36	0.20	0.04	0.07
O_3	0.04	0.25	0.39	0.87	0.10	0.01
NO_2	0.86	0.16	0.05	0.09	0.04	0.30
NH_4^+	0.67	0.00	0.72	−0.05	−0.09	0.08
NO_3^-	0.94	0.07	0.07	−0.23	−0.07	0.10
SO_4^{2-}	0.18	−0.04	0.96	0.17	0.05	0.02
eigenvalue	5.1	3.5	2.9	1.1	1.1	1.0

[a] Underlined values indicate component loadings >0.70.

atmospheric conversion to nitrate and NO_2 has taken place during the course of airflow. However, this hypothesis needs to be rigorously investigated with more data that would be free of possible sampling artifacts.

The second principal component highly correlates with Si, Ca, and Fe, indicating crustal origin. The third principal component is assigned as a sulfate chemistry component since it highly correlates with S and SO_4^{2-}. This component also correlates moderately with NH_4^+, indicating that freshly generated H_2SO_4 is probably neutralized by ambient ammonia resulting in sulfates in the form of $(NH_4)_2SO_4$ or NH_4HSO_4. The fourth principal component correlates well with O_3, a product of atmospheric chemical reactions and a known photochemistry precursor, and it is assigned as ozone photochemistry. The fifth principal component highly correlates with Na, which is a major constituent of sea salt, and is assigned as a marine aerosol component. The sixth principal component highly correlates with Ni, which has been used as a tracer for fuel oil combustion in the Los Angeles basin (*26*). As a result, the last component is assigned as a fuel oil component.

Source Resolution of Fine Aerosol Mass. The fine aerosol mass was apportioned to the six principal components by stepwise regression at the 95% confidence level (Table III). Motor vehicles are responsible for 48%, on the average, of the total calculated fine mass in Duarte, CA, in 1983. Soil dust constitutes 13% of the total fine mass on the average. Atmospheric processes (sulfate chemistry 20% and ozone photochemistry 10%) may contribute up to 30% of the total fine mass. Marine aerosol is responsible for 9% of total mass, while fuel oil fly ash did not have a significant contribution to the fine mass at the 95% confidence level. At the 90% confidence level, however, fuel oil contributed 0.6 $\mu g/m^3$ or 0.9% of the fine aerosol mass at Duarte.

The total calculated mass is within the standard deviation of the yearly average measured mass and 20% higher than its mean. The determination coefficient R^2 of the regression model is excellent, 0.96. These results are in agreement with the common perception of the source contributions to the fine ambient aerosol at an inland Los Angeles site that is strongly affected by photochemical smog (*15*).

Source Resolution of Carbon-Containing Aerosol Compounds. The success of principal component–stepwise regression analysis in resolving the sources of the fine aerosol mass gives confidence in using this method for apportionment of the various carbonaceous aerosol components to their sources (Table III). For the volatile carbon, three sources were found to have statistically significant ($p < 0.05$) contributions. Motor vehicles were responsible for 64% of the total calculated VC mass (and accounted for 41% of the variance, Table IV), and the rest is attributed to atmospheric conversion processes. The total calculated VC mass was close to the yearly average measured volatile carbon mass. However, 28% of the VC variance was not accounted for by these sources (R^2 = 0.72).

Table III. Source Apportionment of Fine Aerosol Mass and Carbonaceous Aerosol Components at Duarte, CA, 1983

	motor vehicles	soil	sulfate	ozone	marine	fuel oil	total
fine mass							
$\mu g/m^3$	33.8	8.9	14.3	7.2	6.2		70.4
%	48	13	20	10	9		
volatile C							
$\mu g/m^3$	2.3		0.7	0.6			3.6
%	64		19	17			
organic C							
$\mu g/m^3$	5.6	2.5	0.7	1.7			10.5
%	53	24	7	16			
black C							
$\mu g/m^3$	4.1					0.3	4.4
%	93					7	
total C							
$\mu g/m^3$	12.0	2.5	1.4	2.3		0.3	18.5
%	65	13	8	12		2	

Motor vehicles contributed about half of the calculated organic carbon, OC, while the other half was made by contributions that were evenly split between the soil dust and the atmospheric conversion processes (R^2 = 0.81). Surprisingly, soil dust was found to contribute a significant amount of organic carbon. Watson (*27*) reported that soil may contain up to 15% carbon. With the results from the source apportionment of the fine mass, carbon is found to make up to 28% of the Duarte soil. The substantial overprediction of the yearly average OC mass and the fact that atmospheric processes and soil dust account for about the same mass of OC indicate that the calculated soil contribution to OC is probably too high.

Finally, motor vehicles are the major source of black carbon (93% of the calculated BC mass, 62% of the BC

Table IV. Variance (Percent of R^2) of the Regression Models Explained by the Principal Components from the Stability Analysis Calculations[a]

	motor vehicles	soil	sulfate	ozone	marine	fuel oil	total
fine mass	49[b]	4	33	9	1		0.96
	(44–55)[c]	(3–6)	(28–40)	(6–15)	(0–2)		
volatile C	4		15	12			0.72
	(35–53)		(10–25)	(8–13)			
organic C	50	11	3	17			0.81
	(43–59)	(6–13)	(0–6)	(14–25)			
black C	62					10	0.72
	(58–67)					(4–14)	

[a] The procedure for the stability analysis calculations is as follows: One daily sample at a time is removed from the 35-sample data set, and principal component analysis is performed on the remaining 34-sample data set. Stepwise regression analysis on the fine aerosol mass and carbonaceous fractions is carried out, and the variance of the regression models explained by each component is recorded (*28*). The previously removed sample is replaced in the data set, and the next daily sample is removed. The procedure is repeated (here for 35 times) until all daily samples have been removed once. [b] Variance from the full 35-sample data set. [c] Range of variance from the stability analysis calculations.

variance), while the rest (7% of mass and 10% of BC variance) come from the fuel oil fly ash component. The low coefficient of determination ($R^2 = 0.72$) of the regression model, however, indicated that other sources in the Los Angeles basin also contribute to ambient BC concentrations.

Overall, motor vehicles constitute the major source of carbonaceous fine aerosol at Duarte, contributing 65% of the total. Secondary carbonaceous aerosols account for 20% of the total or 26% of the nonblack carbonaceous aerosol component. Gray et al. (*1*) estimated by an entirely different procedure that, over long averaging times, 16–22% of the total fine ($d_p < 2.1$ μm) carbon or 27–38% of the nonblack carbon at eastern Los Angeles sites receiving substantial photochemical smog (like Duarte or Azusa) might be due to secondary aerosol formation. The results of this study are in good agreement with the above estimates, considering the differences of the two data bases [sampling (24 h) and thermal analysis techniques (*9*)]. In a similar study in Detroit, Wolff et al. (*28*) found that most of the variance of the nonblack carbon was explained by photochemistry. This was not the case in our study where motor vehicles were found to dominate the variance of both black and nonblack carbon components.

Stability Analysis. A limitation of this study is the small number of samples that was used to derive the principal components of the data set. Although multivariate statistical methods have been often applied to relatively small data sets [Detroit (*20*) and Shenandoah Valley (*29*)], the stability of the results from these methods has to be examined. Considering the number of the present data variables, at least 60 samples are needed for a stable structure of principal components (*30*).

The stability of the results of this study was explored by removing one sample at a time and performing the principal component–stepwise ($p < 0.05$) regression analysis with 34 samples. Each time, the structure of the resulting principal component was examined, and the variance (percent of R^2) of the dependent variables (fine mass and carbonaceous mass fractions) explained by each principal component was recorded (*28*). The structure (Table II) of the principal components was always preserved. Small differences were observed only in the factor loadings (not more than 5%). The range of the principal component variances (percent of R^2) for all dependent variables is shown in Table IV. The averages of the component variances were calculated and were close to the values that were found when all 35 samples were used for principal component–stepwise regression analysis. As a result, the principal component solution (Table II) is stable. Although this is an empirical approach for investigation of the stability of the principal component–stepwise regression analysis, it further supports the integrity of the present results.

Conclusions

Source resolution of the total and carbonaceous fine aerosol at Duarte (near Los Angeles) in 1983 was carried out by principal component–stepwise regression analysis.

Six principal components were found to explain the variance of the data. Four of them were attributed to primary sources of particles: motor vehicles, soil dust, marine aerosol, and fuel oil fly ash. Two were attributed to atmospheric gas to particle conversion processes: sulfate chemistry and ozone photochemistry. Motor vehicles contributed 65% of the total carbonaceous aerosol and 48% of the fine aerosol mass and accounted for about half of the variance of each carbon fraction. Atmospheric conversion processes contributed 30% of the fine aerosol mass, 20% of total carbon, and 26% of nonblack carbon at Duarte. Relatively high contributions were made by soil dust (13% of the mass, 24% of the organic carbon, and 14% of the total carbon), while low carbon contributions were made by fuel oil fly ash (2%).

An important result of this study was the discovery of the close relationship of nitrate and NO_2 to automobile emissions. This shows the power of principal component analysis for revealing underlying relationships between air quality variables.

Although the results of this study were found to be stable by means of an empirical stability analysis, additional studies with larger data bases and good control of sampling and analytical artifacts are needed to understand the source–receptor relationship of ambient carbonaceous and nitrate aerosols.

Acknowledgments

We express our appreciation to Sheldon K. Friedlander of the Department of Chemical Engineering at UCLA and to Petros Koutrakis from the School of Public Health at Harvard University for helpful discussions during the course of this project. We are thankful to T. Novakov from Lawrence Berkeley Laboratories for the thermal analysis of the carbon data and to R. J. Gordon from Global Geochemistry Corp. for the sampling and analysis of the aerosol data.

Registry No. C, 7440-44-0; Na, 7440-23-5; Al, 7429-90-5; Si, 7440-21-3; P, 7723-14-0; S, 7704-34-9; K, 7440-09-7; Ca, 7440-70-2; Ti, 7440-32-6; Mn, 7439-96-5; Fe, 7439-89-6; Ni, 7440-02-0; Cu,

7440-50-8; Zn, 7440-66-6; Br, 7726-95-6; Sr, 7440-24-6; Pb, 7439-92-1; NH_4^+, 14798-03-9; O_3, 10028-15-6; NO_2, 10102-44-0; NO, 10102-43-9; CO, 630-08-0.

Literature Cited

(1) Gray, H. A.; Cass, G. R.; Huntzicker, J. J.; Heyerdahl, E. K.; Rau, J. A. *Environ. Sci. Technol.* **1986**, *20*, 580–589.
(2) Groblicki, P. J.; Wolff, G. T.; Countess, R. J. *Atmos. Environ.* **1981**, *15*, 2473–2484.
(3) Lewis, C. W.; Einfeld, W. *Environ. Int.* **1985**, *11*, 243–247.
(4) Shah, J. J.; Huntzicker, J. J. Presented at the 77th Annual Meeting of the Air Pollution Control Association, San Fransisco, CA, June 24–29, 1984; 84-80.5.
(5) National Institute of Health *Organic Air Pollutants: Carcinogens, Mutagens, Promoters*; Public Health Service, U.S. Department of Health and Human Services, U.S. Government Printing Office: Washington, DC, 1982.
(6) Grosjean, D.; Friedlander, S. K. *J. Air Pollut. Control Assoc.* **1975**, *25*, 1038–1044.
(7) Novakov, T.; Chang, S. G.; Harker, A. B. *Science (Washington, D.C.)* **1974**, *186*, 259–261.
(8) Friedlander, S. K. *Smoke, Dust and Haze*; Wiley: New York, 1977; Chapter 5.
(9) Huntzicker, J. J.; Johnson, R. L; Cary, R. A. In *Particulate Carbon: Atmospheric Life Cycle*; Wolff, G. T., Klimisch, R. L., Eds.; Plenum: New York, 1982.
(10) Ellis, E. C.; Novakov, T. *Sci. Total Environ.* **1982**, *23*, 227–238.
(11) Daisey, J. M.; Hershman, R. J.; Kneip, T. J. *Atmos. Environ.* **1982**, *16*, 2161–2168.
(12) Appel, B. R.; Colodny, P.; Wesolowski, J. J. *Environ. Sci. Technol.* **1976**, *10*, 359–363.
(13) Ip, W. M.; Gordon, R. J.; Ellis, E. C. *Sci. Total Environ.* **1984**, *36*, 203–208.
(14) Lamb, S. I.; Petrowski, C.; Kaplan, I. R.; Simoneit, B. R. T. *J. Air Pollut. Control Assoc.* **1980**, *30*, 1098–1115.
(15) Gartrell, G., Jr.; Friedlander, S. K. *Atmos. Environ.* **1975**, *9*, 279–299.
(16) Pratsinis, S. E.; Ellis, E. C.; Novakov, T.; Friedlander, S. K. *J. Air Pollut. Control Assoc.* **1984**, *34*, 643–650.
(17) Daisey, J. M. *Environ. Int.* **1985**, *11*, 285–291.
(18) Cass, G. R.; Boone, P. M.; Macias, E. S. In *Particulate Carbon: Atmospheric Life Cycle*; Wolff, G. T., Klimisch, R. L., Eds.; Plenum: New York, 1982.
(19) Thurston, G. D.; Spengler, J. D. *Atmos. Environ.* **1985**, *19*, 9–25.
(20) Henry, R. C.; Hidy, G. M. *Environ. Sci. Technol.* **1979**, *13*, 1589–1596.
(21) Dod, R. L.; Rosen, H.; Novakov, T. *Optico-Thermal Analysis of the Carbonaceous Fraction of Aerosol Particles in Atmospheric Aerosol*, Research Annual Report 1977–1978; Lawrence Berkeley Laboratory: Berkeley, CA, 1979; LBL-8696.
(22) Roscoe, B. A.; Hopke, P. K.; Dattner, S. L.; Jenks, J. M. *J. Air Pollut. Control Assoc.* **1982**, *32*, 637–642.
(23) Hopke, P. K. *Atmos. Environ.* **1982**, *16*, 1279–1280.
(24) *SAS User's Guide: Statistics*, 1982 ed.; SAS Institute Inc.: Cary, NC, 1982.
(25) Patterson, R. K. *J. Air Pollut. Control Assoc.* **1980**, *30*, 169–171.
(26) Cass, G. R.; McRae, G. J. *Environ. Sci. Technol.* **1983**, *17*, 129–139.
(27) Watson, J. G. Ph.D. Thesis, Oregon Graduate Center, Beaverton, OR, 1979.
(28) Wolff, G. T.; Korsog, P. E.; Kelly, N. A.; Ferman, M. A. *Atmos. Environ.* **1985**, *19*, 1341–1349.
(29) Tuncel, S. G.; Olmez, I.; Parrington, J. R.; Gordon, G. E.; Stevens, R. K. *Environ. Sci. Technol.* **1985**, *19*, 529–537.
(30) Henry, R. C. In *Aerosols*; Liu, B. Y. H., Pui, D. Y. H., Fissan, H. J., Eds.; Elsevier: New York, 1984.

Received for review April 6, 1987. Accepted September 9, 1987. This work was sponsored by Southern California Edison.

Alkaline Precipitation in Bahia Blanca, Argentina†

M. Cintia Piccolo,* Gerardo M. E. Perillo, and Pedro Varela

CONICET, Instituto Argentino de Oceanografía, 8000 Bahia Blanca, Argentina

■ The spatial, meteorological, and seasonal factors associated with precipitation pH in Bahia Blanca and its surroundings are presented. From April 1984 to April 1985, 85 rain events were studied from 12 sites that represent significant land-use sectors of the city. Mean pH for all sites ranged from 6.5 to 7.2. The area is characterized by alkaline precipitation since most stations reported maximum values in excess of 7.6. The highest values of pH were observed under the influence of continental air masses, which have traveled over the pampas soil, thus introducing large amounts of alkaline cations. The lowest pH values were obtained during the winter season when marine advection introduces high concentrations of spray. Stations located close to the estuary and the industrial park present the larger effect of sea spray but also of the incidence of an incipient atmospheric contamination.

Introduction

The chemical characteristics of precipitation are a well-described phenomenon in most developed countries, especially in Europe and North America because of the everyday increasing problem of rainfall acidity (*1*). In Argentina there are very few studies dealing with atmospheric contamination in general and with acid rain in particular (*2*, *3*).

Bahia Blanca is a relatively small city (275 000 inhabitants) located in the southeast portion of the Buenos Aires Province (Figure 1) and close to the Bahia Blanca estuary. On the banks of the estuary, a large petrochemical industrial park has been established adjacent to a fossil-fueled power plant (600 MW). The plant will be fueled by either oil or coal. The largest deep-water port system of Argentina (Ingeniero White) is adjacent to Bahia Blanca. Most of the grain production of the country is exported through this harbor system. The estuary is also noted for rich fisheries of shrimp and several other local fishes.

In the last few years, the Bahia Blanca community became concerned about future contamination problems in the atmosphere and the estuary caused by the presence of the industrial park. However, no studies were made on the subject prior to the selection of the park site. Therefore, the purposes of the study reported here are threefold: to characterize the spatial and seasonal variations in precipitation pH for Bahia Blanca, to examine the relationship between synoptic scale meteorology factors and rain pH, and to identify base-line rain pH characteristics before full-scale operations in the industrial park and thermoelectric plant.

†Contribution No. 138 from Instituto Argentino de Oceanografía.

 0013-936X/88/0922-0216$01.50/0 © 1988 American Chemical Society

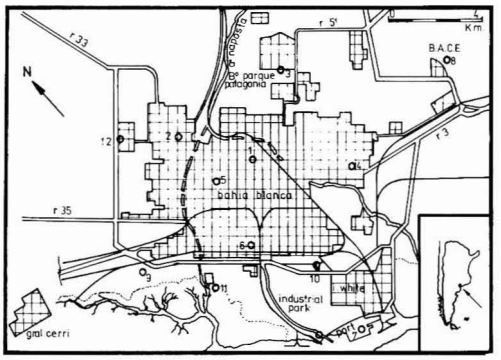


Figure 1. Sampling site locations for wet precipitation study.

Table I. Mean pH Values in Bahia Blanca (1984–1985)

station	mean pH	SD	no. of events	range
1	7.1	0.5	85	5.9–8.1
2	7.1	0.4	42	6.4–8.0
3	7.2	0.4	36	6.4–8.0
4	7.1	0.5	31	6.1–8.3
5	7.1	0.6	52	5.8–8.2
6	7.0	0.6	23	5.3–8.1
7	6.5	0.6	45	5.0–7.6
8	6.6	0.4	6	5.9–7.2
9	6.5	0.6	16	5.3–7.6
10	7.0	0.5	26	6.0–8.4
11	6.8	0.6	24	5.2–8.0
12	6.9	0.6	9	5.8–7.8

Experimental Methods

Rainwater was collected in clean, dried plastic buckets located about 2.5 m above the surface. The collectors were set up prior to the onset of a precipitation event, normally less than 2 h before the event began. Samples were removed immediately after each event and stored in inert-plastic, screw-capped bottles, which had been thoroughly cleaned and rinsed with twice-distilled water and then dried (*4*). All pH measurements were made immediately upon arrival at the laboratory. The time interval between sampling and analysis varied from 1 to 10 h. The weekend samples were analyzed on Monday. However, all samples were stored at 4 °C until they could be analyzed. The pH was determined in a pH meter Metron-Merisan E 488 with an E.A. 121 electrode. Standardization was made with certified buffer solutions of pH 4.0 and pH 8.0.

Data

During the period April 1984 to April 1985, samples were obtained from 85 rain events at 12 sites (Figure 1) distributed in and around Bahia Blanca. Only site 1 has the complete set of records (Table I). In the other stations, the observers were volunteers, and they were not always present at the site during the storm event. Besides the pH data, information about air mass trajectory, type of storm, and synoptic weather patterns were gathered from the National Meteorological Service station at Bahia Blanca Airport (site 8). Meteorological information was also obtained from a station located on the coast of the Bahia Blanca estuary (site 7).

Results and Discussion

The mean pH values and their standard deviations for the 12 stations are presented in Table I. Mean pH for individual sites ranged from 6.5 to 7.2. In all cases, the mean values show nearly neutral conditions. Differences among average pH values for the stations are not significant. However, the spatial distribution of pH isolines (Figure 2) shows a tongue of high-pH values that extends from the northeast into the city. Low pH values are found at the outskirts.

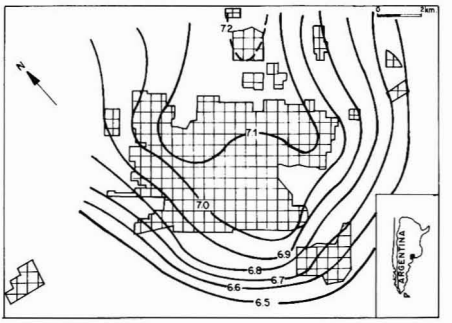


Figure 2. Spatial distribution of mean precipitation pH in Bahia Blanca (April 1984 to April 1985).

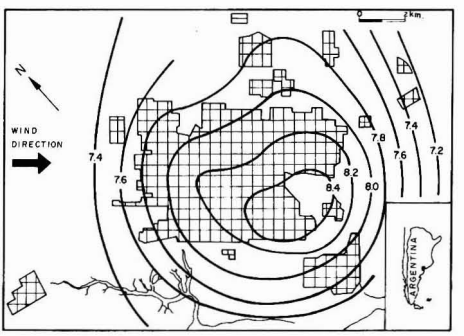


Figure 3. Spatial distribution of the maximum precipitation pH event (Nov 1, 1984).

Table II. Variation in Mean Precipitation pH in Station 1 Related to Air Mass Approach Direction

air mass direction	no. of events	mean pH	SD
S, SE, and E	26	6.8	0.4
W and SW	35	7.3	0.4
NW, N, and NE	24	7.2	0.5

The maximum values for each site are above 7.2 and in most cases are larger or equal to 8.0 (Table I), indicating the presence of alkaline precipitation. Analyses of individual events that produced large pH values show that this situation is normally associated with westerly winds (northwest, west, and southwest) (Table II). An analysis of variance for the groups in Table II resulted in significant differences among the means at $p < 0.001$.

The event of maximum pH for all the period was observed on November 1, 1984 (*5*). The spatial distribution of this episode (Figure 3) presents closed isolines with the maximum value (8.4) at the southeast sector of the city. The weather conditions that caused the rain were associated with a low-pressure center coming from the southwest, originating relatively strong winds (16–27 km/h) from the northwest. Before reaching the city, those winds travel over the "pampas" plain, whose soils are heavily affected by eolic erosion.

The pampas plain soils are mainly composed of sand, important amounts of $CaCO_3$ concretions ("tosca"), and little organic matter (*6*). Chemical analysis of samples

Table III. Comparison of Rainwater Cation Concentrations

cation	concn at Pasadena, CA, mg/L (*1*)	concn at Champaign, IL, mg/L (*8*)	concn at Bahia Blanca, mg/L (*7*)
Ca^{2+}	0.192	0.210	2.614
Mg^{2+}	0.080	0.029	0.479
K^{+}	0.082	0.019	0.750

taken by Balatti and Brevedan (*7*) during a 1-year period (1983, 107 events) at a station close to the study area and associated to typical pampas soils provides average concentrations of Ca^{2+}, Mg^{2+}, and K^{+}. These values are about 1 order of magnitude larger than that observed for acid rain (*1*, *8*) (Table III). Thus, the high values of pH observed for the area are most likely due to the carbonate-rich particulate matter transported by the wind. A similar behavior is mentioned in studies related to alkaline emissions to the atmosphere in the northeast U.S. (*9*).

The peak value close to downtown Bahia Blanca and the concentric distribution of the isolines may be produced by a city source of alkaline substances and/or geographical conditions. To our knowledge, there is no such source within the city; therefore, the first hypothesis may be neglected. The distribution of maximum values of pH closely resembles the mean pattern (Figure 2), since most events resulted in alkaline values associated to similar wind patterns. Figure 3 also presents a tongue coming from the northeast into the city. This characteristic distribution may be produced by the presence of a 76-m terrace that occupies the north, northeast, and east borders of the city (Figure 1). The terrace is constituted of sediments with extremely high concentrations of $CaCO_3$ in form of toscas. This material is rapidly eroded by the winds and transported in suspension over the city. The flank of the terrace enters in the city with a north–south strike following the valley of the Naposta Creek.

This geomorphological structure most likely explains the presence of the tongue because it may originate a secondary flow toward downtown. However, the downtown concentration may be due to the distribution of buildings in the city. Bahia Blanca, as typical of most Latin American cities, has its highest buildings in the center of the town. The effect of these buildings on the wind is to act as a barrier, either producing the drop of suspended substance or resulting in flow separation on their downstream side. If this occurs, alkaline material may be concentrated over the area shown as a maximum in Figure 3.

On the other hand, minimum pH values are in most cases above 5.6, which is considered as the normal pH of pure rainwater in equilibrium with atmospheric CO_2. Only stations 6, 7, 9, and 11 show minimum pH below 5.6 (Table I). Those four sites are located in the southern sector of the city, associated with the industrial park and the Bahia Blanca estuary.

Analysis of storm events that produced minimum values of pH for all stations indicates that the air masses approached the city from the southeastern quadrant (south, southeast, and east). In particular, the minimum pH distribution observed on July 11, 1984 (*5*), is presented in Figure 4. The event was originated by a typical storm that approached from the southeast into the area. The pH isolines are parallel to the wind direction and to the strike of the terrace. The lowest values are found close to the estuary, and they gradually increase toward the northeast.

In this case, two possible causes superimposed may have caused the slightly acidic levels in the rain. First of all, a maritime air mass advected over the continent may have carried in suspension Cl^{-} and Na^{+} ions injected to the

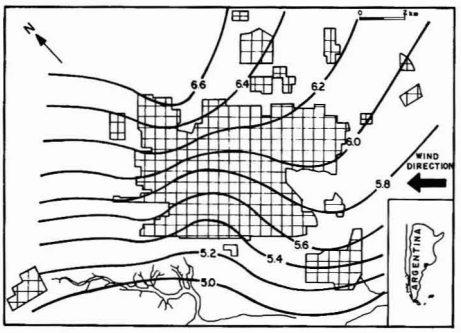


Figure 4. Spatial distribution of the minimum precipitation pH event (July 11, 1984).

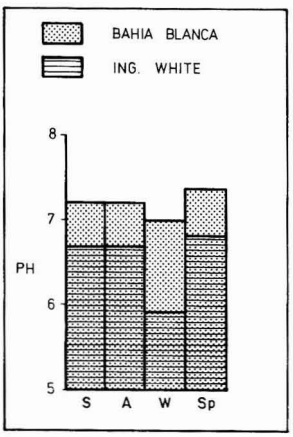


Figure 5. Average seasonal variation of precipitation pH in downtown Bahia Blanca (site 1) and Ingeniero White (site 7). S = summer; A = autumn; W = winter; Sp = spring.

atmosphere by "spray" processes. Although SO_4^{2-}, NO_3^{-}, and H^{+} ions are the major contributors to acid rain pH, Cl^{-} has an important responsibility and must also be considered (*10*). On the other hand, the predominant circulation may produce the dispersion of contaminants from the industrial park over the south and southwest sectors of the city.

The average seasonal variation for stations 1 and 7 are shown in Figure 5. Station 1 was selected because it has the complete record of events and it is localized in downtown Bahia Blanca. Station 7, adjacent to the harbor area and the industrial park, exhibits the lowest pH values in almost every event. In winter, both stations show the lowest values of pH, but at station 7 the differences are remarkable. About 56% of the precipitation events occurring during the winter season have approached from the southeastern sector. This evidence reinforces the idea that marine advection causes in part the reduction of precipitation pH in the area. However, the particular situation of station 7, which receives also low-precipitation pH even with continental air mass trajectories, may indicate an incipient focus of contamination next to Bahia Blanca.

Conclusions

The mean pH of rain falling on different sites in and around the Bahia Blanca area ranges from 6.5 to 7.2. Lowest pH values are measured during the winter season.

However, most stations reported during the 1-year study pH values in excess of 7.6, indicating alkaline conditions. We could not find a significant difference in the pH values depending on the type of storm event. But the values of pH are clearly related to the direction of the air mass approach. The highest values of pH are observed under the influence of continental air masses, which have traveled over the pampas soil, thus introducing large amounts of alkaline cations. The lowest pH values are obtained when marine advection introduces high concentrations of sea spray. Station 7, located close to the estuary and the industrial park, exhibits the largest influence of sea spray but also the presence of an incipient atmospheric contamination.

Acknowledgments

We are grateful to the volunteer observers that made possible this study. We also thank the two anonymous reviewers for the important comments that greatly improved this paper. M. Laura Rubio drew the figures.

Registry No. Ca, 7440-70-2; Mg, 7439-95-4; K, 7440-09-7.

Literature Cited

(1) Liljestrand, H. M.; Morgan, J. J. *Environ. Sci. Technol.* **1978**, *12*, 1271.
(2) Tafuri, V. *Meteorologica* **1977–1978**, *Viii–Ix*, 525.
(3) Lavado, R. S. *Rev. Fac. Agron., Univ. Buenos Aires* **1983**, *4(2)*, 135.
(4) Wolff, G. T.; Lioy, P. J.; Golub, H.; Hawkins, J. S. *Environ. Sci. Technol.* **1979**, *13(2)*, 209.
(5) Piccolo, M. C.; Varela, P. *Rev. Geofis.*, in press.
(6) Glave, A. *El Campo, Suplemento de La Nueva Provincia* **1985**, *346*, 6.
(7) Balatti, A.; Brevedan, R. Final Report, 1984; CONICET: Buenos Aires, Argentina, 1984.
(8) Stensland, G. J.; Semonin, R. G. *Bull. Am. Meteorol. Soc.* **1982**, *63*, 1277.
(9) Smil, V. *Power Engineering (Barrington, Ill.)* **1985**, *89(4)*, 59.
(10) Raynor, G. S.; Hayes, J. V. *Water, Air, Soil Pollut.* **1982**, *17*, 309.

Received for review November 4, 1986. Revised manuscript received June 18, 1987. Accepted September 17, 1987.

A Ferrous Cysteine Based Recyclable Process for the Combined Removal of NO_x and SO_2 from Flue Gas

David K. Liu, Lawrence P. Frick, and Shih-Ger Chang*

Applied Science Division, Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720

■ The use of a neutral or alkaline solution of ferrous cysteine for the removal of NO in wet flue gas cleanup systems is described. This system possesses several advantages over the conventional Fe^{2+}(EDTA)-type chelates. Ferrous cysteine can be oxidized by residual O_2 in flue gas to form inert ferric cysteine, in which rapid electron-transfer reaction occurs to regenerate Fe^{2+}. The oxidation product cystine can be conveniently converted back to cysteine by a simple and potentially cost-effective method using H_2S and SO_2, thus making possible the recycling of the reagents. The effects of pH, O_2, SO_2, and various additives on the absorption of NO by ferrous cysteine have also been examined.

Introduction

Several wet flue gas simultaneous desulfurization and denitrification processes using scrubbing liquors containing various ferrous chelates have been developed and patented in the last 15 years. These processes involve the addition of ferrous aminocarboxylate complexes such as Fe^{2+}-(EDTA) (EDTA ≡ ethylenediaminetetraacetate) and Fe^{2+}(NTA) (NTA ≡ nitrilotriacetate) to aqueous scrubbing liquors to enhance the absorption of NO, via the formation of ferrous nitrosyl complexes. The coordinated NO can then react with dissolved SO_2 and O_2 to produce N_2, N_2O, dithionate, sulfate, and various nitrogen–sulfur compounds (*1–5*). Some of the ferrous chelates are oxidized by residual O_2 in flue gas and by intermediates produced in the scrubbing system to form ferric chelates, which are inactive toward NO. Therefore, this type of process requires regeneration of scrubbing liquors by removing dithionate, sulfate, and N–S compounds from the solutions and reduction of ferric chelates back to ferrous chelates. The regeneration of scrubbing liquors and ferrous chelates associated with these Fe^{2+}(EDTA)- or Fe^{2+}(NTA)-based processes are very costly (*6*). Therefore, even though these wet processes are very efficient in SO_2 and NO_x removal (more than 85% for NO_x and 95% for SO_2), they have not yet reached the commercial stage because they are uncompetitive economically (*1*, *6*).

More recently, results from our laboratory and others have demonstrated that ferrous chelates of acetylacetonate (*2*), citrate (*2*, *7*), and aminopolyphosphonates (*8*) can also promote the absorption of NO from flue gas. Mechanistic studies of these systems revealed that a ferrous nitrosyl complex is formed in each case. The reaction of the coordinated NO with dissolved O_2 and SO_2 would result in the formation of undesirable products such as dithionate and N–S compounds, and the same drawbacks encountered in the Fe^{2+}(EDTA)-type processes are fully expected here.

We wish to report a recyclable process for the combined removal of NO_x and SO_2 from flue gas using ferrous cysteine and alkalies. Employment of these new additives creates different and simpler scrubber chemistry compared to existing processes using Fe^{2+}(EDTA)-type chelates. A previous report from our laboratory has addressed some of the chemistry involving ferrous cysteine and NO (*9*). This paper will give a full account of the scrubber chemistry involving ferrous cysteine, NO, O_2, and SO_2 and the regeneration of cysteine for recycling in the scrubber system.

Experimental Section

Materials. All reagents used in this study were of the purest grade available commercially and were used as received. These include L-(+)-cysteine·HCl·H_2O (MCB), $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ (Mallinckrodt), and $Na_2B_4O_7 \cdot 10H_2O$ (Baker) for the NO absorption experiments and ninhydrin

0013-936X/88/0922-0219$01.50/0 © 1988 American Chemical Society

(Pierce), octanoic acid (Spectrum), sodium citrate dihydrate (Baker), and sodium acetate trihydrate (Baker) for amino acid analysis. Nitric oxide was obtained from Matheson Co. as a mixture of 2.55% NO in N_2 with NO_2 impurity of less than 255 ppm.

NO Absorption Experiments. The absorption of NO by ferrous cysteine was studied with a bench-scale gas scrubber following a procedure described previously (*9*). In a typical experiment, 0.2 L of a solution containing 0.01 M $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$, 0.04 M cysteine·HCl·$H_2O$, and 0.18 M $Na_2B_4O_7 \cdot 10H_2O$ as buffer was placed in a Pyrex reaction column (50-mm i.d. × 210 mm). The pH of the solution was adjusted to the desired value by addition of 0.1 M NaOH or concentrated H_2SO_4, and the reaction temperature of the solution was maintained at 55 °C. The experiment was performed by bubbling a mixture of 2.55% NO in N_2, pure N_2, and O_2 through the ferrous cysteine solution at a flow rate of 0.65–0.80 L/min. The NO concentration in the outlet gas was monitored by a Thermoelectron Model 14A chemiluminescent NO_x analyzer.

Identification of Reaction Products. The identification of cysteine derivatives after the absorption of NO by ferrous cysteine at pH ~10 was accomplished by extraction of the final brown slurry (~0.1 L) with 3.0 L of dilute NaOH solution (pH 11), followed by amino acid analysis of the light yellow filtrate. A Dionex 2010i ion chromotrograph with a conductivity detector was used to determine $[NO_2^-]$ and $[NO_3^-]$. Determination of iron content was achieved by acidifying the slurry to pH 2.0, followed by filtration to obtain a dark green solution. The off-white residue was washed with more diluted H_2SO_4 (pH 2) and finally with H_2O. The iron content of the combined filtrate was determined by the 1,10-phenanthroline method (*10*). The off-white solid collected can then be suspended in a pH 10.0 borate buffer and treated with $H_2S/SO_2/OH^-$ as described below to recover cysteine for recycling.

Regeneration of Cysteine. A total of 0.2 L of a cystine solution (0.04 M) buffered with sodium borate (0.05 M Na^+) at pH 10.0 was allowed to equilibrate at 60 °C. H_2S and SO_2 (6.11% in N_2) were bubbled through the cystine solution for 20 min at flow rates of 0.01 and 0.9 L/min, respectively. Aliquots of the reaction mixture were taken at designated time intervals and monitored by amino acid analysis. The amino acid analyzer used was built in-house, and the detailed procedure has been described previously (*11*). Basically, cystine, cysteine, *S*-thiocysteine, and cysteinesulfonate were separated by cation-exchange chromatography and were detected by quantitative photometric ninhydrin method. After the reaction had reached equilibrium, the solution was neutralized to pH ~7 and tested for HS^- by treatment with Fe^{2+}.

Results and Discussion

The coordination chemistry of ferrous cysteine has been the subject of many investigations (*12–16*). It is generally agreed that in weakly acidic solution a 1:1 complex is formed, whereas as a 1:2 complex is the predominant species in alkaline medium (*12–14*). Spectroscopic studies (*13, 14*) have indicated that cysteine (CySH) is bound to iron through sulfur, nitrogen, and oxygen in the 1:1 complex while behaving as a bidentate S,N ligand in the 1:2 complex. Ferrous cysteine is easily oxidized in air, via the formation of a short-lived violet intermediate (*12*), presumably a ferric cysteine complex. Rapid intramolecular electron transfer from the coordinated cysteine to Fe^{3+} results in the regeneration of Fe^{2+} and the formation of cystine (CySSCy) (*17, 18*). Another advantage of the ferrous cysteine system is that the formation of dithionate from the reaction between Fe^{3+} and HSO_3^- can be prevented. The reaction of ferrous cysteine with O_2 is summarized in eq 1. It is the ability of CySH to reduce Fe^{3+}

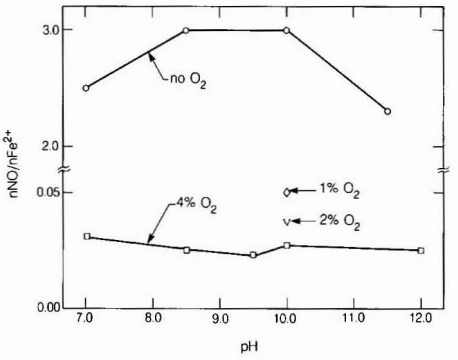


Figure 1. NO absorption capacity of ferrous cysteine as a function of pH. Reaction conditions were $[Fe^{2+}] = 0.01$ M, [CySH] = 0.04 M, $[B_4O_7^{2-}] = 0.09$ M, $P_{NO} = 500$ ppm, and $T = 55$ °C.

$$Fe^{2+}(CyS^-)_2 \xrightarrow[O_2]{+CyS^-} Fe^{3+}(CyS^-)_3 \longrightarrow Fe^{2+}(CyS^-)_2(CyS\bullet) \quad (1)$$

$$-\tfrac{1}{2}CySSCy$$

back to Fe^{2+} that first led us to investigate the use of ferrous cysteine as an additive for NO removal.

The absorption of NO by an alkaline ferrous cysteine solution using a bench-scale gas scrubber has recently been demonstrated in our laboratory (*9*). Infrared spectroscopic and elemental analyses of the solid residue revealed that, if the reaction was carried out at pH ~7, part of the NO absorbed was bound to the ferrous chelate to form a dinitrosyl complex with the empirical formula [Fe(CyS-SCy)$(NO)_2$]. The coordinated NO could be released when the solid was subjected to heating (~155 °C) or placed under vacuum ($\leq 10^{-2}$ Torr). Gas-phase products were determined by mass spectral analysis to contain N_2 and N_2O. The latter could be produced from the reaction of NO with ferrous cysteine and/or the thermal decomposition of NO in the reaction chamber. However, the same reaction at pH ≥8 yielded no nitrosyl complex; most of the NO absorbed was reduced to N_2 (*9*).

Variables Controlling NO Absorption by Ferrous Cysteine. The important factors affecting the absorption of NO by ferrous cysteine are the pH of the solution, the amount of O_2 and SO_2 in flue gas, the ratio $[CySH]/[Fe^{2+}]$, and the presence of different additives in the scrubbing liquor. The effects of pH and O_2 on the NO absorption capacity of a ferrous cysteine solution are shown in Figure 1. In the absence of O_2, the number of moles of NO absorbed per mole of Fe^{2+}, $n\text{NO}/n\text{Fe}^{2+}$, reaches a maximum between pH 8 and pH 10 ($n\text{NO}/n\text{Fe}^{2+} = 3.0$) and drops off rapidly when the solution becomes either acidic (pH ≥6) or strongly alkaline (pH ≥12). When a gas mixture containing between 1 and 4% O_2 and 500 ppm NO (typical concentrations for these components in flue gas) was used, the amount of NO absorbed was reduced significantly compared to the cases with no O_2 present. The decrease in $n\text{NO}/n\text{Fe}^{2+}$ is attributed to the rapid oxidation of CySH to CySSCy by O_2, catalyzed by the Fe^{2+} in solution (*17, 18*).

The effects of several additives on the NO removal efficiency of ferrous cysteine were examined, and the results are summarized in Table I. Power plant flue gas typically contains several thousand ppm SO_2 in addition to NO and O_2. SO_2 is quite soluble in water and hydrolyzes to form

Table I. Effects of Various Additives on NO Absorption Capacity of Ferrous Cysteine[a]

additive	concn, M	nNO/nFe^{2+}	additive	concn, M	nNO/nFe^{2+}
none		0.023	$AlCl_3$	0.01	0.022
Na_2SO_3	0.05	0.040	imidazole	0.05	0.023
	0.10	0.050	penicillamine	0.01	0.031
	0.50	0.068		0.05	0.067
	1.00	0.062			
$Na_2S_2O_3$	0.05	0.030			
	1.00	0.080			

[a] The concentrations of Fe^{2+} and CySH were 0.01 and 0.04 M, respectively. The reaction was carried out at pH 9.5 (borate buffer) and 55 °C with a gas mixture of 500 ppm NO and 4% O_2, and the balance was N_2.

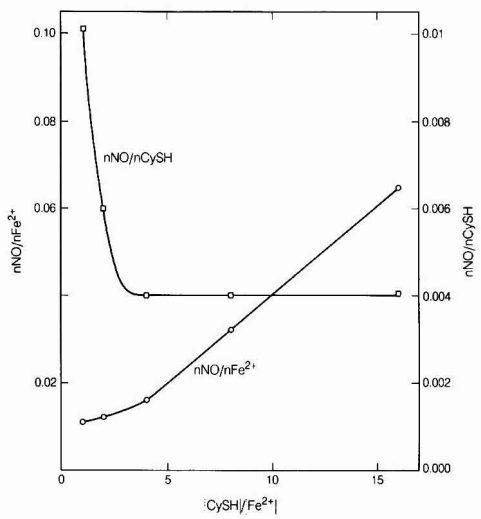


Figure 2. NO absorption capacity of ferrous cysteine as a function of [CySH]/[Fe^{2+}]. Reaction conditions were [Fe^{2+}] = 0.05 M, [$B_4O_7^{2-}$] = 0.18 M, P_{NO} = 500 ppm, P_{O_2} = 4%, pH 9.5, and T = 55 °C.

primarily SO_3^{2-} at pH >9. The effect of SO_2 on the NO absorption capacity can therefore be studied by the addition of SO_3^{2-} to the ferrous cysteine solution. Addition of SO_3^{2-} to the scrubbing solution increases nNO/nFe^{2+}, up to a SO_3^{2-} concentration of ~0.5 M. The SO_3^{2-} additive can improve the NO removal efficiency via two routes: (i) by its reaction with O_2 to form SO_4^{2-}, and (ii) by its reaction with CySSCy to form CySH and cysteinesulfonate (vide infra). High concentrations of $S_2O_3^{2-}$ also appear to enhance NO removal, whereas additives such as Al^{3+} and imidazole at the levels employed have little influence on NO absorption by ferrous cysteine. In the case of penicillamine, or β,β'-dimethylcysteine, the improvement can be attributed to the presence of Fe^{2+}(penicillamine)$_2$ and/or Fe^{2+}(penicillamine)(cysteine) in solution, in addition to Fe^{2+}(cysteine)$_2$.

As mentioned earlier, residual O_2 in flue gas can oxidize CySH to CySSCy rapidly in the presence of Fe^{2+} catalyst. Therefore, the use of excess CySH should improve the performance of ferrous cysteine. As shown in Figure 2, increasing [CySH] at a fixed [Fe^{2+}] increases nNO/nFe^{2+} from 0.01 at [CySH]/[Fe^{2+}] = 1 to 0.065 at [CySH]/[Fe^{2+}] = 16. However, the number of moles of NO absorbed per mole of CySH, nNO/nCySH, decreases from 0.01 at [CySH]/[Fe^{2+}] = 1 to 0.004 at [CySH]/[Fe^{2+}] >4.

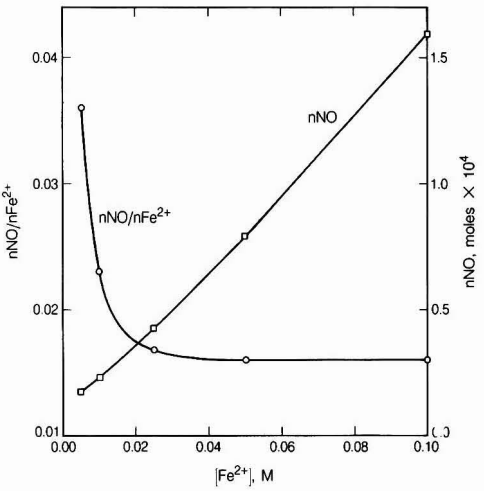


Figure 3. NO absorption capacity of ferrous cysteine as a function of [Fe^{2+}] and [CySH] at a fixed [CySH]/[Fe^{2+}] ratio of 4. Reaction conditions were [$B_4O_7^{2-}$] = 0.18 M, P_{NO} = 500 ppm, P_{O_2} = 4%, pH 9.5, and T = 55 °C.

Therefore, the exact ratio of CySH to Fe^{2+} to be used would depend on whether NO removal efficiency of the ferrous cysteine system is to be maximized with respect to Fe^{2+} or CySH. Finally, the effect of increasing both [Fe^{2+}] and [CySH] at a fixed [CySH]/[Fe^{2+}] ratio is shown in Figure 3. When the concentrations of Fe^{2+} and CySH were increased from 5×10^{-3} and 2×10^{-2} M to 0.10 and 0.40 M, respectively, nNO/nFe^{2+} was lowered exponentially from 0.036 to 0.016. Therefore, it appears the efficiency of the ferrous cysteine system is higher at lower reactant concentrations. The reason for this behavior is unclear and will be the subject of further investigation.

NO removal efficiency of ferrous cysteine with respect to Fe^{2+} can be maximized by using a high nCySH/nFe^{2+} ratio and by the addition of SO_3^{2-} to the reaction mixture. For example, using a ferrous cysteine solution containing 0.1 M Fe^{2+}, 1.0 M CySH, and 1.0 M SO_3^{2-} at pH 8.0, we have obtained nNO/nFe^{2+} = 0.18. On the contrary, the NO removal efficiency based on CySH can be optimized when a low nCySH/nFe^{2+} ratio is employed. Thus a value of nNO/nCySH = 0.04 was obtained when a ferrous cysteine solution containing 0.01 M Fe^{2+}, 0.01 M CySH, and 0.05 M SO_3^{2-} at pH 9.0 was used to absorb NO. As mentioned above, the limiting factor for the ferrous cysteine system appears to be the rate of oxidation of CySH to CySSCy by O_2 in the presence of Fe^{2+} catalyst (*17, 18*). Recent results in our laboratory have demonstrated that ferrous complexes of other SH-containing amino acids and peptides such as ferrous penicillamine and ferrous glutathione are more resistant to O_2 and are substantially more efficient than ferrous cysteine in the absorption of NO from simulated flue gas mixture containing both NO and O_2 (*19*).

Regeneration of CySH from CySSCy and $CySSO_3^-$. The solid residue collected after the absorption of NO by ferrous cysteine in the absence of O_2 has been shown to be comprised of iron(II)/(III) hydroxide, cystine, and under certain conditions, a dinitrosyl complex with the empirical formula [Fe(CySSCy)$(NO)_2$] (*9*). In this study, where between 1 and 4% O_2 was present, we could not detect any metal nitrosyl complex in the solid residue by infrared spectroscopy. Since only small amounts (6 ± 2% of the NO absorbed) of NO_2^- and no NO_3^- were detected

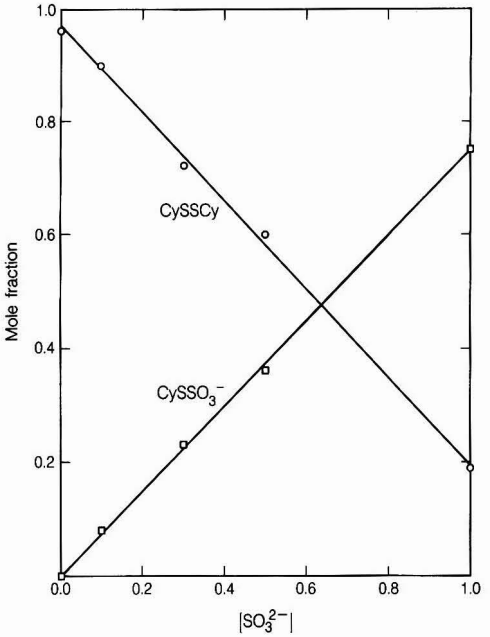


Figure 4. Recovery of CySH as CySSCy and $CySSO_3^-$ at various $[SO_3^{2-}]$. Reaction conditions were $[Fe^{2+}]$ = 0.1 M, [CySH] = 1.0 M, $[B_4O_7^{2-}]$ = 0.2 M, P_{NO} = 500 ppm, P_{O_2} = 4%, pH 9.0, and T = 55 °C.

Table II. Regeneration of CySH from CySSCy under Various Conditions

method[a]	pH	T, °C	CySH, %	$CySSO_3^-$, %	CySSCy, %
I	10	60	59	17	15
II	10	60	36	3	58
III	10	60	90	5	4
IVa	10	60	85	8	6
IVb	10	80	84	10	6
IVc	12	60	84	6	5

[a] See text for description of experimental methods.

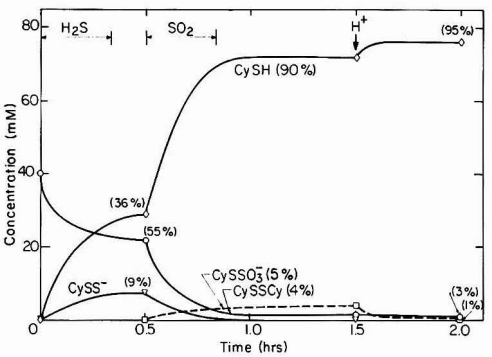


Figure 5. Concentration–time profile of the regeneration of CySH from CySSCy at pH 10 and 60 °C by the reaction of CySSCy first with H_2S and then with SO_2, followed by neutralization to pH ~7.

in the liquid phase by ion chromatography, most of the NO absorbed was presumably reduced to N_2/N_2O. As a result, minimal formation of nitrogen–sulfur compounds is expected from the reaction between NO_2^- and HSO_3^- in the ferrous cysteine system. On the other hand, >90% of the iron was recovered as insoluble hydroxides in the solid residue, of which ~80% was Fe(II) and ~20% was Fe(III) as determined by the 1,10-phenanthroline method (*10*). The mass balance for CySH in the reaction between ferrous cysteine and NO/O_2 was also studied. In the absence of SO_3^{2-}, all of the CySH was recovered as CySSCy, as shown in Figure 4. However, if SO_3^{2-} was present in the scrubbing solution, cysteinesulfonate ($CySSO_3^-$) was also formed via the reaction of CySSCy with SO_3^{2-} (*20*), as shown in eq 2. It appears that the decrease in [CySSCy] and the increase in $[CySSO_3^-]$ are linear with respect to increasing $[SO_3^{2-}]$. In each case, 96 ± 2% of the CySH can be recovered as a combination of CySSCy and $CySSO_3^-$. It is clear from Figure 4 that unless high concentrations (>0.5 M) of SO_3^{2-} are present in the ferrous cysteine system, most of the CySH would end up as CySSCy. It is therefore necessary to convert CySSCy back to CySH in order to make this process recyclable and cost effective. Existing methods for converting CySSCy to CySH include electroreduction and chemical (e.g., Na/NH_3 and Zn/HCl) reductions. However, these methods require the use of electric energy or expensive reagents and are not suitable for large-scale applications in flue gas cleanup systems. The recovery of CySH from $CySSO_3^-$ can in principle be accomplished by the acid hydrolysis of $CySSO_3^-$ (eq 3).

$$CyS^- + SO_3^{2-} \rightleftarrows CyS^- + CySSO_3^- \quad (2)$$

$$CySSO_3^- + H_2O \overset{H^+}{\rightleftharpoons} CySH + H_2SO_4 \quad (3)$$

However, this reaction proceeds extremely slowly, even upon boiling in concentrated HCl and the yield of CySH is low (*21*). In our search for a simple and potentially cost-effective method for the regeneration of CySH from CySSCy and $CySSO_3^-$, we have discovered that CySH can be recovered from $CySSCy/CySSO_3^-$ in high yield, with H_2S (or sulfide/hydrogen sulfide ion) and SO_2 (or sulfite/bisulfite).

The regeneration of CySH from CySSCy was carried out between pH 10 and pH 12 because of (i) the low solubility of CySSCy in the pH range 2–8 (*22*) and (ii) the lack of reaction between HS^- and SO_3^{2-} at pH ≥10 as reported by Heunisch (*23*). However, experiments in our laboratory indicated that HS^- and SO_3^{2-} do react slowly to form $S_2O_3^{2-}$ at pH 10.0 and 60 °C. The results for the regeneration of CySH from CySSCy are presented in Table II. When a 0.01 M CySSCy solution at pH 10.0 and 60 °C was allowed to react first with 2.0 equiv of $Na_2S{\cdot}9H_2O$, followed by 3.0 equiv of Na_2SO_3 (method I), the reaction reached equilibrium in ~30 min with 59% CySH, 17% $CySSO_3^-$, and 15% CySSCy in the reaction mixture. No HS^- remained in the reaction mixture after neutralization to pH 7, as evidenced by the absence of FeS precipitate upon addition of the reaction mixture to a Fe^{2+} solution. This is attributed to the reaction of HS^- and HSO_3^- to form $S_2O_3^{2-}$ (*23*). The simultaneous addition of $Na_2S{\cdot}9H_2O$ and Na_2SO_3 to CySSCy solutions under the same conditions (method II) yielded less CySH (36%), presumably due to the slow reaction between HS^- and SO_3^{2-} at pH 10.0 and 60 °C.

The best result was obtained from the reaction of CySSCy with H_2S and then SO_2 at pH 10.0 and 60 °C (method III). The concentrations of HS^- and SO_3^{2-} resulting from the hydrolysis of dissolved H_2S and SO_2 were estimated to be 0.04 and 0.22 M, respectively. In this case, a 90% yield of CySH was attained together with small amounts of $CySSO_3^-$ and unreacted CySSCy. The yield of CySH was increased to 95% upon neutralization of the reaction

mixture to pH ~7. The concentration–time profile of this reaction is shown in Figure 5. When H_2S and SO_2 were applied simultaneously under the same conditions (method IVa), CySH was obtained in 85% yield. Again, the slightly lower yield could be attributed to the slow reaction between HS^- and SO_3^{2-} at 60 °C.

The effects of temperature and pH on this CySH regeneration were examined. Raising the reaction temperature to 80 °C did not affect the yield of CySH (method IVb), although the equilibrium was achieved in ~15 min, as opposed to ~30 min when the reaction was carried out at 60 °C. Finally, increasing the pH to 12.0 also had no effect on the CySH yield (method IVc). The mechanism for the conversion of CySSCy to CySH is summarized as

$$CySSCy + HS^- \rightleftarrows CySH + CySS^- \quad (4)$$

$$CySS^- + HS^- \rightleftarrows CySH + S_2^{2-} \quad (5)$$

$$CySS^- + SO_3^{2-} \rightleftarrows CyS^- + S_2O_3^{2-} \quad (6)$$

$$CySSCy + SO_3^{2-} \rightleftarrows CyS^- + CySSO_3^- \quad (7)$$

$$CySSO_3^- + HS^- \rightleftarrows CySH + S_2O_3^{2-} \quad (8)$$

where $CySS^-$ represent *S*-thiocysteine. Equations 4 and 5 were first reported by Rao and Gorin (*24*), and we have recently completed a kinetic study of these reactions (*11*). The reaction between CySSCy and SO_3^{2-} (eq 2 and 7) is also well established (*20*). Preliminary experiments in our laboratory have provided evidence for eq 6 and 8, the latter of which may provide an efficient method for converting $CySSO_3^-$ to CySH. Therefore, the conversion of both CySSCy and $CySSO_3^-$ to CySH is possible according to the above procedure.

The overall reaction for the regeneration of CySH from CySSCy using HS^- and SO_3^{2-} can be expressed as

$$CySSCy + HS^- + SO_3^{2-} \rightleftarrows 2CyS^- + S_2O_3^{2-} + H^+ \quad (9)$$

In an acidic medium, thiosulfate decomposes to form HSO_3^- (and/or SO_2) and colloidal sulfur, as shown in eq 10. By adding eq 9 and 10 and taking into account the

$$S_2O_3^{2-} + H^+ \rightarrow HSO_3^- + S\downarrow \quad (10)$$

equilibrium between SO_3^{2-} and HSO_3^-, we obtain the net equation

$$CySSCy + HS^- \rightleftarrows 2CyS^- + S\downarrow + H^+ \quad (11)$$

Thus the only reagent consumed in the conversion of CySSCy to CySH is HS^-, and elemental sulfur is formed as a product. The latter can be converted back to H_2S by reaction with H_2, which can be derived from CO and H_2O (water–gas shift reaction) (*25*). Therefore, in essence, the reducing agent consumed in this CySH regeneration scheme is CO, which can be easily obtained from the incomplete combustion of coal. It can be inferred from eq 11 that 1 mol of CO is required for the regeneration of 2 mol of cysteine.

Conclusions

We have demonstrated that ferrous cysteine can remove NO in the presence of O_2 and SO_3^{2-} (from SO_2 dissolution). This system possesses several advantages over the conventional Fe^{2+}(EDTA)-type chelates, including the suppression of dithionate and nitrogen–sulfur compound formations. Cysteine is also capable of rapidly reducing Fe^{3+} to Fe^{2+}, thus prolonging the NO absorption process. The oxidation product cystine can be conveniently converted back to cysteine by $H_2S/SO_2/OH^-$, making possible the recycling of the reagents. Finally, the NO absorption capacity of ferrous cysteine is slightly higher than that of Fe^{2+}(EDTA), in both the absence or presence of O_2 (*9*). Experiments are underway in our laboratory to study the use of ferrous chelates of cysteine derivatives as well as other thiol-containing ligands for the combined removal of NO_x and SO_2 from flue gas.

Acknowledgments

We appreciate the support and encouragement of Charles Drummond, Gilbert McGurl, and Michael Perlsweig.

Registry No. SO_2, 7446-09-5; Na_2SO_3, 7757-83-7; $Na_2S_2O_3$, 7772-98-7; $AlCl_3$, 7446-70-0; NO_x, 11104-93-1; imidazole, 288-32-4; penicillamine, 52-67-5; $Fe^{2+}(CyS^-)_2$, 84214-30-2.

Literature Cited

(1) Chang, S. G. In *Fossil Fuels Utilization: Environmental Concerns*; Markuszewski, R., Blaustein, B. D., Eds.; ACS Symposium Series 319; American Chemical Society: Washington, DC, 1986; pp 159–175.
(2) Chang, S. G.; Littlejohn, D.; Lynn, S. *Environ. Sci. Technol.* **1983**, *17*, 649.
(3) Chang, S. G.; Littlejohn, D.; Lin, N. H. In *Flue Gas Desulfurization*; Hudson, J. L., Rochelle, G. T., Eds.; ACS Symposium Series 188; American Chemical Society: Washington, DC, 1982; pp 127–152.
(4) Littlejohn, D.; Chang, S. G. *Environ. Sci. Technol.* **1984**, *18*, 305.
(5) Littlejohn, D.; Chang, S. G. *Anal. Chem.* **1986**, *58*, 158.
(6) Maxwell, J. D.; Tarkington, T. W.; Burnett, T. A. "Preliminary Economic Analysis of NO_x Flue Gas Treatment Processes Using TVA and EPRI Economic Premises"; EPRI Report CS-2075; Electric Power Research Institute, Inc.: Palo Alto, CA, Dec 1981.
(7) Griffiths, E. A.; Chang, S. G. *Ind. Eng. Chem. Fundam.* **1986**, *25*, 356.
(8) Zhuang, Y.; Deng, Y. *Acta Sci. Circumstantiae* **1985**, *5*, 347.
(9) Tu, M. D.; Chang, S. G. *AIChE Environ. Progr.* **1987**, *6*, 51.
(10) Harvey, A. E., Jr.; Smart, J. A.; Amis, E. S. *Anal. Chem.* **1955**, *27*, 26.
(11) Liu, D. K.; Chang, S. G. *Can. J. Chem.* **1987**, *65*, 770.
(12) Schubert, M. *J. Am. Chem. Soc.* **1932**, *54*, 4077.
(13) Tanaka, N.; Kolthoff, L. M.; Stricks, W. *J. Am. Chem. Soc.* **1955**, *77*, 1996.
(14) Gilmour, A. D.; McAuley, A. *J. Chem. Soc. A* **1970**, 1006.
(15) Murray, K. S.; Newman, P. J. *Aust. J. Chem.* **1975**, *28*, 773.
(16) Panossian, R.; Terzian, G.; Guiliano, M. *Spectrosc. Lett.* **1979**, *12*, 715.
(17) Mathus, H. B.; Gupta, M. P.; Kavedia, C. V. *Indian J. Chem.* **1966**, *4*, 337.
(18) Taylor, J. E.; Yan, J. F.; Wang, J.-L. *J. Am. Chem. Soc.* **1966**, *88*, 1663.
(19) Chang, S. G.; Liu, D. K.; Littlejohn, D. Presented at the AIChE National Meeting, Houston, TX, March 1987; paper 76b.
(20) Stricks, W.; Kolthoff, I. M. *J. Am. Chem. Soc.* **1951**, *73*, 4569.
(21) Clarke, H. T. *J. Biol. Chem.* **1932**, *97*, 233.
(22) Sano, K. *Biochem. Z.* **1926**, *168*, 14.
(23) Heunisch, G. W. *Inorg. Chem.* **1977**, *16*, 1411.
(24) Rao, G. S.; Gorin, G. *J. Org. Chem.* **1959**, *24*, 749.
(25) *Riegels Handbook of Industrial Chemistry*, 7th ed.; Kent, J. A., Ed.; Van Nostrand Reinhold: New York, 1974; p 87.

Received for review February 2, 1987. Accepted August 7, 1987. This work was supported by the Assistant Secretary for Fossil Energy, U.S. Department of Energy, under Contract DE-AC03-76SF00098 through the Pittsburgh Energy Technology Center, Pittsburgh, PA.

Environ. Sci. Technol. 1988, 22, 224–228

Isolation and Detection of Genotoxic Components in a Black River Sediment

W. Raymond West, Philip A. Smith, Gary M. Booth,* and Milton L. Lee*

Departments of Chemistry and Zoology, Brigham Young University, Provo, Utah 84602

■ Unusually high levels of epidermal and liver cancer have been observed in brown bullhead catfish taken from a river in an industrialized area in Ohio. Four chemical class fractions isolated from a sediment extract in this area were analyzed by capillary column gas chromatography–mass spectrometry and tested for mutagenicity in the Ames assay and for induction of unscheduled DNA synthesis (UDS) in primary rat hepatocytes. Significant UDS was detected in two of these fractions, which contained high levels of polycyclic aromatic compounds (PAC). Furthermore, all of the weight-normalized UDS of the total crude extract was found to be in these two fractions. These results indicate that the PAC-containing fractions account for most of the genotoxic activity observed in this polluted river sediment extract. Furthermore, our data indicate that UDS was a more sensitive indicator of genotoxicity than the Ames assay.

Introduction

The presence of polycyclic aromatic compounds (PAC) in aquatic sediments presents a health hazard not only to aquatic organisms but to other life that are eventually exposed to these compounds. These compounds, which originate from incomplete combustion of organic matter, may accumulate in tissues, their metabolites may bind to DNA, and they may ultimately cause mutations and/or cancer.

Chemical class fractions of PAC-contaminated sediments can be evaluated by relevant bioassays to determine the contribution of PAC to the genotoxicity of the total crude extract. Such analyses have been applied previously to coal-derived materials (*1–3*). These procedures are also applicable to PAC fractions isolated from environmental samples, such as river sediments.

The observation of tumors in bottom-feeding fish is a good indicator of the presence of environmental carcinogens in the sediment (*4*). In several species of fish at a variety of locations, cancer has been associated with PAC pollution of the sediment (*4, 5*). One study in particular (*6*) reported a high incidence (33%) of liver tumors for brown bullhead catfish 3 years and older taken from the Black River. Recently, it was concluded by microscopy of liver sections that 84% of these fish had precursor lesions (*7*). These fish were caught in a heavily industralized area near Lorain, OH, where the principal pollution source was a coking plant used for the production of steel. No tumors were found in the same species of fish taken from nonpolluted waters. In the laboratory, hyperplasia and neoplasia have been induced in brown bullhead catfish painted weekly with a 5% solution of a PAC-containing extract from a Buffalo River sediment (*8, 9*).

Observations in our laboratory using scanning electron microscopy have shown that significant pathology of the liver and gill results when young trout and catfish are exposed to PAC-containing extracts from a Black River, OH, sediment (*10, 11*). Although not entirely conclusive, these studies suggest that PAC of complex organic extracts of polluted river sediments may participate in causing chemically induced neoplasms in fish. High levels of polycyclic aromatic hydrocarbons (PAH), sulfur heterocycles, and nitrogen heterocycles have been found in the sediment where the fish were caught (*12, 13*). Several catfish samples were also found to contain high levels of PAC (*6, 13, 14*); however, this was not the case for a larger sample size (*12*). Significant levels of unscheduled DNA synthesis (UDS) were observed in rat hepatocytes exposed to PAC-containing fractions of the sediment extract (*12*).

The objective of this paper was to apply analytical and short-term biological testing to verify the genotoxicity of these fractions and to show that the other chemical class fractions were not genotoxic. This was done by testing the crude sediment extract and four chemical class fractions for mutagenicity in the Ames assay and for induction of UDS in primary rat hepatocytes.

Experimental Section

Sediment Analysis. Sediment from the Black River (near Lorain, OH) was collected near the outfall of a coking plant associated with a steel production facility. The methods of extraction, fractionation, and analysis of the sediment have been reported in detail previously (*12*). Briefly, the dried sediment was ground to a powder and extracted with benzene/methanol (3:2) and then with methylene chloride. About 6 g of crude extract was adsorbed onto 100 g of neutral alumina, which was added to the top of 150 g of neutral alumina packed in a 5 cm i.d. glass column. Four chemical class fractions were obtained by eluting sequentially with 300 mL of *n*-hexane (A1), 1300 mL of benzene (A2), 1600 mL of chloroform (A3), and 1000 mL of methanol (A4). This is an adaptation of the fractionation scheme developed for isolating PAC in synthetic fuels by Later et al. (*15*). In that work, aliphatic hydrocarbons, PAH and sulfur heterocycles, nitrogen heterocycles, and hydroxylated PAH eluted in the A1–A4 fractions, respectively. After fractionation, each fraction was weighed, and appropriate portions of each were recombined to obtain a reconstituted crude. In addition, portions of fractions A2 and A3 were recombined in their proper ratio.

Chemical analysis of the four alumina fractions was performed by gas chromatography and gas chromatography–mass spectrometry (GC–MS). The gas chromatographic column was a 22 m × 0.2 mm i.d. fused silica capillary coated with SE-54. The chromatographic oven was held at 50 °C for 2 min and then programmed to 290 °C at 4 deg min^{-1}. The carrier gas was hydrogen at a linear velocity of 71 cm s^{-1}. Fraction A3 was also analyzed with nitrogen-selective thermionic detection. The same column was used except that helium was the carrier gas at 37 cm s^{-1}. GC–MS was accomplished by use of a fused silica column (15 m × 0.3 mm i.d.) with helium carrier gas. PAC identifications were verified by comparison of mass spectra and retention indexes of mixture components with those of authentic standards. The concentrations of selected components were determined by GC peak area measurements.

Genotoxicity Testing. The crude extract, each of the four alumina fractions, and the two recombined fractions were evaluated for genotoxicity by the Ames assay with metabolic activation and by unscheduled DNA synthesis in rat hepatocytes. Stock solutions of the test mixtures were prepared by dissolving each in dimethyl sulfoxide

 0013-936X/88/0922-0224$01.50/0 © 1988 American Chemical Society

(DMSO) at a concentration of 10 mg mL^{-1}. The Ames assay was performed as described by Ames et al. (*16*) with some modifications: instead of 30 mL of medium per dish, 20 mL were used; instead of 2 mL of top agar, 4 mL were used. These modifications seem to give a more even distribution of the top agar on the plates. The tester strain *Salmonella typhimurium* TA98 was provided by Dr. Bruce Ames, Berkeley, CA. Only TA98 was used because we have demonstrated previously (*17*) that TA98 generally responds most favorably to PAC compared to other *Salmonella* strains. Aroclor 1254 induced S9 rat liver homogenate (Litton Bionetics, Kensington, MD) was used for all tests at 0.04 mL of S9 per mL of S9 buffer. The mixtures described above were tested at concentrations between 1.0 and 100.0 μg $plate^{-1}$. Dose levels up to 100 $\mu g/plate^{-1}$ seem to be adequate in determining genotoxicity since PAC above 10 μg $plate^{-1}$ were often toxic. A positive control, 2-acetamidofluorene (2-AAF), and a solvent control were included. The number of revertants per plate was determined by direct counting. Correlation coefficients were determined on the linear portion of each curve because of the inherent toxicity of PAC complex mixtures.

UDS was measured in primary hepatocytes of male Fisher-344 rats (Charles River Breeding Laboratories, Inc., Wilmington, MA) that were 7–9 weeks old and weighed 170–190 g. Animals were housed in stainless steel hanging cages and given Rodent Blox (Wayne Research Animal Diets, Chicago, IL) and water ad libitum in a constant photoperiod of alternating 12-h periods of light and darkness. The liver cultures were obtained as described by Williams (*18*). This included a two-step liver perfusion with 0.5 M ethylene glycol bis(β-aminoethyl ether)-*N*,*N*,*N*′,*N*′-tetraacetic acid (EGTA) in Hank's balanced salt solution followed by perfusion with 100 units mL^{-1} of collagenase (type I, Sigma Chemical Co., St. Louis, MO) in Williams' medium E (Flow Laboratories, Inc., McLean, VA). The liver cells were isolated, their viability was determined by trypan blue exclusion, and 4×10^5 hepatocytes were seeded into 4 mL of Williams' medium E supplemented with fetal bovine serum (10%). After a 90-min attachment period, the cell cultures were washed and incubated for 18 h in 2 mL of Williams' medium E containing 10 μCi mL^{-1} of [^{3}H]thymidine (New England Nuclear, Boston, MA) and the test mixture. After incubation, the cells were washed, fixed, and prepared for autoradiography. Each culture was dipped in Kodak NTB-2 emulsion, which was previously diluted 1:1 with water, dried, and placed in a light tight box with desiccant for 10 days at −15 °C. After exposure, the emulsion was developed in D-19 developer, fixed, and washed. Finally, the cells were stained with methyl green pyronin Y for 25 s. The highest concentration of DMSO in the cell media was 1%. Negative solvent and media controls were included, as well as a positive control dimethylnitrosamine (DMN). Thirty cells per slide and three slides per concentration were scored for UDS by automatic grain counting as described by Mirsalis et al. (*19*). The number of net grains (NG) was determined by counting the silver grains over the nucleus minus the highest of two nuclear sized areas over the cytoplasm. A cell with more than 5 NG was considered in repair.

Results and Discussion

The crude extract of the Black River sediment was found to be 1.35% by weight of the dried sediment. Table I summarizes the weight distribution of the extract in the four fractions obtained from the alumina column. The Al fraction was the largest fraction by weight, and it consisted of a complex mixture of aliphatic hydrocarbons with about

Table I. Weight Percent Distribution of Organic Compounds Extracted from a Black River Sediment and Fractionated into Chemical Classes by Neutral Alumina Adsorption Chromatography

	weight percent	
fractions	original extract	dry sediment
A1	35.8	0.50
A2	31.1	0.44
A3	19.9	0.28
A4	9.5	0.13
total	96.3	1.35

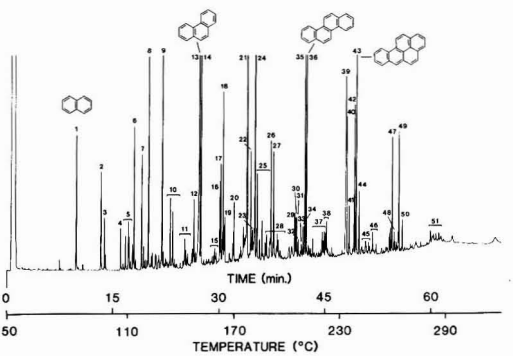


Figure 1. Capillary column gas chromatogram of the polycyclic aromatic hydrocarbon fraction of a Black River sediment extract. See text for chromatographic conditions.

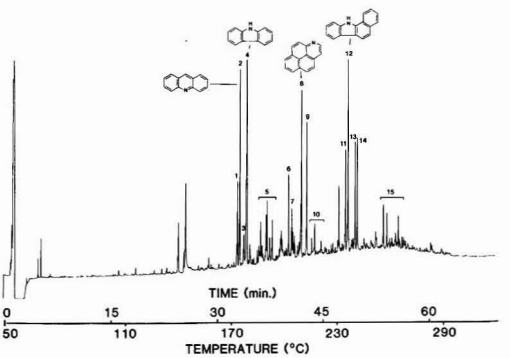


Figure 2. Capillary column gas chromatogram of the nitrogen heterocycle fraction of a Black River sediment extract with nitrogen-selective thermionic detection. See text for chromatographic conditions.

19% elemental sulfur, as determined by the method of Blumer (*20*). As reported previously (*12*), the A2 fraction of the Black River sediment extract contained a complex mixture of PAH and sulfur heterocycles. The gas chromatographic analysis of this sample is shown in Figure 1. This fraction contained PAH ranging from naphthalene to dibenzopyrene, and also contained three-, four-, and five-ring sulfur heterocycles. The concentrations of individual PAH reached as high as 792 μg (g of dry sediment)$^{-1}$ (phenanthrene). Table II lists the concentrations of compounds as determined by gas chromatography. Figure 1 and Table II show that essentially all of the components of fraction A2 are PAH or sulfur-containing PAH.

The A3 fraction contained a number of secondary and tertiary nitrogen heterocycles containing up to five rings, as well as a large amount of non-PAC material that eluted

Table II. Concentrations of Polycyclic Aromatic Compounds in Fraction A2 Isolated from a Black River Sediment

peak no.[a]	compound	% of A2	% of total extract
1	naphthalene	1.3	0.39
2	2-methylnaphthalene	1.1	0.33
3	3-methylnaphthalene	0.55	0.17
4	biphenyl	0.46	0.14
5	C_2 naphthalene	1.9	0.58
6	acenaphthylene	1.5	0.46
7	acenaphthene	1.3	0.40
8	dibenzofuran	2.3	0.72
9	fluorene	4.2	1.31
10	C_1 dibenzofuran	1.9	0.60
11	C_1 fluorene	1.2	0.38
12	dibenzothiophene	0.84	0.26
13	phenanthrene	18.0	5.60
14	anthracene	3.0	0.92
15	C_1 dibenzothiophene	0.43	0.13
16	3-methylphenanthrene	0.88	0.27
17	2-methylphenanthrene	1.0	0.32
18	4*H*-cyclopenta[*def*]phenanthrene	1.8	0.56
19	1-methylphenanthrene	0.53	0.16
20	2-phenylnaphthalene	0.68	0.21
21	fluoranthene	11.4	3.55
22	acephenanthrylene	1.1	0.33
23	phenanthro[4,5-*bcd*]thiophene	0.31	0.10
24	pyrene	7.7	2.39
25	MW 218	1.8	0.54
26	benzo[*a*]fluorene	1.3	0.39
27	benzo[*b*]fluorene	1.7	0.53
28	C_1 fluoranthene, C_1 acephenanthrylene, C_1 pyrene	1.2	0.37
29	benzo[*b*]naphtho[2,1-*d*]thiophene	0.51	0.16
30	benzo[*ghi*]fluoranthene	0.43	0.13
31	benzo[*c*]phenanthrene	0.46	0.14
32	benzo[*b*]naphtho[1,2-*d*]thiophene	0.24	0.07
33	benzo[*b*]naphtho[2,3-*d*]thiophene	0.10	0.03
34	cyclopenta[*cd*]pyrene	0.31	0.10
35	benz[*a*]anthracene	3.0	0.92
36	chrysene, triphenylene	3.0	0.92
37	C_1 benz[*a*]anthracene, C_1 chrysene, C_1 triphenylene	1.3	0.39
38	MW 240	0.77	0.24
39	benzo[*b*]fluoranthene, benzo[*j*]fluoranthene	3.2	0.99
40	benzo[*k*]fluoranthene	1.2	0.36
41	MW 252	0.44	0.14
42	benzo[*e*]pyrene	1.6	0.50
43	benzo[*a*]pyrene	3.0	0.92
44	perylene	0.66	0.21
45	dibenzofluorene	0.25	0.08
46	MW 264	0.30	0.09
47	indeno[1,2,3-*cd*]pyrene	1.0	0.32
48	dibenz[*a,h*]anthracene	0.17	0.05
49	benzo[*ghi*]perylene	1.1	0.35
50	dibenzo[*def,mno*]chrysene	0.33	0.10
51	MW 302	0.34	0.11
	total	94.7	29.4

[a] Peak numbers correspond to those in Figure 1.

Table III. Concentrations of Nitrogen-Containing Polycyclic Aromatic Compounds in Fraction A3 Isolated from a Black River Sediment

peak no.[a]	compound	% of A3	% of total extract
1	benzo[*h*]quinoline	0.81	0.16
2	acridine	1.9	0.37
3	benzo[*f*]quinoline, phenanthridine	0.34	0.07
4	carbazole	7.5	1.49
5	C_1 benzoquinoline, C_1 carbazole	2.1	0.41
6	2-azafluoranthene	0.63	0.13
7	7-azafluoranthene	0.53	0.11
8	1- or 4-azapyrene	1.6	0.32
9	benzo[*def*]carbazole	1.6	0.31
10	C_1 azafluoranthene/azapyrene	0.62	0.12
11	benz[*a*]acridine	1.2	0.24
12	11*H*-benzo[*a*]carbazole	2.5	0.50
13	5*H*-benzo[*b*]carbazole	1.2	0.24
14	7*H*-benzo[*c*]carbazole	1.2	0.23
15	MW 253	2.5	0.50
	total	26.2	5.2

[a] Peak numbers correspond to those in Figure 2.

Table IV. Microbial Mutagenicity (Ames Assay) of Chemical Class Fractions Isolated on Neutral Alumina from a Black River Sediment Extract[a]

fraction	revertants μg^{-1}	linear correlation coefficient
A2	4.74	0.93[b]
A3	3.51	0.97[b]
A4	0.29	0.94[c]
A(2,3)	5.31	0.95[b]
A(1–4)	0.38	0.97

[a] *Salmonella typhimurium* TA98 with S9. Solvent control: 40 ± 8 revertants plate^{-1}. Positive control (2-AAF): 658 ± 112 revertants/11 μg plate^{-1}. [b] Linear regression analysis for data points of 1, 2, 5, and 10 μg plate^{-1}. [c] Linear regression analysis for data points of 2, 5, 10, 50, and 100 μg plate^{-1}.

with the chloroform. Figure 2 is the gas chromatogram of this fraction with nitrogen-selective detection. Table III lists the concentrations of nitrogen heterocycles identified. In contrast to fraction A2, PAC of fraction A3 made up only 26% of the fraction. However, essentially all of the components containing nitrogen were nitrogen heterocycles. One might expect quinoline to be present in the pool of PAC associated with fossil fuels. However quinoline is very water soluble (6 g/100 mL = 60 000 ppm) and would not be expected to stay in sediments that are continuously "extracted" with water in aquatic ecosystems. Moreover, we have never detected quinoline in analytical investigations of river sediments (*21*).

The A4 fraction was the smallest by weight and contained a mixture of polar non-PAC compounds. For fossil fuels, the hydroxylated PAH elute in this fraction, however, there were none detected in the A4 fraction of the sediment extract.

The four fractions isolated from the alumina column and the two recombined fractions had very low responses in the Ames assay. The highest response obtained was for the A3 fraction (96 revertants at 100 μg plate^{-1}). Furthermore, there was not a good linear correlation over the entire concentration range. Table IV gives the mutagenicity for the positive fractions over the most linear portion of the dose–response curve. The original extract and the Al fraction were similar in mutagenicity compared to the spontaneous revertant background level of the solvent control. The same stock solutions used for Ames testing were also used for induction of DNA repair in primary rat hepatocytes. The fractions were tested at concentrations representative of their weight percent contributions to the total crude extract; the crude was tested at 0.10 mg mL^{-1}, A1 at 0.038 mg mL^{-1}, A2 at 0.033 mg mL^{-1}, A3 at 0.021 mg mL^{-1}, A4 at 0.010 mg mL^{-1}, A(2,3) at 0.54 mg mL^{-1}, and A(1–4) at 0.10 mg mL^{-1} (see Table I). Each fraction was also tested at half the first concentration to verify a dose response for the assay. The dose–response range for this assay was small (essentially no UDS at concentrations below 0.010 mg mL^{-1} and toxicity at concentrations greater than 0.1 mg mL^{-1}). Table V gives the results of the assay in terms of NG per nucleus and percent of cells in repair. The media and DMSO controls were negative, and the positive control DMN gave the expected positive response. Cloudiness was observed in the cell media when the test

Table V. Induction of Unscheduled DNA Synthesis in Rat Hepatocytes by Chemical Class Fractions from a Black River Sediment Extract

test mixture	concn, mg mL^{-1}	NG ± SE[a]	% IR ± SE[b]
crude extract	0.10	16.0 ± 12.0	70 ± 23
	0.050	11.8 ± 5.8	66 ± 32
fraction A1	0.038	−14.9 ± 3.5	0
	0.019	−14.2 ± 3.2	0
fraction A2	0.033	16.6 ± 8.0	67 ± 32
	0.017	11.8 ± 4.1	69 ± 16
fraction A3	0.021	8.5 ± 6.6	53 ± 41
	0.011	−6.3 ± 1.1	4 ± 5
fraction A4	0.010	−0.3 ± 6.3	26 ± 33
	0.005	−7.3 ± 0.6	0
fraction A(2,3)	0.054	28.3 ± 6.3	93 ± 0
	0.027	1.9 ± 4.0	32 ± 33
fraction A(1–4)	0.10	17.5 ± 11.6	73 ± 33
	0.050	1.3 ± 5.2	30 ± 42
DMN	10 mM	37.9 ± 6.8	96 ± 5
control (DMSO)	1%	−17.4 ± 5.6	2 ± 4
control (media)		−13.3 ± 1.6	3 ± 3

[a] Standard error (SE) represents slide-to-slide variation for three slides at each concentration, 30 cells counted per slide. [b] Percent in repair (IR) is defined as those cells with ≥ 5 NG.

mixtures were added, indicating incomplete solubility. The cell viability in these experiments ranged from 55 to 75%. The A1 fraction was negative both in terms of NG and percent of cells in repair. The A2 and A3 fractions induced UDS in metabolically competent rat hepatocytes. Furthermore, essentially all of the genotoxicity of the crude extract was accounted for in these two fractions, with the greater activity due to the PAH fraction (A2). The A4 fraction did not yield a positive number of NG, although there was a significant number of cells in repair.

The indication of major UDS activity in fractions A2 and A3 was confirmed by the number of NG counted in the recombined A(2,3) fraction. The activity of this fraction was slightly greater than that for the total crude extract. The nearly identical response of the recombined fraction A(1–4) with the original crude extract indicates that the genotoxic activity was not lost during the fractionation.

In this study, we found that the induction of UDS was a more sensitive indicator of genotoxicity than was the standard Ames assay. This is not surprising since a study by Holland et al. (*3*) showed that complex mixtures of PAC from coal liquids did not give correlative results when tested by the Ames test and for skin tumorigenesis. The Ames assay was chosen initially because of its rapidity and relative ease of use. It was used previously to investigate the mutagenicity of sediment extracts and fractions obtained by acid–base extraction and silica gel column chromatography (*22*). In this previous work, mutagenicity was greatest in the neutral fraction in which several PAH were found. In another study, the mutagenicity of a sediment extract was thought to be due more to unidentified polar organic material than PAH (*23*). In our work, the Ames test did not indicate that any of the fractions were strongly mutagenic. However, the highest activity was found in the two PAC-containing fractions. It has been suggested that crude oil mixtures require increased amounts of S9 over standard assay conditions in order to obtain an optimal response of mutagens present in the mixture (*24*), which may be a factor in the low activity observed in the PAC-containing fractions. In addition, the effect of toxicity to the activity of these fractions is not known. Therefore, UDS in hepatocytes was measured in order to determine genotoxity with greater sensitivity. Ideally, it would have been best to demonstrate UDS in primary catfish hepatocytes exposed to the individual fractions in vivo. However, recent work to adapt the UDS assay to aquatic organisms suggests that due to a lower DNA excision repair capacity of aquatic organisms the assay is not very sensitive (*25*, *26*) and that modifications are necessary to enhance grain production (*27*). This implies that it is difficult to measure UDS in fish because fish cannot rapidly repair the lesions, which also indicates that they may be in greater danger than a mammal under similar exposure conditions (*28*).

Since fish metabolize PAH carcinogens by pathways similar to mammals (*29*), significant information concerning the genotoxicity of these fractions can be obtained from UDS determined in rat hepatocytes. A feature of this assay is that it offers the advantage of looking at genotoxicity in the target cell. The positive UDS response of the PAH fraction isolated from the Black River sediment extract is consistent with previous studies of UDS of complex mixtures of PAC that are carcinogenic. Several complex mixtures containing PAC have been shown to induce UDS (*30*, *31*). One sample, the methylene chloride extract of a coke oven emission, which may contain PAC similar to the compounds identified in this study, produced 65.2 NG at 0.1 mg mL^{-1}. Furthermore, a tumor-initiation study of the alumina column fractions of a solvent refined coal has shown that the PAH fraction accounts for most of the tumorigenic activity (32). Two known carcinogens, benzo[*a*]pyrene and benz[*a*]anthracene, were present in fraction A2 at a concentration of 1 μg mL^{-1}. On the basis of UDS results of these standard compounds (*33*), it appears that they contribute some, but not all, of the activity of the entire fraction. In addition, benzo[*b*]fluoranthene, a known potent carcinogen (*34*), was also present in about the same concentration. The complex interactions of the many polycyclic aromatic hydrocarbons make it virtually impossible to assign genotoxicity to just one or two components. While it is clear that the genotoxicity of the A2 fraction is a result of the PAC present, the exact contribution to genotoxity of the nitrogen-containing PAC is not as clear because of many non-PAC that coelute in fraction A3.

Acknowledgments

We thank Jon C. Mirsalis and Karen L. Steinmetz of SRI International for automatic grain counting of slides from the UDS assays and for helpful discussions. We also thank Byron E. Butterworth for helpful comments and critique. We thank Paul Baumann and Larry Ludke from the Columbia National Fisheries Research Laboratory (CNFRL) for collection of sediment samples and for continued collaboration in this study.

Registry No. Naphthalene, 91-20-3; 2-methylnaphthalene, 91-57-6; biphenyl, 92-52-4; acenaphthylene, 208-96-8; acenaphthene, 83-32-9; dibenzofuran, 132-64-9; fluorene, 86-73-7; dibenzothiophene, 132-65-0; phenanthrene, 85-01-8; anthracene, 120-12-7; 3-methylphenanthrene, 832-71-3; 2-methylphenanthrene, 2531-84-2; 4*H*-cyclopenta[*def*]phenanthrene, 203-64-5; 1-methylphenanthrene, 832-69-9; 2-phenylnaphthalene, 612-94-2; fluoranthene, 206-44-0; acephenanthrylene, 201-06-9; phenanthro[4,5-*bcd*]thiophene, 30796-92-0; pyrene, 129-00-0; benzo[*a*]-fluorene, 30777-18-5; benzo[*b*]fluorene, 30777-19-6; benzo[*b*]-naphtho[2,1-*d*]thiophene, 239-35-0; benzo[*ghi*]fluoranthene, 203-12-3; benzo[*c*]phenanthrene, 195-19-7; benzo[*b*]naphtho-[1,2-*d*]thiophene, 205-43-6; benzo[*b*]naphtho[2,3-*d*]thiophene, 243-46-9; cyclopenta[*cd*]pyrene, 27208-37-3; benz[*a*]anthracene, 56-55-3; chrysene, 218-01-9; benzo[*b*]fluoranthene, 205-99-2; benzo[*k*]fluoranthene, 207-08-9; benzo[*e*]pyrene, 192-97-2; benzo[*a*]pyrene, 50-32-8; perylene, 198-55-0; dibenzofluorene, 73560-78-8; indeno[1,2,3-*cd*]pyrene, 193-39-5; dibenz[*a,h*]-anthracene, 53-70-3; benzo[*ghi*]perylene, 191-24-2; dibenzo-

[*def,mno*]chrysene, 191-26-4; benzo[*j*]fluoranthene, 205-82-3; benzo[*h*]quinoline, 230-27-3; acridine, 260-94-6; benzo[*f*]quinoline, 85-02-9; carbazole, 86-74-8; 2-azafluoranthene, 7148-92-7; 7-azafluoranthene, 206-49-5; 4-azapyrene, 194-03-6; benzo[*def*]carbazole, 203-65-6; 1-azapyrene, 313-80-4; benz[*a*]acridine, 225-11-6; 11*H*-benzo[*a*]carbazole, 239-01-0; 5*H*-benzo[*b*]carbazole, 243-28-7; 7*H*-benzo[*c*]carbazole, 34777-33-8; phenanthridine, 229-87-8.

Literature Cited

(1) Epler, J. L.; Larimer, F. W.; Rao, T. K.; Nix, C. E.; Ho, C.-H. *EHP, Environ. Health Perspect.* **1978**, *27*, 11–20.
(2) Later, D. W.; Pelroy, R. A.; Mahlum, D. D.; Wright, C. W.; Lee, M. L.; Weimer, W. C.; Wilson, B. W. In *Polynuclear Aromatic Hydrocarbons: Formation, Metabolism and Measurement*; Cook, M., Dennis, A. J., Eds.; Battelle Press: Columbus, OH, 1983; pp 771–783.
(3) Holland, J. M.; Larimer, F. W.; Rao, T. K.; Epler, J. L.; Ho, C.-H.; Buchanan, M. V.; Guerin, M. R. *J. Appl. Toxicol.* **1984**, *4*, 117–123.
(4) Black, J. J. *Transplant. Proc.* **1984**, *16*, 406–411.
(5) Black, J. J. *Mar. Environ. Res.* **1984**, *14*, 529–534.
(6) Baumann, P. C.; Smith, W. D.; Ribick, M. In *Polynuclear Aromatic Hydrocarbons: Physical and Biological Chemistry*; Cook, M., Dennis, A. J., Fisher, G. L., Eds.; Battelle Press: Columbus, OH, 1982; pp 93–102.
(7) Harshbarger, J. C., Smithsonian Institute, personal communication, 1985.
(8) Black, J. J. In *Polynuclear Aromatic Hydrocarbons: Formation, Metabolism and Measurement*; Cook, M., Dennis, A. J., Eds.; Battelle Press: Columbus, OH, 1983; pp 99–111.
(9) Black, J. J. *J. Great Lakes Res.* **1983**, *9*, 326–334.
(10) Stoker, P. W.; Plasterer, M. R.; McDowell, R. L.; Campbell, R.; Fields, S.; Price, R.; Muehle, C.; West, W. R.; Booth, G. M.; Larsen, J. R.; Lee, M. L. In *Polynuclear Aromatic Hydrocarbons: Mechanisms, Methods and Metabolism*; Cooke, M., Dennis, A. J., Eds.; Battelle Press: Columbus, OH, 1985; pp 1239–1257.
(11) Stoker, P. W.; Larson, J. R.; Booth, G. M.; Lee, M. L. *J. Fish Biol.* **1985**, *27*, 31–46.
(12) West, W. R.; Smith, P. A.; Stoker, P. W.; Booth, G. M.; Smith-Oliver, T.; Butterworth, B. E.; Lee, M. L. In *Polynuclear Aromatic Hydrocarbons: Mechanisms, Methods and Metabolism*; Cooke, M., Dennis, A. J., Eds.; Battelle Press: Columbus, OH, 1985; pp 1395–1411.
(13) Vassilaros, D. L.; Eastmond, D. A.; West, W. R.; Booth, G. M.; Lee, M. L. In *Polynuclear Aromatic Hydrocarbons: Physical and Biological Chemistry*; Cooke, M., Dennis, A. J., Fisher, G. L., Eds.; Battelle Press: Columbus, OH, 1982; pp 845–857.
(14) Vassilaros, D. L.; Stoker, P. W.; Booth, G. M.; Lee, M. L. *Anal. Chem.* **1982**, *54*, 106–112.
(15) Later, D. W.; Lee, M. L.; Bartle, K. D.; Kong, R. C.; Vassilaros, D. L. *Anal. Chem.* **1981**, *53*, 1612–1620.
(16) Ames, B. N.; McCann, J. M.; Yamasaki, E. *Mutat. Res.* **1975**, *31*, 347–364.
(17) Later, D. W.; Lee, M. L.; Pelroy, R. A.; Wilson, B. W. In *Polynuclear Aromatic Hydrocarbons: Physical and Biological Chemistry*; Cook, M., Dennis, A. J., Fisher, G. L., Eds.; Battelle Press: Columbus, OH, 1982; pp 427–432.
(18) Williams, G. M. *Cancer Res.* **1977**, *37*, 1845–1851.
(19) Mirsalis, J. C.; Tyson, C. K.; Butterworth, B. E. *Environ. Mutagen.* **1982**, *4*, 553–562.
(20) Blumer, M. *Anal. Chem.* **1957**, *29*, 1039–1041.
(21) West, W. R.; Smith, P. A.; Booth, G. M.; Lee, M. L. *Environ. Toxicol. Chem.* **1986**, *5*, 511–519.
(22) Sato, T.; Momma, T.; Ose, Y.; Ishikawa, T.; Kato, K. *Mutat. Res.* **1983**, *118*, 257–267.
(23) Suzuki, J.; Sadamasu, T.; Suzuki, S. *Environ. Pollut., Ser. A* **1982**, *29*, 91–99.
(24) Carver, J. H.; Machado, M. L.; Macgregor, J. A. *Environ. Mutagen.* **1985**, *7*, 369–379.
(25) Walton, D. G.; Acton, A. B.; Stich, H. F. *Mutat. Res.* **1983**, *124*, 153–161.
(26) Walton, D. G.; Acton, A. B.; Stich, H. F. *Cancer Res.* **1984**, *44*, 1120–1121.
(27) Walton, D. G.; Acton, A. B.; Stich, H. F. *Bull. Environ. Contam. Toxicol.* **1985**, *34*, 340–348.
(28) Regan, J. D.; Snyder, R. D.; Francis, A. A.; Olla, B. L. *Aquat. Toxicol.* **1983**, *4*, 181–188.
(29) Melius, P.; Elam, D.; Swain, L. *Fed. Proc., Fed. Am. Soc. Exp. Biol.* **1983**, *42*, 2108.
(30) Ved Brat, S.; Tong, C.; Williams, G. M. In *Genotoxic Effects of Airborne Agents*; Tice, R. R., Costa, D. L., Schaich, K. M., Eds.; Plenum: New York, 1982; pp 619–631.
(31) Tong, C.; Ved Brat, S.; Telang, S.; Laspia, M. F.; Fazio, M.; Reiss, B.; Williams, G. M. In *Polynuclear Aromatic Hydrocarbons: Formation, Metabolism and Measurement*; Cooke, M., Dennis, A. J., Eds.; Battelle Press: Columbus, OH, 1983; pp 1189–1203.
(32) Mahlum, D. D.; Wright, C. W.; Chess, E. K.; Wilson, B. W. *Cancer Res.* **1984**, *44*, 5176–5181.
(33) Probst, G. S.; McMahon, R. E.; Hill, L. E.; Thompson, C. Z.; Epp, J. K.; Neal, S. B. *Environ. Mutagen.* **1981**, *3*, 11–32.
(34) Lee, M. L.; Novotny, M.; Bartle, K. D. *Analytical Chemistry of Polycyclic Aromatic Compounds*; Academic: New York, 1981; p 444.

Received for review December 9, 1985. Revised manuscript received April 10, 1987. Accepted September 25, 1987. This work was supported in part by a cooperative research agreement between Brigham Young University and the Columbia National Fisheries Research Laboratory.

Environ. Sci. Technol. 1988, 22, 229–230

CORRESPONDENCE

Comment on "Estimation of the Atmospheric and Nonatmospheric Contributions and Losses of Polychlorinated Biphenyls for Lake Michigan on the Basis of Sediment Records of Remote Lakes"

SIR: Swackhamer and Armstrong (*1*) recently estimated the magnitude and the relative importance of the different sources and sinks of polychlorinated biphenyls (PCBs) in Lake Michigan (LM). To distinguish between atmospheric and nonatmospheric sources of PCBs, they used an atmospheric deposition model calibrated on several small Wisconsin lakes (WLs) whose only known source of PCBs is the atmosphere. Estimates of the total inputs to all of the lakes were based on the accumulations in the sediments. Their conclusions are based on a number of assumptions. I would like to discuss four of their assumptions.

(1) The atmospheric deposition model calibrated on the WLs indicates that 75% of the PCBs that enter from the atmosphere evaporate and only 25% accumulate in the sediments. Swackhamer and Armstrong applied the same ratio of evaporation to accumulation to LM. Thus, the 1.9 $\mu g/(m^2 \cdot yr)$ of the PCBs accumulated in the sediments of LM, which they assume came from the atmosphere, implies a loading of 7.5 $\mu g/(m^2 \cdot yr)$ from the atmosphere. However, in determining the loading of nonatmospherically derived PCBs to LM, they assume with no explanation that *none* of these PCBs evaporate! Thus the sediment accumulation, 5.7 $\mu g/(m^2 \cdot yr)$, *equals* the lake loading from this source. This results in the atmospheric loading being 57–67% of the total loading. However, if one assumes that PCBs from all sources have similar tendencies to evaporate, only 25% now comes from the atmosphere—a big difference. Their assumption that nonatmospherically derived PCBs behave very differently in the lake than atmospherically derived PCBs do has a major effect on their conclusions and needs to be justified.

Also, if the atmospheric contribution to the sediment accumulation in LM is closer to 1.08 $\mu g/(m^2 \cdot yr)$, see below, then the atmosphere may contribute only ≈16% of the total lake loading.

(2) There is abundant evidence that PCB inputs to the environment have increased over time, at least through the mid-1970s, since they were first manufactured in the late 1920s. The sediment data presented by Swackhamer and Armstrong support these findings. However, in calculating the sediment fluxes of PCBs, Swackhamer and Armstrong averaged the accumulations found in the sediments in Lake Michigan over 51 years (1930–1980). But the average accumulations found in the WLs were based on an average of only the last 30 years. By averaging the sediment accumulations in LM over an additional 20 years of much lower accumulations, the average flux to the LM sediments is lowered. If their assumption is true that atmospheric inputs to LM have been the same as to the WLs, then the PCB accumulations found in the WLs should also be divided by 51 years. If this is done, an average flux to the WLs sediments of 1.08 ± 0.53 $\mu g/(m^2 \cdot yr)$ is found, with a range of 0.25–1.75 $\mu g/(m^2 \cdot yr)$. This is only ≈60% of the 1.9 ± 1.1 $\mu g/(m^2 \cdot yr)$ they used for those lakes.

Also, the mean total flux of PCBs to the four WLs differs by as much as a factor of 4 (a factor of 8 in the 51-year means). This casts doubt on the assumption of uniformity of atmospheric inputs, or it is a reflection of errors in correcting for sediment focusing in the WLs.

(3) In applying the WLs results to LM, Swackhamer and Armstrong assume that the meteorological, climatological, hydrological, and hydrodynamic environment of LM (58 000 km^2; 5000 km^3) is the same as that of the WLs (0.1–3 km^2; 0.001–0.03 km^3). But there are significant differences that need to be taken into account. In particular, the Great Lakes with their large surface area and very large heat capacity significantly affect the regional climatology and local meteorology (*2–4*). This should affect atmospheric inputs to them compared to smaller lakes. For instance, the ice cover on LM, averaged over the 4 months of the typical ice season, is only 19% (*5*). The higher average wind speeds and the unstable atmospheric conditions over LM during this time, caused by the water being warmer than the air, should enhance dry deposition and vapor exchange with the atmosphere. In contrast, the WLs are completely frozen over and isolated from the atmosphere during the winter.

Also, to the extent that wind speeds affect the exchange of PCBs between air and water, the PCB exchange should be lower with the more sheltered WI lakes, due to lower wind speeds and shorter fetches, than with LM.

(4) Swackhamer and Armstrong assumed that the PCB inputs/m^2 from the atmosphere to LM were the same as to the WLs. However, the Milwaukee–Chicago–Gary urban/industrial area is along the southwest shore of LM. Air concentrations of PCBs in Chicago, IL (*6*), Madison, WI (*7*), and Minneapolis, MN (*8*), are all a factor of 5 or more above the concentrations measured over LM (*7*). This is in agreement with literature reviews that indicate that PCB concentrations are a factor of 10 higher in urban areas than in rural areas (*9*). Precipitation inputs of PCBs are also higher in Chicago than in the more remote, northern regions of Lakes Michigan and Huron. PCB concentrations determined in event wet-only rain samples in 1979–1980 averaged 75 ng/L in Chicago (41°55′ N) (*6*). Monthly integrated wet-only samples collected during a similar time period averaged 12 ng/L at Point Betsie, MI (44°41′ N), and 45 ng/L at Waukegan, IL (42°42′ N). In addition, 32 wet-only event rain samples collected during 1977–1978 at Whitestone Point (44°06′ N) on Saginaw Bay along Lake Huron averaged only 13 ng/L (*10*, *11*).

The legitimacy of the conclusions in a modeling paper such as this is very dependent on the soundness of the assumptions made. And the important assumptions need to be thoroughly justified. To me, the lack of justification and reasonableness of some of the assumptions made in this paper severely limits the validity of the conclusions reached.

Literature Cited

(1) Swackhamer, D. L.; Armstrong, D. E. *Environ. Sci. Technol.* **1986**, *20*, 879–83.

0013-936X/88/0922-0229$01.50/0 © 1988 American Chemical Society

(2) Changnon, S. A.; Jones, D. M. A. *Water Resour. Res.* **1972**, *8*, 360–71.
(3) Eichenlaub, V. L. *Weather and Climate of the Great Lakes Region*; University of Notre Dame Press: Notre Dame, IN, 1979.
(4) Cole, H. S.; Lyons, W. A. *Proceedings of the 14th Conference on Great Lakes Research*; International Association for Great Lakes Research: Ann Arbor, MI, 1971; pp 436–63.
(5) Assel, R. A.; Quinn, F. H.; Leshkevich, G. A.; Bolsenga, S. J. *Great Lakes Ice Atlas*; Great Lakes Environmental Research Laboratory: Ann Arbor, MI, 1983; Table 2.
(6) Murphy, T. J.; Rzeszutko, C. P. *J. Great Lakes Res.* **1977**, *3*, 303–12.
(7) Doskey, P. V.; Andren, A. W. *J. Great Lakes Res.* **1981**, *7*, 15–20.
(8) Hollod, G. J. Ph.D. Thesis, University of Minnesota, Minneapolis, MN, 1979.
(9) Eisenreich, S. J.; Looney, B. B.; Hollod, G. J. *Environ. Sci. Technol.* **1981**, *15*, 879–83.
(10) Murphy, T. J.; Paolucci, G.; Schinsky, A. W.; Combs, M. L.; Pokojowczyk, J. C. "Inputs of PCBs from the Atmosphere to Lakes Huron and Michigan"; report of U.S. EPA project R-805325; Duluth Environmental Laboratory: Duluth, MN, May 1982.
(11) Murphy. T. J. In *Toxic Contaminants in the Great Lakes*; Simmons, M., Nriagu, J., Eds.; Wiley: New York, 1984.

Thomas J. Murphy

Chemistry Department
DePaul University
Chicago, Illinois 60604

SIR: Murphy questions assumptions made in our estimations of the atmospheric and nonatmospheric contributions of PCBs to Lake Michigan (*1*). Although we explained our assumptions at some length, we are happy to provide further clarification.

Murphy argues that we assumed PCBs from nonatmospheric sources do not evaporate and that this assumption leads to an overestimate of the fraction of the PCB loading to Lake Michigan derived from nonatmospheric sources. However, we did *not* make this assumption. Clearly, PCBs from nonatmospheric sources are also subject to volatilization. We chose to use the calculated loss to the atmosphere from remote lakes as a *conservative* estimate of the corresponding loss from Lake Michigan. We did not feel that alternative assumptions, such as Murphy's suggestion that loss to the atmosphere is directly proportional to loading, were justified. Importantly, our estimate of the nonatmospheric loading to Lake Michigan was presented as the *net* rather than the total value, representing the amount remaining (in the lake sediments) after losses by volatilization or other processes. As a point of further clarification, we did *not* obtain the atmospheric loading (7.5 $\mu g\ m^{-2}\ yr^{-1}$) on the basis of a ratio of evaporation to sediment accumulation of PCBs, as indicated by Murphy. The atmospheric loading was obtained from a separate investigation (*2*). We measured sediment accumulation of PCBs in remote lakes and calculated loss to the atmosphere as the difference between atmospheric loading and sediment accumulation of PCBs.

Our use of different periods of time for the remote lakes and Lake Michigan in calculating average sediment fluxes of PCBs was also questioned. Fluxes were averaged over the periods for which PCBs were detectable in the sediments. This time interval was longer in Lake Michigan than in the remote lakes. We believe it would be erroneous to use a time period other than the period over which PCBs were actually deposited. In contrast to Murphy's conclusion, we believe PCBs could have been delivered to Lake Michigan earlier than to the remote lakes, i.e., from nonatmospheric sources. As discussed previously (*1*), the range in sediment fluxes of PCBs in the remote lakes probably reflects uncertainties in time resolution (sectioning sediment cores and calculating sedimentation rates), measurement of low PCB concentrations, and sediment focusing. We did not attempt to correct for differences in sediment focusing among remote lakes. Were sediment focusing occurring in the remote lakes, the difference between the remote lakes and Lake Michigan would be even greater, making our estimates conservative.

We share Murphy's concern regarding meteorological and physical differences between Lake Michigan and the remote lakes and acknowledged this limitation (*1*). In the absence of a pristine lake identical in size and climate with Lake Michigan, the remote lakes served as a useful first approximation. The suitability of the remote lakes is supported by data from Lake Superior. Lake Superior receives approximately 80% of its PCBs through atmospheric input (*3*, *4*). The average sediment PCB flux in Lake Superior is estimated to be 4 $\mu g\ m^{-2}\ yr^{-1}$ (*4*), which makes the atmospheric contribution similar to the flux for the remote lakes (*1*). Furthermore, sediment PCB cogener fluxes in Siskiwit Lake on Isle Royale in Lake Superior are similar to those of Lake Superior, even though Siskiwit Lake is ice-covered during winter months (*5*). Two factors may account for the agreement in fluxes: (1) although possibly enhanced by high wind speeds, dry deposition is not the dominant process involved in transport of atmospheric PCBs to lakes (*2*), and (2) during winter, vapor exchange from ice-free lakes may be reduced through the influence of low surface water and air temperatures on Henry's Law constants. In fact, Murphy (*6*) suggests this temperature effect in a recent publication.

Our assumption that atmospheric inputs per unit area are similar for Lake Michigan and the remote lakes is supported by air and rain measurements, including data cited by Murphy. Air concentrations of PCBs over the open waters of Lake Michigan (*7*), Wisconsin remote sites (*8*), and Lake Superior (*4*) are similar. As we stated previously (*1*), concentrations in air and rain are higher in urbanized areas in localized regions along the southern shores of Lake Michigan, possibly resulting in higher atmospheric inputs of PCBs to Lake Michigan than to the remote lakes. However, the major portion of the Lake's surface is apparently influenced by air concentrations similar to those in remote areas.

We reemphasize that assumptions made in comparing Lake Michigan and the remote lakes will lead to some uncertainty in the calculated fluxes. We encourage continued examination of the air–water transfer processes to improve the reliability of flux estimates. However, we believe the comparison clearly shows the loss of PCBs from the lake to the atmosphere is significant and that atmospheric and net nonatmospheric inputs of PCBs to Lake Michigan have been of similar magnitude.

Literature Cited

(1) Swackhamer, D. L.; Armstrong, D. E. *Environ. Sci. Technol.* **1986**, *20*, 879–83.
(2) Andren, A. W. In *Physical Behavior of PCBs in the Great Lakes*; Mackay, D., Paterson, S., Eisenreich, S. J., Simmons, M. S., Eds.; Ann Arbor Science: Ann Arbor, MI, 1983; Chapter 8.
(3) Eisenreich, S. J.; Looney, B. B.; Thornton, J. D. *Environ. Sci. Technol.* **1981**, *15*, 30–38.

 Not subject to U.S. Copyright. Published 1988 by the American Chemical Society

(4) Eisenreich, S. J. In *The Sources and Fates of Aquatic Pollutants*; Hites, R. A., Eisenreich, S. J., Eds.; Advances in Chemistry 316; American Chemical Society: Washington, DC, 1987; Chapter 13.
(5) Swackhamer, D. L.; McVeety, B. D.; Hites, R. A., unpublished data.
(6) Murphy, T. J.; Pokojowczyk, J. C.; Mullin, M. D. In *Physical Behavior of PCBs in the Great Lakes*; Mackay, D., Paterson, S., Eisenreich, S. J., Simmons, M. S., Eds.; Ann Arbor Science: Ann Arbor, MI, 1983; Chapter 3.
(7) Doskey, P. D.; Andren, A. W. *J. Great Lakes Res.* 1981, *7*, 15-20.
(8) Andren, A. W., personal communication.

Deborah L. Swackhamer*

Environmental and Occupational Health
University of Minnesota
Minneapolis, Minnesota 55455

David E. Armstrong

Water Chemistry Program
University of Wisconsin
Madison, Wisconsin 53706

Comment on "Reaction Products and Rates of Disappearance of Simple Bromoalkanes, 1,2-Dibromopropane, and 1,2-Dibromoethane in Water"

SIR: A recent article in this journal by T. M. Vogel and M. Reinhard (*1*) concerned itself with the disappearance, rates, and reaction products of mono- and dibromoalkanes in water. One conclusion of this article was that 1,2-dibromoethane (EDB) degraded to the bromoalkane vinyl bromide as a "main product" causing them to conclude that "...dehydrobromination is the most significant degradation mechanism for alkanes with two bromines in vicinal position, although substitution cannot be ruled out from the data due to analytical limitations". Since the authors did not specify at what EDB concentrations their studies were performed, it is impossible to put such observations in perspective with those of ours (*2*) and Jungclaus and Cohen (*3*). We have shown that, in natural groundwaters, ethylene glycol and bromide ions account for nearly all the degradation of EDB when studies are done at EDB concentrations that have been observed in groundwater (*2*; 10–100 μg/L). Vogel and Reinhard (*1*) did not look for water-soluble products but concentrated their effors on pentane-soluble ones.

When your readers consider the relative mammalian toxicities of ethylene glycol and vinyl bromide, it is important for them to know that the more innocuous ethylene glycol accounts for nearly all the degradation of EDB in groundwaters.

Registry No. EDB, 106-93-4; $BrCH_2CHBrCH_3$, 78-75-1.

Literature Cited

(1) Vogel, M. T.; Reinhard, M. *Environ. Sci. Technol.* **1986**, *20*(*10*), 992-997.
(2) Weintraub, R. A.; Jex, G. W.; Moye, H. A. *Evaluation of Pesticides in Ground Water*; Garner, Willa Y., Honeycutt, Richard C., Nigg, Herbert N., Eds.; ACS Symposium Series 315; American Chemical Society: Washington, DC, 1986; Chapter 15.
(3) Jungclaus, G. A.; Cohen, S. Z. *Extended Abstracts*, 191st National Meeting of the American Chemical Society, Division of Environmental Chemistry, New York, NY; American Chemical Society: Washington, DC, 1986: paper 6.

H. Anson Moye,* Randy Weintraub

Pesticide Research Laboratory
Institute of Food and Agricultural Sciences
University of Florida
Gainesville, Florida 32611

SIR: Weintraub et al. (*1*) and Jungclaus and Cohen (*2*) report that 1,2-dibromoethane (EDB) hydrolyzes in aqueous buffers to form ethylene glycol as the primary product. Recent data obtained in this laboratory are consistent with this finding (*3*). In addition, Vogel and Reinhard (*4*), Jungclaus and Cohen (*2*), and recently Haag and Mill (*5*) have found vinyl bromide as a product of EDB decomposition in water. Haag and Mill (*5*) have found degradation via elimination to be 9 times slower than hydrolysis. Although ethylene glycol is quantitatively the major product of aqueous EDB degradation, vinyl bromide may be the more significant product because of its elevated toxicity.

We specified that the initial EDB concentrations in our studies were 10 mg/L (*4*). However, product distribution is not expected to change with the initial concentration since the rates of both elimination and hydrolysis are first order with respect to organic reactant. Degradation of 100 μg/L EDB (the upper limit in groundwater quoted by Moye and Weintraub) in water may react to form approximately 30 μg/L ethylene glycol via hydrolysis and 6 μg/L vinyl bromide via elimination. For the purpose of comparison, the final maximum contaminant levels set by the U.S. EPA for vinyl chloride (the chlorinated analogue of vinyl bromide) is 2 μg/L.

Registry No. EDB, 106-93-4; $BrCH_2CHBrCH_3$, 78-75-1.

Literature Cited

(1) Weintraub, R. A.; Jex, G. W.; Moye, H. A. *Evaluation of Pesticides in Ground Water*; Garner, Willa Y., Honeycutt, Richard C., Nigg, Herbert, N., Eds.; ACS Symposium Series 315; American Chemical Society: Washington, DC, 1986; Chapter 15.
(2) Jungclaus, G. A.; Cohen, S. Z. *Extended Abstracts*, 191st National Meeting of the American Chemical Society, Division of Environmental Chemistry, New York, NY; American Chemical Society: Washington, DC, 1986; paper 6.
(3) Barbash, J. E.; Reinhard, M. *Extended Abstracts*, 194th National Meeting of the American Chemical Society, Division of Environmental Chemistry, New Orleans, LA; American Chemical Society: Washington, DC, 1987.
(4) Vogel, T. M.; Reinhard, M. *Environ. Sci. Technol.* **1986**, *20*, 992-997.
(5) Haag, W. R.; Mill, T., personal communication, 1987.

Martin Reinhard*

Department of Civil Engineering
Stanford University
Stanford, California 94305

Timothy M. Vogel

Environmental Engineering
Michigan State University
East Lansing, Michigan 48824-1212

0013-936X/88/0922-0231$01.50/0 © 1988 American Chemical Society

❑ **ACCOUNTS OF CHEMICAL RESEARCH**
Editor, F.W. McLafferty
Cornell University
12 issues a year. ISSN 0001-4842
Member $23 Nonmember $105

❑ **ANALYTICAL CHEMISTRY**
Editor, George H. Morrison
Cornell University
24 issues a year. ISSN 0003-2700
Member $25 Nonmember $38

❑ **BIOCHEMISTRY**
Editor, Hans Neurath
University of Washington
26 issues a year. ISSN 0006-2960
Member $75 Nonmember $439

❑ **CHEMICAL & ENGINEERING NEWS**
Editor, Michael Heylin
51 issues a year. ISSN 0009-2347
Nonmember $49

❑ **CHEMICAL RESEARCH IN TOXICOLOGY**
Editor, Lawrence J. Marnett
Wayne State University
6 issues a year. ISSN 0893-228X
Member $46 Nonmember $269

❑ **CHEMICAL REVIEWS**
Editor, Josef Michl
University of Texas
8 issues a year. ISSN 0009-2665
Member $22 Nonmember $129

❑ **CHEMTECH**
Editor, Benjamin J. Luberoff
12 issues a year. ISSN 0009-2703
Member $34 Nonmember (Pers.) **$55**
Nonmember (Inst.) **$252**

❑ **ENERGY & FUELS**
Editor, John W. Larsen
Lehigh University
6 issues a year. ISSN 0887-0624
Member $46 Nonmember $269

❑ **ENVIRONMENTAL SCIENCE & TECHNOLOGY**
Editor, William H. Glaze
University of California, Los Angeles
12 issues a year. ISSN 0013-936X
Member $30 Nonmember (Pers.) **$55**
Nonmember (Inst.) **$192**

❑ **INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH**
Editor, Donald R. Paul
University of Texas, Austin
12 issues a year. ISSN 0888-5885
Member $52 Nonmember $299

❑ **INORGANIC CHEMISTRY**
Editor, M. Frederick Hawthorne
University of California, Los Angeles
26 issues a year. ISSN 0020-1669
Member $79 Nonmember $443

❑ **JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY**
Editor, Irvin E. Liener
University of Minnesota
6 issues a year. ISSN 0021-8561
Member $24 Nonmember $131

❑ **JOURNAL OF THE AMERICAN CHEMICAL SOCIETY**
Editor, Allen J. Bard
University of Texas, Austin
26 issues a year. ISSN 0002-7863
Member $70 Nonmember $399

❑ **JOURNAL OF CHEMICAL AND ENGINEERING DATA**
Editor, Bruno J. Zwolinski
Texas A&M University
4 issues a year. ISSN 0021-9568
Member $29 Nonmember $171

❑ **JOURNAL OF CHEMICAL INFORMATION AND COMPUTER SCIENCES**
Editor, Thomas L. Isenhour
Utah State University
4 issues a year. ISSN 0095-2338
Member $17 Nonmember $90

❑ **JOURNAL OF MEDICINAL CHEMISTRY**
Editor, Philip S. Portoghese
University of Minnesota
12 issues a year. ISSN 0022-2623
Member $40 Nonmember $234

❑ **THE JOURNAL OF ORGANIC CHEMISTRY**
Editor, Frederick D. Greene
Massachusetts Institute of Technology
26 issues a year. ISSN 0022-3263
Member $53 Nonmember $309

❑ **JOURNAL OF PHYSICAL AND CHEMICAL REFERENCE DATA**
Editor, David R. Lide, Jr.
National Bureau of Standards
4 issues a year. ISSN 0047-2689
Member $60 Nonmember $265

❑ **THE JOURNAL OF PHYSICAL CHEMISTRY**
Editor, Mostafa A. El-Sayed
University of California, Los Angeles
26 issues a year. ISSN 0022-3654
Member $65 Nonmember $432

❑ **LANGMUIR**
Editor, Arthur W. Adamson
University of Southern California
6 issues a year. ISSN 0743-7463
Member $55 Nonmember $342

❑ **MACROMOLECULES**
Editor, Field H. Winslow
AT&T Bell Laboratories
12 issues a year. ISSN 0024-9297
Member $53 Nonmember $342

❑ **ORGANOMETALLICS**
Editor, Dietmar Seyferth
Massachusetts Institute of Technology
12 issues a year. ISSN 0276-7333
Member $55 Nonmember $360

Call Toll Free (U.S.)

800-227-5558

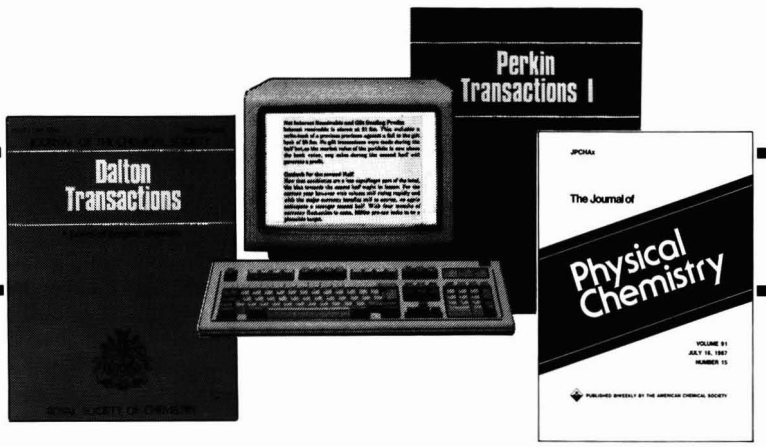
Telex: 440159 ACSP UI or
892582 ACSPUBS
Cable Address: JIECHEM
Telecopier (SANYO Group 1,2,3): 202-872-4615

American Chemical Society
Marketing Communications Department
1155 Sixteenth St., N.W.
Washington, D.C. 20036
U.S.A.

Rates listed are for 1988 U.S. subscriptions. For subscription rates outside the U.S., contact American Chemical Society or your subscription agency. Member rates are for personal use only. For nonmember subscriptions in Japan, write Maruzen Co., Ltd.

Now you can search the worlds major primary chemical journals in minutes using:-

CHEMICAL JOURNALS ONLINE (CJO)



CJO... is a family of new online files from the American Chemical Society which contains the complete papers published in the worlds leading primary chemical journals.

CJO... presently includes journals published by the Royal Society of Chemistry (since Jan 87), the American Chemical Society (since 1982), the polymer journals from Wiley (since Jan 87), although plans are in hand to include other publishers.

CJO... is updated fortnightly and is searchable via STN International to provide you with one of the most up-to-date and invaluable chemical information data bases in the world.

CJO... is linked to CAS ONLINE via STN's crossover facility. This enables you to perform the same search on CJO and CAS ONLINE thereby combining the breadth of coverage of Chemical Abstracts with the depth of coverage of full-text journals.

For more information, call (614) 421-3600, or return the form below to: STN International, c/o Chemical Abstracts Service, 2540 Olentangy River Road, P.O. Box 02228, Columbus, OH 43210.

Please send me more information on CJRSC and the Chemical Journals Online data base.

Name .....

Address .....

.....

.....

CHEMICAL JOURNALS ONLINE

To digest or not to digest?

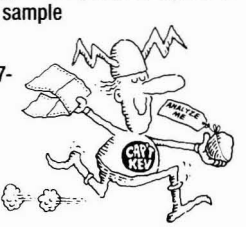
That is the question...

Art thou weary of:	yea	nay
Singed eyebrows?	—	—
Holes in thy labcoat?	—	—
Yellow fingers?	—	—
Samples that disappear?	—	—

Just one *yea* means you know that acid digestion can cause acid indigestion in a hurry. There's all that tedious prep like weighing and pipetting and serial dilution. Positively medieval. Plus acid consumes your sample while leaving some compounds undissolved. Silicates for instance.

Now, a modern answer. New STXRF™ analysis does away with the acid and most of the prep. And still delivers optimum sensitivity. Quickly. You simply select the right excitation radiation to get a complete composition rundown. Even of light elements.

STXRF can pre-screen and analyze just about any substance known or unknown. Large or small. Solid, liquid, or any state in-between. This lets you save time, aggravation, and money. Not to mention labcoats. You also save your sample for further studies.



Call Capt. Kev TOLL FREE 1-800-227-0277 (In CA: 1-800-624-4374) for a demonstration, or request our literature packet. STXRF. The noble solution that's not part of the problem.

*STXRF (source tuned X-ray fluorescence) is a trademark of Kevex Corporation.

See us at the Pittsburgh Conference in New Orleans Booth 2356-2365.

Kevex Corporation 1101 Chess Drive, Foster City, CA 94404 415-573-5866 1-800-227-0277 (In CA: 1-800-624-4374)
Kevex Affiliate (Getac GmbH) Tel 49-6131-40091 Kevex Canada, Ltd. Tel 416-731-2161 Kevex France (Fondis, S.A.) Tel 33-1-34810024 Kevex UK Tel 44-582-400596