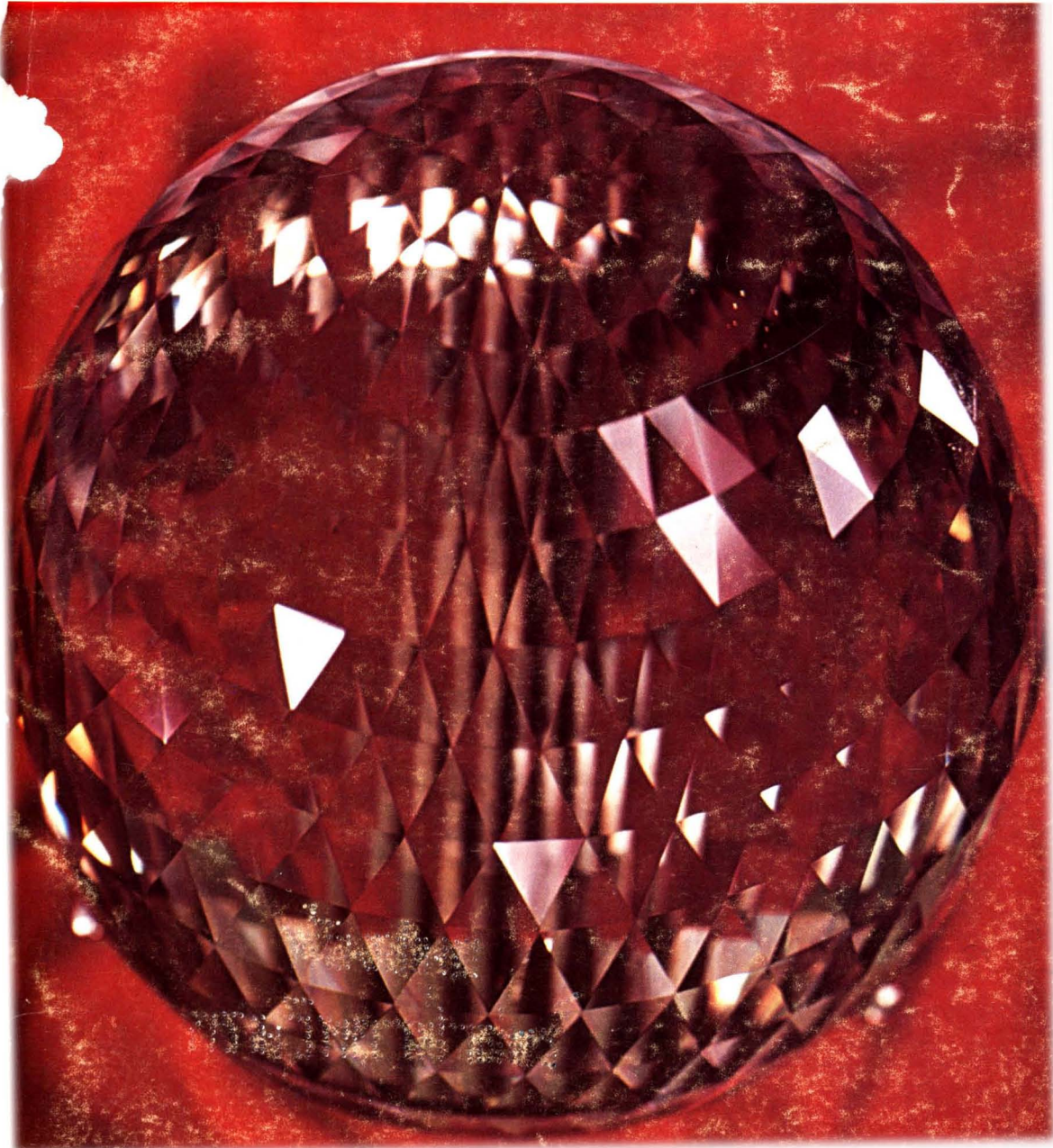


Environmental

Science & Technology

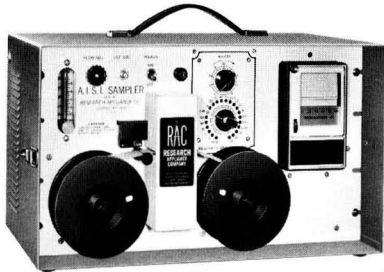
MARCH 1976

GEMS: global monitoring 230



For automatic, cyclical sampling of particulates, H₂S gas, and fluorides in ambient air...

specify RAC filter tape instruments

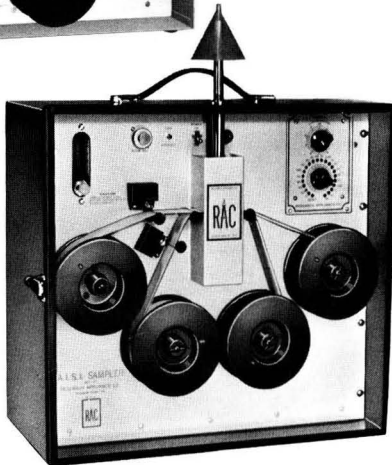


RAC Model G2 SER Monitor

this line of versatile, precision samplers & monitors provides a wide range of capabilities to meet air sampling requirements

RAC offers a variety of portable, automated, timer-controlled instruments designed to sample/monitor airborne *particulate matter*—to **ASTM D1704** specs—by means of filter tapes. Particles down to 3.4 microns (and smaller) are collected automatically and accurately during preset sampling cycles. In addition, RAC particle samplers can be easily adapted to sample *hydrogen sulfide gas* (H₂S) in concentrations ranging from 0.02 to 20 ppm. *Fluorides*, both gaseous and particulate, are sampled simultaneously with a dual-tape instrument.

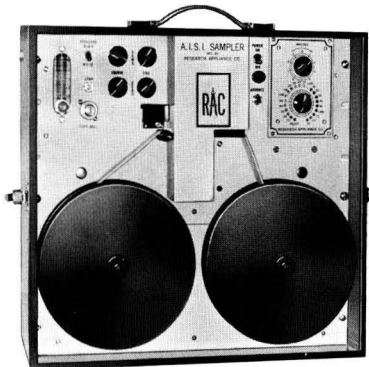
RAC Model G2DT Fluoride Sampler



Engineered to operate unattended and with optimum repeatability, these precision designs are among the most versatile, adaptable devices available for both indoor and outdoor air sampling/monitoring operations. RAC **monitor** configurations automatically evaluate sample spots by means of an integral densitometer, and provide an output signal that can transmit the densitometer readings to a remote data collection device or station.

The scope of application for RAC tape instruments depends largely on users' needs and ingenuity. They can be used to detect air pollutants, to indicate the rate and frequency of change in ambient pollution concentrations, to provide data for determining source and distribution of atmospheric contaminants, to check the efficiency of dust collection and air filtration equipment, to plot traffic flow/density patterns, to correlate wind direction with ambient pollution levels, and for similar types of air sampling/monitoring operations.

Ten different models . . . plus a variety of specialized options . . . are available to meet virtually any air sampling/monitoring requirement within the capabilities of RAC filter tape designs.



RAC Model G2-T-600 Monitor

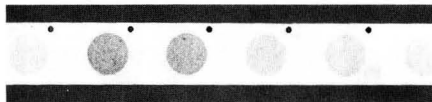
For details on *particle & H₂S samplers*, send for **BULLETIN 2300**.

CIRCLE 19 ON READER SERVICE CARD

For details on *dual-tape fluoride sampler*, send for **BULLETIN 2356**.

CIRCLE 20 ON READER SERVICE CARD

Section of filter tape showing typical 1" dia sample spots.



STACK SAMPLING SEMINARS

Since 1970, RAC has sponsored an annual series of 2-day, technical, practical seminars on stack sampling parameters & procedures (EPA methods). **Write for descriptive folder.**

CIRCLE 21 ON READER SERVICE CARD



RESEARCH APPLIANCE COMPANY

Route 8, Gibsonsia, Pennsylvania 15044

Environmental Instruments / Laboratory Products

Whatman® Filters and Media FOR POLLUTION CONTROL PROCEDURES

Products of Superior Quality and Performance for Filtration, Extraction, Absorption, Chromatography and Electrophoresis.

Glass Microfiber Filters

Qualitative Filter Papers

Quantitative Filter Papers

**Roll and Sheet Filters for
Air Sampling**

**Roll, Sheet and Circle Filters for
Water Testing**

Indicator Papers

Spot Test Papers

Glass Fiber Filter Tubes

**Disposable Phase Separators for
Sample Preparation**

**Full Range of Chromatography
Products**

Whatman products are famous for excellence—of performance, quality, uniformity. *Standard procedures call for Whatman.* They are applicable to virtually every sampling and analytical pollution control procedure calling for filtration and/or extraction. Whatman offers an extremely broad line of filters and media to fill nearly any requirement.

Whatman products for pollution control procedures are available from selected laboratory supply dealers worldwide. For the dealer nearest you, please write or phone.

® Registered trademark of Whatman Ltd.



Whatman

Whatman Inc. ■ 9 Bridewell Place, Clifton, New Jersey 07014 ■ Tel. (201) 777-4825 ■ Telex 133426.

Whatman Ltd. ■ Springfield Mill, Maidstone, Kent ME14 2LE, England ■ Tel. (0622) 61681 ■ Telex 96113.

Whatman S.a.r.l. ■ Zone Industrielle, BP N.12, 45210 Ferrieres, France ■ Tel. 95 74 15 ■ Telex 78229.

See us at FAISEB, Booth 016-017

CIRCLE 15 ON READER SERVICE CARD



WHEN IT COMES TO SMOKE, NO TWO STACKS ARE ALIKE. THEIR MONITORING SYSTEMS DON'T HAVE TO BE EITHER.

The new smoke regulations are very specific. But how you comply with them is up to you. And that's exactly what an Ethyl Intertech Smoke Monitoring System lets you do. Comply in the way that's best suited to your stack, your operation, your economics.

The most important aspect of this is that we offer *two* highly sensitive double-pass optical transmissometers, the DR-116 and the DR-110.

The new DR-116 is an economically-priced instrument designed to meet all anticipated regulations for stacks up to 10 feet in diameter. It offers automatic zero compensation, built-in alarm contacts, and an output signal linear with opacity.

The dual-beam DR-110, on the other hand, is for stacks from 5 to 50 feet in diameter—and adds a number of automatic, labor-saving features.

For instance, it continuously compensates itself for window deposits, and also indicates the amount of these deposits so that cleaning can be efficiently scheduled. It corrects its opacity readings for stack exit conditions. In addition, the DR-110 can perform its

own span and window calibration checks.

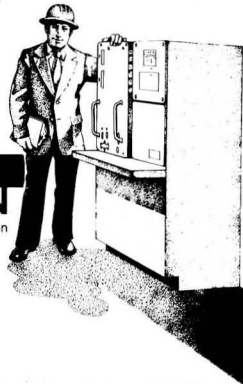
Both transmissometers meet proposed EPA specifications. Both are manufactured for Intertech by Durag GmbH in West Germany where there are thousands operating successfully. And both are available with many compatible options and accessories to provide the exact system you need.

Your system, for example, could include an air-purge capability for long-term unattended operation. Automatic fail-safe shutters. Remote control and annunciator panels. And of course output devices such as integrators and recorders.

But the added extra with Ethyl Intertech is Total Project Capability. So write or call for details and the name of your nearest rep, c/o Ethyl Intertech Corporation

Dept. T., 19
Roszel Road,
Princeton, N.J.
08540. Phone:
(609) 452-8600.

"You can't beat the system."



**ETHYL
INTERTECH
CORPORATION**

A Subsidiary of Ethyl Corporation/Instrument Division

CIRCLE 29 ON READER SERVICE CARD

Environmental

Science & Technology

Volume 10, Number 3, March 1976

ESTHAG 10(3) 205-302 (1976)
ISSN 0013-936X

CONTENTS

Features

- 230 The global environmental monitoring system—U. N. Environment Program's Martin & Sella
- 234 The arguments in court cases involving public health issues—attorney Hills
- 239 The Coast Guard oil spill control program—Lt. Ard of the USCG Reserve

PAT Report

- 228 Aerial photos can be used to assess eutrophication of lakes

Outlook

- 220 Government: EPA computer modeling of environmental economics still to pay off
- 222 How much environmental manpower is really needed? NRC committee asks
- 224 The pollution control industry: a recent reassessment of its size
- 226 Ground water: The growing concern that subsurface water is clean and safe to use

Departments

- 211 Editorial
- 212 Letters
- 215 Currents
- 286 Industry trends
- 287 New products
- 290 New literature
- 292 Books
- 295 Meeting guide
- 297 Classified section
- 298 Consulting services

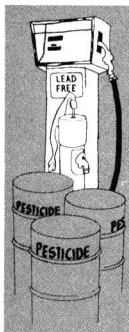
Current research

- 208 Contents
- 243 Papers

220



228



234

219



© Copyright 1976 by the American Chemical Society.

Published monthly, with additional Pollution Control Directory in October, by the American Chemical Society, from 20th and Northampton Sts., Easton, Pa. 18042. Executive offices: Editorial Headquarters, 1155 16th St., N.W., Washington, D.C. 20036. Advertising office: 50 West State St., Westport, Conn. 06880. Second-class postage paid at Washington, D.C., and at additional mailing offices.

ES&T ON MICROFILM: This publication is available on microfilm. For information, write to: Microfilm, Special Issues Sales, ACS, 1155 16th St., N.W., Washington, D.C. 20036.

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

SUBSCRIPTION RATES 1976: Members, 1 year \$10.00; three years \$24.00. Nonmember individuals, 1 year 15.00; 3 years \$36.00. Nonmember institutions, 1 year 30.00. Foreign postage: Pan American Union, \$4.75 per year; Canada and others, \$5.00 per year. Air freight rates per year available on request. Single copies: current issues, \$3.50; Pollution Control Directory, \$4.00; rates for back issues and volumes are available from Special Issues Sales Department, 1155 16th St., N.W., Washington, D.C. 20036. Claims for missing numbers will not be allowed if loss was due to failure of notice of change of address to be received in the time specified: if claim is dated (a) North America: more than 90 days beyond issue date, (b) all other foreign: more than one year beyond issue date; or if the reason given is "missing from files." Hard copy claims are handled at the ACS Columbus address.

Those interested in joining the American Chemical Society should write to Admissions Department of Washington Office. The American Chemical Society assumes no responsibility for the statements and opinions advanced by contributors to its publications.

CURRENT RESEARCH

Preliminary small-scale combustion tests of coal liquids 243

J. E. Haebig*, B. E. Davis, and E. R. Dzuna

Nonupgraded coal liquids were burned in a modified boiler equipped with an air atomizer and examined for smoke and NO_x emissions. These were compared with emissions from nitrogen-doped petroleum and full-boiling range and distillate coal liquids.

Test of theory of ozone generation in Los Angeles atmosphere 248

J. G. Calvert

The data from the LARPP Operation #33 are analyzed to test present theories of O₃ generation in photochemical smog. The data collected after 0920 are in accord with the models considered, and they confirm the presently accepted ozone formation mechanism.

Hydrocarbon involvement in photochemical smog formation in Los Angeles atmosphere 256

J. G. Calvert

The extensive measurements made by the LARPP on November 5, 1973, were analyzed to test theories of smog formation. Consideration of concentrations and reaction rates indicates that smog models must involve all classes of hydrocarbons as important reactants.

Kinetics of limestone neutralization of acid waters 262

Paul Barton* and Terdthai Vatanatham

Rate of neutralization of H₂SO₄ by limestone is shown to be controlled by hydrogen diffusion in the pH range 2-6. A shrinking particle model describes the dissolution of the limestone. Effects of temperature, stoichiometry, turbulence, and CO₂ are analyzed.

Records of lead deposition in Lake Michigan sediments since 1800 266

D. N. Edgington* and J. A. Robbins

Lead distribution in sediment cores from Lake Michigan was determined using the ²¹⁰Pb technique. A model was developed that gives a quantitative description of historical Pb input. The model was applied to Pb distribution in sediment cores measured previously by others.

Diffusive collection of aerosol particles on Nuclepore membrane filter 274

T. N. Smith, C. R. Phillips*, and O. T. Melo

Recoveries of particles on 3.0- μ m pore diameter Nuclepore filters were measured. Diffusion to the face of the filter was concluded to be the main mechanism for recovery on this filter. A generalization to filters with different pore length to diameter ratios is suggested.

Continuous determination of free cyanide in effluents using silver ion selective electrode 277

M. Hofton

A method is presented for continuous monitoring of free cyanide in effluents using a silver ion selective electrode. Potential interferences are discussed, and results of a two-week trial monitoring of a steelworks effluent are presented.

NOTES

Transport of atmospheric sea salt in the coastal zone 281

S. A. Hsu* and Thomas Whelan III

A model is developed to explain vertical distribution of sea salt aerosol above two beaches. Each beach was under the influence of different winds. The proposed model is supported by data from independent sources.

CORRESPONDENCE

Characterization of Australian crudes and condensates by gas chromatographic analysis 284

E. R. Adlard

J. L. Powell

Trace elements in corn grown on long-term sludge disposal site 284

G. W. Leeper

M. B. Kirkham

* To whom correspondence should be addressed

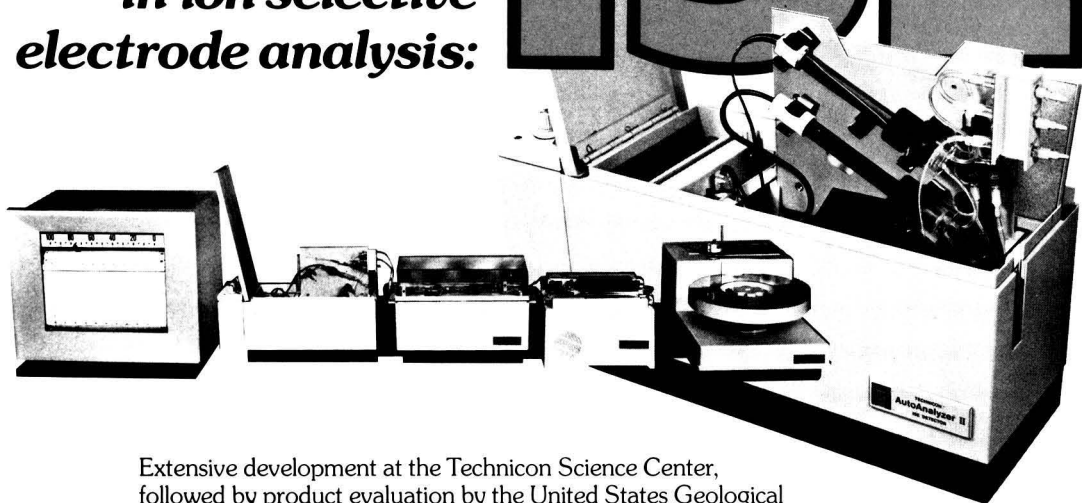
This issue contains no papers for which there is supplementary material in microform

Credits: 219 (upper), Research-Cottrell; 220, 221, Rob Sugar; 222, ES&T's Julian Josephson; 232, General Electric

Cover: Smithsonian Institution

AUTOMATED ISE

**Technicon presents
the major advance
in ion selective
electrode analysis:**



Extensive development at the Technicon Science Center, followed by product evaluation by the United States Geological Survey laboratories* of a new temperature controlled, ISE detector module integrated with the Technicon™ AutoAnalyzer™ II Continuous-flow Analytical system has resulted in a dramatic improvement in ion selective electrode analysis.

- **Significantly improved precision, easily and practically achieved** – The need for ionic strength and pH adjustments, electrode washing between samples, and other manual manipulations affecting precision are eliminated. In addition, automatic temperature control of the analytical system ensures overall stability and precision to a level impractical by manual procedures.
- **Speed of Analysis** – Up to 40 samples per hour can be routinely handled with the Technicon AutoAnalyzer II system, allowing steady state to be reached over a wide range of matrices and concentrations.
- **Selectivity** – The sample can be automatically pretreated in the manifold of the AutoAnalyzer II system to optimally eliminate potential interferences using techniques such as automatic distillation and dialysis.

Currently, three parameters have been evaluated – fluoride, pH and ammonia, with many other automated ISE parameters and matrices presently in various stages of development.

For additional information, write Department 225

*Environmental Science and Technology, Vol. 9, No. 3, P. 252, March 1975 – Automated Ion Selective Electrode Method for Determining Fluoride in Natural Waters, David E. Erdmann, U.S.G.S.



**Technicon
Industrial Systems**
Tarrytown, New York 10591.

EXPANDING HORIZONS IN AUTOMATED ANALYSIS

Wear our new *Hipster*: Instant alarm and accurate analysis of H₂S... on a strap!

Meet our new ECOLYZER 6000 H₂S Personnel Alarm. It's also an H₂S Analyzer.

Strap it to your waist . . . or sling it around your neck like a camera. It goes where you go.

Turn it on and read H₂S levels directly from the meter in ppm or grains. Leave it on and you have a continuous, fast, accurate personnel alarm as you move from site to site.

Like our other ECOLYZER H₂S units, *Hipster*:

- alarms audibly to preset H₂S levels . . . *instantly*. . . at concentrations as low as 5 ppm (.32 grains);
- operates reliably in a wide range of interfering gases;
- provides quantitative data accurately and rapidly . . . to $\pm 2\%$ F.S.

Consider this, too. The *Hipster* is just as easy to calibrate, zero and operate as our larger ECOLYZER 2000 H₂S Analyzers.

And, *Hipster* provides the most reliable way to protect personnel . . . *anywhere!*

For additional information on the *Hipster*, the available detection ranges, and the availability of other 6000 Series ECOLYZER units for measuring CO, NO, or NO₂, just use this publication's reader service card. Or write or call:

energetics
science, inc.

85 EXECUTIVE BOULEVARD, ELMSFORD
NEW YORK, U.S.A. 10523 914-592-3010
CIRCLE 26 ON READER SERVICE CARD

TOXIC EFFECTS OF H₂S ON HUMAN LIFE

Concentrations in Air
ppm grains/100 ft.³

<1	<0.07
>10	>0.65
20	1.30
100	6.48
200	12.96
500	32.96
700	45.36

Physical Effects

Detectable by odor.
Protective breathing apparatus necessary.
Allowable for 8 hours exposure. (OSHA)
Kills smell in 3-15 minutes. May sting eyes and throat.
Kills smell quickly. May burn eyes and throat.
Dizziness with loss of balance and reasoning.
Breathing stops within 15 minutes. Prompt resuscitation needed.
Unconsciousness occurs quickly. Breathing stops. Death may result unless immediate resuscitation is applied.
Immediate unconsciousness followed by death or permanent brain damage in minutes.

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

WASHINGTON EDITORIAL STAFF

Managing Editor: Stanton S. Miller
Associate Editor: Julian Josephson
Assistant Editor: Lois R. Ember

MANUSCRIPT REVIEWING

Manager: Katherine I. Biggs
Assistant Editor: David Hanson

MANUSCRIPT EDITING

Associate Production Manager:
Charlotte C. Sayre

Assistant Editor:
Gloria L. Dinote

GRAPHICS AND PRODUCTION

Production Manager: Leroy L. Corcoran
Art Director: Norman Favin
Artist: Diane J. Reich

Advisory Board: P. L. Brezonik, Joseph J. Bufalini,
Arthur A. Levin, James J. Morgan, Sidney R.
Orem, Frank P. Sebastian, John H. Seinfeld, C.
Joseph Touhill, Charles S. Tuesday

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

Executive Director: Robert W. Cairns

BOOKS AND JOURNALS DIVISION
D. H. Michael Bowen, Director

Charles R. Bertsch, Head
Editorial Department

Bacil Guiley, Head, Graphics and
Production Department

Seldon W. Terrant, Head, Research and
Development Department

Marion Gurfein, Head, Circulation Development

ADVERTISING MANAGEMENT
Centcom, Ltd.

For offices and advertisers, see page 300

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

For author's guide and editorial policy, see June
1975 issue, page 547, or write Katherine I. Biggs,
Manuscript Reviewing Office *ES&T*

Water cleanup strategies

Strategies for water quality control require the establishment of standards. These may be either effluent standards for waste discharges or "stream" standards for receiving waters. Selection of the type of standard affects the management strategy to be adopted, the costs of that strategy, and the benefits that are derived from it.

Quality standards for receiving waters are based primarily on the protection of human health, the preservation of aquatic ecosystems, and the prevention of aesthetically unpleasant conditions. They are established chiefly by the effects of water pollution and not by its causes.

Effluent standards are often based on technical or economic feasibility. The inevitable result is that the costs of pollution control are too high and the benefits are too few. For example, present requirements for secondary treatment of *all* point-source municipal discharges necessitate aerobic biological treatment and chlorination. Application of this requirement to cities such as Los Angeles that discharge into well-flushed oceanic waters results in enormous costs and no discernible benefits. Similarly, aerobic biological treatment is of little use for municipal discharges to many lakes. Here nutrients such as nitrogen and phosphorus are proper concerns, and these are not removed by conventional secondary treatment.

Effluent standards *can* be based on stream standards by relating discharge rates to the quality that results in receiving waters. This requires knowledge of physical, chemical, and biological phenomena and is usually expressed mathematically in a model. Specific models are needed for specific pollutants and specific locations. Costs are incurred by developing these models, but significantly greater costs can be incurred by not developing them. Such models have been formulated in the past by environmental scientists and engineers to provide a base for strategies for controlling pathogens, for managing dissolved oxygen resources and, more recently, for controlling eutrophication and thermal pollution.

Prudent management of our economic resources requires that we discard present uniform treatment requirements. We should then expand our efforts at the development of models for regional water quality management, encourage research to perceive and solve new problems as they arise, and promote the education of environmental scientists and engineers who are needed to develop and implement sound strategies for pollution abatement.

Charles R. O'Melia

For filtering
samples to
instruments—

BalstonTM Filters are the best on the market!

You get:

A cleaner sample, with a lower pressure drop, compared to any other filter!

**A bold statement—
but we can
prove it!**

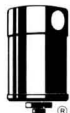
1. Instant Proof

Ask for your FREE "You're the Judge" kit . . . price and performance comparisons. Plus — names of Balston customers, stating why they selected Balston Filters. Plus — the easiest-to-understand technical and product data you ever saw!

2. Seeing is Believing

Match a Balston Filter against the filter you're using now. See which works better! Our portable demonstrator does it quickly — enables you to test any filter you have against a Balston Filter by merely turning a valve and watching a counter. Details are in the "You're the Judge" kit.

To get Balston's FREE "You're the Judge" kit, just phone or write us at Dept. 8-EST.



BALSTON, INC.

P.O. Box C, 703 Massachusetts Ave.
Lexington, Massachusetts 02173
(617) 861-7240 • (617) 862-7455
Telex 92-3481

CIRCLE 32 ON READER SERVICE CARD

LETTERS

Ozone correction

Dear Sir: In the story, "Ozone can help clean water and air" (*ES&T*, July 1975, p 618) there are some words about my city, Quebec, and its water treatment plant. Since we are very proud of our treatment plant, we are always very happy when it is the subject of a discussion or when it is stated as an example of water treatment technology.

In that issue, it was written, "Interestingly enough, Quebec City ozonates prior to activated carbon filtration, whereas . . ." Such a statement is incorrect since our water is ozonated in the final steps of the treatment. In fact, the treatment goes like this:

- pre-chlorination of the raw water at a rate of $<2 \text{ mg/l Cl}_2$
- addition of chemicals (alum, lime and polyelectrolyte) according to actual conditions
- flocculation and settling (4 hours)
- filtration through a bed of anthracite, sand and gravel
- ozonation
- pH adjustment (lime) and post-chlorination.

Since our treatment plant ranks among the largest drinking water ozonation plants ($\approx 200,000 \text{ m}^3/\text{day}$) and because other groups might want to contact us for more information or on-site tests, I wanted to make this point clear.

Let me assure you and ACS that I look forward to receiving my copy of *ES&T* each month. It is an essential tool for my work in the field of sanitary control as applied to water treatment and distribution.

Pierre-A. Côté

Jacques Rousset

La Ville de Quebec

2,480 de la Canardière

Que., P.Q., Canada G1J 2G1

Offshore drilling

Dear Sir: The item under Currents regarding the California Air Resources Board (CARB) (*ES&T*, November 1975, pp 1007-1008) and offshore oil is one of the many printed quoting numbers stated by the CARB. However, I have yet to see one printed quoting the CARB as making a correction or retraction. The enclosed material, taken from data of the Western Oil and Gas Association (WOGA) clearly illustrates the irresponsible actions of Tom Quinn and the entire CARB, and items such as yours only add to the problem in that thousands of readers only hear the CARB side of what is happening to California and unfortunately the poor results of the

CARB and the voice of the taxpayer go unheard.

CHARGE: CARB reported that the Federal Government's proposed offshore oil-drilling program could have disastrous air quality impacts in Southern California—creating as much smog as at least 900 000 new cars. (CARB press release, Sept. 29, 1975)

RESPONSE: This didn't make any sense at all to the WOGA, which charged that CARB apparently couldn't tell an oil well from an oil refinery. The WOGA found that CARB took Environmental Protection Agency refinery emission factors that are to be used to estimate total emissions from all the valves in a refinery and applied those factors to each valve on offshore platforms, to each valve in the treating facilities, and to each valve in the loading and unloading facilities. In other words, CARB took the EPA's 28 lb/day/1000 barrels refining capacity for all valves in a refinery, and applied that number to each valve in the anticipated production facilities.

CARB compounded these errors by applying an emission factor for an entire refinery to a production facility that is equal to no more than a small part, such as a single unit, of a refinery. Further, CARB disregarded the fact that the vast majority of these production facilities handles liquids and gases of a less volatile nature and usually at much lower temperatures and pressures. All of this contributes to CARB's gross overstatement of emissions from Outer Continental Shelf (OCS) production facilities.

CARB also assumed erroneously that all crude oil would be stored in tanks of 40 000-gallon (952-barrel) capacity or smaller, without vapor control devices. Crude tanks being built at the present time are far larger than 952-barrel capacity and have the most modern vapor control devices.

In calculating impact, CARB estimated more than 17 tons a day of reactive hydrocarbons from 100 000 barrels a day of production, whereas WOGA estimates less than one ton a day from the same amount of production.

Moreover, CARB assumed the efficiency of a sulfur removal unit in a gas-treating facility to be only 80% and thus concluded that 8.1 tons of SO_2 /day/100 000 barrels of produced crude would be emitted. The facts are that gas-treating facilities would have an efficiency greater than 99.5% and thus less than 0.1 tons/day/100 000 barrels would be emitted.

Raymond H. Bever

Huntington Beach, Calif. 92646



Enter your personal subscription to ENVIRONMENTAL SCIENCE AND TECHNOLOGY. Provides monthly information on research and technology involved in water, air, and waste chemistry. Also includes news of political and industrial aspects of environmental management.

ENVIRONMENTAL SCIENCE AND TECHNOLOGY 1976

	U.S.	PUAS	Canada and Other Nations
Member (Personal)	\$10.00	\$14.75	\$15.00
Nonmember (Personal)	\$15.00	\$19.75	\$20.00
Institutions, Libraries, Companies	\$30.00	\$34.75	\$35.00

Payment enclosed (payable to American Chemical Society).

Bill me Bill company

Name _____ Position _____

Your Employer _____
 Address Home Business _____

City _____ State _____ Zip _____

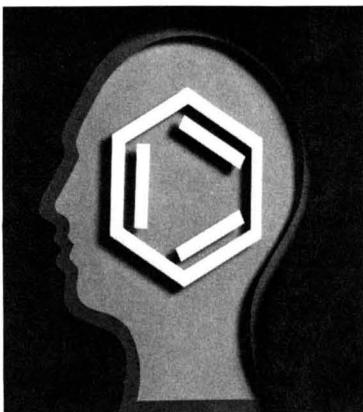
Employer's Business: Manufacturing Government Academic Other _____

If Manufacturer, Type of Products Produced _____

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

INQUIRE ABOUT 2 AND 3 YEAR PRICES.

**Formula
for a better tomorrow...**



**THE PUBLICATIONS
OF THE
AMERICAN CHEMICAL SOCIETY**

BUSINESS REPLY MAIL

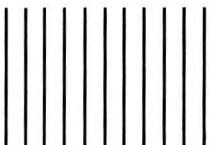
No postage stamp necessary if mailed in the United States

Postage will be paid by

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

ATTN: G. HEBRON

FIRST CLASS
Permit No. 1411-R
Washington, D.C.



Without these logos

NSF-pw

Potable water

NSF-dwv

Drain, waste, vent

NSF-cw

Corrosive waste

NSF-sewer

Sewer

NSF-drain

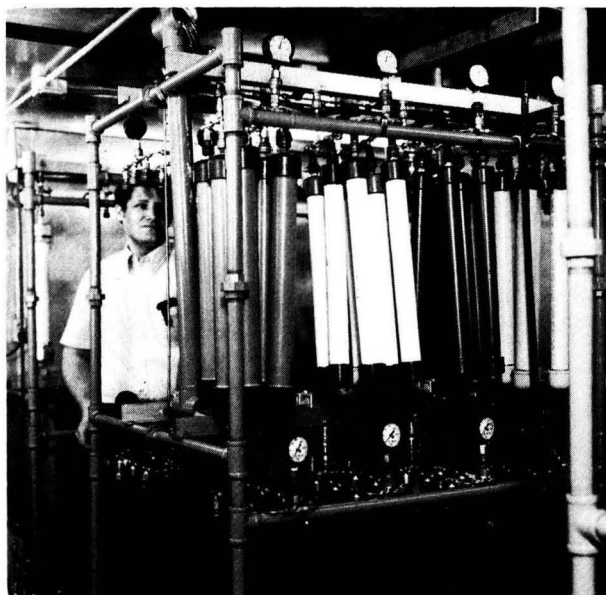
Drain

how do you know the substitute pipe is "as good as NSF"?

At a glance the substitute pipe looks okay and, of course, you can check it for dimensions, but how will it *perform*? What about crush resistance and hydrostatic burst? How about joint tightness and specific resistance to flattening, or invasion by water or chemicals? How is its resistance to impact at room temperature—or impact below zero° F?

Pipe with the NSF logo is tested at repeated intervals throughout the year in the NSF laboratory to make sure the pipe fulfills the requirements of its NSF standard.

When you bury a pipe in the ground or within a wall you won't be burying your reputation if it's marked with an NSF logo.



Send for
your copy
of NSF
pipe
standards.
FREE to
public officials.
Only \$1 to
non-official
professionals.

National Sanitation Foundation—an independent non profit, non governmental organization dedicated to environmental quality. Offices and laboratories: NSF Building, Ann Arbor, Mich. 48105 (313)-769-8010

NSF

CIRCLE 31 ON READER SERVICE CARD

The Calgon® Adsorption Report

Presenting summary reports of lab studies on effectiveness of granular carbon in removing dissolved organics from water.

Industrial wastewater survey shows adsorption effectiveness.

A study of wastewater samples from 68 different industrial operations has shown carbon adsorption to be almost universally applicable as a viable wastewater treatment method for dissolved organics removal.

A total of 324 samples were tested for pH, suspended solids, TOC, and carbon adsorption applicability. Color and phenol were also checked on 59 and 22 samples, respectively.

TOC was reduced 85% or better in 253 of the samples. Color removal was 90% or better in 58 samples; and phenol removal, 99% in 21 of the samples checked.

As requirements for higher levels of TOC reduction become more common, combined-treatment systems using carbon's specialized ability against dissolved organics will be used in more industrial locations.

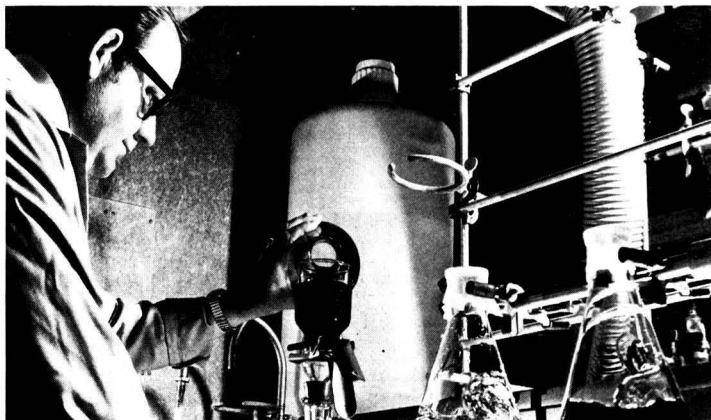
Fish toxicity tests compare raw and treated wastewater.

In addition to the isotherm tests reported at right, seven industrial effluents were tested with bluegill sunfish. The fish were exposed to samples of both untreated and treated wastewater containing toxic organics. In the bioassays conducted at independent labs, the raw wastewater produced a 100% mortality in from 1/4 hour to 5 hours, while the carbon-treated water produced no mortality for up to 10 days.

While these fish tests were cursory in nature, the dramatic survival rate in carbon-treated wastewater helps confirm the efficacy of carbon adsorption in removal of toxic dissolved organic chemicals.

EFFECT OF CARBON TREATMENT ON TOXICITY OF BLUEGILL SUNFISH

Plant	Raw water		Treated water	
	Exposure	% mortality	Exposure	% mortality
A	5 hours	100	5 hours	0
			48 hours	63
B	1/4 hour	100	72 hours	100
			10 days	0
C	2 hours	100	7 days	0
D	2 hours	100	7 days	0
E	1/4 hour	100	96 hours	0



Carbon isotherm tests at Calgon Water Laboratory

Toxic organics study shows carbon to be 98% effective.

Concern about hazardous and toxic organics has focused interest on effective treatment methods for removing these chemicals from wastewater. Conventional biological systems are generally ineffective against these compounds.

By contrast, adsorption using granular activated carbon is a process which meets the combined objectives of removal from water and practical ultimate disposal during thermal reactivation of the carbon. This process is already at work in dozens of industrial systems removing dissolved organics from process waters and wastewaters. When the adsorbing capacity of the carbon is exhausted, it can be reactivated for reuse. During reactivation, the organics are completely oxidized to harmless compounds.

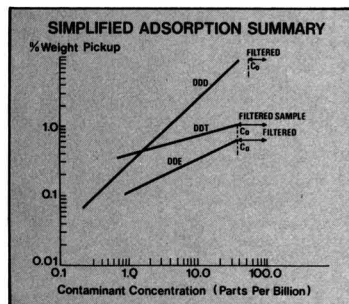
Report on studies.

Since not every organic is amenable to this treatment, a series of carbon isotherm tests was run on 16 of 21 compounds. This isotherm is a standard lab method of evaluating effluent levels after treatment and the weight of contaminant that will be adsorbed by the carbon at the concentration studied.

Effective reduction of effluent concentration was realized for all of the toxic organics—ranging from a reduction from 38.0 to 1.0 ppb to a reduction from 62 to 0.07 ppb. Weight-

pickup percentage ranged from 1.4% for heptachlor to 130% for dichlorodiphenyldichloroethane.

While these tests are certainly not all inclusive and more work must be done on the relationship of adsorption to toxic organics, the results to date indicate that activated carbon is feasible for removal of hazardous and toxic organics.



Papers available.

For reprints of the papers and reports on which these summaries are based, write Calgon Adsorption Systems, Calgon Corp., Pittsburgh, Pa. 15230.

In Europe contact Chemviron, 1135 Chaussée de Waterloo, B-1180, Brussels, Belgium. Phone 375.24.20.



SUBSIDIARY OF MERCK & CO., INC.

CIRCLE 4 ON READER SERVICE CARD

CURRENTS

INTERNATIONAL

West Germany is proving that strip-mined land can be productively reclaimed back to forests, farms and lakes. West Germany sits on an estimated 55 billion tons of soft brown coal reserves; about 42 million tons/yr are extracted to fuel about 27% of the country's power generating plants. Rheinische Braunkohlenwerke (Cologne), a company now mining at Fortuna-Garsdorf near Bergheim, claims that in the last 20 years, of the 400 000 acres of land taken for open-pit mining, more than half has been returned to productivity. Last December, for their efforts, five mining company specialists and a government planner received a \$200 000 industrial prize awarded by West Germany's Alfred Krupp Foundation.

WASHINGTON

Under proposed rulemaking (40 CRF 116) EPA would designate 306 substances as hazardous and would limit their discharge under Section 311 of the Federal Water Pollution Control Act (P.L. 92-500). Materials were considered for inclusion on the list according to six criteria for toxicity. According to the EPA, the hazardous substances on the list cannot, in the language of P.L. 92-500, "actually be removed." The Agency has proposed four categories of hazardous substances; it adopted, but modified, a scheme used by the Intergovernmental Maritime Consultative Organization, an agency of the United Nations. The proposed rulemaking also sets out a schedule of penalties.

Final air pollution standards for new and modified primary copper, lead and zinc smelters were set by the EPA. The regulations are designed to reduce the average emissions of particulates and sulfur dioxide by about 95%. Discharge of particulate matter is set at 50 mg/dry m³ at standard conditions, SO₂ is limited to 0.065% of volume and smokestack emissions opacity is set at 20% or less.

The House Subcommittee on Transportation and Commerce has completed a discussion draft of a Solid Waste Utilization Act that tackles the problems of resource recovery and solid waste disposal. The draft does not commit the Subcommittee to any



Subcommittee chairman Rooney

legislative language or provision. Provisions of the draft provide for such economic incentives as a national solid waste disposal charge and a subsidy program for use of recycled materials. According to Rep. Fred B. Rooney (D-Pa.), Chairman of the Subcommittee, the draft is "a first step toward legislation which will effectively encourage the recovery of economically valuable resources now being wasted, and which will encourage the safe and efficient disposal of those wastes which cannot be reclaimed."

In a recent report, GAO reviewed the federal pesticide registration program and found that "The American consumer has not been adequately protected from the potential hazards of pesticide use . . ." Among other things, the General Accounting Office found that: there is little or no information on the long-term effects of pesticides as marketed on human health and the environment; many labels do not comply with regulations; pesticide residue tolerances are not monitored or reviewed; and statutory registration requirements are not carried out on a timely basis. GAO has issued three other reports citing EPA's inadequate program to regulate the use of pesticides.

A National Registry of Marine Pathology has been established by the National Oceanic and Atmospheric Administration (NOAA) at the Middle Atlantic Coastal Fisheries Center laboratory at Oxford, Md. The Registry is a repository for information on diseases and abnormalities of marine and estuarine organisms.

A delay in the sale of offshore leases in the Gulf of Alaska has been requested by the Council on Environmental Quality (CEQ). In a letter to Thomas Kleppe, Secretary of the Department of the Interior, CEQ asked

for more time to allow further analysis of the environmental impact of drilling for oil and gas in the area. If Kleppe should conclude that a blanket delay of the sale is not in the national interest, CEQ asked that the sale be restricted to Icy Bay tracts in the northeastern zone of the Gulf of Alaska.

STATES

California Air Resources Board has fined American Motors Corp. \$4.3 million for producing polluting cars and falsifying test reports, and has halted the sale of all AMC cars containing the company's V-8 engine. This was the strongest disciplinary action yet taken by the ARB, and far surpasses that taken by the Board against Chrysler Corp. last year. Despite the company's test records, 85% of all AMC cars tested by the ARB failed to meet California's carbon monoxide or oxides of nitrogen standards. The ARB will consider waiving 75% of the fine if American Motors immediately pays 25% and commits the remaining amount to improving its emission control and fuel economy program.

Wisconsin Department of Natural Resources recently adopted regulations setting limits to PCB's discharged into state waters. Effective January 1, 1977, 0.01 mg/l as measured in a 24-h composite sample of polychlorinated biphenyls may be discharged; this will decrease to 0.005 mg/l by February 2, 1979. In the meantime, the Department has asked the state legislature to ban the use, sale, purchase, or manufacture of PCB's after February 1, 1977, except in limited instances. On another water matter, the Department announced that the state had been awarded almost \$1 million from the U.S. EPA for five lake and rehabilitation projects. Wisconsin thus received about 50% of all federal monies granted for this purpose.

The 1975 Annual Report of the Interstate Sanitation Commission was recently released. The report describes the air and water pollution abatement activities of New York, New Jersey, and Connecticut, the states that comprise the Interstate Sanitation District. More than \$4.5 million has been allocated, over the next few years, for the upgrading and expansion of present wastewater treatment systems to provide at least secondary treatment.

ANNOUNCING ENVIROSPHERE

The complete environmental service company.

Envirosphere is a company organized to provide professional environmental engineering and scientific services to industry, utilities, and government. Envirosphere's services assist clients in satisfying current and emerging regulatory requirements and ensuring environmental compatibility in an economic manner.

Envirosphere Company is a division of Ebasco Services Incorporated—one of America's largest Engineering, Construction, and Consulting firms—which enjoys a worldwide reputation for its experience, professionalism, progressiveness, and results. Ebasco has organized Envirosphere as a separate company in order to make available to all sectors of industry and government the environmental services currently provided to Ebasco clients.

Envirosphere offers a complete range of services

covering all aspects of:

- Environmental Engineering
- Environmental Management and Planning
- Environmental Assessment Analyses
- Environmental Monitoring.

These services are performed by a staff of experienced engineers and scientists, whose collective capabilities have been utilized by Ebasco since the late 1960's to provide cost-effective solutions to pollution control problems and to support the licensing activities of industry.

Envirosphere is prepared to discuss with you your environmental service needs—from site selection through expert testimony. For detailed information, please write: Harvey S. Sands, Director of Client Services, Envirosphere Company, 21 West Street, New York, N.Y. 10006. Or call him at (212) 785-4488.



envirosphere

**envirosphere
company**

21 West Street, New York, N.Y. 10006 • (212) 785-4488

A DIVISION OF EBASCO SERVICES INCORPORATED

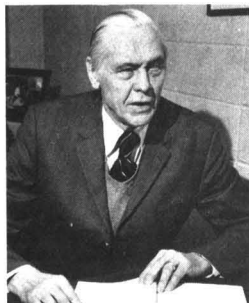
Air pollution engineers • Aquatic ecologists • Archaeologists • Biochemists • Botanists • Chemical engineers • Chemists • Civil engineers • Demographers • Economists • Environmental engineers • Environmental geologists • Environmental planners • Health physicists • Hydrodynamics • Hydrogeologists • Industrial hygienists • Landscape architects • Land use planners • Limnologists • Marine biologists • Mathematical modeling specialists • Mechanical engineers • Meteorologists • Noise control engineers • Oceanographers • Physicists • Sanitary engineers • Sociologists • Terrestrial ecologists • Zoologists

A HALLIBURTON Company

CIRCLE 25 ON READER SERVICE CARD

Phase 2 of a three-phase study—in depth studies of alternatives to ocean dumping of sewage sludge—has begun, as has a biological monitoring program to monitor biological conditions in the District. The Commission's air pollution activities included the coordination of the Air Pollution Warning System; characterization of photochemical oxidants; and an investigation of rural sulfates.

A plan to convert New York City's trash to a clean fuel gas and reusable materials has been submitted to city officials. The plan, developed by a research team headed by H. W. Schulz at Columbia University's School of Engineering and Applied Science, calls for pyrolysis of solid waste with pure oxygen to a clean fuel gas, and the co-combustion of prepared refuse (refuse-derived fuel) in a utility boiler (see



Schulz & N.Y.'s plan

ES&T, May 1975, pp 423–427). This plan, along with others, was considered by a task force formed to design a master waste disposal plan for the city. A preliminary draft report of this master plan, released last December, calls for continued in-house feasibility studies and a "go-slow" implementation of projects because of the city's financial situation.

New Hill, North Carolina is the site of a 4000-ft well now being drilled to test the liquid waste storage potential of deep geologic basins in the Middle and North Atlantic regions. These basins have been suggested as natural underground storage reservoirs where toxic wastes and other unusable liquid materials might be contained and controlled without harm to natural resources or the environment. The Triassic basins in North Carolina, Virginia, Connecticut, and New Jersey are especially attractive waste disposal sites because they are accessible to major industrial areas, contain little known mineral worth and unusable saline water. This test well is considered a significant first step in determining the basins' storage potential.

Tennessee, Alabama, Virginia, Kentucky and the Tennessee Valley Authority will begin to reclaim abandoned "orphan" coal strip mines this spring. This demonstration program is expected to cover a five-year period, reclaim some 87 000 acres of orphan strip mines and haul roads and cost an estimated \$22.8 million. Only orphan lands that were mined and abandoned before effective reclamation laws were enacted are to be reclaimed under this program. Congress recently approved \$2.9 million in funds for this TVA-administered project, and a similar amount is contained in the President's budget request for fiscal 1977. This is the first multistate effort to reclaim abandoned mines and haul roads.

Thirteen experimental computer-produced land-use maps have been prepared of the New Haven, Conn., area by the U.S. Geological Survey; these maps were part of USGS' Census Cities Project. Prepared with the use of cameras and other remote sensors on aircraft and satellites, each map delineates one of 13 categories of land use such as residential, commercial, industrial and agricultural. According to J. R. Wray of the USGS, "These maps are expected to be of particular use to urban and regional planners, administrators, environmentalists and others concerned with monitoring and planning urban growth and changing land use." The Northeastern Illinois Planning Commission and Argonne National Laboratory have also developed computer techniques to analyze soil data and produce graphics of this analysis.

MONITORING

Determining occupational exposure of a worker to mercury is the task of a new sensitive monitor developed by Eugene Scheide and John Taylor of the National Bureau of Standards (NBS, Gaithersburg, Md.). This monitor, portable, easy and inexpensive to build, and reusable, gives the worker's total accumulated dose over a workday, rather than concentrations of mercury at a given time. It can measure to parts per billion, and is to help protect some 150 000 workers in industries where mercury exposure is still a hazard. Other pollutants do not interfere with the NBS monitor's readings. Permissible mercury exposure for an 8-h day and 40-h week must not exceed 0.05 mg/m³.

TECHNOLOGY

Production of ammonia from solid waste can be realized when the organic fraction of that waste is pyrolyzed, and resulting gases are cleaned and the

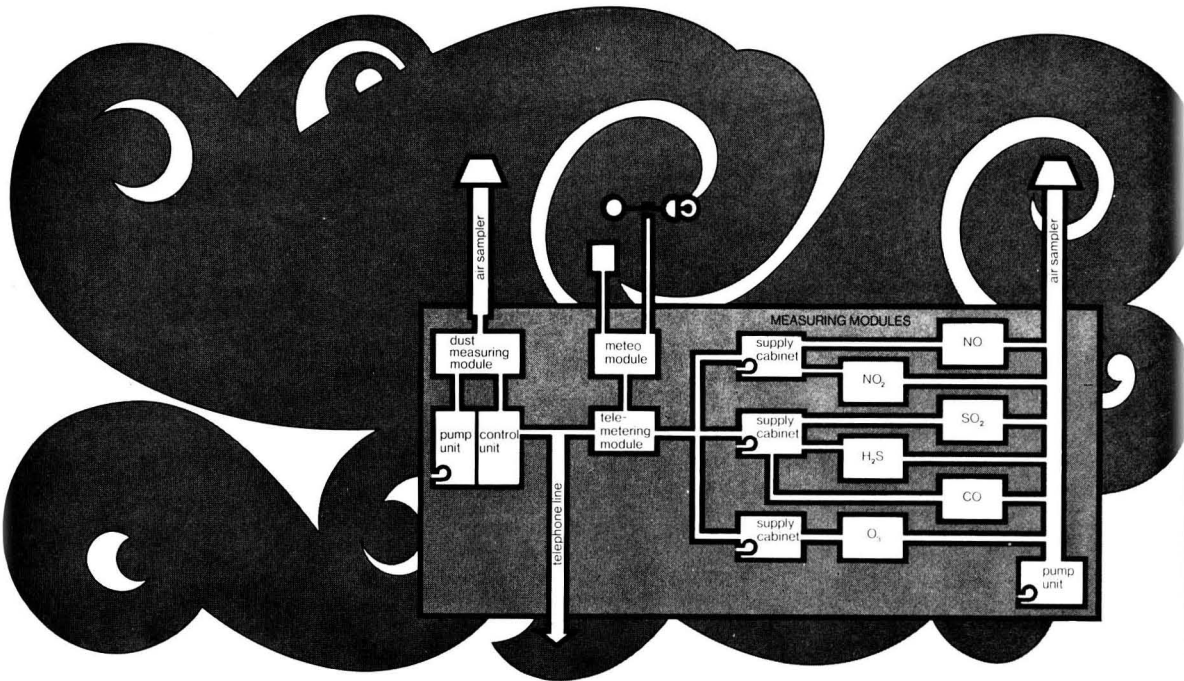
hydrogen component is treated with atmospheric nitrogen over a catalyst. According to Coyne Chemical Co. (Philadelphia, Pa.), process developer, the hydrogen is derived from the gasified waste. Coyne, with Union Carbide, is negotiating with the City of Seattle (Wash.) to build a \$90 million plant to process waste to 140 000 t/yr of ammonia. Estimated savings of natural gas, a present ammonia feedstock, are 5 billion ft³/yr. Alternatively, 550 000 t/yr of solid waste, Seattle's projected production, could make 32 million gal/yr of methanol, with a slight modification of the Coyne process. The firm offers financing and plant construction, and end-product marketing and distribution, as well as the process.

Substantial reduction of toxic industrial waste materials is possible with a new process that is being used in the carbon and alloy steels and cast iron industries. Developed by Degussa (Hanau, Ger.) and marketed in the U.S. by Kolene Corp. (Detroit, Mich.) the new process uses cyanates rather than cyanides. The new process—"Tenifer" in Germany and Melonite in the U.S. and Canada—yields no more than 1–2 kg of iron oxide sludge from the bath. These baths are used in the surface hardening of carbon, alloy steels and cast irons to increase their wear and fatigue resistance.

Cyanides can be removed from electroplating wastes with concentration and recovery of cyanide and metal cyanides. A Union Carbide process uses a continuous countercurrent solvent extraction technique based on a quaternary amine solvent. The resulting decontaminated aqueous raffinate solution can be recycled to the plating rinse bath or to other plant uses, or sent to the sewer. The amine solvent is regenerated by dilute sodium hydroxide stripping, and metal and cyanides can be recycled to the plating bath, or salvaged. Regenerated amine solvent goes back to the cyanide extraction section. The process has been demonstrated with zinc and cadmium plating lines, and will be evaluated for nickel, silver, and gold plating and recovery.

An energy-conserving solvent vapor recovery system handles a wider range of hydrocarbon (HC) vapors. The CA-66 system, developed by Oxy-Catalyst, Inc., a division of Research-Cottrell, Inc., regenerates adsorbent under vacuum, without steam, thereby extending its applicability to HC's with boiling points higher than those to which conventional techniques are limited. Cartridge heaters or recirculation of recovered heat are steam substitutes. The adsorbent is

THIS SOLUTION



...fits any multi-component air-pollution monitoring problem.

With such a wide variety of requirements associated with air pollution monitoring, you may be surprised to learn there's a single solution that fits them all.

The Philips Multi-Component Air Pollution Monitoring System.

You decide exactly what you need. Which pollutants and parameters you want to monitor. Within which environmental limits. Whether or not you need automatic operation. At a single location only or as part of a network. What type of data transmission, if any, you need.

We deliver the system that fits the problem.

The secret to the Philips system's versatility is its modular design. Standard measuring modules are provided for pollutants such as SO₂, H₂S, NO, NO₂, CO, O₃ and particulate matter. The appropriate units ... supported by sampling, calibration, supply, control and

communication elements ... are all housed in a monitoring station of appropriate size and construction. Space is also provided for meteorological modules.

All modules are designed to operate continuously and automatically for at least three months, without need of attention. Data communication can be over switched or leased telephone lines, or by radio links. When your needs change, you simply change the modules.

Simple? Of course. Let us send you free details.

Please direct all enquiries to:
Philips Electronic Instruments, Inc.,
750 South Fulton Avenue,
Mount Vernon, N.Y. 10550.
... enquiries outside U.S.A., to:
Philips Industries,
Pollution Monitoring Department,
Building TQ 111-4,
Eindhoven, The Netherlands.



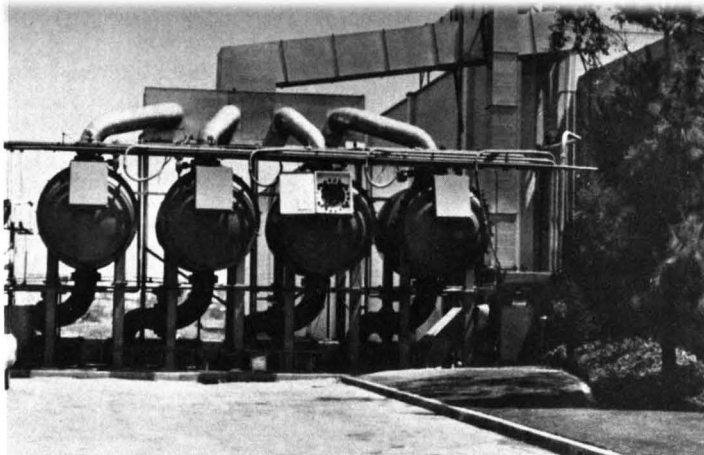
A Philips multi-component air monitor within typical weatherproof housing. This forms part of the Dutch national air monitoring network.



**Philips
Environmental
Protection**

CIRCLE 7 ON READER SERVICE CARD

PHILIPS



Recovering solvent vapors

activated carbon; the vapors driven from it by the CA-66 system can be condensed and made available for reuse or sale. The system, which uses 5% of the energy of afterburner incineration, and uses no oil or gas, meets air rules as tough as those of Los Angeles.

An automatic acid mine drainage water neutralization system is on-stream at a Pennsylvania coal mine. The system mixes acid mine drainage water with slaked lime in a flash mixer, and then transfers it into a second reactor where the iron content is oxidized. Designed by Mine Safety Appliances Co. (MSA, Pittsburgh, Pa.) to treat 4 mgd of mine drainage, the system acts when a pH probe in the flash mixing pond signals a sufficiently acid pH. Then, a feeder unit delivers a metered amount of quicklime to a slaker; next, the lime slurry is sluiced to the flash mixer. A dust collector prevents quicklime dust from venting to the atmosphere.

Were adverse effects of chlorofluorocarbons on upper atmospheric ozone overestimated? A study for the Manufacturing Chemists Association (MCA, Washington, D.C.), performed by N. D. Sze and M. F. Wu of Environmental Research & Technology, Inc. (ERT, Concord, Mass.) so concludes. It proposes that fluorocarbon effects may have been overestimated fivefold or more, because 80% or more of these compounds may be destroyed by unidentified natural tropospheric processes other than photolysis before they reach the stratospheric ozone layer. The ERT model predicts a 1.2% ozone depletion by the year 2100, rather than the approximately 10% depletion foreseen through models that assume photolysis to be the only fluorocarbon destruction mechanism.

INDUSTRY

U.S. Ozonair Corp. (South San Francisco, Calif.) has recently completed four months of field tests on ozonation of raw St. Lawrence River water at Pointe Claire, Québec (near Montreal). This water is considered to be among North America's worst. According to Ozonair president Karel Stopka, his company's Film Layer Purifying Chamber (FLPC) ozone (O_3) contact system reduced color from 40-60 Jackson Units to 3-4 J.U., after 12 seconds of treatment. Total bacteria and E. Coli were always down to zero. Stopka believes that the FLPC system will remove viruses and suspected carcinogens from water. The new high-frequency O_3 generator delivers 1.84% concentration by weight, as against 0.994% for other generators, and can instantly dissolve up to 2 mg/l of O_3 in water, as compared to the usual 0.4-0.6 mg/l.



Ozonair president Stopka

The American Paper Institute (API, New York, N.Y.) warned that 63 000 jobs in the paper industry will not be created in 1984, because of steep advances in environmental outlays and other rising capital costs. Speaking on API's behalf, Eugene Ellis, Jr., vice president of International Paper Co., noted that "those 63 000 jobs multiply to 440 000 when you include the

impact on all those who supply our raw materials and use our products." Speaking to the National Commission on Water Quality, he said, "Dollars spent to meet unrealistic 1983 requirements simply would not be there to finance growth and create new jobs in this industry." He warned that costs for 1983 would far outweigh minor benefits achieved.

Frank Sebastian, senior vice president of Envirotech Corp., said that modern sewage sludge incineration technology is responsive to environmental protection and energy conservation needs. "Thermal processing of sewage sludge is environmentally attractive because hazardous substances such as PCB's, chlordane, and heptachlor are almost completely destroyed in the combustion process," Sebastian said. He noted that this benefit is not achieved when sewage sludge is used as landfill or dumped in waterways. Sebastian also pointed out that since "close-loop" sludge incineration systems now being built can recycle heat, their energy consumption drops to near zero, and their air pollution is "insignificant."

Enviro-Systems & Research, Inc. (ES&R, Roanoke, Va.) will demonstrate a high-efficiency fabric filter device at the Kerr Finishing Division of FabricsAmerica Corp., a textile maker at Concord, N.C. ES&R will construct and operate its proprietary Enviro-Clean RAC-3 collector on two 60 000-lb coal-fired stoker boilers. This demonstration, to last almost 3 yrs, is funded by a \$1.23 million EPA allocation. According to ES&R, fly ash removal efficiencies can exceed 99.9%, and the device is more economical than conventional systems. The fly ash is collected in a dry form, so the need for water and sludge disposal problems, encountered with scrubbers, are essentially eliminated. ES&R aims to develop the most comprehensive fabric filter data ever obtained.

AJAX International Corp. (Santa Barbara, Calif.) has assembled and shipped the largest reverse osmosis (RO) wastewater treatment plant yet sold in Europe. The plant has a daily output of 730 m³ (192 800 gal); it will be used at a \$7 million water purification and recycling facility in Switzerland. When that facility is completed early this year, it will purify contaminated wastewater from the Zurich engineering facility of Swissair, one of Europe's major airlines. Recycling the cleaned wastewater will reduce consumption of fresh water and the output of polluted water, and contribute to the alleviation of one of Switzerland's nagging problems.

EPA rides the stormy SEAS

OUTLOOK

The Strategic Environmental Assessment System (SEAS) has been embroiled in controversy since its inception in the fall of 1972. The questions then being debated, and not fully answered even today, were:

- whether SEAS, being such a complex model, is the best way to study environmental problems
- whether a federal agency should be involved in such an extensive and costly modeling adventure
- whether the assumptions and limitations set during development were "correct."

This latter issue is the pivot on which the very utility of the system turns. And, after 3.5 years and \$3-8 million, the operational status of the system is still being bandied about. The developers claim it's operational while EPA's present staff claims it's in a "research mode."

The system

Seas is a collection of 13 interdependent modules (see box material) and 28 independent computer programs designed to forecast the interrelated effects, at the national level, of the economy and environment as both are affected by environmental policies and socioeconomic trends. The system incorporates preexisting economic, technological and demographic projections, and is capable of forecasting, on an annual basis, through 1985.

The programs do not require user-supplied information, but can be run under what is termed a "default scenario" in which forecasts are developed based on data available from government sources. The user, however, has the option of overriding the default data and can also select optional scenario conditions as input to all programs. The National Commission on Water Quality (*ES&T*, April 1975, pp 297-299) primarily chose to use its own data for its draft report, and may not use SEAS at all for its final report (scheduled for release in the second quarter 1976).

INFORUM, a macroeconomic inter-industry input/output (I/O) model

developed by Clopper Almon, Jr., at the University of Maryland was utilized and expanded by EPA to obtain the national economic forecasts that drive the other SEAS modules. INFORUM is generally accepted as being state-of-the-art.

In the early phases of building SEAS, the development of the national modules was emphasized; but, for reasons perceived to increase its utility, the regional modules were expanded in the third and fourth (present) phases. These regional modules have received much criticism and, in at least one known instance, by the U.S. Water Resources Council, the regional output data were actually rejected. The focus of the criticism is that in going from the national level to the regional level, a top-down approach, the system makes certain assumptions in the allocation of national aggregates, such as the generation of pollution residuals, that result in imprecise assessments at the regional level. And, so, as some argue, since the major effects of policy decisions and regulations are to be felt at the local level, this imprecision is a major deficiency in the model.

To build a better widget

SEAS was developed within the Office of Research and Development (ORD) by Peter House, Ted Williams, Philip Patterson, Sam Ratick, and outside contractors. Only Ratick remains on the SEAS project, and then only part time. Thus a vast amount of expertise, not only in the development of the model but in the perspective, a "feel" for economically linked environmental problems, acquired by these four men has been lost to EPA. Although Calvin Lawrence, who is now the project's acting manager, is doing an admirable job in learning the system, he lacks the perspective of the original developers.

According to House, the model attempts to define or predict: the magnitude of the pollution problem including the cost to clean up the problem; the problems that will be created as a result of cleanup efforts; and the regions of the U.S. in which the problems will

be most severe. He claims that SEAS offers the user a consistent data base and a consistent set of assumptions on which the synergistic effects of air, water and solid waste pollution abatement practices on the economics of a specific industry (or region) can be ascertained.

It is a unique model, so EPA claims, in that it links economics to residuals generation at the national level; the secondary effects of environmental policy can, in a fashion, be projected by this model. Others, including Edwin Clark of the Council of Environmental Quality, claim that SEAS is not so unique and that other, though less detailed, models exist, including one developed several years ago by Ronald G. Ridker, who is now with Resources for the Future, which link an I/O model with residuals generation and cost abatement coefficients; Ridker's model, however, has not been updated.

As a policy analysis tool, one of the mechanisms for which SEAS was purported to be developed, the system is seen as being too cumbersome and too costly to operate. For this purpose, many feel, SEAS would have to be greatly simplified and restructured. In this redesigning, it would help if the modelers had some feeling for problems policy decision-makers face.

The developers and the current staff see the system as a macro model, not suitable for microeconomic or specific regional studies.

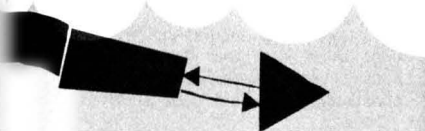
Struggle to survive

In its short history, SEAS as a program has been on the verge of termination at least twice. Each time, its charismatic developer, Peter House, began evangelical efforts, mainly briefings, to save it. At these briefings, House was said to overwhelm his audience with the possibilities inherent in SEAS. Through his efforts and those of the other developers, the list of users expanded and SEAS survived.

When Wilson K. Talley, assistant administrator for research and development, came to EPA in December 1974

...still

The system is a \$3-8 million modeling effort that the agency calls unique and its detractors term unwieldy



he instituted a reorganization within ORD and ordered reviews of all its programs. SEAS, subject to this order, was reviewed by an ad hoc review panel, a group of outside experts, co-chaired by Nobel Laureate Wassily Leontief of New York University and Thomas Crocker of the University of Wyoming.

In its report dated December 3, 1975, the panel recommended that SEAS be retained within EPA, but that the Topsy-like growth pattern that had characterized its development be halted. No new modules (sub-models) should be added to the system and existing capabilities should be refined through the

- development of better data bases
- improvement of structure
- verification of results.

Other recommendations included the maintenance of a stable in-house staff of professionals and the establishment of a continuous peer review group, which may end up being the ad hoc review panel itself.

Prior to surviving the review panel's scrutiny, the SEAS project had been funded at about \$1.1 million for fiscal 1976, half of which covered ADP costs. EPA has recently requested continued support for SEAS in its fiscal 1977 budget at the previous year's level of funding. This figure, and even the very existence of the program, has been discussed in the Office of Management and Budget.

Problems and potentials

All those who criticized SEAS have used the system or are themselves modelers or intrigued by the utility of models. They all saw a need for some modeling capability within EPA, and they consistently recognized the formidable task undertaken and to some measure successfully achieved by the agency. But in general they characterized SEAS as cumbersome, unwieldy, overgrown and very costly, both to develop and to use.

Most detractors saw the system as presently constituted as being too costly and too complex to use either as a

policy-making tool or as a repository for data. To use the system properly, they stated, the user has to know it in exquisite detail. But, most importantly, the user must be able to interpret the output, and know enough about the problem in the "real world" to be able to reject spurious data. They felt that as a policy-making tool, the level of detail supplied by SEAS is far in excess of that needed by decision-makers, and that the added refinement serves only to add to the cost and confusion.

Because of excessive costs, some previous users stated that they would not have used SEAS had it been in the hands of private contractors. Bill Watson at Resources for the Future, however, stated that he would continue to use the system at the current costs. For his purposes, a study for the National Institutes of Health, there is no other model available, he claimed, that he could use as effectively. Watson has made many modifications to SEAS and, in fact, has helped to develop it. But there are not many who have the expertise or the propensity of a Bill Watson to spend the time required to adapt the system to specific needs.

Dan Sokoloski, now with the Department of the Interior but formerly with the NCWQ, Edwin Clark with CEQ and Fred Abel, now with ERDA but formerly with EPA, feel that the system, if pared down, would become cost effective for developing annualized reports.

SEAS was used to develop the (1975) Cost of Air and Water Pollution Control: 1976-1985, a report that EPA is required to submit to Congress annually. This report cost as much to develop as did the previous two reports (the 1973 Economics of Clean Water and the 1974 Cost of Clean Air). But much

of this expenditure (\$500 000) can be justified if meaningful, standardized reports can be developed in the future on an annual basis. At press time, the draft 1975 report, now about a year late, was being circulated to other federal agencies and to interested public groups for comment.

SEAS could be an excellent repository for data, according to Clark, if the data collectors could be made to conform to rigid formats so that the collected information is in a form for direct insertion into the computer. This storage capacity would make data readily accessible to EPA and other users.

The data presently going into the system are not those continuously collected from EPA's own National Emissions Data System (NEDS), nor are provisions being made to insert the water data from EPA's Needs Survey and the 208 studies mandated by P.L. 92-500. Ted Williams claims that some NEDS data, in a modified form, are being fed into SEAS. Edward Pechan in ERDA's Office of Environmental Analysis and formerly with EPA, feels that the SEAS projections for air and water are already outdated by the Regional Emission Projection System, which uses NEDS data, and the National Residuals Discharge Inventory (NRDI) developed by the National Academy of Sciences for the NCWQ. In its latest assessment of water quality in the U.S., the Water Resources Council used the NRDI model rather than SEAS.

The next move

Randall Shobe, director of the Technical Information Division in ORD and Calvin Lawrence's immediate superior, told *ES&T* that SEAS is now undergoing an in-house management review. This latest scrutiny will consider the Leontief/Crocker panel review recommendations, and then decide the best direction for SEAS' future development.

Shobe felt that the model's architecture would not be expanded. But whether the resources required to streamline and simplify the system would be forthcoming was not yet known. Both Shobe and Lawrence stressed the need to develop more user-oriented documentation, although they did emphasize that SEAS was technically well-documented now. They did stress, as did Talley, that SEAS in the next two years could, with appropriate applications engineering, be moved from a research project to a more efficient operational system.

With proper restructuring, SEAS could become both a useful policy-making tool and a data bank. How EPA spends its current \$1.1 million on SEAS will be interesting to watch. At press time it was learned that SEAS will be funded for fiscal 1977. But the monies, another \$1 million, will come from EPA's discretionary funds. LRE

The 13 functional units

National economic modules

INFORUM

Industry & consumption disaggregation

Abatement costs

Prices/wages

Materials flow modules

Stocks

Solid waste and recycling

National residuals module

Transportation module

Energy budgets module

Regional modules

Regional industrial & residuals
disaggregation

Land-use residuals

Ambients

Benefits

Clearing the employment picture

An NRC committee aims to replace speculation about environmental manpower needs with hard numbers

At all times, but especially during times of high unemployment, questions of where, how, and what types of manpower are and will be needed elicit much interest. Thus, manpower needs in the environmental field are a subject of considerable interest, particularly since the President's Council on Environmental Quality (CEQ) sees this field as one of the few areas of relative job strength at present.

In an attempt at a more systematic understanding of present and future manpower and related training needs, and funding related to these needs, the National Research Council (NRC) formed a Committee for the Study of Environmental Manpower (*ES&T*, May 1975, p 405), with Earnest Gloyna, dean of the College of Engineering of the University of Texas (Austin) as its chairman, and Stanton Ware as NRC's staff

maintenance (O&M) of collection systems as in actual treatment systems.

Wagner said that the WPCF is really interested in how many properly trained and educated employees there are, capable of making the correct O&M decisions, in treatment plants. For 1974, the WPCF estimated that 40 800 people were so employed. Wagner cited National Commission on Water Quality (NCWQ) estimates of manpower needs of 85 000 by 1990, for treatment alone, if clean water criteria, based on 1983 goals of P.L. 92-500, are to be met.

Will the requisite personnel be available? One answer to this query might be gleaned from a statistic from the WPCF Government Affairs Seminar of last April, that in 1971-1972, there were 2406 graduate students in the water pollution control (wpc) field. By 1974-1975, there were 1635 such stu-

but in industry or engineering organizations these data are inadequate because, in the private sector, apc often constitutes a part-time responsibility.

Some industry inputs

Speaking for the National Association of Manufacturers (NAM, Washington, D.C.), Richard Nalesnik, the NAM's vice president for natural resources and technology, said that manufacturing companies are not experiencing immediate or critical manpower problems. He pointed out that in-house pollution control (pc) staffs have been expanded through on-the-job training, outside seminars, and short courses. He also noted that some firms augment pc staff capabilities by engaging consultants, and others rely on makers of installed pc equipment. Nalesnik did predict, however, the more than 50% of future environmental manpower demand will be for professionals.

Offering some numbers, Isaiah Gellman, technical director of the National Council of the Paper Industry for Air and Stream Improvement (NCASI, New York, N.Y.), predicted that paper industry environmental expenditures could rise 33%/yr from 1975 to 1980. These outlays could boost professional personnel needs by 1700-1850; technician needs by 1600-1750; operator needs by 3200-3400; and administrative employee needs by 800-900. Outside consultants to the paper industry may need 750-1200 more engineers; and regulatory agencies, 200-300 people to oversee the industry, for example, Gellman told the committee.

Its work is cut out!

In any case, the NRC committee has its work cut out for it. It must compile and interpret environmental employment statistics, many of which are nebulous or haphazard at present. For instance, it heard some speakers say that there is not, and probably will not be, a shortage of qualified manpower. At the same meeting, other speakers warned of a possible serious shortage of such personnel several years hence. Thus, the committee has a hard row to hoe, and the type of people rendering it assistance, it should succeed admirably in "telling it like it is" about environmental manpower needs. JJ



Earnest Gloyna and Stanton Ware
Numbers instead of guesses

director for the committee. This effort is one of several being conducted under a contract with the EPA. On January 16, the NRC held an open meeting at which prominent representatives of trade and professional associations, government, industry, and academe presented their views on the subject.

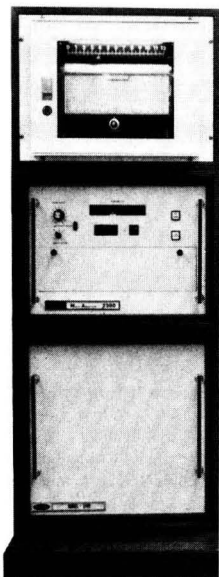
Wet and airy numbers

Victor Wagner, president of the Water Pollution Control Federation (WPCF, Washington, D.C.), said, "A major problem lies in defining what is to be counted." For example, a U.S. Census report gave a figure of 86 000 for 1974 employment in a category called "sewerage". What clouds this figure is that there are as many or more employees engaged in operation and

students, since federal training grant support to universities and students was being phased out. Over the same time period, the number of master's degree students in wpc dropped from 1271 to 722, for much the same reason.

Lewis Rogers, executive vice president of the Air Pollution Control Association (APCA, Pittsburgh, Pa.), recommended that the NRC committee "seek to establish some mechanism for regular and continuing surveys of manpower in the air pollution control [apc] field, together with salary data for the various types of air pollution specialists." These data, Rogers said, should include recipients of degrees in environmental science and engineering. He said that statistics concerning apc manpower in public employment are "fairly good,"

Reliable multi-parameter water quality monitoring.



Raytheon 2200 Multi-Parameter Analyzer.

Now, you can reliably monitor any or all of these basic water quality parameters, simultaneously:

temperature • pH • conductivity • dissolved oxygen • turbidity • stage height • oxidation reduction potential.

The 2200 features rugged construction that includes a non-corrosive flow chamber. It is designed for easy expansion of capabilities in the field and offers such options as adjustable high-low set points, automatic range changing, isolated current outputs and a wide selection of application-oriented accessories.

The 2200 will bring new efficiency and convenience to dynamic monitoring in waste-water, waste treatment and industrial process control applications.

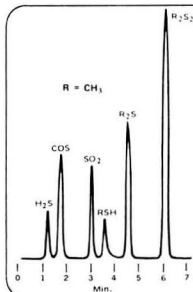
For complete technical data, contact Raytheon Company, Environmental Systems Center, Portsmouth, R.I. (401) 847-8000.



CIRCLE 24 ON READER SERVICE CARD

SUPELCO, INC.

New GC Column for Trace Sulfur Gases in Stack Gas



Kraft Pulp Mill Stack Gases

Teflon 30" x 1/8" OD, column packed with 18" of 80/100 Supelpak-S. Temp.: 30°C for 1 min., programmed to 210°C @ 40°/min. Det.: Flame photometric.

No Water Interference

Water elutes very rapidly and will not interfere with H₂S, COS or SO₂.

Low Back Pressure

The column is very short, 30" of 1/8" section packed, and requires a lower pressure for operation; therefore, less chance for leaks.



FREE Technical Bulletin 722B provides much more detail and lists three other columns which can be used for trace sulfur analysis.

Teflon column fits any instrument
Available from stock for immediate shipment.

Cat. No.
1-2255

Description
Column, Supelpak-S

Price
\$85



SUPELCO, INC.

Supelco Park • Bellefonte, Pennsylvania 16823
Phone (814) 359-2784 TWX 510 670-3600

CIRCLE 30 ON READER SERVICE CARD

$$G_n = 1/P$$

The number of grades required is inversely proportional to the purity

DISTILLED IN GLASS™ SOLVENTS

from
BURDICK & JACKSON LABORATORIES

Ask for Data Sheet BJ-25
Distilled in Glass Solvents
BJ-21 Liquid Scintillation
Counting



BURDICK & JACKSON LABORATORIES, INC.

MUSKEGON MICHIGAN 49442

(616) 726-3171

CIRCLE 13 ON READER SERVICE CARD

Pollution control industry optimism

The CEQ reports that for jobs and profits, this sector is a bright spot in a generally gloomy economy

Often in the learning process, one encounters many truisms. One such truism is that if environmental controls, mandated by various laws and regulations, must actually be installed and operated, many businesses and industries will be forced to close down, profits and jobs will be lost, goods and services will become unavailable, and a horrific depression with no end in sight will result. In times past, many truisms were taught; these included the terracentric nature of the universe and the flatness of the earth. Much more recently, truisms regarding bad health effects of cholesterol and cyclamates, now increasingly open to debate, have been circulated. Apparently, there is no end to truisms!

Shutdowns

To be sure, there have been instances in which the need for environmental controls closed a facility, with concomitant job losses, or would have, had there not been court decisions or agency-granted variances to the contrary. One case in point is that of Reserve Mining Co. (Silver Bay, Minn.), which was enjoined from further dumping of taconite tailings into Lake Superior by Judge Miles Lord. If not for a successful appeal, with the proviso that Reserve must find new disposal methods, the facility would have had to close, cancel out about 3000 jobs, and deprive the U.S. of a source of iron for steel. Incidentally, in January, Judge Lord was disqualified from hearing the Reserve case on grounds that he ceased to be impartial.

Also in January, U.S. Steel at Gary, Ind., decided to shut down three coke ovens rather than face criminal charges for air pollution; about 200 workers were affected. It often happens, however, that a plant which shuts down under environmental fire is obsolescent and uneconomical, and would have closed anyhow; environmental actions simply catalyzed the shutdown. One should, however, sympathize with adversely affected employees, and ask whether there might be a place for

them in the burgeoning pollution control (pc) industry, especially in a recession.

Job creation

Nevertheless, when environmental controls are implemented, goods and services are needed, funds are allocated, purchase orders are made, and jobs are created. Russell Peterson, chairman of the President's Council on Environmental Quality (CEQ), estimated that each \$1 billion expended for pc will

Will cleanup costs break the economy?

Here are dollar gains expected by 1980 from water cleanup alone

Water-based activities	Cumulative dollar gains (millions)
Salt-water fishing	\$4961.0
Swimming	2917.6
Fresh-water fishing	1714.2
Commercial fishing	1663.9
Other boating	1373.0
Property values	230.8
TOTAL	\$12 860.5

Source: National Commission on Water Quality

lead to 66 900 new jobs. He also told a Washington Affairs Forum of the Water and Wastewater Equipment Manufacturers Association (WWEMA—McLean, Va.) that pc expenditures for 1975 amounted to \$10 billion by private industry, \$4.2 billion by the federal establishment, and \$1.5 billion by state and local governments.

Indeed, Peterson predicted that environmental controls will be one of the relatively few areas of job strength during 1976. He noted that since 1971, controls figured in about 75 plant closings; many of these plants were marginally productive and would have been shut down in any case. These closings involved about 15 700 jobs.

As an important step in quantifying jobs created and job-creating potential of pc, the CEQ commissioned an analy-

sis of the pc industry itself. Kenneth Ch'uan-k'ai Leung of F. Eberstadt & Co., Inc. (New York, N.Y.), and independent consultant Jeffrey Klein, now with Kidder, Peabody, & Co., both financial analysts, prepared the analysis. At least 600 firms, not counting 10 000 waste collection companies, were studied.

The analysis indicates that industrial, federal, state, and local environmental spending, plus associated disbursements for operation and maintenance, provide over a million jobs (compare that with 15 700 jobs lost). This finding, along with prospects for federal outlays of \$2.2 billion in 1976 for sewage treatment plant construction alone, not to mention other environmental areas, leads the CEQ to state that environmental control-related employment presents one of the few bright economic pictures. The analysis predicts a several-fold expansion of employment levels as pc programs are implemented, and spending rises accordingly.

Profits for the pc industry

What about profits for the pc industry? Leung and Klein feel that the industry is maturing, and that profit margins are stabilizing, and will expand in the future. Better engineering know-how, more experienced management, and streamlined contract terms and payment schedules are among reasons given for these happier prospects. However, the real opportunities and challenges for pc equipment makers, according to the analysis, are in working with industry to improve process technologies in terms of cost effectiveness and energy efficiency.

Certainly there has been some—even fairly considerable—economic displacement involved in meeting environmental standards. However, with environmental quality goals more clearly set in terms of the national economic framework, displacement should be minimized, and a goodly number of people and companies might have the pleasure of expressing a "truism" that in the pc business, one can cry all the way to the bank. JJ

"HYDRO-PRECIPITROL" Industry's solution to air pollution.

The "HYDRO-PRECIPITROL" is an integrated wetted-wall electrostatic precipitator that effectively collects particulates and aerosols from industrial gas streams. Lightweight, compact and easily installed, it removes pollutants of less than 1 micron — even below .01 micron. It has been successfully demonstrated in a wide range of applications, including chemicals, glass, meat smoking, pulp and paper, fertilizer, ferrous and non-ferrous metals, and coal-fired power boilers.

Basically, the unit consists of a series of concentric cylinders and concentric cages equally spaced between the cylinders. High voltage is applied to the electrode discharge cages. A high energy field is created wherein particulates in the gas stream are charged and collected by a thin film of liquid flowing down the cylinder wall. The gas stream flows vertically upward through the "HYDRO-PRECIPITROL."

The "HYDRO-PRECIPITROL" can be used with existing equipment or can be custom-tailored. Compactness allows it to be assembled and factory-tested before delivery.

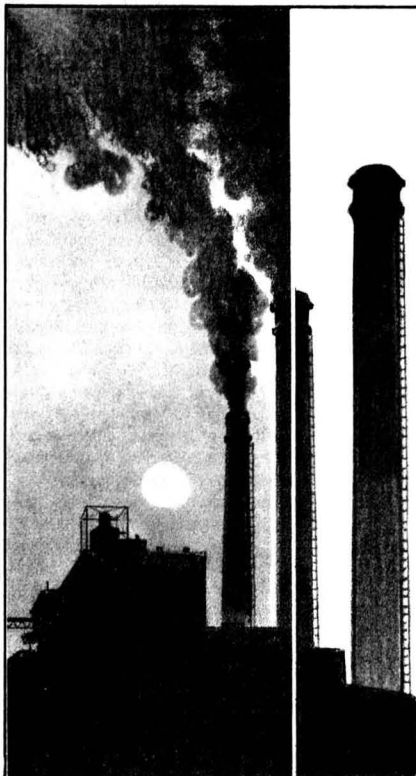
For a detailed brochure, or more information on how you can test the "HYDRO-PRECIPITROL" at your own plant, call collect or write:



Fluid-Ionic Systems

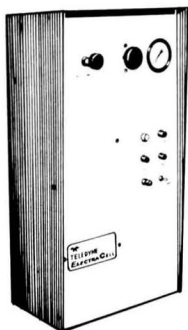
a division of Dart Industries, Inc. Chemical Group
2525 East Magnolia Phoenix, Arizona 85034
Phone: (602) 275-6301

"HYDRO-PRECIPITROL" is a trademark of Fluid-Ionic Systems, which is the sole and exclusive licensed manufacturer and distributor of the "HYDRO-PRECIPITROL."



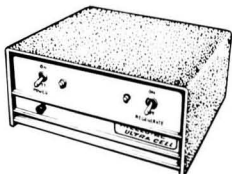
CIRCLE 5 ON READER SERVICE CARD

more RELIABILITY than ever before



HYDROGEN GENERATOR

Just introduced at a level of reliability not previously available in the industry. Produces 250 sccm of pure gas at 10 to 60 psig. Other models provide 500 and 1000 sccm.



HYDROGEN PURIFIER

A new Teledyne Energy Systems product that converts hydrogen gas into analytical quality or better. Will supply up to 400 sccm.

TELEDYNE ENERGY SYSTEMS

110 W. Timonium Rd., Timonium, Md. 21093
Phone: 310-252-8220 Telex: 8-7780 Cable: TELISES

CIRCLE 10 ON READER SERVICE CARD

reagents

E. P. A. METHODS
STANDARD METHODS
GENERAL LABORATORY
CUSTOM

IMPROVE YOUR WATER TESTING
EFFICIENCY WITH OUR QUALITY

LINE OF REAGENTS

For full particulars, call or write:

taylor

(301) 823-1573 CHEMICALS, Inc.
7300 YORK RD. / BALTIMORE, MD. / 21204

CIRCLE 9 ON READER SERVICE CARD

Quality assurance for groundwater

The main idea is to see that subsurface water is clean and safe to use.
The WHO, EPA, and private groups are working to accomplish this mission

An American traveling through the French countryside not far from Dijon, the old capital of Burgundy, on an anomalously hot day a few summers ago, stopped at a well in a Burgundian village. The water looked and tasted good. When the American noticed the villagers' shock at the fact that he drank the well water, he was naturally a bit curious as to the reason for this shock. He was told that during the reign of Charlemagne, in approximately the year 800, a dog had drowned in that well. Since then, no one ever used the well's water. "Besides, with all our excellent wine here in Burgundy, who needs water? Water is bad enough in your shoes; imagine what it does to your stomach!"

The degree to which well water actually satisfies French water needs, such as they may be, is beyond the scope of this story, but as of last August, 100 million Americans were dependent upon underground sources of drinking water. Historically, for the most part, these sources have been relatively free of contaminants. More recently, however, underground injection of waste substances, and other ways by which groundwater could become contaminated—thereby degrading groundwater and possibly threatening public health—have become a matter of concern. For this reason, the Safe Drinking Water Act of 1974 (P.L. 92-523) provides a statutory mandate for establishment of state programs for protection of underground drinking water sources from subsurface injection and other means of introducing contaminants.

"Part C"

When P.L. 92-523 was passed by Congress, many were betting on a Presidential veto, and were flabbergasted when the President signed the measure on December 16, 1974 (*ES&T*, March 1975, p 194). The New Orleans drinking water carcinogen scare is believed to be a principal factor that prevented a veto of the bill. Be that as it may, Part C of the law contains the provisions for the protection of underground sources of drinking water.

One of the protection provisions involves the monitoring of groundwater quality, the main thrust of P.L. 93-523 emphasizing quality rather than degree of contamination. The implementation of this provision differs from that called for by the National Pollution Discharge Elimination System (NPDES) of the Federal Water Pollution Control Act Amendments of 1972 (P.L. 92-500). According to the NPDES, all states are required to devise monitoring, permitting, and related functions acceptable to the administrator of EPA, with EPA itself stepping in when a state's programs are unsatisfactory. Pursuant to the drinking water law, however, the EPA administrator designates which states must formulate groundwater quality control programs.

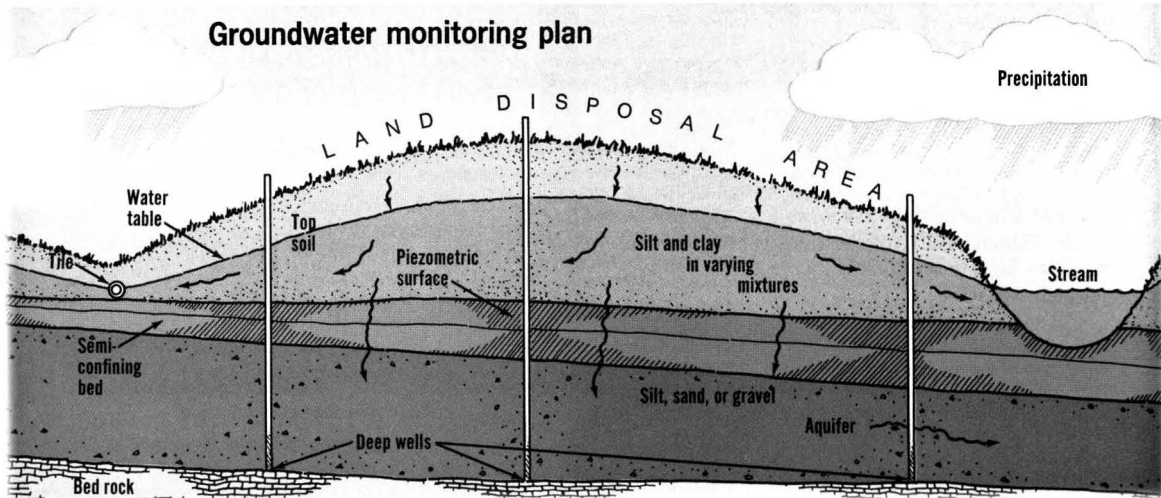
If a designated state does not come up with a satisfactory program, the EPA will then organize and run such a program in that state. By contrast, if a non-designated state wishes to have a groundwater protection program, it can obtain EPA help in setting one up; how-

ever, EPA will not operate the program if the nondesignated state's program does not meet regulatory requirements.

Part C mandated that by 180 days after enactment of P.L. 93-523, the EPA administrator must have published proposed regulations for state underground injection control programs. Promulgation of these regulations, modified as the administrator deems appropriate, was to have occurred by the next 180 days. As this goes to press, these regulations have not been promulgated; indeed, the most recent draft of proposed regulations, for the *Federal Register*, has yet to be finalized. Debate over the determination of the specific types of potentially contaminating activities intended to be regulated by the legislation has caused the delay.

By statute, an injector who violates injection control requirements, and is not in compliance by 60 days after his violation notice; and if a state either fails to submit a report, or the state has not brought the offender into compliance, the EPA may assess civil penalties. These penalties can be as high as \$5000/day after the 60-day grace period, or \$10 000/day if the violation was willful. Also, there is to be a permit program for new injection wells where there is no health hazard, with \$5000/day (or \$10 000/day, if a violation is willful) civil penalties for permit violations. The EPA may also issue injunctions against violative injections, and can prescribe controls on any injections found to contaminate an aquifer used as a sole or principal source of drinking water.

Groundwater monitoring plan



Contaminants, not pollutants

Before any discussion of groundwater problems, it is worthwhile to mention that in such discussions, according to what an EPA spokesman told *ES&T*, one uses the term "contamination", rather than "pollution", particularly when matters concerning P.L. 93-523 come up. A reason given was that certain substances, such as brine used in secondary recovery of petroleum, for example, are excluded from the class of "pollutants" under P.L. 92-500. "Contaminants", by comparison, is taken to mean anything at all that should not be in drinking water.

An EPA Office of Water Supply (OWS) spokesman said that a large portion of groundwater contamination can stem from oil and gas operations, especially where secondary and tertiary oil recovery is taking place. Waste brine is the principal contaminant. The OWS spokesman told *ES&T* that there are about 70 000 brine injection wells in the 32 states that produce oil and gas, with the majority of them in Louisiana and Texas.

In addition, it is estimated that 390 industrial waste injection wells have been permitted by various states. These industrial waste injection wells are seen by Congress to pose a potential hazard to underground sources of drinking water. For example, heavy metals and organic compounds from petrochemical operations present a groundwater contamination problem. The primary sources of the heavy metals are catalysts from the petroleum cracking process; these are sometimes disposed of by underground injection. Another waste occasionally disposed of by injection is spent pickle liquor from iron and steel plants.

The OWS spokesman said that human and animal waste has been detected in groundwater supplies. He also said that the U.S. Army Corps of Engineers found such waste in some groundwaters of Oregon and Washington State. Enteric viruses from human wastes have also been detected in groundwater (*ES&T*, December 1975, p 1124). The major source of these viruses turned out to be leachates from "sanitary" landfills in which many disposable diapers containing untreated fecal matter had been buried. Hopefully, more data as to what effects land application of sewage, pesticides, fertilizers, and the like, as well as landfill leachates and injected materials, may have on groundwater will become available from studies requested by Congress in P.L. 93-523.

Permit and monitoring mechanisms

States must establish a two-part monitoring program. First, a state must require an injector to monitor and report on groundwater quality. Second, a

state is to have capabilities to do its own monitoring. However, the EPA/OWS would monitor at a state's reasonable request, or if a state failed (or refused, as has happened) to monitor properly.

Injection is authorized by permits issued by states or the EPA. Injection of brine or other fluids brought to the surface for oil and gas production, or used for secondary or tertiary oil and gas recovery are not exempt from permit provisions of P.L. 93-523. In some cases, a state could issue temporary injection permits for existing wells, but these permits must expire by December 16, 1978.

The EPA/OWS oversees underground injection on a federal level, and will be working with the states to help them develop their injection control programs and monitoring requirements. The OWS is concerned with all injection wells, including recharge wells, salt water barrier wells, subsidence control wells, and solution mining wells. The last category increases in importance, since solution mining is one way of extracting uranium.

Incidentally, some states, such as Missouri, do not require injection permits. The reason is that they flatly ban underground waste injection.

Water quality watch

One agency keeping watch on surface and ground water is the World Health Organization Collaborating Committee on Surface and Ground Water Quality (WHO/CC). Its coordinator is Dr. Silvio Barabas of the Canada Centre for Inland Water of Environment Canada (Burlington, Ont.). Its calling is to establish on a worldwide basis

- uniform or compatible methods of measuring and monitoring water quality in bodies of surface and ground water as a basis for public health action

- uniform or compatible instrumentation for these purposes

- uniform or compatible data storage and retrieval systems.

The WHO/CC will also work at establishing an international network of monitoring stations under the Global Environmental Monitoring System. According to Barabas, there are approximately 326 million mi^3 of water on this earth,

Environment Canada's Barabas

Assessing world water quality



"Good grief! It can't be!"

That is what a Minnesota physician exclaimed when he came across several cases of arsenic poisoning. After all, arsenic poisoning takes place only in medical textbooks, old Broadway plays, and "whodunit" novels.

Apparently, a rather small Minnesota community had been obtaining its water from underground sources. When the poisoning symptoms showed up in the summer of 1972, and the arsenic proved to come from the well water, the question as to how the arsenic got there arose. Exhaustive investigation revealed that an arsenic-based pesticide had been massively applied in 1934, in order to deal with a grasshopper infestation. The arsenic took 38 years to percolate down to the underlying groundwater, but, like the proverbial bedbug which has no wings, "got there just the same!"

of which about 8 million mi^3 is fresh water. Of the 8 million mi^3 of fresh water, in turn, about 1 million mi^3 are underground; 33 400 mi^3 comprise rivers and lakes; and the remainder is frozen in polar ice caps and glaciers.

Closer to home, the National Water Well Association (NWWA, Worthington, Ohio) is the national groundwater industry "spokesman" and information clearing house. Its executive director is Dr. Jay Lehr who is also a member of the National Drinking Water Advisory Council established pursuant to P.L. 93-523.

The NWWA offers correspondence courses, trade shows, scientific symposia, periodicals, texts and manuals, legal and business aid, insurance, and promotion help for the water well industry. Its research staff also does contract work. This year, one of the jobs the NWWA hopes to do involves an EPA contract to develop permit requirements for sanitary landfills, aimed at groundwater contamination reduction. A project that the NWWA recently completed for the EPA (\$115 000) was preparation of model laws, regulations, and institutions for groundwater contamination control. An ongoing EPA contract for \$120 000 involves the development of an engineering guide for construction of deep disposal wells where permitted, along with an evaluation of the environmental impact of abandoned wells; expected completion, 1977.

Comprising 95% of the U.S. fresh water supply, groundwater is a precious resource; abundant, but not inexhaustible. Government, industrial, and international organizations are beginning to join forces to ensure that groundwater supplies, in the U.S., and worldwide, are properly protected from contamination and excessive depletion. Perhaps it can be said that the ultimate idea is to see to it that water is, in fact, better in one's stomach than in one's shoes. JJ

The aerial photo-water quality link

Calspan Corp. finds that going up in planes and satellites to monitor algae in lakes may seem far out, but it works

A new technique in the interpretation of aerial photographs—growing out of the 1972 International Field Year on the Great Lakes (IFYGL)—is helping investigators monitor the age and health of fresh water lakes.

The death of a lake through eutrophication, an aging process in which it becomes overly rich in nutrients, fills with algae, and eventually degrades to a swamp, happens too slowly for a person to observe it all in a lifetime. An important indicator is algal concentration.

Algae are tiny plants at the bottom of the food chain. Like other vegetation, they contain chlorophyll, which gives them a characteristic green color. The algae remove oxygen from the water; fish suffocate, and, with fewer fish to eat the algae, the propagation can increase until the lake's natural balance is destroyed.

Limnologists, scientists who study fresh water, monitor algal growth to help determine lake age and, wherever possible, detect and assist in reducing the amount of manufactured nutrients entering the lake. These nutrients can accelerate eutrophication by causing algae to propagate in tremendous numbers.

Until recently, algal monitoring procedures have been restricted to cruising the lake in a boat and taking water samples at predetermined stations. This monitoring is not consistent, however; a steady wind can blow the algal concentration from one side of the lake to the other, resulting in false readings.

Moving ahead

The new technique, developed by the Remote Sensing Section of Calspan Corp., a Buffalo, N.Y., research and development company, uses minute changes in the colors of a photographic transparency as indicators of the location and concentration of the green, chlorophyll-containing algae.

"Clear, pure water is blue," says Dr. Kenneth R. Piech, a physicist in the Remote Sensing Section, who acted as project scientist. "Water containing algae has a greenish cast. The higher the concentration of algae, the greener the water; and the difference in color is measurable."

It's a simple proposal in theory, but many questions had to be answered on the way to practical application. One important question concerned the scale needed for the photographs. Could the

small scale of a very high altitude satellite photo be used, or would it be necessary to take relatively low altitude photographs from an airplane? That became the basis for an experimental project, using the facilities of IFYGL, sponsored by the National Science Foundation, aerial photographs from Skylab, a NASA project, interpretation techniques and equipment developed for the U.S. Air Force, and Calspan's own twin-engine airplane, which is outfitted for aerial photography.

Data about Lake Ontario were collected from three levels. Photographs were taken by the Skylab astronauts in orbit 270 miles above the earth and from Calspan's aircraft flying at an altitude of about 10 000 feet. The aircraft exposed about 20 frames of film in each of four tracks across the lake. Water samples were taken from the surface of the lake by the IFYGL boat, "Researcher."

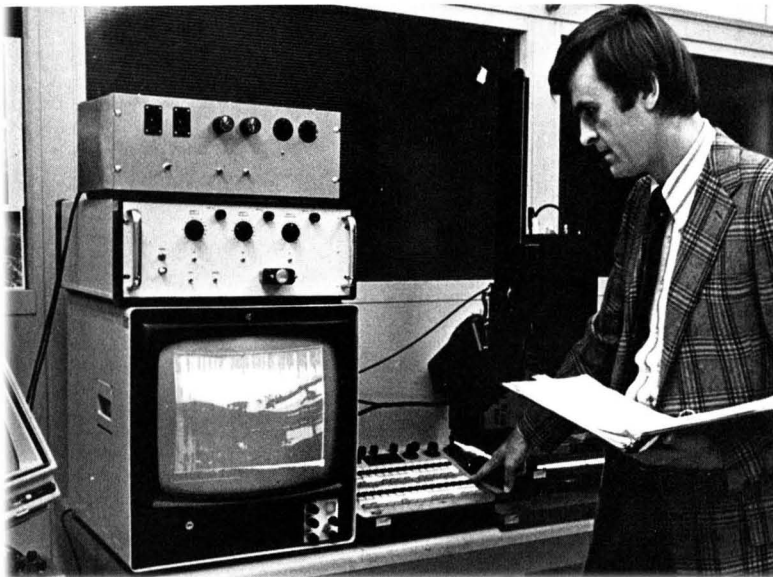
"The time differential was an interesting part of the experiment," Piech reports. "Skylab orbited over the lake in a matter of minutes. Our airplane completed its flights in about 2.5 hours from takeoff to landing in Buffalo. 'Researcher' took about a week to cruise the lake and stop at all sampling stations. This is the value of aerial photography in this application. Pictures can be taken which preserve data on the condition of the lake at a relative moment in time. By comparison, surface sampling takes much longer and conditions can change from the time a cruise starts and ends."

The pictures taken from the aircraft were made with four Hasselblad motorized cameras equipped with normal 80 mm lenses, aimed straight down at the lake surface. The film Piech used was 74 mm Kodak Aerochrome MS film 2448 (Estar base).

Using standard film

"We could have used an exotic film," Piech recalls, "but we wanted the experiment to be repeatable by someone else, so we used an off-the-shelf film which can be purchased in a camera store and processed commercially. The 2 1/4 by 2 1/4-inch transparen-

Photo analysis. Density changes indicate changes in quality



cies contained more data than we needed." The film also nearly matched, in size and emulsions, that used in Skylab.

Interpretation of the data was done on a sophisticated console whose prototype was developed by Calspan for the U.S. Air Force. Through filtration on a copying camera, processing control with a mini-computer, and reconstruction with a color analyzer, the console can isolate a single color from the original transparency and measure minute changes in that color. It also can compare two or three colors in a mathematical relationship and play the comparison on the screen of a television monitor.

"Each color transparency contains data in three layers of emulsion," Piech summarizes. "But the eye sees all three at the same time and cannot discriminate between them. The console allows us to segregate one layer—one color as black-and-white negative, which eliminates the confusion of the other colors."

For his fresh water studies, Piech focuses on two colors—the blue of pure water and the green of chlorophyll—and measures their relationship in a mathematical ratio. "When one sees all three colors together, the result is the end product of all three—red times blue times green," Piech says. "We divide one color by the other to arrive at the ratio."

To do this, he uses a copying camera to duplicate the transparency as black-and-white negatives. Filters are used so that one negative represents just blue; the other, green. Viewing the two negatives together, however, would still be multiplication of the data, so he recopies the green negative, changing it to positive representation of the scene. In this way, Piech divides the data when they are viewed in the color analyzer and the result is a ratio of the blue and green layers in the original transparency. "The color analyzer is really a densitometer. Instead of providing readings in numbers, it does it in colors," he explains. "We can analyze up to 32 different densities, but we need only eight for our lake studies."

The densities in the copies that the analyzer reads must be critically controlled to provide accurate data. One of the controls is the exposure of a step wedge—a series of known densities—at the beginning of the color film. This acts as a guide to film processing by establishing a known, measurable checkpoint. Another control is the exposure and processing of the duplicate negatives and positives.

When the aerial photography is first received, the step wedge and specific transparency areas are read with a specially built micro-densitometer. Readings are entered into a mini-computer,

which prints out the proper exposures as well as processing solutions, times, and temperatures for the duplicates.

The copies usually are exposed on 4 X 5-inch Kodak Plus-X pan professional film. This sheet film is preferred because its contrast can be controlled easily through variations in exposure and processing. It also has very fine grain and high resolution to record fine details in the transparency.

Atmospheric correction

"The key to this operation, however, is knowing how much atmospheric interference we have in the original transparencies," Piech notes. "For example, about 70% of the light reaching the satellite's cameras was reflected off water droplets and other components of the air."

Determining the amount of atmospheric interference begins with the special measurement of shadows cast by objects within the scene, such as buildings. From these measurements, the computer plots three calibration curves—one for each color layer of the film—and prints out atmospheric correction factors for each color. These data determine the exposure and processing procedures of the black-and-white copies that contain the information on variations of the ratio of blue lake color to green lake color.

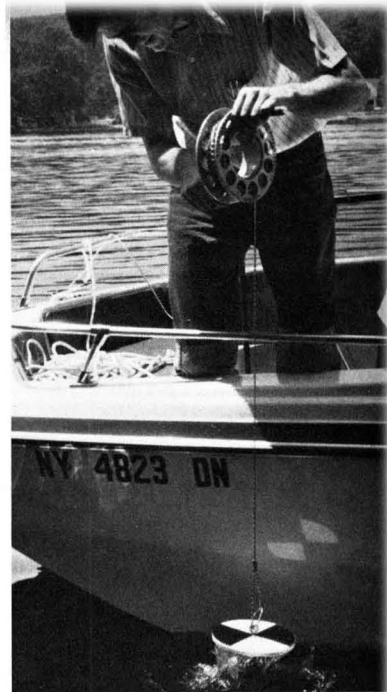
The color analyzer encodes the variations in the blue-green ratio and displays them on the monitor tube as different colors. This visualizes changes that cannot be seen with the eye and pinpoints areas of chlorophyll concentration.

The display is then photographed as a color negative on 4 X 5-inch Kodak Vericolor II professional film, and color prints are made for analysis.

"Through many studies, we have found a direct correlation between the blue-green color ratio and the concentration of chlorophyll in the water," Piech reports. "In the Skylab experiment, we applied our knowledge to determine if satellite photographs, which are taken through the whole atmosphere, could be processed accurately enough to provide adequate data. We concluded that the atmospheric corrections could be made accurately enough so that satellite photographs could be used to measure the blue-green ratio."

Further potential

The ability to use satellite photographs is very significant. Skylab covered Lake Ontario in two frames, providing a detailed picture of every point in the lake at a single instant. The low altitude photography required about 80 frames, and even then large areas of the lake were not covered. Measurements by boat cruise would provide data from only about fifty points in one



Ground truth. Taking water samples for comparison with photos

week of sampling. Satellites imagery provides a unique and powerful perspective from which to study such a lake.

Piech is now applying his findings to smaller lakes in upstate New York. "We're also studying the signatures for humic acid and lignin in the water," he adds. "Humic acids emanate from decaying leaves and vegetation and lignin results from the decay of fibrous material that accumulates in the lake. These can be detected by studying the green-red reflectance ratio.

"And we're getting to the point of quantification of the data," Piech reports. "For example, we compare photographs taken in early summer, mid-summer, and early fall; measure them; and reduce the measurements to numbers to associate the changes taking place. But we're not limnologists; we just gather data that provide information for their decisions."

Repetitive photography, which provides the basis for comparison, will indicate changes to the limnologist, Piech feels. "It's a convenient tool and one which is very inexpensive to use," he says. "If the limnologist had a means of photographing the lake biweekly, it would take only an hour or two for the interpretation. If changes take place—such as a blooming of the algae—the analysis could pinpoint the time, and possibly even the place, to go for water sampling. Measurements would be far more comprehensive and to the point than if the investigator guessed or sampled at random."

FEATURE

Earthwatching on a macroscale

GEMS: The global environmental monitoring system of the United Nations aims to assess conditions on planet Earth

Brian Martin and Francesco Sella

*United Nations Environment Programme
Nairobi, Kenya*

Public concern about the environment can probably be traced back to 1962, the year of publication of Rachel Carson's book *Silent Spring*. Concern mounted to such an extent in the following years that the United Nations convened a Conference on the Human Environment in June 1972. A report was produced and resulted in the establishment, by the UN General Assembly, of the United Nations Environment Programme (UNEP) in December 1972, and within UNEP the development of the concept of Earthwatch—a program for environmental assessment, which was seen by the Conference as a vital input to the process of environmental management.

Earthwatch consists of four functional components: Evaluation and Review, Research, Monitoring and Information Exchange. These four functions provide the necessary knowledge and understanding for the rational planning needed to guide environmental management activities. The monitoring component within Earthwatch is the Global Environmental Monitoring System (GEMS).

The concept

GEMS may be viewed as a co-ordinated effort on the part of the world community to gather data of significance to the rational management of the environment. It encompasses the United Nations family, national governments and any concerned organization that has an input of relevant data. The GEMS Programme Activity Centre (PAC) within UNEP basically performs a co-ordinating role between on-going national and international monitoring projects. By providing a small amount of financial support, UNEP also encourages, along with other members of the UN family, the participation of developing countries in monitoring activities so that a truly global system of data gathering might eventually be established in conformity with the seven program goals of GEMS:

- An expanded human health warning system.
- An assessment of global atmospheric pollution and its impact on climate.
- An assessment of the extent and distribution of contaminants in biological systems, particularly food chains.
- An assessment of critical environmental problems related to agriculture and land and water use.
- An assessment of the response of terrestrial ecosystems to pressures exerted on the environment.
- An assessment of the state of ocean pollution and its impact on marine ecosystems.
- An improved international system allowing monitoring of factors necessary for understanding and forecasting disasters and implementation of an efficient warning system.

These program goals, identified by the Intergovernmental Meeting on Monitoring (IMM) in February 1974 and endorsed by the third session of UNEP's Governing Council, provide a focus for GEM's activities within the overall priority subject areas of UNEP.

Monitoring

There are several fundamental questions that must be addressed if monitoring is to produce meaningful data. First, what is meant by monitoring? Second, what is being monitored and why? Third, what will be done with the data once they are collected?

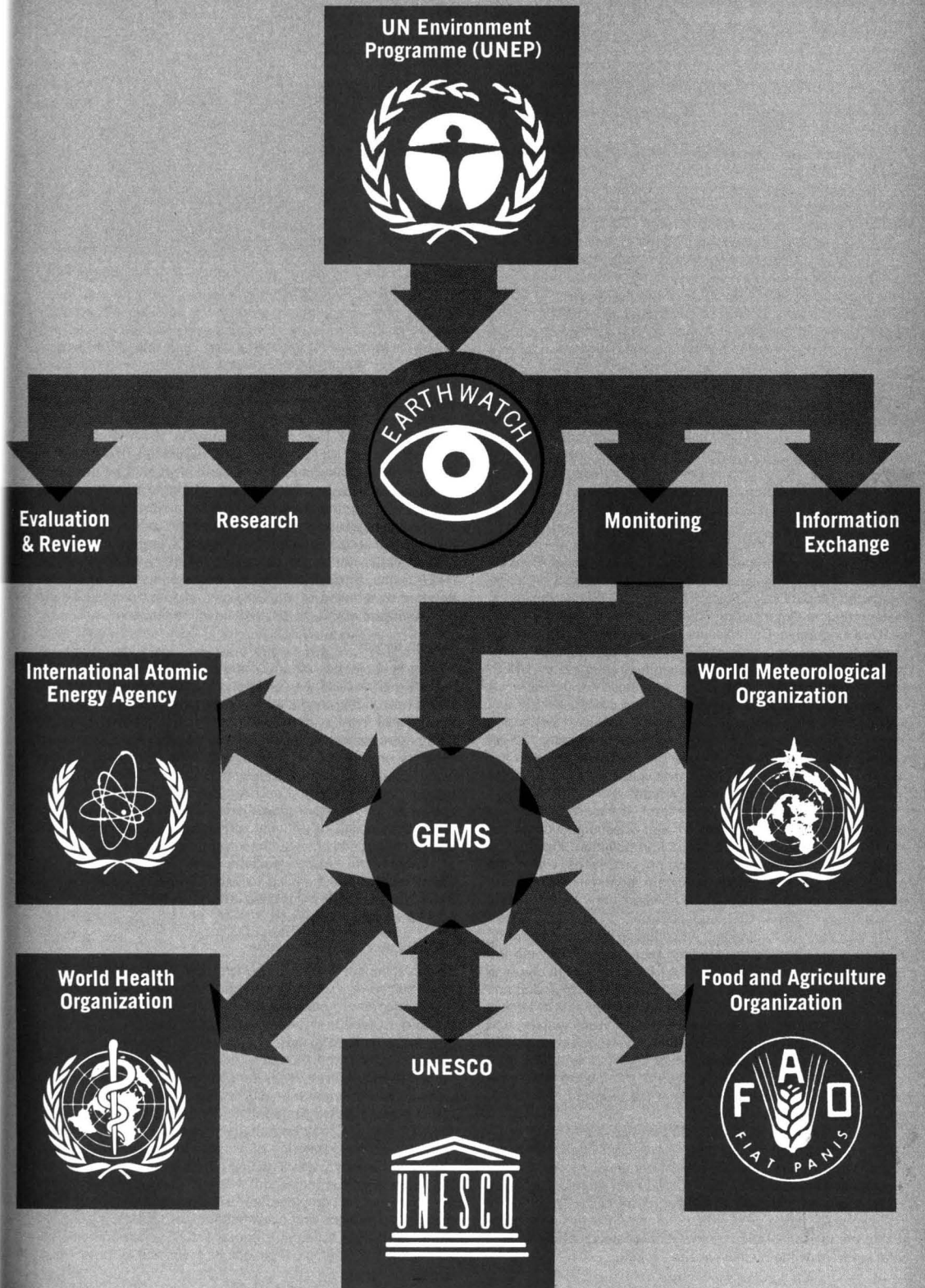
Monitoring can be defined as the process of repeated observation and measurement, for defined purposes, of one or more indicators of the physical, chemical or biological state of an environmental element or medium, according to pre-arranged schedules in space and time. It is evident that comparable methodologies must be used to produce consistent and comparable data. Standards are generally employed as they are in most systems of measurement.

The decision as to what is monitored is obviously a critical one, and carries with it an implied evaluation of its importance as an indicator of changes, deleterious or otherwise, in an environmental medium or element. It should be evident that any system of monitoring is not just measurement but should be a developing and a self-modifying system of data-gathering for a specific purpose. As data are gathered and assessed, a feedback as to what element or indicator is monitored—and how and why—should periodically alter priorities and methods. In a sense, monitoring is a component of a research effort to understand the complex physical, chemical and biological interplays in the Earth's ecosystems with a view of identifying man's harmful effects.

In an attempt to give the system a start in the right direction, an Interagency Working Group produced a report on the development of GEMS and presented a set of proposals to the IMM in February 1974. These proposals were considered by the various governments and a list of priority pollutants were recommended. Recommendations on other aspects of monitoring involved factors useful in predicting climatic changes, degradation of various ecosystems, and the health status of populations.

Once monitoring data are received, they must be interpreted (evaluated) in the light of current research knowledge. Since the physics, chemistry and biology of the many ecosystems are imperfectly understood, such interpretations will be the subject of periodic revisions. Ideally, data and knowledge should be such that a set of outer limits may be placed

GEMS' interactions with other U.N. programs



on various pollutants or indicators of deleterious changes in the environment, and the process of environmental management would then concern itself with containment within these limits.

UNEP's co-ordinating role

No attempt will be made here to cover all the national and international monitoring programs. Emphasis will be placed on a few of the projects that are receiving direct financial assistance from the Environment Fund of UNEP. These projects should illustrate the way the GEMS PAC within UNEP is co-operating and co-ordinating with other agencies within the UN Family to produce a truly global system directed toward the attainment of the defined goals.

In accordance with a decision of the last Governing Council of UNEP (GC IV), groups of government experts are being convened on various priority topics. Two such meetings to be held with the co-operation of several UN agencies are to take place in March 1976: one on the monitoring of background levels of pollution in open ocean waters (to be held in Geneva) and one on monitoring for the assessment of critical environmental problems related to agricultural and land-use practices (to be held in Rome). Other government meetings that UNEP will convene, during 1976 will include those on climate and on health-related monitoring and on the inter-media transfer processes of pollutants with emphasis on the effects on man and/or ecosystems.

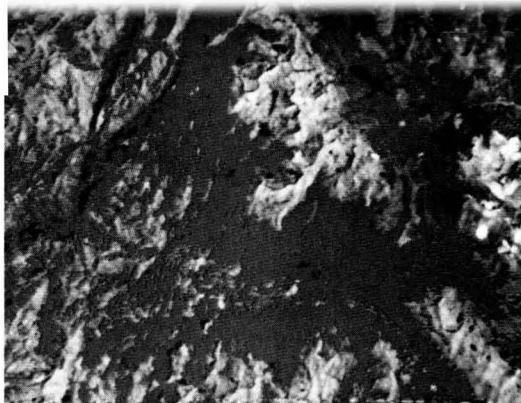
Oceans

The Government Expert Meeting on Open Ocean Monitoring, to be held jointly with IPLAN (the planning group for the Integrated Global Ocean Station System (IGOSS) of the World Meteorological Organization (WMO) and the Intergovernmental Oceanographic Commission (IOC) of UNESCO), and attended by representatives of the 12 countries that are members of IPLAN and 6 additional countries selected by UNEP, will consider detailed proposals, formulated on the basis of recommendations of consultants, by the UNEP, WMO, and IOC secretariats. These proposals will consider monitoring the background levels of certain pollutants in open ocean waters. The secretariats' propose the implementation in the Atlantic Ocean of a pilot phase that will test the methodologies and the organizational arrangements.

The open ocean monitoring project, if successful, should contribute to solving a number of vital questions such as the role of atmospheric transport in ocean pollution; the relative importance of various concentration processes within the ocean; and the interactions between sediments, ocean and atmosphere in the distribution of pollutants and in the control of the levels of CO₂ in the atmosphere.

Other UNEP co-ordinating activities in ocean monitoring have centered around the Mediterranean Sea. Following the Barcelona Conference in 1974, UNEP has taken initiatives to set up a co-ordinated Mediterranean Pollution Monitoring and Research Program, which will, among other things, provide a continuous source of data on pollution in these waters, and on the uptake of petroleum, organochlorine compounds and trace metals by the organisms found in these waters. An inventory of land-based sources of pollutants on the Mediterranean coastline, which is also part of the program, will be another valuable input to GEMS.

Even before the Barcelona Conference some monitoring was undertaken on the Mediterranean coast between Sete, France, and Genoa, Italy, by the International Atomic Energy Agency Marine Radioactivity Laboratory in Monaco, with the support of UNEP. Besides providing information on a heavily polluted area, these studies have become the basis for organizing the intercalibration of analytical methods that will be a vital element of the Mediterranean Project.



Forests. Satellite image of Yosemite National Park (Calif.) after multispectral analysis

The atmosphere

The main meteorological program input into GEMS is provided by the World Weather Watch (WWW), which has been operated by the WMO since 1963. A component of the WWW is the monitoring of background atmospheric pollution at baseline stations. This program (see *ES&T*, January 1975, pp 30-34), which became operational in 1971, is now being expanded with UNEP's support. In particular, UNEP is supporting a feasibility study of the establishment of an atmospheric baseline station in East Africa that will provide, through the participation in a global monitoring scheme of local scientists and institutions, information on background levels of pollution in one of the world's largest continental areas. Similar initiatives are being taken in South America. UNEP is now also supporting part of the costs of the preparation and distribution of standard gas mixtures needed for the measurement of CO₂ in air at all baseline stations.

Human health

Man is subject to the influence of the air he breathes, the water he drinks and the food he eats. Various types of monitoring have been conducted for a number of years, mainly at the national level in developed countries, to try to ensure that these necessary elements are relatively pollutant-free. Projects on monitoring air pollution, food contamination and water quality are being developed or expanded by UNEP through WHO, the Food and Agriculture Organization (FAO) and other interested organizations. These projects' aim is to make the results of national monitoring efforts comparable and to collect and analyze the information of global or regional importance. Such projects also enable developing countries that are planning to establish health-related monitoring programs to focus their efforts in the right areas and avoid a waste of resources.

Renewable natural resources

Man's impact on the biosphere and its complex ecosystems can have extremely serious repercussions. The developing countries predominantly rely on their agricultural productivity to feed their people and obtain foreign exchange to buy manufactured goods. If this productivity is exhausted, starvation and extreme economic deprivation can and does result. UNEP has involved itself, to date, in two monitoring projects of importance in this regard: monitoring of tropical forest cover and soil degradation monitoring.

UNEP and FAO have agreed to undertake pilot activities in remote sensing monitoring of tropical forest cover, from satellites and aircraft, which will encompass four West African countries (Benin, Cameroon, Nigeria and Togo). The pilot phase should be completed in 1977 and should provide information on methods and classifications of forest cover. WMO will also provide an input to these activities through its studies on the meteorological conditions favorable to forest fires.

On the question of soil degradation—a question of major importance in all countries—soil surveys have been conducted for a number of years by FAO and UNESCO, and have resulted in the publication of the World Map of Soils in addition to a vast store of unpublished detail. FAO and UNESCO, with UNEP support, have started to monitor soil degradation (loss of fertility and erosion) by making use of information collected during the preparation of the map, information supplied by WMO, and the new data collected on an ad hoc basis through field studies and aerial surveys. At present, the first stage of activity covers Africa north of the equator.

It is expected that the projects on soil degradation and forest cover monitoring will form the basis for a comprehensive and integrated program of monitoring soil and vegetation cover that will also include the monitoring of rangeland degradation. These three main components will be linked by the use of compatible classifications and data-handling methodologies that will, to a large extent, need to be developed in the course of pilot projects. Such a program will be discussed by the government expert group on monitoring for the assessment of critical environmental problems related to agricultural and land-use practices.

Information dissemination

As information and data gradually flow into the various components of GEMS, evaluation will usually take place as part of the programs under which the information is collected. The evaluated information will be further reviewed, analyzed and published as an input to the State of the Environment Report of UNEP, but this is unlikely before 1977.

It is evident that much background-level monitoring will yield meaningful trends only gradually and that the interpretation of these trends must proceed with caution and thoroughness. The role of UNEP in this procedure is one of co-ordinator and synthesizer, whereas the operational responsibility will rest, in most cases, with the international organization concerned. UNEP's annual State of the Environment Report to which GEMS will soon be making major contributions should eventually become a definitive document to which national environmental management authorities may look to for guidance and advice.

Additional reading

Jensen, C. E., et al., *Earthwatch. Science*, **190**, 432-438 (1975).
Anon., *Environ. Sci. Technol.*, March 1974, pp 214-216.



Brian Martin is a geochemist with UNEP's Global Environmental Monitoring System. Dr. Martin was formerly engaged in experimental research.

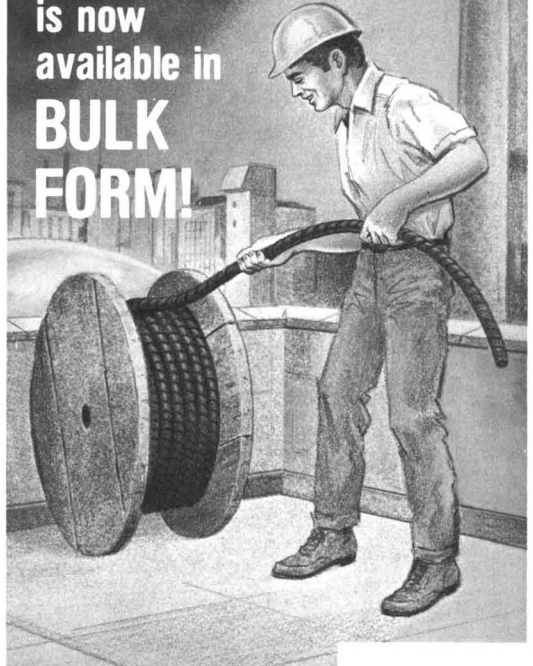


Francesco Sella, director of the Global Environmental Monitoring System, was for 14 years Secretary to the United Nations Scientific Committee on the Effects of Atomic Radiation. Dr. Sella has a medical background and was engaged in genetic and epidemiological research before entering the UN.

Coordinated by LRE

High-Temperature SAMPLING HOSE

is now available in BULK FORM!



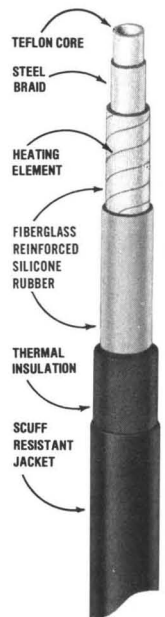
For the first time, large volume users can buy high-heat bulk sampling hose in lengths from 100' up to 1000'. This new product is designed for firms who don't know their requirements in advance and therefore prefer to cut the length they need from stock.

Heat/Line Bulk Hose may be operated up to 50W per lineal foot and provides uniform heat capability up to 400°F. Since all components are bonded into one integral unit, the hose is extremely pliable and flexible.

Heat/Line Bulk Hose offers other important features, too . . . Like a Teflon core to assure contamination-free inner surface. Plus thermal insulation and scuff-resistant jacket. Choice of 1/4", 3/8", or 1/2" diameters. 115 or 230VAC operating voltage. Electrical hardware and temperature controllers can be supplied, if desired.

NOTE: For customers with specific needs, we recommend our regular Heat/Line Sampling Hoses which are provided in the exact length desired and come completely assembled with fittings and electrical connections, ready to use.

Want more data on our new bulk sampling hose? Write for full details!



TECHNICAL HEATERS, INC.

1730 First St. • San Fernando, Ca. 91340 • (213) 361-7185

Legal decisions and opinions in pollution cases

John P. Hills

*Messenger, Lynch, Hills and Miller
Attorneys and Counselors at Law
Beltsville, Md. 20705*

A medical doctor involved in asbestos research who is convinced that low-level exposure to asbestos causes cancer asks: "Where are we in translating what I know as a doctor into the law of the land?" Significant advances in federal case law have, in fact, occurred. Although the law is groping, and the field is enmeshed in controversy, there are strong indications that the courts will assess present scientific knowledge and opinion so as to protect public health.

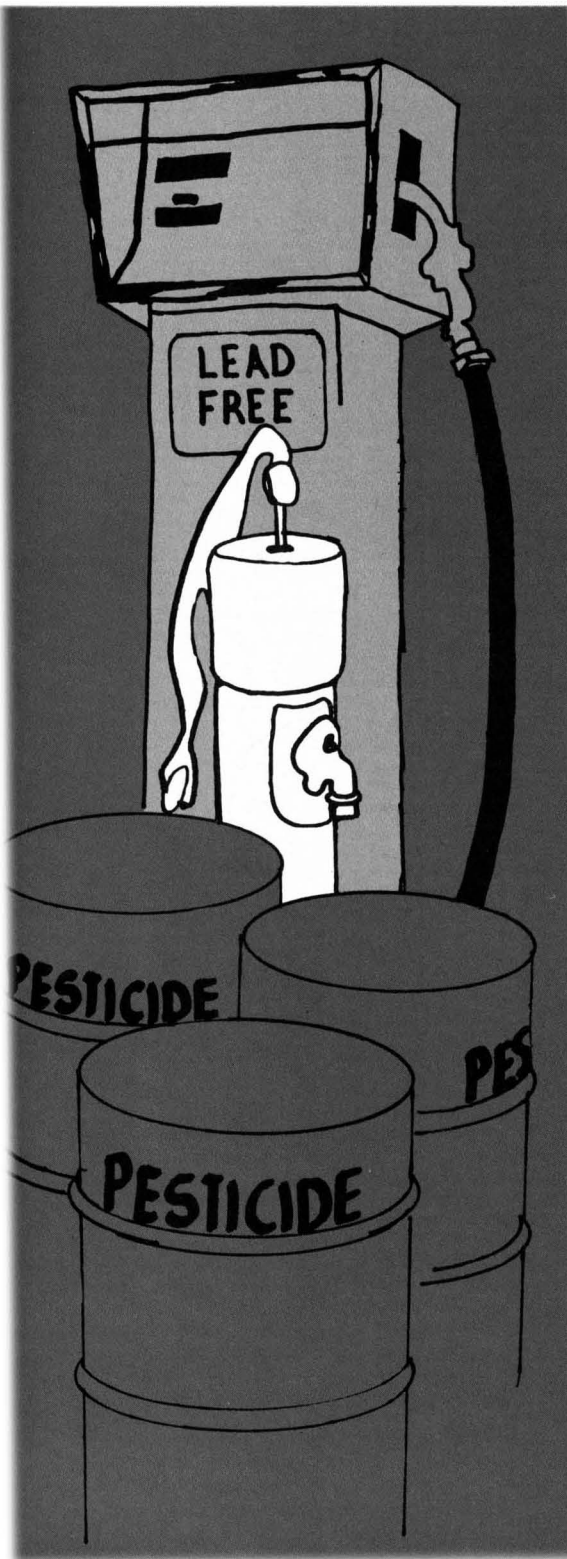
Unique problems are presented by toxic substances such as asbestos, vinyl chloride, organochlorine pesticides, and lead, which have all been subjected to recent court cases. The question has been whether these substances constitute a significant health hazard to the portion of the public exposed to low levels over a period of years. Substances that cause cancer present an additional problem to researchers and lawyers in that a 15- to 45-year latency period between exposure and disease is usual.

Traditional vs. scientific proof

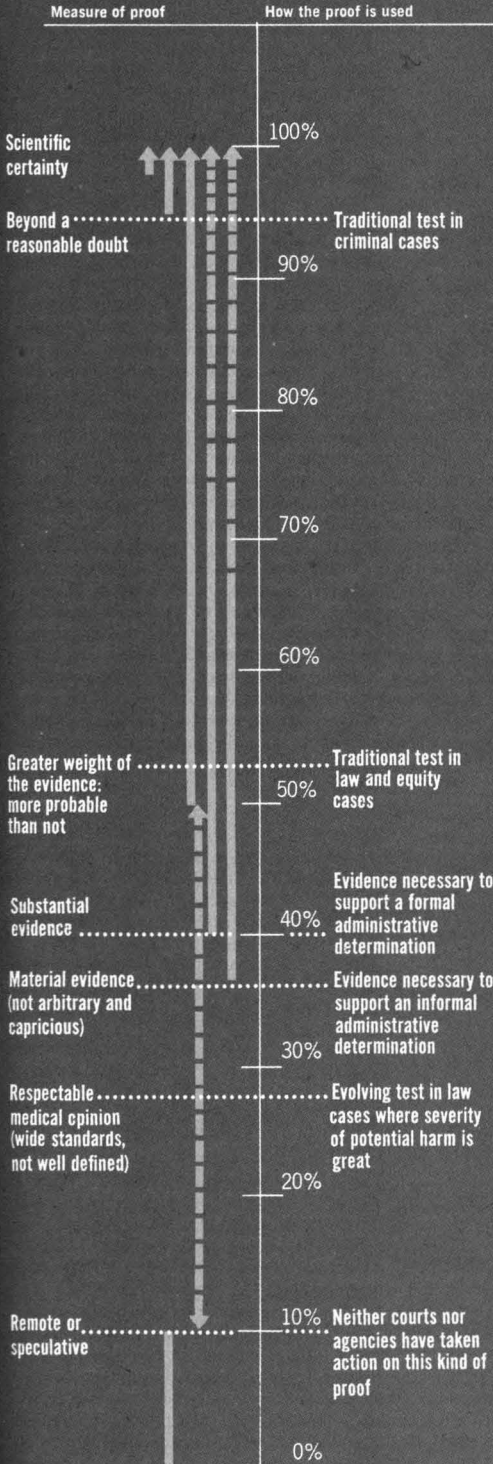
When studying toxicants, the scientist can accumulate some hard facts and make some strong correlations. However, he may reach a point in the investigation where he forms an opinion not supported by scientific "proof." When testifying he is asked for this opinion. It may be an uncomfortable experience, but the court needs his opinion and allows him to give it. This is the classic use of expert opinion testimony.

The scientist prefers to support his conclusions with data verifiable at the 99.9% confidence level. He is truly comfortable only after his work has stood the test of peer review and is accepted by the scientific community. Courts have never asked for such proof; this level of proof traditionally has been impossible to attain because the court system evolved before the days of the scientific method.

It has always been one man's word against another's, and the court has resolved conflicts by hearing both sides, judging the truthfulness of the witnesses, and deciding in favor of the stronger or more likely contention. Thus the legal test for civil cases remains: Is it more likely than not that the proposition asserted is true? Where the plaintiff has alleged a chain of events he must meet this standard for each of his material assertions. Here a man's liberty is at stake and proof must be beyond a reasonable doubt.



Legal burdens of proof in various cases



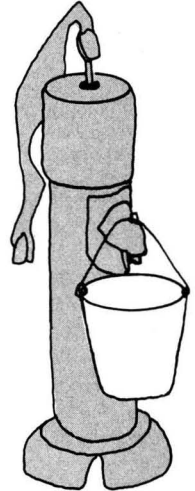
..... —not well defined

When dealing with the "frontier of scientific knowledge," and questions of public health, U.S. courts are waiving traditional burdens of proof, giving increased weight to expert opinions and/or lowering their standard of necessary proof

However, even this traditional legal test has been inadequate in the face of the allegation that thousands or even millions of people are at an increased risk of disease from long-term, low-level exposure to a cancer-causing substance. The indications are that the courts, instead of demanding scientific proof when hearing scientific evidence, are in fact applying a more lenient standard than the traditional legal one. A discussion of a few recent cases shows why this is logical, and in fact necessary, in these types of cases.

Asbestos in the water

On April 21, 1974, the Honorable Miles Lord, U.S. District Judge sitting at Minneapolis, ordered Reserve Mining Company to immediately cease dumping asbestos-laden taconite tailings into Lake Superior. The tailings are finely ground amphibole mineral from which iron ore is extracted to produce taconite pellets that are used in place of raw ore by the steel industry. Billions of asbestos fibers found in the tailings were swept along the north shore of Lake Superior to Duluth by normal counter-clockwise currents.



North shore communities, including Duluth, draw their drinking water from the Lake. People were, and still are, ingesting asbestos fibers, about 42 million fibers/liter, with their drinking water.

Asbestos is a human carcinogen when inhaled; asbestos workers who inhale the dust contract, after a latency period of 15-45 yr, various diseases. Among these are lung cancer, pleural and peritoneal mesothelioma, and gastro-intestinal cancer. Since no asbestos worker ingests asbestos without inhaling, there is no direct evidence that ingestion without inhalation causes disease. Because medical research has been directed toward occupational exposure, there are no

animal data that implicate ingested asbestos alone as the cause of disease in animals.

However, medical proof is that asbestos workers swallow a large part of the asbestos that they inhale, and suffer a three-fold increase in stomach cancer. Medical opinion presented to the Court was that swallowing asbestos fibers caused stomach cancer. There was no scientific proof that this was so because none existed. No increase in stomach cancer could be demonstrated in the Duluth population because sufficient time had not elapsed. There had been only 15 years of exposure. Epidemiologists were of the opinion that many more years of exposure would have to occur before a valid study could be performed. Judge Lord found, after an 8½-month trial, a substantial danger to the general public drinking the water and ordered the asbestos discharge stopped immediately. The decision was important and controversial. The plant employed thousands of workers and supported two Minnesota north shore communities. Its product, which was about 17% of U.S. taconite pellet production, was deemed to be essential to the steel industry.

The 8th Circuit Court of Appeals agreed to an immediate hearing and two days after Judge Lord's order a Circuit judge asked the lawyers, "Can you show me one death or serious illness?" The answer was, of course, no. The Court ordered the plant reopened and agreed to an accelerated hearing schedule, with another preliminary hearing to more fully consider the evidence.

In June 1974, the 8th Circuit published its preliminary findings, based on the same evidence considered by the District Court. It found that no basis existed, save a theoretical one, for assuming the drinking water dangerous to health. Given the state of medical and scientific knowledge, the case was based on medical hypothesis and was simply "beyond proof." The Appeals Court found that the District Court had erred by resolving all uncertainties in favor of public health safety. The plant remained open pending the final decision.

In August, Senators Gaylord Nelson (D-Wis.) and Gary Hart (D-Colo.) jointly sponsored a bill that would have changed the burden of proof in public health cases. Their idea was to require the plaintiff to establish more than a remote risk, and then require the industry to come forward and prove that there was no risk. In other words, the bill would place the burden of proof of safety of an emission into the air or effluent into the water on the person who stood to make a profit from the activity, rather than on a citizens' group or public health agencies. The amendment was a direct response to the 8th Circuit's opinion in the *Reserve Mining* case.

The case was characterized as follows in the bill's prefatory remarks:

"First there was a course of conduct which created a potentially serious health hazard. Second, the risk of harm was potential—not a certainty or a clear probability. And finally, in both situations it was decided that, since no one could be certain that a tragic result would occur, the course of conduct should not be stopped.

This, I submit, is more than misguided conduct: it is irresponsible in the extreme.

Cong. Rec. 93d Cong. 2d Sess.
Aug. 19, 1974: S. 15186"

The preliminary opinion of the 8th Circuit was appealed to the U.S. Supreme Court, but was not set aside. Justice William O. Douglas wrote a dissenting opinion in October 1974 that read: "I would vacate the stay issued by the Court of Appeals . . . I am not aware of a constitutional principle that allows either private or public enterprises to despoil any part of the domain that belongs to all of the people."

In March 1975, the 8th Circuit rendered its final decision in the case, this time with five judges participating. The Court had now considered the record more fully and made findings not only on water pollution but also on asbestos air contamination in the vicinity of the plant. The Court modified its ear-

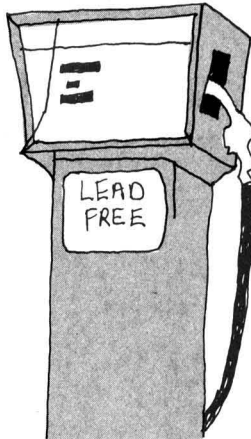
lier opinion and quoted Judge Wright's language from the dissent in the lead in gasoline case (a discussion of which follows) on the issue of risk and harm.

The opinion stated in part that

"While 'risk' and 'harm' are separate concepts that cannot be compared and ranked . . . there is a reciprocal relationship between them, and they may not really be assessed in isolation . . . The 'significance' of the risk . . . can only be ascertained through knowledge of the threatened harm, and it is the total 'risk of harm' that must be sufficient to endanger the public health. This relationship does not, however, invalidate the separate analysis . . . for the parameters of each must be identified before their interaction can be studied."

In assessing probabilities of death or disease from asbestos exposure in the water and air the Court determined that, "it cannot be said that the probability of harm is more likely than not." It found that respectable medical opinion gave a "reasonable medical concern for the public health." With respect to probability of disease from drinking the water the Court found that because there was no past history of harm, the probability was low. Those who breathed the air around the plant were found to be at greater risk because there was an established history of illness in occupationally exposed groups. In balancing equities between the Duluth populace and the large manufacturing concern it chose to give the plant a period of years to convert to an on-land system of tailings disposal and required immediate steps to abate the plant's discharge of asbestos into the air.

The case stands as an important legal precedent because it holds that relief can be given even though traditional legal tests were not, in its opinion, met. In other words, a court applying traditional tests would require that the reality of the risk be more likely than not or be supported by the greater weight or preponderance of the evidence, before taking action. In this case the court took action but found the reality of the risk to be only in the realm of respectable medical opinion. But given this lesser degree of risk, it declined to take drastic or immediate action, but stipulated that time be allowed for the risk to be minimized.



Lead in gasoline

While the *Reserve Mining* controversy was still boiling, EPA's order reducing lead in gasoline was considered by the U.S. Court of Appeals for the District of Columbia. The order was issued by the administrator of EPA and would

have reduced the content of lead in gasoline to 0.5 g/gal over a period of years. EPA was acting under the Clean Air Act that gave it specific authority to take this step if it found that lead emissions will endanger public health.

It can be stated with certainty that there is lead in gasoline; that there is lead in auto exhaust emissions; that this lead is airborne; and that people breathe the air. It is known that lead in air enters the human system through the lungs, and increased lead levels have been established for exposed populations working near highways, for traffic policemen and for garagemen. However, the food we eat is the major source of

lead; most lead poisoning in children comes from eating lead-based paint. Most lead levels from ingestion are well below the 0.8 ppm or above required to produce clinical illness. There is little medical evidence of the effects of chronic low-level lead levels in the body.

The majority of the three-judge panel considering the appealed EPA order held that the statute required an administrative finding that lead emissions presented a significant health hazard to a substantial portion of the population, and that a causal connection must be established between lead emissions and harm. The majority held, given this standard, that the EPA order was not supported by the record and was, therefore, arbitrary and capricious.

As part of a strongly worded 97-page dissenting opinion, Judge Skelly Wright observed that confusion is typical when the legal process must address questions on the frontiers of scientific knowledge. In law, "mere 'correlations' whether statistical or otherwise, are used to prove causal connections," and that courts, "after centuries of balking, have finally realized that circumstantial evidence can have probative value as great as that of direct evidence." Judge Wright interpreted "will endanger" as encompassing both risk and harm. Assessment of risks could be made from suspected, but unproven hypothesis, trends, imperfect data or probative preliminary data not yet certifiable as "fact." Judge Wright would have upheld EPA's regulation as supported by material evidence in the absence of scientific proof of actual harm.

A petition to rehear the case was subsequently granted and a second hearing was held in May 1975 with all nine circuit judges participating. At this writing, no final decision has been given.

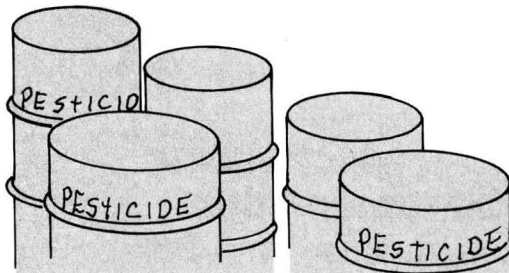
VC: An occupational hazard

The vinyl chloride standard set by the Secretary of Labor was challenged and the case was decided in January 1975. In the wake of death and controversy, the Department had set a standard of 1 ppm for exposure to workmen. The vinyl chloride industry is large; it employs 6500 workers directly in the manufacturing field and hundreds of thousands more in the fabricating fields. The 5.4 billion pounds of polyvinyl chloride resin produced annually in the U.S. is used in a myriad of wares from pipes and conduits to phonograph records, and packaging.

Conclusive proof of the danger of vinyl chloride resulted from an unintentional scientific experiment in which workers served as guinea pigs. Angiosarcoma, a rare type of cancer of the liver, began to occur in the industry with alarming frequency. Eighteen American workers have now died from the disease.

In animal experiments cancer was inducible at exposures as low as 50 ppm. The Secretary set the 1 ppm standard as a precautionary measure because no one could say if a threshold level existed at which cancer could not be induced. There appears to be no level below which it can be demonstrated that vinyl chloride does not cause cancer.

The special three-judge U.S. District Court panel sustained the Secretary's determination with Justice Tom Clarke, retired from the Supreme Court, writing the opinion. The Court was critical of industry for withholding data that could have saved the lives of its workmen. The Court noted that it was dealing with the "frontiers of scientific knowledge," and that it was dealing with human lives. The Court accepted the proposition that there must be a safety factor between levels known to cause cancer and the standard set. Relying on expert opinion based on sound toxicological principles the Court recognized a safety factor of 1/100 as sufficient for worker protection and the Secretary's promulgation of 1 ppm standard was found to be supported by substantial evidence.



A pesticide ban

The *Shell Chemical* case challenged EPA's ban on the pesticide aldrin/dieldrin. Judge Leventhal of the U.S. Court of Appeals for the District of Columbia rendered the opinion in April 1975. EPA had acted under the federal pesticide statute that authorizes suspension of any pesticide upon a showing of imminent health hazard.

The Court observed that aldrin/dieldrin had been shown to be carcinogenic in several strains of mice and probably in rats. There were no separate data that it was carcinogenic in humans. Evidence was placed in the record that showed that the chemicals persisted in the environment and that more than 96% of U.S. citizens have about 0.27 ppb in their fatty tissue. The defendants argued that there was no proof of a human health hazard because one could not extrapolate mice data to humans; therefore, no threshold level of exposure at which cancers would be caused in humans could be determined.

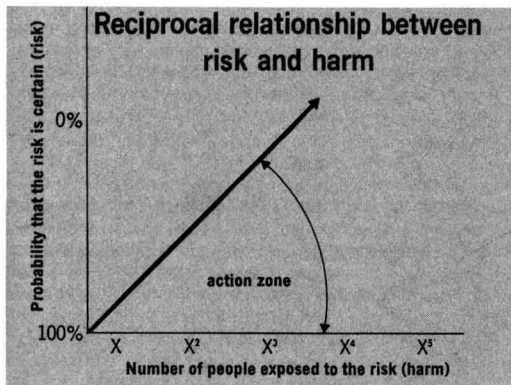
The Court stated:

"The Administrator's failure to determine a threshold level of exposure to aldrin/dieldrin does not render his determination improper, for he has concluded that the concept of a threshold level has no practical significance where carcinogens are concerned. This is due in part to the irreversibility and long latency period of carcinogens. '(W)here the matter involved is as sensitive and fright-laden as cancer,' and the statute places the burden on the registrant to establish the safety of his product, *we shall not, assuming a substantial showing of danger, require the Administrator to make impossible proofs.*" (emphasis added)

The Court found that EPA's suspension was supported by substantial evidence and upheld the administrative decision.

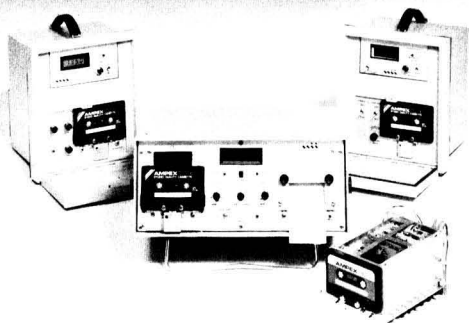
Summation

Although the above cases arose under different statutes and the courts were not uniform in their treatment of the evidence, there are some striking similarities. The cases are consistent with the proposition that there is a reciprocal rela-



Although the reciprocal relationship between risk and harm is highly judgmental and can never be reduced to formula, it might be viewed in this fashion. As the risk becomes greater, action is more clearly justified. As the number of people at risk becomes greater, action is still justified even though the certainty of the risk may be greatly decreased

Martek measures up



with water quality instrumentation

The Martek DAS Series is a portable, economical data acquisition system designed to meet a wide range of applications and provide complete acquisition and retrieval of data from water quality monitors and other environmental instrumentation.

Take the Model EDP Environmental Data Printer. It can record — continuously or intermittently — up to 15 data signals and time of day on a magnetic tape cassette and/or digital paper printer. Data recorded on magnetic tape can be processed subsequently via external data converters.

If your application requires a low-cost, portable, self-contained data logger capable of long-term remote operation, the Martek Model DAL is your answer.

To retrieve data from magnetic tape cassettes, Martek offers the Model DAR Data Reader. Its digital LED display permits visual reading of the tape while the information is simultaneously available at the output connectors for external data processors.

For recording of water quality data and time during unattended operation in remote areas, Martek has designed the Model SDL Submersible Data Logger.

For the full story on the full DAS line of Martek modules, write to:



MARTEK INSTRUMENTS, INC.
879 West 16th Street, Newport Beach, CA 92663 (714) 645-1170
Manufacturers of Environmental Instrumentation
CIRCLE 6 ON READER SERVICE CARD

tionship between risk and harm, and in each there were gaps in scientific knowledge that made scientific "proof" of some elements of the cases impossible.

In *Reserve Mining*, the only way to prove that ingestion of asbestos fibers causes stomach cancer in humans is to expose a human population and then perform an epidemiological study. With vinyl chloride the workers have already suffered the results of a high-dosage experiment. One can only hope that 1 ppm is low enough to protect workers. In the case of aldrin/dieldrin, since we all have been exposed, an experiment is impossible because among other reasons, a control group cannot be formed. Most importantly, however, all such experimentation is immoral and unethical: We as a society simply cannot condone intentional human experimentation with carcinogens.

The law has traditionally dealt with a single plaintiff who sues a defendant and claims injury. It has traditionally required a showing that the defendant was more likely than not responsible for the injury.

In public health cases, hundreds, thousands, and perhaps millions stand to be injured if the cited activity is not stopped. This is where the reciprocal relationship between risk and harm becomes important. Risk is the probability that the substance will cause harm at the exposures involved. What is the probability that the risk is real? Is it certain, comparable to dropping a bomb upon a population, or is it remote?

Next we consider the disease caused and the number of people at risk. This is harm. Is one person exposed, in which case we might require the usual standard, or are many people exposed? Where a great many people are at risk and the risk is one of death, the potential harm is great. In these cases there is no question but that action should be taken even if the probability or certainty of the risk being real is low. Where the potential harm is slight, the probability of risk should be greater before action is taken. In some cases the potential harm is so great that action should be taken even though the risk is remote or speculative, although no court has yet gone this far. An example is the case of fluorocarbons. If the ozone layer in the stratosphere is reduced, the entire population of the earth will be at increased risk of skin cancer. With that sort of harm at issue, the risk might be very small, and yet justify action.

The cases cited above are encouraging to those who view public health in terms of prevention of disease. It is apparent that courts will be called upon to make hard decisions affecting large numbers of people even though all the evidence is not yet in. In making these decisions courts will have to rely on expert opinion and available data. Where there is a gap in the proof or the matter is impossible of proof, either the expert opinion will be given considerable weight, or the courts will lower their standard of necessary proof within the reciprocal risk theory. Ultimate decisions will consider all the equities, including severity of harm, number of people affected, number of jobs affected and capital structures jeopardized. The probability that the risk is real has become, and hopefully will remain, no more than one of these equitable factors.



John P. Hills is an attorney in private practice in the law firm of Messenger, Lynch, Hills and Miller. Hills was a senior trial attorney for the Pollution Control Section of the U.S. Department of Justice. In this position, he was chief government counselor in the Reserve Mining case. As a senior staff member of the Council on Environmental Quality, Hills handled situations involving public health questions.

Coordinated by LRE

Coast Guard's response to spilled oil

Lt. R. W. Ard, Jr.

U.S. Coast Guard Reserve
Office of Research & Development
Washington, D.C. 20590

The Coast Guard has widely differing oil spill control responsibilities depending on whether the location in question is inside or outside the territorial limits (nominally 12 miles out from the coast). Outside the territorial limits and in accordance with the Outer Continental Shelf Lands Act, the Department of the Interior has primary responsibility. A Memorandum of Understanding (MOU) exists between Interior and the Department of Transportation, the department in which the Coast Guard resides. This MOU gives the Coast Guard responsibility for containment and clean up of oil spills, while the U.S. Geological Survey (USGS), as the representative of Interior, has the responsibility of coordinating cleanup efforts and abating the source of pollution.

In other words, the USGS is primarily responsible for pollution abatement outside the territorial limits of the U.S.; it develops all regulations including those for pollution abatement, and is the on-scene coordinator in the event of a spill. The Coast Guard provides cleanup expertise and equipment if requested by the USGS.

Inside the territorial limits, the Federal Water Pollution Control Act applies. Under this Act, the Coast Guard can fine oil dischargers with civil penalties of up to \$5000. Additionally, any supervisor of an offshore facility is required to notify the Coast Guard of an oil discharge immediately or be personally liable to a \$10 000 fine and imprisonment for one year. Under the National Oil and Hazardous Substances Pollution Contingency Plan, the Coast Guard is required to provide an on-scene coordinator for a spill. The on-scene coordinator is responsible for overseeing private cleanup activities.

If sufficient private response is not provided, the Coast Guard will personally clean up the spill and bill the polluter. The Coast Guard maintains a pollution revolving fund for cleanup measures that are normally reimbursed by the polluter. The Coast Guard also maintains a National Response Center whose National Response Team, a group of representatives from various government agencies, assumes an advisory role during a major oil or hazardous substances discharge. Three Coast Guard teams on the Atlantic, Gulf, and Pacific coasts are specially trained and equipped to contain and clean up spills of oils and hazardous substances.

The Federal Water Pollution Control Act also authorized regulations to prevent oil spills; regulation authority was delegated to the Environmental Protection Agency (EPA) for non-transportation-related facilities and to the Coast Guard for transportation-related facilities. A MOU between EPA and the Coast Guard has defined oil and gas rigs as non-transportation-related facilities and, therefore, under EPA's control. Explicitly, EPA is responsible for the first valve closest to storage and the Coast Guard is responsible outboard of that valve.

Remote sensing of oil spills

The Coast Guard's Office of Research and Development has an extensive remote sensing program to detect oil spills. This program is broken down into two major categories: in-

A number of monitoring detectors, sensors, and techniques help this federal agency to find, recover, and identify this pollutant

situ and airborne. In-situ sensors are used to survey the immediate area of the sensor and are typically mounted on bridge piers, buoys, and piles. Studies have been conducted by the Coast Guard to determine high-risk areas and potential oil drift patterns within these areas. Using this information, sensors can be strategically located to provide continuous, all-weather surveillance.

Airborne remote sensing, or using appropriate sensors on an aircraft, can cover tremendous areas over short periods of time and can map the extent of the spill with appropriate documentation for later legal action. Unfortunately, remote sensing is not continuous and is expensive. Still, for the vast coastal regions of the U.S., an aircraft with an all-weather capability of detecting oil slicks is a powerful surveillance tool.

Many in-situ sensor concepts have been investigated by the Coast Guard including those that use vapor detectors, various mechanical schemes, and visible, ultraviolet, and infrared detectors.

Hydrocarbon vapor sensor. At least seven different hydrocarbon vapor sensors exist, but the Coast Guard required one that could be used on buoys in a marine environment. This sensor must provide reliable monitoring over wide ranges of temperature, humidity, and salt spray as well as declining battery voltage, automatic response and resetting to hydrocarbon vapors, and minimal maintenance features. The Taguchi gas sensor was determined to best meet these requirements.

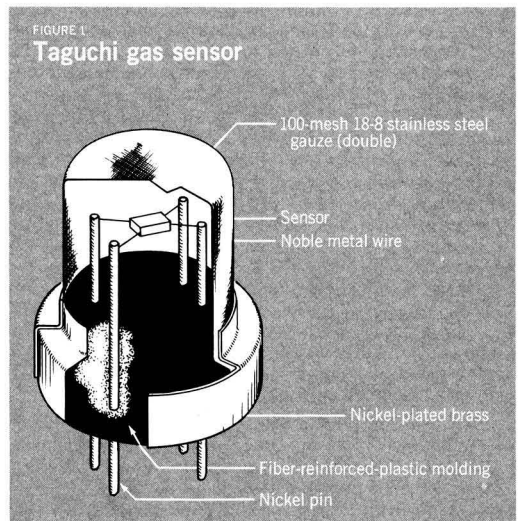


Figure 1. Taguchi gas sensor

The Taguchi gas sensor, as shown in Figure 1, uses a semi-conductor to detect charge-transfer phenomena as a function of hydrocarbon vapors adsorbed onto its surface. As these vapors are adsorbed, conductivity is increased. There is a built-in heater that periodically warms up the semi-conductor to drive off the vapors and allows the sensor to detect vapors at minimum intervals of one to five seconds.

While the potential for this sensor is very good, there are certain disadvantages. Since this device responds to hydrocarbon vapors and not to oil directly, it can react to hydrocarbon vapor sources (such as boat exhausts) other than oil spills. In addition, heavy oils with small amounts of volatile constituents such as No. 6 and lubricating oils are not detected.

Infrared detectors. The Wright & Wright Environmental Engineering and Rambie, Inc. detectors use an active infrared light source to detect oil. There is a convenient sharp increase in the reflectivity of infrared light from water between 2.5μ and 3.4μ ; this same phenomenon occurs from oil but at wavelengths approximately 0.5μ longer. These instruments utilize infrared reflectance at both frequencies but sound an alarm when the ratio is near that of oil rather than that of water.

These units must be rigidly mounted above the water and be properly aligned and field calibrated as shown in Figure 2. They are effective day and night and in all weather except heavy rain, which will cause returned signals to approach zero and produce a failure alarm. Generally these infrared sensors have been proven reliable in service, but they can only survey a small spot immediately below the instrument.

Buoy fluorescence detector. When oils are irradiated with an ultraviolet light they re-radiate a long wavelength emission in the near ultraviolet and blue end of the visible spectrum. Living organisms and some other marine materials fluoresce and reliable oil detection on these waters requires appropriate tuning of the detectors to select the oil fluorescence peaks, signal processing parameters, and field sensitivity adjustments. The Spectrogram Corporation's Buoy System selectively discriminates among the various oils.

This device can be modified to selectively detect any particular oil from crude to kerosene. Under contract with the Coast Guard, the Spectrogram Corporation has produced and extensively tested a buoy that operates from a 12 V dc power supply (Figure 3). The buoy beam is directed down beneath a sunshade; this means that the oil must pass directly below the buoy before it can be detected, but the system is then effective day or night.

Scanning fluorescence detector. The Baird-Atomic, Inc. Multispectral Active Passive Scanner (MAPS) (Figure 4), is capable of detecting and to some extent classifying oils while scanning in azimuth and range at night only. The MAPS has demonstrated a maximum range capability of 650 ft in clear weather, an elevation scan from $6-30^\circ$ below horizontal, an azimuth scan of $\pm 165^\circ$, and a minimum detectable oil thickness of one micron.

The fact that this sensor operates only at night is a sizeable disadvantage even though many spills do occur during this period and are only reported at first daylight when they are widely dispersed. Thus, being able to detect a spill when it is least likely to be seen by the casual observer, who usually is the first to see a discharge, is a very real advantage.

Laser polarimeter. The design of this device is based on the fact that the presence of oil on turbid water (normally present in the marine environment) can be detected as an equal attenuation of both the horizontal and vertical components of a laser-irradiated-backscatter signal. When the backscatter is significantly different in the horizontal and vertical components, there is turbid water without oil, but when

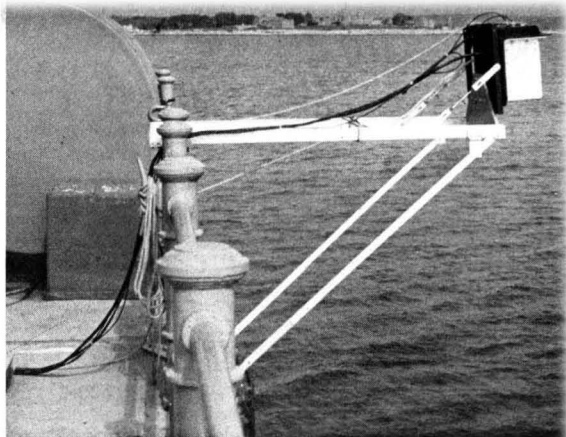


Figure 2. Rambie, Inc.'s active IR detector

both polarizations attenuate radically and equally, oil is present. Since the spectral absorption of different oils vary, two or more frequencies can be used to provide identification data.

Airborne sensors

Airborne remote sensing requires an expensive vehicle with sufficient payload capacity to carry the sensor package and ancillary equipment. Flying sensors have some very important advantages:

- they are able to survey a very wide area
- they possess sufficient speed to allow a rapid deployment in areas of suspected spills
- they occasionally possess a mapping capability that permits the extent of the spill to be determined
- they require the presence of a human operator who can make rational decisions and collect data. Under this program, fixed-wing aircraft, helicopters, and satellites have been investigated. While many sensors have been looked at by the Coast Guard, including visible, infrared, ultraviolet, radar, passive microwave, and lasers, only the most promising sensors are described below.

All sensors are subject to operational limitations. Therefore, to cover differences in weather and oil types and to allow for false alarm rejection, source identification, and quantification, an array of complementary sensors is required. The Coast Guard's Airborne Oil Surveillance System (AOSS) is a prototype of such a system that includes infrared and ultraviolet line scanners, passive microwave imagery, low-light-level television, and side-looking-airborne radar. This research package has proven highly successful in both testing and actual operational flights.

Low-light-level television (LLLTV). In addition to airborne photography, a LLLTV may be used to view visual images. It was hoped that the low-light-level feature would enhance oil spill detection into the range of starlight, but the major problem with this sensor was found to be "blooming," which obscures the image when sun glint or even vessel lights are observed. Unfortunately, this problem has severely limited the applicability of this device even though it has proven useful in enhancing the visual powers of the observer where ship, shore, or offshore structure lights do not interfere.

IR scanners, forward-looking-infrared (FLIR). Unlike visual sensors, infrared systems can operate 24 hours a day, but not in fog or precipitation. During the day, oil will usually absorb and re-radiate more heat than the surrounding water. At night, the water gives its heat up more slowly than the oil. Another phenomenon that establishes a temperature difference between the oil and the water is the cooling effect on fresh oil from evaporation of the more volatile constituents.

Since the sensitivity of these scanners is usually about 1 °F, temperature differences between very thin slicks and water are insufficient to be detected, and thermal anomalies such as power plant discharges can produce an image very much like an oil slick.

An IR line scanner consists of a fixed detector and a 45° mirror that rotates about the axes on the centerline of the detector. If the aircraft proceeds in the direction of the axis of rotation, a line of data perpendicular to the aircraft heading is obtained that can be used to draw a map on film, video display, or for storage on magnetic tape.

FLIR devices detect infrared radiation and project it visually on a TV-like screen. These scanners have the panning ability of low-light-level TV without the serious "blooming" problem or the requirement for ambient light.

Ultraviolet (UV) sensors. The UV scanner may be included in the previously described IR scanner pod. The UV image brightness of oil on water depends on the oil type, oil thickness, water quality and, especially, the level of sunlight. While this passive UV system cannot be used at night and would not be very useful alone, it serves the very important function of discriminating thermal anomalies from oil slicks, both of which are detectable by the IR scanner.

Side-looking-airborne radar (SLAR). Radar detects the small wave suppression effect of an oil spill and is the best of all the airborne sensors. Unlike the previously discussed sensors, radar is an active system. Microwaves are radiated to the sea surface and returned by small waves to produce a dense light pattern on the radar scope. By suppressing these waves, oil appears as a black area amidst the white glitter on the radar scope. The radar used for this application must be a mapping type of unit with sufficient resolution to detect the normally occurring small waves.

A Motorola APS-94D radar (a side-looking radar) was modified and installed on the Coast Guard AOSS aircraft. Testing and operational uses have proven this device to be highly effective. It has detected oil in solid overcast with a 100-ft ceiling while flying at 1300 ft and at a range of 13.2 nautical miles.

Passive microwave imagery (PMI). Passive radiometry can be used to detect oil because the microwave radiation emitted by oil is usually different from the water and penetrates clouds and haze. The image produced by PMI is much like a mosaic and consists of rectangular, uniform areas of "bright-

ness temperature" of particular areas. While the imagery is difficult to interpret, PMI's sensitivity to oil thickness is such that it can be used in airborne quantification of the slick.

Thus, it can be seen that the Coast Guard is in the process of developing a very comprehensive, multifaceted oil spill detection system that will be able to reliably detect oil spills under a wide variety of situations. It is hoped that this detection capability will deter deliberate discharges and allow the timely detection and recovery of accidental spills before they disperse over a wide area.

Oil spill recovery

Once a spill has been detected, the next problem is to contain and recover the oil. The Coast Guard Office of Research and Development (ORD) has conducted a very extensive program to produce effective oil containment and recovery equipment. Several different systems have been developed to provide the Coast Guard with clean up capability.

Air deployable anti-pollution transfer system (ADAPTS). This independent pumping system, developed by Ocean Science and Engineering Inc., is used to remove oil from stricken tankers to minimize or prevent major oil spills. It consists of a 40 horsepower diesel prime mover unit that hydraulically drives a variable displacement, two-stage centrifugal, submersible pump unit. The pump unit is designed to fit into a 12-in. diameter hatch so that it can be lowered through standard Butterworth fittings or deck plates. This system is capable of transferring typical cargo crude oils at flow rates of up to 1000 gpm against a 40-ft head and through 200 ft of 6-in. diameter transfer hose.

This device was designed for air delivery from a C-130 aircraft by parachute in a delivery container; however, this delivery mode has not been implemented operationally. It can also be delivered to the deck of a stricken vessel by helicopter. There are 21 systems in the Coast Guard's oil spill control equipment inventory. This equipment has been used successfully several times in actual pollution incidents.

High seas oil containment system. The high seas containment barrier was designed to be functional in 5-ft seas, 2-knot currents, and 20-knot winds with sufficient strength to withstand 10-ft seas, 5-knot currents, and 40-knot winds. This barrier features a 4-ft high flexible curtain with rigid vertical struts on 6-ft centers; this combination provides the requisite sea following ability (Figure 5). An inflatable float with a

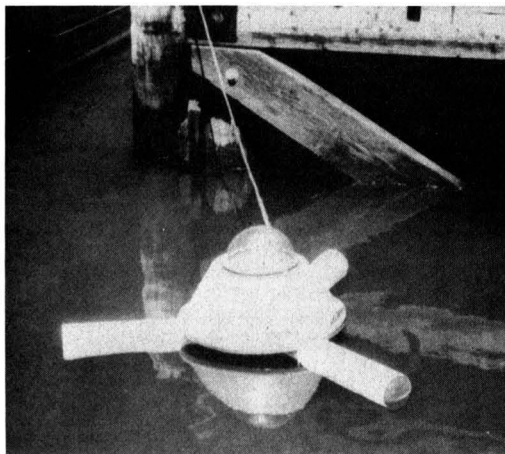


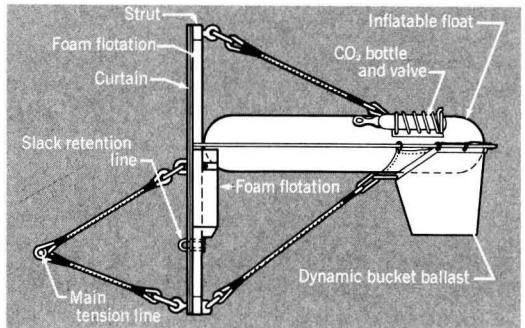
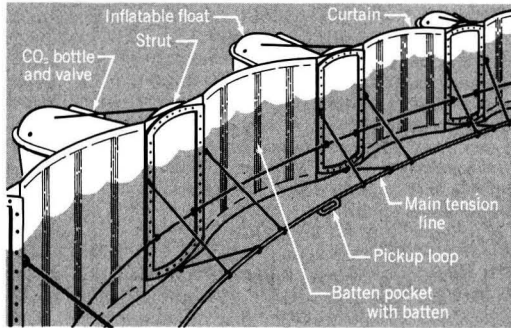
Figure 3. Spectrogram's buoy system



Figure 4. Baird-Atomic's UV fluorescence scanner

FIGURE 5

A high seas oil containment system



"bucket" in its end acts as an outrigger stabilizer for the deployed barrier. The barrier is fastened to an external tension line that prevents the accumulation of loading forces upon the curtain proper and thus allows the barrier to better follow and maintain a proper attitude to the seas.

A 612-ft length of the barrier is stored, transported, and deployed in an aluminum container 18-ft long, 9-ft wide, and 5-ft high. This system is air transportable from storage to staging site and is designed for air delivery by C-130 aircraft with parachutes. The air delivery capability has not been implemented operationally. The system may be deployed from a support ship with a crane large enough to handle the 18 000 lb system weight. Once the container is in the water, the barrier is withdrawn directly from it.

A mooring system is also provided to allow the barrier to be located in a desired position. A barrier handling system is used to retrieve, transport, and refurbish the barrier after use. Fifteen barriers, built by Offshore Devices, Inc., were procured for use and are stored at strategic sites around the country.

Rotating-disc-drum-high-seas-oil-recovery system. This unit, developed by Lockheed Missiles and Space Company, Inc., is capable of operation in sea state 3 with currents up to 2 knots and of survival in sea state 6, with 40-knot winds, and 8-ft seas. It is 22-ft long, 27-ft wide, and 12-ft high and uses 65 vertical rotating discs. The oil adheres to the discs but water does not; the oil is then wiped off the rotating discs with wipers into a central trough. An air-cooled diesel engine powers an air compressor to inflate the pontoons that support the device, the three hydraulic pumps that drive the discs, and four oil-discharge pumps. The pontoons are used so that this device can fit into a C-130 aircraft.

This system weighs about 7 tons and can be transported by a C-130 aircraft. It can be deployed from a support vessel with a suitable crane and can recover up to 1000 gpm of oil.

Fast-current-oil-recovery devices. At the present time there is no effective way to recover oil in currents in excess of 1-2 knots. This has severely limited effective oil spill cleanup in areas where current is a factor such as rivers, bays, and estuaries. To remedy this situation, the Coast Guard has initiated a program to recover oil in currents up to 10 knots. Stage I: Concept Feasibility of this program has been completed and two contractors, Shell Development Company, Inc., and Seaward, Inc., have been selected to continue into Stage II: Advanced Model Demonstration.

The Shell concept uses an oleophilic (oil absorbing)/hydrophobic (water rejecting) continuous belt that is laid down on the oil slick at the same speed as the current. There is zero relative velocity (ZRV) between the belt and the slick and the oil is rapidly absorbed on the belt to be later wrung out.

The Seaward concept uses bundles of fibers to isolate the oil slick from the water and allow the water to drain out of the device while the oil is slowed and thickened for subsequent pickup.

After Stage II is completed, it is anticipated that prototypes of these devices will be built in Stage III for field testing and evaluation. These devices should allow the Coast Guard to effectively recover oil in high-current situations.

Oil spill identification

Once a spill has been detected and recovered, the next problem is to determine the violator so that he may be required to reimburse the Coast Guard's oil spill cleanup revolving fund.

The Coast Guard Research and Development Center is developing a system that will determine the source of a spill with sufficient confidence that violators can be prosecuted. Every promising technique was evaluated for its ability to characterize oils. The most promising techniques have been infrared and fluorescence spectroscopy, gas chromatography, and thin-layer chromatography. The detection probabilities for each method in ten simulated spills involving 63 samples were: infrared 94.4%; fluorescence 91.1%; gas chromatography 91.1%; and thin-layer chromatography 62.9%, for a combined probability of 99.9%.

These oil spill identification fingerprinting techniques have been used in 38 real-world spill cases. In every case, each of the techniques agreed on one source as responsible for the oil spill. In all of the cases that could be verified, these techniques correctly identified the source.

The opinions or assertions contained herein are the private ones of the writer and are not to be construed as official or reflecting the views of the Commandant or the Coast Guard at large.



Lt. Roswell W. Ard is a project officer at the Coast Guard's Office of Research and Development. As a registered professional engineer he has worked on marine sewage systems, vessel stack emission control, shipboard solid waste management and high-speed oil recovery devices. He has previously been assigned to various Coast Guard ships, but he will be leaving the service soon.

Coordinated by LRE

CURRENT RESEARCH

Preliminary Small-Scale Combustion Tests of Coal Liquids

Jon E. Haebig*, B. E. Davis, E. R. Dzuna

Gulf Research & Development Co., Pittsburgh, Pa. 15230

■ Nonupgraded coal liquids contain high concentrations of nitrogen and aromatics; the tendency for such fuels to emit excessive amounts of NO_x and smoke was examined in burning tests in a modified 1-gph boiler equipped with an air-atomizing nozzle. Full-boiling range and distillate coal liquids were tested, and conventional nitrogen-doped petroleum fuel oils were used for comparison. At 80% excess air, the fraction of the fuel-bound nitrogen converted to NO_x was 80%, but the conversion decreased to 35% at 25% excess air. Petroleum oils exhibited similar behavior. Smoke levels from the full-range and distillate coal liquids were similar to those from petroleum No. 4 and No. 2 fuel oils, respectively. The use of a set of modified burners showed that increasing the air-fuel mixing rate decreased the smoke emissions, but increased the conversion of fuel-bound nitrogen.

Because of recent intense concern for environmental conservation, air pollutants that originate from combustion sources have attracted a great deal of attention, including sulfur oxides, nitrogen oxides (NO_x), and smoke particulates. Emission factors for stationary sources have been determined which relate the rate of pollutant emission to the types of boilers and furnaces and grades of fuel oils and other fuels (1). Studies have demonstrated that NO_x emissions arise from two sources: (1) molecular nitrogen in the combustion air is oxidized via a thermal process to form "thermal NO_x "; and (2) nitrogen, which is chemically bound in the fuel, is converted to "fuel NO_x " (2-4). The most effective approach to eliminating NO_x emissions from combustion sources is the modification of the combustion process. Several combustion modification techniques have been developed to combat NO_x emissions, and staged combustion has been shown to be the most effective technique for the suppression of the oxidation of fuel nitrogen (5, 6). The smoking tendencies of fuel oils have been related to their API gravity and other properties (1, 7).

The growing imbalance between energy consumption and fuel production has created a need to supplement petroleum-derived fuels by the conversion of coal and other fossil fuel forms into liquid fuels. Studies by many organizations, including the Gulf Oil Corp., have shown that low severity processing is sufficient to convert coal to a low-sulfur liquid fuel. However, such liquids still differ from conventional petroleum-derived fuel oils in the same viscosity range; the coal liquids contain more nitrogen and aromatic compounds, being hydrogen deficient. As a result, the combustion of such liquids can be expected to produce greater emissions of NO_x and smoke and will require upgrading to produce suitable fuel products.

To obtain more information about the relationships between coal liquid composition and combustion emissions, we have submitted several coal liquids to the combustion tests to be described in this paper. In these tests, a modified 1-gph (3.8 dm³/h) residential boiler was used, which required relatively small samples; the coal liquids were tested as produced and were in the quality range of a No. 4 fuel oil. Thus, these tests are preliminary in nature, and neither the boiler nor the liquids used are intended to represent future commercial equipment or fuel products. The results of these tests of coal liquids are instead to be interpreted by referring to some tests of conventional petroleum-derived fuel oils in the same boiler, which served to "calibrate" it. Some operating parameters of the burners and boiler were also varied to further establish their role in the combustion behavior of the coal liquids.

Experimental

Equipment and Procedures. The structure of the test boiler and associated equipment used is shown in Figure 1. The burner was fired horizontally into a firebrick-lined combustion chamber 38 cm (15 in.) long, 28 cm (11 in.) wide, and 35.5 cm (14 in.) high; the flame gases then passed upward into the boiler section, where they were cooled to 230-290 °C (450-550 °F). Gases were sampled from the flue immediately above the boiler section, and were delivered through 6.25-mm o.d. stainless steel tubing to an ice bath and a train of continuous analyzers for NO_x (electrochemical or chemiluminescent), CO_2 and CO (NDIR), and O_2 . Instrument accuracy was verified with Orsat readings for CO_2 and CO, and by comparison with combustion stoi-

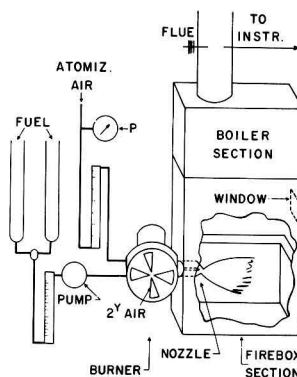


Figure 1. Residential boiler and associated equipment

chiometric calculations. A Bacharach smoke number sampler (ASTM D 2156) was also positioned in the flue; smoke filter disks were read photometrically. The low velocity of the flue gases made isokinetic sampling impractical.

A modified residential "gun-type" burner was used, which had a motor-driven fan. The small orifice of the pressure-atomizing nozzle tended to become plugged by the coal liquids, and it was necessary to substitute an air-atomizing nozzle that had no small orifices. The burner was also equipped with an efficient flame retention head, so positioned that all the combustion air emerged through it into the combustion chamber. Although this produced a high swirl and turbulence in the flame, it permitted measurements at low excess air levels without the formation of excessive smoke that tends to degrade the reliability of the flue gas analysis instruments. (The behavior of other burners with less air turbulence was also ascertained; these are described in the section on burner design.) A further advantage of the air-atomizing nozzle (compared to pressure-atomizing nozzles) is the independent variability of fuel flow (controlled by a peristaltic pump), atomizing pressure, and fuel viscosity.

In a typical run, the fuel flow rate was held constant at 3.8 dm³/h (1.0 gph), and the combustion air input was varied. The atomizing air pressure was 34.4 kPa (5 psi) unless otherwise noted. The boiler was fired initially with No. 2 fuel oil to bring the system to equilibrium before introducing samples. Periodically, the No. 2 oil was fed into the system to check instrumentation and to serve as a reference. During a run, the combustion air was varied and measurements of Smoke Number, CO, CO₂, O₂, NO_x, and unburned hydrocarbon were taken. At each change of the air gate opening or other operating variable, the excess air level was calculated in the conventional manner from the measured CO₂ and the C/H content of the test fuel.

In addition to the measured total concentrations of NO_x in the flue gas, a parameter of interest is the portion of the NO_x that originated from the fuel nitrogen and the fraction of the fuel nitrogen converted to NO_x (the remainder of the fuel nitrogen emerging as N₂). The concentration of thermal NO_x in the flue gases from the combustion of the test fuel was assumed to be the same as that measured in the combustion of No. 2 fuel oil, and was subtracted from the total value to obtain the fuel-NO_x concentration. (Two slight differences between the combustion of No. 2 fuel oil and of coal liquids that are neglected in this procedure are the different volumes of dry stack gases and the different flame temperatures, resulting from the use of the same volumetric fuel feed rate but different heat input rates. The resulting error is estimated to be less than 5%. The heavier

oils and No. 2 fuel oil differed in their atomization and fuel-air mixing behavior; this may also contribute to differences between the thermal NO produced from the test and reference fuels, but the effect is hard to estimate.) The fraction of fuel nitrogen converted to NO_x was obtained as the ratio of the observed fuel-NO_x concentration and the theoretical fuel-NO_x concentration computed for complete conversion by combustion stoichiometry. The nitrogen contents of the test fuels were determined by Kjeldahl analyses.

Properties of Fuels. The properties of the fuels tested are listed in Table I. The coal liquids were produced in a bench-scale version of the Gulf Catalytic Coal Liquefaction process, which is based on the hydrogenation of a pulverized coal-solvent slurry. These liquids contained less than 0.1% sulfur. Samples F1 and F2 are filtered full-boiling range process effluents; they were produced from western subbituminous and Pittsburgh Seam bituminous coals, respectively. These full-range liquids contained 0.5% nitrogen, and their viscosities were in the range of No. 4 or No. 5 fuel oils. Coal liquid "D" was a 130–350 °C (270–670 °F) distillate obtained from the full-range liquid F1; it contained 0.31% nitrogen and its viscosity was near that of No. 2 fuel oil.

Results and Discussion

Emissions from Coal Liquids. Emissions of sulfur dioxide were very low because of the low sulfur content of these liquids. The concentrations of carbon monoxide and hydrocarbons in the flue gases were less than 5 ppm except at times when the smoke number exceeded eight. The smoke data are presented in the section on smoke emissions; these coal liquids produced much less smoke than that encountered while burning typical petroleum-derived fuel oils having such low API gravities (7–14 °API). When the excess air was greater than 25%, a relatively low air requirement, the smoke from the distillate and full-range coal liquids were within the limits corresponding (respectively) to home furnaces and industrial uses. The only emission which seemed to be problematic was NO_x.

Conversion of Fuel-Bound Nitrogen. The NO_x concentrations in the flue gas measured in the tests of the coal liquids in the air-atomizing test burner are shown in Figure 2. The distillate produced between 250 and 300 ppm of NO_x, and the full-range liquids produced between 300 and 400 ppm of NO_x. The emissions from No. 2 fuel oil are also shown. The concentration of NO_x in the flue gas did not vary greatly with excess air, but correction for dilution by excess air shows (Figure 3) that the amount of NO_x emitted from the burning of coal liquids increased with excess

Table I. Properties of Fuels Tested

	Coal liquids						
	Distillate D	Full-range		Anthracene oil	Cycle oil	No. 2 fuel oil	No. 4 fuel oil
F1		F2					
Gravity °API	14.1	7.0	10.4	—	15.3	34.5	28.3
Density, 15°C, kg/l.	0.9730	1.0217	0.9970	—	0.9638	0.8524	0.8854
Ash, wt %	0.0030	0.010	0.013	0.002	—	—	—
Carbon wt %	89.56	89.93	89.0	91.02	90.7	86.9	86.41
Hydrogen wt %	9.54	8.84	9.44	5.90	9.3	13.1	12.36
Nitrogen wt %	0.31	0.51	0.50	0.98	—	0.01	—
Sulfur wt %	0.04	0.07	—	0.58	0.50	0.10	—
Dist. range, °C	130–364	—	—	>200	204–338	182–338	—
Dist. range, °F	266–688	—	—	>392	400–640	360–640	—

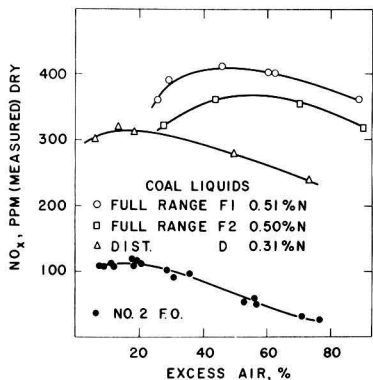


Figure 2. Measured NO_x concentration

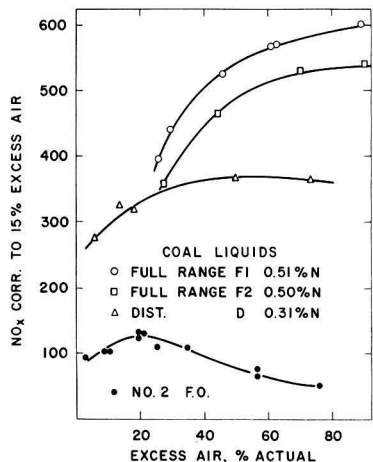


Figure 3. Amount of NO_x

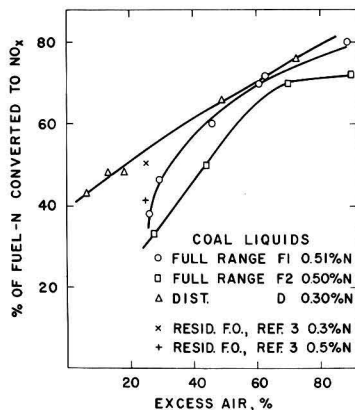


Figure 4. Conversion of fuel-N

air; this was due to increased oxidation of the fuel-bound nitrogen. The amount of thermal NO_x produced by the No. 2 fuel oil decreased with increasing excess air, owing to cooling of the flame by the additional air.

The effects of the nitrogen content of the fuels and of the excess air levels in the tests can best be seen in Figure 4, which presents the fraction of fuel nitrogen converted to NO_x as a function of the excess air level. We first compare the behavior of the coal liquids and petroleum fuels when the excess air was 25%. Thirty-two and forty percent of the nitrogen in the full-range coal liquids was converted to NO_x . These conversion values are close to those for 0.5% nitrogen petroleum oils reported by Turner and Siegmund (3); in that study, a 10-gph boiler was used, which contained an insulation-lined combustion chamber and an air-atomizing nozzle. The fuel nitrogen conversion exhibited by the distillate coal liquid in our tests was 52%, which is higher than that of the full-range liquids; this value is also close to that of a petroleum fuel oil containing 0.3% nitrogen, observed by Turner and Siegmund (3). These values for fuel nitrogen conversion in the coal liquids are also consistent with the observation by others that more of the fuel nitrogen is converted in less nitrogen-rich fuels (2, 3, 6). It is possible that the test unit used in this study and in the large unit reported in Reference 3 involves flames which

are similar in aspects that affect fuel nitrogen conversion; if so, one can conclude that the NO_x emissions from coal liquids will generally resemble those from petroleum fuel oils in such boilers. Observations of the effects of burner-operating parameters are described in the section on burner design.

Thus, the distillate coal liquid contained only 60% as much nitrogen as the full-range coal liquids, but it yielded nearly as much NO_x in combustion, as a result of the higher fuel nitrogen conversion associated with its lower nitrogen concentration.

In addition to the effect of the nitrogen concentration on the conversion levels, other differences between the distillate and full-range liquids may have influenced the nitrogen conversions in these liquids. The viscosity of the full-range liquid was four times that of the distillate; and from a correlation for pneumatic atomizers (8), it was estimated that the mass mean diameter of the droplets in the filtrate spray was twice that of the distillate droplets. Furthermore, the droplets of the full-range liquid probably volatilized in the flame more slowly than those of the distillate.

There are also a few indications of effects of the volatility and composition of the nitrogen compounds in the fuels. Approximately one-half of the nitrogen compounds in the full-range liquid F1 boiled above 350 °C (670 °F), in contrast to the nonvolatile components of the distillate, which of course all boiled below that temperature. Tests of pyridine-doped No. 2 fuel oil in the test burner (curve "10" in Figure 7) also indicate that the pyridine was more extensively oxidized than were the nitrogen compounds in the distillate coal liquid. [The conversion of the 0.5% N oil (as pyridine) was close to the nitrogen conversion (52% at 25% excess air) of the distillate coal liquid (which contained 0.3% nitrogen), and the conversion of 0.3% N oil (as pyridine) would then definitely exceed 52%.] Finally, in three of the burners employed in tests described in the burner design section, the conversion of piperidine in No. 2 fuel oil was 10–15% greater than the conversion of pyridine; the dopant level was 0.50% N in both cases, and this difference occurred only between 50% and 100% excess air.

Effect of Excess Air. The major operating parameter that affects combustion emissions is the excess air level. In tests of the coal liquids in the test burner, between 70% and 80% of the fuel nitrogen in all the coal liquids was converted to NO_x at very high excess air levels. The fuel nitrogen conversion exhibited by the distillate liquid decreased regularly to 40% as the excess air level was reduced to 6%. These conversion levels are close to those observed by

Turner and Siegmund (3). They also found that the conversion continued to decrease as the air feed was reduced below stoichiometric values, in a simulation of the first stage of staged combustion; this accounted for the success of this technique. The conversion of the fuel nitrogen in the full-range coal liquids exhibited a similar response to decreasing excess air, although in the lower excess air range, its decrease appears to be unusually rapid. Others have also noted dramatic decreases in conversion with decreasing excess air (5). Thus, staged combustion may serve to limit the NO_x emissions arising from the nitrogen in coal liquids. This technique is also likely to be more effective in larger furnaces whose residence time is longer than that of the test unit used here. However, staged combustion is limited by the soot formed in the fuel-rich first stage, and this limitation will become problematic with coal liquids.

Smoke Emissions. The smoke measurements made during these tests of the coal liquids in the test burner are shown in Figure 5. Data are also included from tests of anthracene oil and No. 4 fuel oil [the latter at 138 kPa (20 psi) atomizing air pressure]. No. 2 fuel oil gave no smoke when the excess air exceeded 12%. When the excess air was greater than 25%, the smoke from the distillate coal liquid was less than ASTM smoke No. 2 (a typical performance requirement for a home furnace) and the smoke from the full-range liquids was less than approximately a Ringelman number one—a common limit for industrial furnaces. This is a relatively low air requirement. When the excess air was increased above 50%, the smoke from the distillate fuels (including anthracene oil) decreased to less than ASTM smoke No. 1; in contrast, the residual fuels (the full-range coal liquids and the No. 4 fuel oil) produced moderately persistent smoke.

There is a relationship between the smoking tendencies of these fuels and of their compositional properties. The most influential of these properties is apparently the non-volatile content of the full-range fuels, whose persistent smoking places them in a separate group from the distillate fuels. Further comparisons of smoke formation from full-range coal liquids and from petroleum residual fuels are needed and may be made possible by using a variable fuel preheater in the test burner. The API gravity of the distillate fuels is closely related to their tendency to form soot in the low excess air range. Viscosities and carbon numbers do not seem to bear any regular relationship to the smoking tendencies of this set of fuels, although these properties are also important.

To obtain further information about the effect of the aromatic content of fuels on their smoking tendencies, a middle distillate cycle oil was tested. It resembled the distillate coal liquid, since its API gravity was 15.3; but it did not

pressure-atomizing nozzles, permitting the use of a conventional but efficient home furnace burner. No. 2 fuel oil was also burned for comparison. The No. 2 fuel oil required 17% excess air to limit the smoke from its combustion to a number one spot; and the cycle oil required a moderate increase in excess air, to 27%, to reduce its smoke to this limit.

Effect of Burner Design on Emissions

As we have described, the combustion of the coal liquids in the residential-size test burner produced fuel nitrogen conversion levels close to the conversions reported for residual petroleum fuel oils burned in somewhat larger units. These latter furnaces had air-atomizing nozzles; and in comparison with residential burners, they had longer residence times and higher flame temperatures. In contrast, tests by Martin (2) in a representative residential furnace produced fuel nitrogen conversions that were generally 50% lower than those observed in our modified residential test furnace and in the larger units mentioned above. A pressure-atomizing nozzle was employed by Martin to burn a series of No. 2 fuel oils doped with pyridine and other nitrogen compounds; this unit had a high tendency to form smoke.

On the other hand, much greater fuel nitrogen conversion has been observed in small combustors in which very high combustion intensities were produced by accelerated mixing of combustion air and fuel, and also by the fine atomization of the oil (4, 9). In such units between 50% and 100% of the fuel nitrogen was converted to NO_x . To relate our results to these various studies, several burners were assembled having various air-handling parts that varied the air-mixing rate over a wide range; these burners were used in a series of tests with No. 2 fuel oil doped with pyridine at the level of 0.50% nitrogen. Since the smoke-forming tendency of such burners decreases with an increasing air-fuel mixing rate, the smoke number curve of each burner was used to empirically characterize its mixing rate as shown in Figure 6. Each burner is designated by the excess air level that it required to reduce the smoke to a number one spot; for example, the test burner used in the coal liquids test required only 10% excess air, while the least efficient residential burner required 120% excess air. Pressure-atomizing nozzles were employed in all burners except Unit 10, and the droplets produced by the former were probably several times larger than those produced by the air-atomizing nozzle in Unit 10. Burners 40A, 40B, and 120 were fired in the same test boiler as Unit 10 but had various air-handling parts and/or flame retention heads. Curve "75" is plotted from data obtained (10) from the test furnace em-

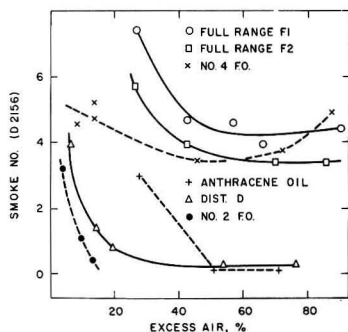


Figure 5. Smoke from coal liquids and other fuels

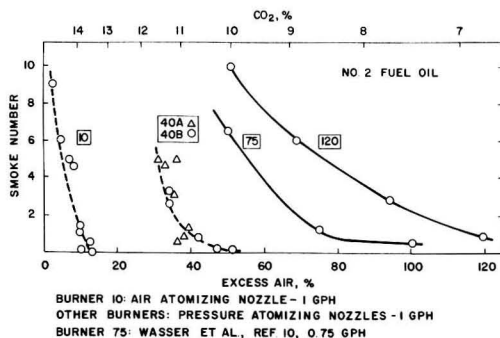


Figure 6. Smoke from variety of burners

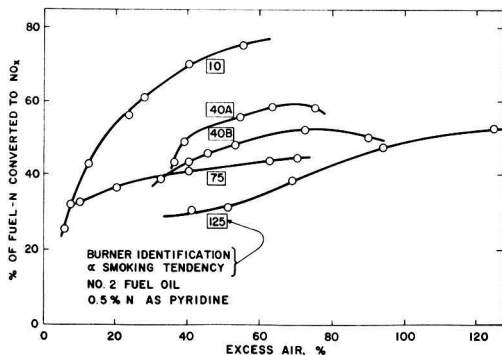


Figure 7. Effect of burners on fuel-N conversion

ployed by Martin and Berkau in the tests of pyridine-doped No. 2 fuel oil which we cited above (2).

Each of these burners was used to fire No. 2 fuel oil which contained 0.5% nitrogen as pyridine; Figure 7 displays the fuel nitrogen conversion observed in each burner plotted as a function of excess air. At any excess air value, the fuel nitrogen conversion was greater in burners having lower smoking tendencies or faster air-fuel mixing. For example, at 50% excess air, Burner 120, which produced the most smoke, converted only 35% of the fuel nitrogen to NO_x . In contrast, in Unit 10, the fuel nitrogen conversion to NO_x was 70%.

Conclusions

In the following, we summarize the observations made with the particular fuels and boiler used here, and note some implications of these results.

1. Generally, the combustion of the coal liquids produced negligible amounts of sulfur oxides (because of their low sulfur content) and CO and hydrocarbons. The amounts of smoke from the combustion of the distillate and the full-range liquids was less than the typical limits for (respectively) home furnaces and for industrial units. Only the NO_x emissions were potentially problematic. This problem can be solved with the removal of nitrogen from some coal liquids by upgrading; the minimum processing requirements for this are now being ascertained.

2. The coal liquids tested contained 0.3% and 0.5% nitrogen, and the concentration of NO_x in the flue gas resulting from their combustion ranged between 240 and 400 ppm. The behavior of the coal liquids in the test burner used here was similar to that observed by Turner and Siegmund in their tests of petroleum residual oils in a 10-gph boiler. At 25% excess air, 35–50% of the fuel-bound nitrogen was converted to NO_x . Although the nitrogen content of the distillate coal liquid was 40% less than that of the full-

range liquid, NO_x emissions from the former were not appreciably reduced. The reduction in NO_x emissions with decreasing excess air suggests that staged combustion will be effective when applied to coal liquids combustion, although smoke formation may then be problematic.

3. Pyridine-doped No. 2 fuel oil exhibited more extensive conversion to NO_x than did the distillate coal liquid, probably due to the lower volatility of the nitrogen content of the latter. Piperidine appeared to exhibit slightly higher conversion than did pyridine, at high excess air levels. There was little difference between the emissions from the combustion of full-range liquids derived from bituminous and subbituminous coal.

4. Tests of pyridine-doped No. 2 fuel oil in a series of modified burners showed that as the fuel-air mixing rate was increased and smoke formation decreased, the conversion of fuel nitrogen was increased. The fuel-air mixing rate in the test burner used in the coal liquids tests was greater than that in conventional home furnace burners.

In conclusion, these tests of coal liquids illustrate how several fuel properties and equipment and operating parameters affect the emissions of NO_x and smoke from these fuels. These effects are similar to those noted in others' observations of the combustion of petroleum fuel oils, although more definitive testing is indicated.

Literature Cited

- (1) Barrett, R. E., Miller, S. E., Locklin, D. W., "Field Investigations of Emissions from Combustion Equipment for Space Heating", EPA Contract No. 68-02-0251, June 1973.
- (2) Martin, G. B., Berkau, E. E., "An Investigation of the Conversion of Various Fuel Nitrogen Compounds to NO in Oil Combustion", presented at 70th National AIChE Meeting, Atlantic City, N.J., August 1971.
- (3) Turner, D. W., Siegmund, C. W., "Staged Combustion and Flue Gas Recycle: Potential for Minimizing NO_x from Oil Combustion", Presented at AFRC/EPA "American Flame Days", Chicago, Ill., September 1972.
- (4) Appleton, J. P., Heywood, J. B., Fourteenth Symposium (International) on Combustion, Combustion Institute, Pittsburgh, Pa., p 777, 1973.
- (5) Pershing, D. W., et al., "Effect of Design Variables on the Production of Thermal and Fuel NO_x from Residual Oil and Coal Combustion", Presented at the 66th Annual AIChE Meeting, Philadelphia, Pa., November 1973.
- (6) Muzio, L. J., et al., "Package Boiler Flame Modifications for Reducing Nitric Oxide Emissions, Phase II", June 1974, EPA Contract No. R2-73-292-b.
- (7) Kraus, B. J., Coburn, J. F., "Emissions from Domestic Heating Oil Combustion", ACS Div. of Fuel Chemistry *Preprints*, 19 (5), 49 (1974).
- (8) Wigg, L. D., *J. Inst. Fuel*, 37, 500 (1964).
- (9) Merryman, E. L., et al., "Recent Studies of the Conversion of Fuel Nitrogen to NO_x ", presented at a Meeting of the Central States Section of the Combustion Institute, March 26–27, 1974.
- (10) Wasser, J. H., et al., *J. Air Pollut. Control Assoc.*, 18 (5), 332 (1968).

Received for review June 19, 1975. Accepted November 26, 1975.

Test of the Theory of Ozone Generation in Los Angeles Atmosphere

Jack G. Calvert

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210

The chemical changes which occur in photochemical smog have been the subject of extensive speculation and research in the physical, biological, and engineering sciences for over 20 years. Most of the information available today and related to the chemistry of these systems was derived in laboratory experiments, smog chamber studies based upon rather simple analogues to the complex atmospheric mixtures, or fixed ground-level studies of a continually changing air mass. It is not clear that these data may be extrapolated to rationalize well the chemical changes that occur in the complex, real atmosphere.

The LARPP Program was designed to measure the chemical reactions occurring in well-defined parcels of air as they moved about the Los Angeles Basin under the influence of prevailing winds. The parcels were followed using radar-tracked tetroons equipped with transponders. Two twin-engine instrumented helicopters (Smog #2 and Smog #3) and a mobile instrumented van made possible pollutant concentration measurements throughout the moving air parcel at ground level and at elevations about 200, 400, 600, and 800 ft above ground. These studies have provided for the first time extensive physical and chemical

observations that should allow significant tests of existing theories of smog formation and the development of new concepts useful to the modeling of photochemical smog formation. An analysis is given in this report of some of the chemical aspects of the LARPP data for a selected, single day's Operation #33 that took place in Los Angeles on November 5, 1973.

The Los Angeles Reactive Pollutant Program (LARPP) was carried out in Los Angeles from September to November 1973. It was jointly sponsored by the Coordinating Research Council and the Environmental Protection Agency with participation of the EPA (helicopter instruments and ultraviolet solar radiation measurements), National Oceanographic and Atmospheric Administration (tetroon operations and radar tracking), the California Air Resources Board (mobile van and laboratory support for GC analysis of bag samples), General Research Corp. (data management), Systems Innovations Corp. (Lidar), Metronics Associates, Inc. (tracer and overall operation control). All basic data from the 35 days of successful operations have been archived on magnetic tape and are available at the National Technical Information Service, Washington, D.C.

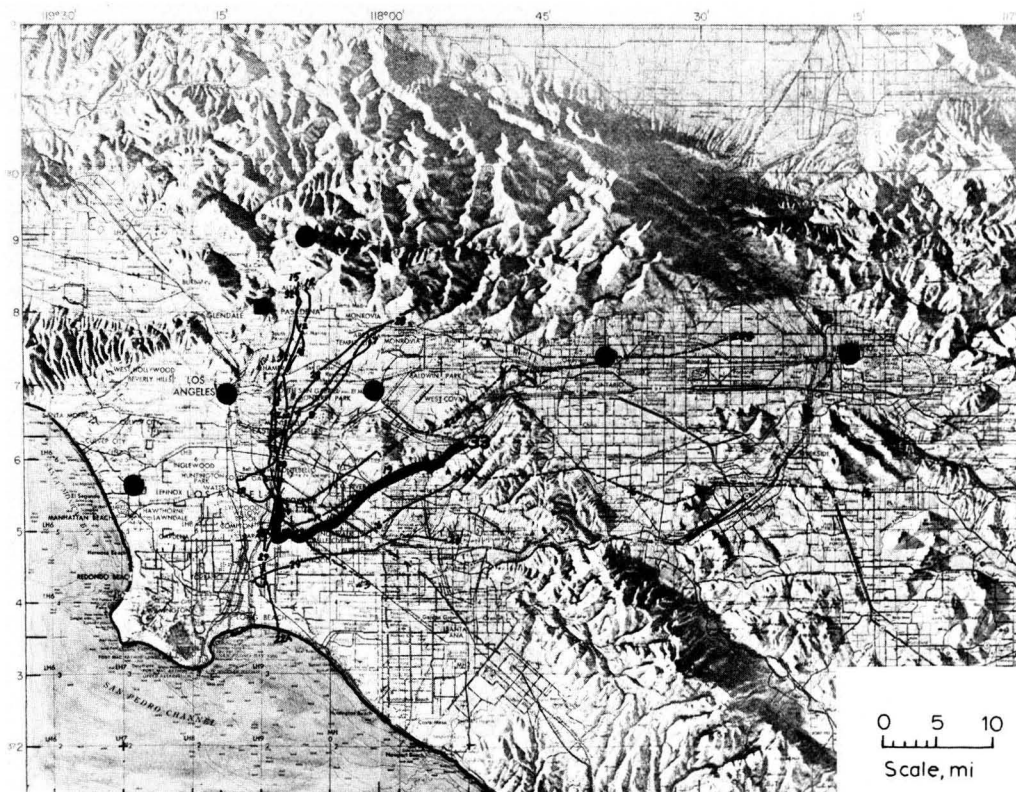


Figure 1. Trajectory of tetroon centroid for LARPP operation #33 of November 5, 1973 (dark line labeled 33). Darkened circles give location of ultraviolet irradiance monitoring stations; darkened square near Glendale is location of radar tracking station.

■ The extensive chemical and physical measurements of the Los Angeles Reactive Pollutant Program (LARPP), Operation #33, are analyzed to test the suitability of current mechanistic hypotheses related to ozone generation in photochemical smog. The pollutant concentrations and certain physical variables were determined from aircraft observations at various elevations and times within a well-defined air mass which moved across the Los Angeles Basin. Ground-level pollutant concentrations and ultraviolet intensities were also obtained from sites near the track of the air mass. These data, simple theory, and reaction rate constant estimates, are utilized to calculate the rate

constant ratio, k_1/k_3 , which is approximately equal in theory to the pollutant concentration ratio $[O_3][NO]/[NO_2]$, $NO_2 + h\nu \rightarrow O(^3P) + NO$ (Reaction 1), or $O_3 + NO \rightarrow O_2 + NO_2$ (Reaction 3). Two theoretical models are considered. The first neglects uv light attenuation within the polluted layer and reflected light from the surface of Los Angeles, while in the second model account is taken of both of these factors. The experimental data from observations made later than the 0920 hour are in reasonable accord with the results of the two models, and within the accuracy of the data they confirm the presently accepted ozone formation mechanism.

Physical Factors Related to Operation #33

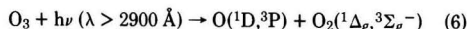
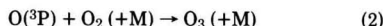
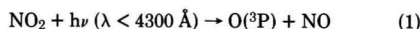
The air mass studied moved across the Los Angeles Basin from the tetroon launching site at Downey toward the Puente Hills as shown in Figure 1 (heavy line). The temperature-elevation profile taken at 0530 showed a temperature inversion at about 1600 ft at El Monte and at about 740 ft (AGL) at the Los Angeles airport. Some indication of a temperature inversion in the early morning hours is seen in the plot of the temperature-time record of the helicopter sampling planes given in Figure 2. Note at 0815 the temperature at the 200-ft region was somewhat lower than that at the upper levels sampled (768–838 ft AGL). The height of the temperature inversion increased throughout the day; it can be seen in Figure 2 that the temperature equality of the 800- and 200-ft levels occurred at about 0845. At 1130 hr, radiosonde data taken at the Los Angeles International Airport showed the mixing height to be approximately 2000 ft (AGL).

Shown in Figure 3 are the intensities of the total ultraviolet light (2900–3900 Å) which were incident on a horizontal plane at ground level for the six different observation points in the Los Angeles Basin for November 5, 1973; the locations of these stations are marked by darkened circles in Figure 1. Five were located at ground level in the Los Angeles Basin and one at the 5640-ft elevation on Mt. Disappointment. The blackened square near Glendale in Figure 1 was the location of the radar tracking equipment. The trends of the ultraviolet intensity with time observed at the downtown Los Angeles and the El Monte stations are probably the most representative of the actual ultraviolet light distribution which would have been encountered at ground level along the trajectory of the air parcel followed in Oper-

ation #33 (Figure 1). Obviously an apparent attenuation of the ultraviolet component of the sunlight occurred during this period.

Chemical Considerations of the Nitric Oxide–Nitrogen Dioxide–Ozone Data

One aspect of the chemistry of the urban atmosphere, which would appear to be well accepted on the basis of much laboratory work and on theoretical grounds, is the ozone formation mechanism. An effort was made by the author to test current ideas in this area with this extensive new set of atmospheric data. Present knowledge of the smog systems points to only three reactions, Reactions 1–3, as the major ones which control the relationship between the ozone–NO–NO₂ in the usual NO_x-polluted, sunlight-irradiated atmosphere (1–6). The rate of Reactions 4–6 are relatively less important, though not negligible, for the reactant concentrations encountered in the lower atmosphere.



Thus the approximate instantaneous rate of ozone generation in the absence of atmospheric turbulence, heterogene-

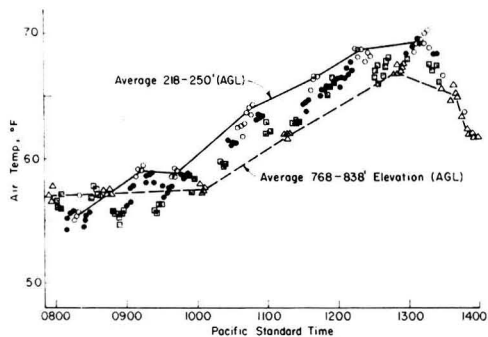


Figure 2. Variation of air temperature (°F) with time along flight path of Smog #2 and Smog #3 during operation #33 of LARPP. Symbols designate different elevation regions monitored (AGL). Triangles, 768–838 ft; squares, 600–664 ft; darkened circles, 420–437 ft; open circles, 218–230 ft.

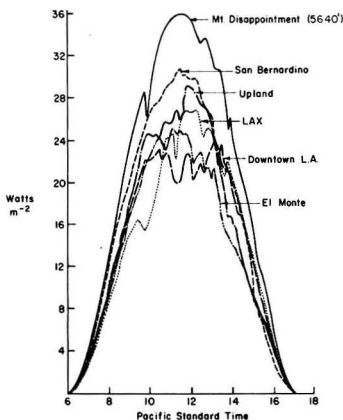


Figure 3. Time dependence of ultraviolet intensities (2900–3900 Å) incident on a horizontal plane as received at six monitoring sites on November 5, 1973

Table I. Estimates of Approximate Instantaneous Magnitude of Ozone Reaction Rate Terms of Relation I for Reactant Conditions and Solar Intensities of LARPP Operation #33^a

Time, PST	(1) $\frac{d[O_3]}{dt}$	(2) $[NO_2]k_1 - [O_3]$	(3) $\{[NO]k_3 + [NO_2]k_4 + [RH]k_5 + k_6\}$	(4) $\{[NO]k_3 + [NO_2]k_4 + [RH]k_5 + k_6\}$
1000	0.0005	0.100	1.82	0.044
1200	0.0005	0.0830	0.85	0.039
1400	0.0005	0.0410	0.29	0.032

^a Rates are in units of ppm min⁻¹.

ity, and dilution of the polluted layer, should be given by Equation I:

$$\frac{d[O_3]}{dt} = [NO_2]k_1 - [O_3] \{ [NO]k_3 + [NO_2]k_4 + [RH]k_5 + k_6 \} \quad (I)$$

If it is assumed that ozone is at its steady state concentration, $d[O_3]/dt = 0$, and that ozone is destroyed largely in Reaction 3, that is, $k_3[NO] \gg k_4[NO_2] + k_5[RH] + k_6$, then the approximate useful Equation II results:

$$\frac{[O_3][NO]}{[NO_2]} \approx \frac{k_1}{k_3} \quad (II)$$

The magnitude of the error introduced through the assumptions made in deriving Equation II can be seen in Table I for the conditions of reactant concentrations and solar intensity typical of those present during specific time periods of Operation #33. It can be seen from these data that the assumption that $d[O_3]/dt = 0$ used in deriving Equation II introduces at most about 1% error for these conditions. The neglect of the rates of Reactions 4-6 compared to that of Reaction 3 is the source of somewhat greater error: 2.4% at 1000, 4.6% at 1200, and about 11% at 1400 hours for the conditions of Operation #33. Although this error could not be tolerated for some applications, the precision of Equation II will be adequate here to provide a test of the simple mechanism of ozone formation using the data of Operation #33.

The analytical data for Operation #33 for [NO], [NO₂], and [O₃] as a function of time and elevation are summarized in Figure 4. These are averages of the analyses made during each leg of the rectangular, constant elevation helicopter flights which were made about the tetraon position during a given time period. In the early morning (0755) the ozone level of about 0.05 ppm is present at the higher altitudes; this may be from pollutant hangover from the previous day's accumulation. There is a general decline in O₃, probably as a result of Reaction 3 largely, as the early morning massive insertion of NO occurs with the rise in the traffic. A series of chemical reactions (involving HO₂, RO₂, etc.) cause conversion of the NO to NO₂, and the [NO]/[NO₂] ratio decreases regularly as the day progresses (Figure 5). In qualitative accord with Equation II, the [O₃] rises steadily as this occurs (Figure 4). Note that a given time period in the early morning hours the [NO], [NO₂], and [O₃] vary rather widely with the elevation of the sample taken. The concentrations of the gases are rather insensitive to elevation at any given time after the 1000 hour; mixing of the reactants in the polluted layer is obviously effective from 200-800 ft by this time.

We may attempt a quantitative test of present theory using these data and the theoretical relationship between

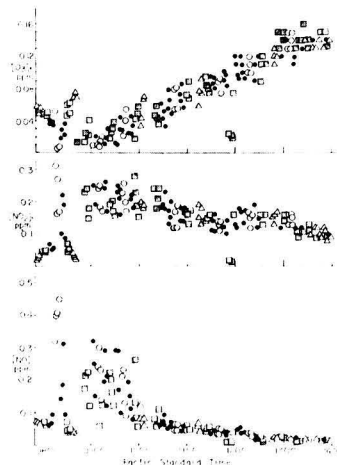


Figure 4. Time dependence of concentrations of NO, NO₂, and O₃ as monitored in LARPP operation #33
Symbols as in Figure 2

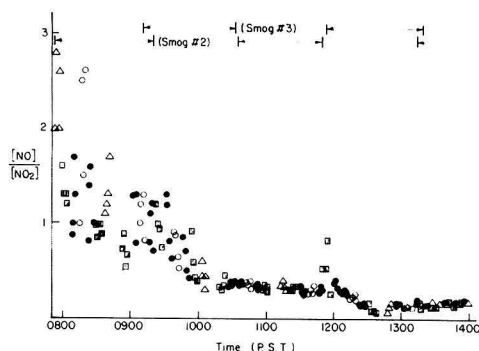


Figure 5. [NO]/[NO₂] ratio as a function of time in LARPP operation #33
Symbols as in Figure 2

[O₃], [NO], and [NO₂] given by Equation II. The theoretical values of k_1/k_3 may be derived for the conditions present in Los Angeles on November 5, 1973, and a test made of the fit of the present data to the Equation II. Two different models of different sophistication will be employed. In the first and simpler of the models, we will assume there is no attenuation of the ultraviolet component of the sunlight as it enters the atmosphere. In view of the apparent attenuation of the uv light experimentally observed by the detectors at ground level, a reasonable rationale for such a seemingly inappropriate assumption should exist. In principle, the apparent attenuation may have resulted from the preferential sensitivity of the detector to the direct component of the solar uv light. The instrumental attenuation of the higher incidence angle, scattered light component of the total radiation may have occurred inadvertently as a result of the instrument receiver design. If a nonlight absorbing aerosol was the source of the increased scatter throughout the day, then an apparent attenuation of the direct component of the sunlight would be observed while the total radiation including both the scattered and the direct light should be little changed. In this regard note the data presented in Table II. Here we have estimated the intensity of the ultraviolet in the sunlight (2900-3900 Å, the approxi-

Table II. Theoretical Effect of Increased Scatter by Nonlight Absorbing Aerosol for Simulation of LARRP Operation #33, 1200, November 5, 1973, Los Angeles, Calif.^a

	Case I (<i>b</i> = 0.042)	Case II (<i>b</i> = 0.0105)	I/II
<i>I_d</i>	2.70 × 10 ¹⁵	3.76 × 10 ¹⁵	0.72
<i>I_s</i>	3.85 × 10 ¹⁵	2.95 × 10 ¹⁵	1.31
<i>I_d</i> + <i>I_s</i>	6.55 × 10 ¹⁵	6.71 × 10 ¹⁵	0.98

^a Form of particulate scatter transmissivity term (*T_{pλ}*) was log₁₀ *T_{pλ}* = -*bλ*^{-1.5}; *b* values were used as indicated above for Cases I and II.

mate range of sensitivity of the detector) for the direct component (*I_d*), the scattered component (*I_s*), and the total uv light (*I_d* + *I_s*), received on a horizontal surface for the conditions present at 1200 (*z* = 50°) on November 5, 1973 in Los Angeles.

Two different loadings of a nonlight absorbing aerosol were chosen which differ by a factor of four. Note that although we expect in theory an attenuation of the direct component of the uv light by a factor of 0.72 in the case of aerosol increase, the theory also predicts that very little attenuation of the total direct plus scattered light will result; (*I_d* + *I_s*)_I / (*I_d* + *I_s*)_{II} = 0.98. Although this "apparent attenuation" hypothesis is possible in theory, our later considerations will show that it is probably not accurate for the present system. However the errors introduced by the neglect of attenuation of the uv light are probably about equal in magnitude but opposite in sign to those that result from the neglect of surface reflections in this model. Thus, the fortuitous partial cancellation of the two major errors in this simplified model is expected.

In our second model which we will consider, a more quantitative attenuation theory is adopted, and the results should be more realistic. However this greater sophistication leads to much greater complication in the calculations so that application of Model II will be limited to special cases where the need for greater accuracy outweighs the additional computational time required.

Model I of Ozone Mechanism

The theoretical value of *k*₁ may be estimated following a procedure similar to that employed by Leighton (1). In theory, *k*₁ is a time-dependent function determined by the position of the sun, the atmospheric conditions, and the absorptive and photodissociative properties of NO₂. For a given set of atmospheric conditions, *k*₁ should be given approximately by Equation III:

$$k_1 = 2.303 \int_{\lambda_1}^{\lambda_2} J_\lambda \alpha_\lambda \phi_{1\lambda} (1 + a_\lambda) d\lambda \quad (III)$$

α_λ is the absorption coefficient of NO₂ at λ ; $\phi_{1\lambda}$ is the quantum yield of O(³P) atom formation from NO₂ photolysis at λ ; *a_λ* is the albedo, the fraction of the incident light of wavelength λ reflected from the earth's surface under the point of the observation. *J_λ* is a time-dependent function related to the solar irradiance. Leighton (1) considered it to be approximately equal to the solar irradiance (photons cm⁻² sec⁻¹ per wavelength interval about λ) which would be measured by a weakly absorbing chemical actinometer with a flat horizontal surface exposed to the sun and sky when placed at the desired observation point within the atmosphere. The integrand of Equation III contributes significantly to the value of *k*₁ only within the wavelength

range 2900–4300 Å. In practice, the evaluation of *k*₁ is accomplished using a summation of products of $\overline{J_\lambda \alpha_\lambda \phi_{1\lambda}}$ obtained from averages of the *J*, α , and ϕ_1 values over some wavelength interval such as 100 Å.

If no significant attenuation of the sunlight occurs within the relatively small polluted layer of the lower atmosphere, then *J_λ* can be calculated by the approximate Equation IV (1):

$$J_\lambda = I_{0\lambda} T_{a\lambda} [T_{m\lambda} T_{p\lambda} + \cos Z (1 - T_{m\lambda} T_{p\lambda})] \quad (IV)$$

Here *I_{0λ}* is the intensity of the sunlight (*q* cm⁻² sec⁻¹) within the small band of wavelengths centered at λ which is incident on a surface perpendicular to the direction of the sun's rays outside the earth's atmosphere. *T_{aλ}*, *T_{mλ}*, and *T_{pλ}* are attenuation factors which result from light absorption by atmospheric ozone (*T_{aλ}*) and light scatter from molecules (*T_{mλ}*) and suspended particulate matter (*T_{pλ}*) in the atmosphere. *Z* is the solar zenith angle. Values of *I_{0λ}* are available from several studies for the wavelength range of interest here (2900–4300 Å); however, the data from the different sources are not in complete accord; the early re-

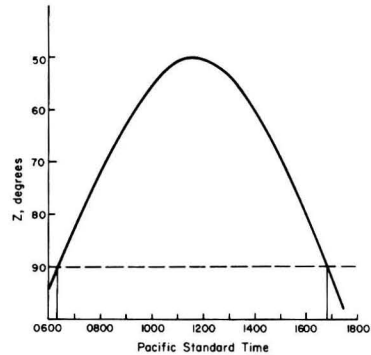


Figure 6. Theoretical variation of solar zenith angle (*Z*) in Los Angeles with hour of the day calculated for November 5, 1973, operation #33

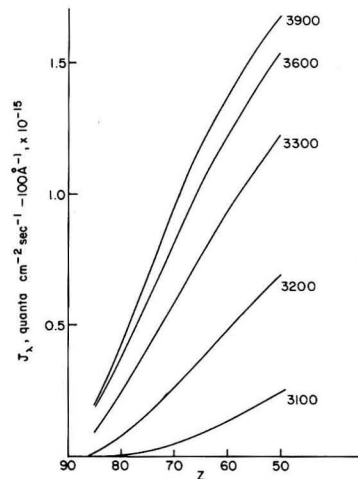


Figure 7. Theoretical variation of solar irradiance within atmosphere of Los Angeles for November 5, 1973, for various solar zenith angles and band centers. No attenuation of the radiation within the polluted layer has been assumed here

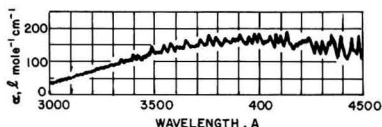


Figure 8. Variation of molar absorption coefficient of NO_2 with wavelength
Data from reference 13

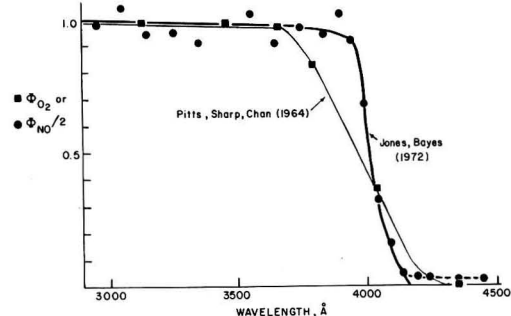


Figure 9. Variation of quantum yield of $\text{O}(^2\text{P})$ formation in NO_2 photolysis as function of wavelength
Data are from Pitts et al. (14) and Jones and Bayes (15)

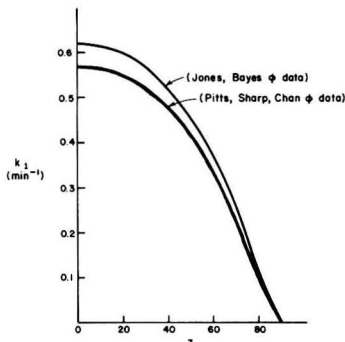


Figure 10. Theoretical magnitude of rate constant k_1 for formation of $\text{O}(^2\text{P})$ atoms through NO_2 photolysis at different solar zenith angles as estimated for atmosphere of Los Angeles. Values are calculated for the conditions of no attenuation of the ultraviolet within the polluted layer and no reflection from the surface of Los Angeles

sults of Johnson (7) and the recent work of Ackerman (8) give values about 10% higher than those recommended by Arvesen et al. (9) and Thekaekara (10). We have used here the higher estimates for $J_{O\lambda}$ which will lead to maximum values of k_1 in theory. The attenuation resulting from ozone absorption in the upper atmosphere, molecular scatter, and particulate scatter were estimated using standard relations (1) adjusted to the conditions that approximate those for Operation #33. For the latitude of Los Angeles ($34^\circ 3'$) on November 5, 1973, the equivalent column of uv filtering O_3 overhead was taken as 2.8 mm (STP) following the estimates of Dutsch (11).

The solar zenith angle, Z , was estimated using standard relations and data of the Nautical Almanac (12) for November 5, 1973. The estimated time dependence of Z for this date in Los Angeles is shown in Figure 6. Some idea of the wavelength and Z dependence of the $J_{O\lambda}$ values can be had from Figure 7, estimated for conditions of Operation #33, but outside of the polluted layer. The wavelength dependence of the absorption coefficient for NO_2 (α_λ) was taken from data determined by Hall and Blacet (13) and summarized by Leighton (1) (Figure 8). The wavelength dependence of $\phi_{1\lambda}$, as determined by two sets of workers (14, 15), is summarized in Figure 9. In this model we will assume the albedo $a_\lambda = 0$ at the outset and then introduce an empirical but appropriate number consistent with the match of theory and experiment later. The results of the calculation of k_1 are given in Figure 10 for both sets of ϕ_1 data. The more extensive data for the 3800–4300 Å wavelength dependence of $\phi_{1\lambda}$ presented by Jones and Bayes (15) seems to establish this set as the most reliable data for the region of divergence of the two data sets. Thus the higher curve is considered the most reliable estimate of k_1 .

To test the fit of the $[\text{NO}][\text{O}_3]/[\text{NO}_2]$ experimental data to the theory, we require the ratio of k_1/k_3 . The value of k_3 was estimated for each time period by the experimental temperature-dependent function for k_3 estimated by Clyne, Thrush, and Wayne (16):

$$\log_{10} k_3 (\text{l. mol}^{-1} \text{sec}^{-1}) = 8.78 - 2460 / (2.303)(1.987)(T^\circ \text{K})$$

The k_3 was calculated for the specific temperatures of the air as measured at the places and times of the NO_2 - O_3 measurements (Figure 2). Then the ratio of k_1/k_3 was calculated as a function of time for the particular conditions of Operation #33 (Figure 11). Here the k_1/k_3 data are shown also as estimated using k_3 values for 25°C . It is evident that one should use the actual values of k_3 at the true temperatures of the measurements or a significant error (about 10% in this case) will be introduced.

Experimental values of the function $[\text{O}_3][\text{NO}]/[\text{NO}_2]$ were calculated for each individual 6–7-s record of the instrument readings provided on the second level archive computer readouts for Operation #33. Then the averages and the standard deviations of the $[\text{O}_3][\text{NO}]/[\text{NO}_2]$ function were calculated for each leg of the constant elevation helicopter flights. The experimental results are compared with our theoretical estimated ratios for Model I in Figure 12. Error bars drawn vertically through each point represent one standard deviation from the average $[\text{O}_3][\text{NO}]/[\text{NO}_2]$ experimental function for each leg. In general, fair agreement between the simple theoretical Model I and experiment is seen for data after about the 0920 hour. However, extremely large positive deviations of the averages from theory occur for data collected in flights before 0920. A similar effect has been observed previously by Eschenroeder et al. (17) in air samples of low average ozone content (and presumably high NO) collected at ground level. They considered several possible sources of the apparent deviation from simple theory, although they were not able to choose between the alternatives.

It is not clear from the results of this single run whether the apparent deviation seen here is really an artifact resulting from errors inherent in the measurement of small O_3 and NO_2 levels. Electrical interference may account for part of the problem; note that helicopter Smog #3 data give ratios well above the theoretical curve for analyses at the start of its run at about 1200 on this day (Figure 12). However, normal values in reasonable accord with theory were recorded at this time by the departing aircraft, Smog #2, flying under similar conditions. Although some rf-interference with the analytical instrumentation was noted to occur during radio communication aboard the aircraft, it is highly unlikely that the entire effect has this origin. It seems probable to this author that the early morning divergence between $[\text{O}_3][\text{NO}]/[\text{NO}_2]$ ratios and theoretical k_1/k_3 values arises in large part from the heterogeneity of the air

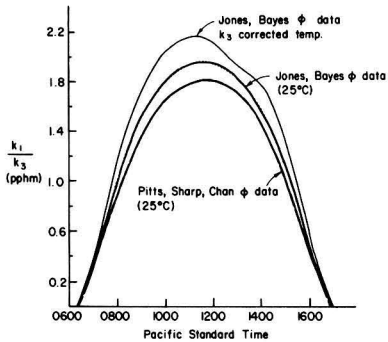


Figure 11. Theoretical rate constant ratio k_1/k_3 vs. time as estimated for atmosphere of Los Angeles

Top curve is considered to be the most reliable estimate. Comparison with the lower curves indicates the magnitude of the error expected for the use of different ϕ_1 data and the 25°C value for k_3

at this time period. In the early morning hours, pockets of NO-rich air that originate from the surface layer and pockets of O₃-rich air that come from the old air at the higher elevations mix turbulently to produce the relatively homogeneous air mass of the later hours. The O₃ will be at very low concentrations in the NO-rich pockets while NO will be at very low concentrations in the O₃-rich pockets. If the response time of the analytical equipment for NO_x and O₃ is long compared to the average time between the arrival of O₃-rich and O₃-poor pockets of inhomogeneous early morning air at the detector, then the product of the "average" concentrations of NO and O₃ recorded by the equipment must exceed the true average of the [O₃][NO] product in the individual pockets. Thus, an artificial enhancement of the [O₃][NO]/[NO₂] ratio may occur in the measured data even though the pseudosteady-state Equation II may apply quite well both within the O₃-rich and the NO-rich pockets. Further details related to the response time of the various instruments and the physical structure of the heterogeneous air masses of the early morning are necessary before any more sophisticated and meaningful treatment of the divergent early morning data can be made.

Although the data of Figure 12 show considerable scatter, it appears that the values of the experimental function, [O₃][NO]/[NO₂], are somewhat higher than those expected from the simple theoretical model employed. Note that the data points would better fit a theoretical curve that was about 10% greater in ordinate value at each time. In a very simplistic fashion we could assume that this suggests the use of an "apparent" albedo term, $1 + a = 1.10$, in Equation III. To interpret the difference as due to a reflection correction alone is, of course, an oversimplification of the problem. There are several other factors we have not considered here which should also cause significant deviations between theory and experiment. Thus no correction was made in the present estimates for the ultraviolet attenuation that apparently occurred during the midday hours. See Figure 3. A second problem inherent in the instrumental methods employed in the NO_x determination, also should lead to a negative deviation of the function [O₃][NO]/[NO₂] from the theoretical values of k_1/k_3 . Nitrogen compounds other than NO₂ and NO are recorded during the NO_x cycle. In particular, PAN levels are detected almost quantitatively as NO_x (18). Thus the actual [NO₂] must be somewhat lower than that calculated by this author using [NO₂] = [NO_x] - [NO]. There is a further potential problem associated with the EPA analytical stan-

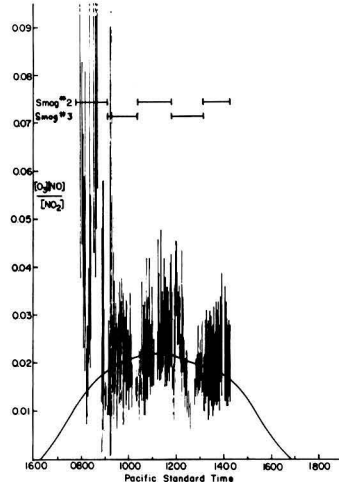


Figure 12. Plot of function $[O_3][NO]/[NO_2]$ as estimated from experimental data from operation #33

Length of vertical lines indicate range of standard deviation of average over given leg of flight. Solid curve is the theoretical function k_1/k_3 , calculated assuming no uv-attenuation within the polluted layer and no reflection from surface of Los Angeles

dard method for ozone upon which the chemiluminescence O₃ instruments were calibrated (19). In spite of the very approximate nature of the model employed here, it gives reasonably good agreement with the experimental data. It can be used to provide approximate ozone estimates by neglecting attenuation of the uv light and assuming an "apparent" albedo term, $a = 0.1$ for uv light (2900–3900 Å) at the surface of Los Angeles.

Model II of Ozone Mechanism

A more quantitative treatment of the O₃, NO, NO₂ data of Operation #33 is desirable to provide a more valid test of the theory of ozone generation. In particular, the apparent attenuation of ultraviolet light at ground level (Figure 3) should be better understood and taken into account in the treatment. First we can test the characteristics of the uv monitoring equipment using experimentally observed time dependence of the intensity of uv light (2900–3900 Å) received at Mt. Disappointment (5640-ft elevation), well above the polluted layer, with that expected for the direct (I_d) and scattered (I_s) components of the light in terms of theory. These can be calculated from the summation of the $I_{d\lambda}$ and $I_{s\lambda}$ values obtained using Equations V and VI for small wavelength intervals (100 Å) in the range 2900–3900 Å:

$$I_{d\lambda} = I_{0\lambda} T_{a\lambda} T_{m\lambda} T_{p\lambda} \cos Z \quad (V)$$

$$I_{s\lambda} = I_{0\lambda} T_{a\lambda} \cos Z (g)(1 - T_{m\lambda} T_{p\lambda}) \quad (VI)$$

Here g has been taken as 0.5 (equal forward and back scattering assumed), and the other terms are as outlined previously. The results of these calculations are shown in Figure 13 (solid curves) together with the experimental measured intensities (open circles). The quantitative agreement between the theoretical and experimentally measured intensities of total radiation and the shape of the time variation of the energy received suggests that the measuring instrument was indeed monitoring quite well both the scattered and the direct components of the sunlight. The only significant deviations between the theoretical curve and the experimental points occur for times near sunset and

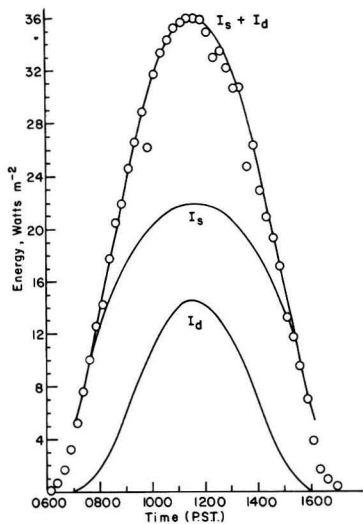


Figure 13. Comparison of theoretical ultraviolet energy (2900–3900 Å) for direct (I_d) and scattered (I_s) light components received on a horizontal surface within the atmosphere as function of time for Los Angeles (above polluted layer) on November 5, 1973. Open circles are experimental data collected on Mt. Disappointment (5640 ft) for this day.

sunrise when the approximations in the theory applied are accentuated, the incident angles of much of the radiation are large, and quantitative light collection by any measuring instrument is difficult. We must conclude that the measuring instrument does a reasonably good job of monitoring both the scattered and direct uv radiation. The apparent attenuation of the light observed in the data of Figure 3 must be a real effect and not an artifact of the instrumentation. It must result in large part from light absorption within the polluted layer.

We should consider the nature of the light absorber so that a theoretically sound model for the attenuation may be developed. Uv light attenuation in Los Angeles has been attributed to particulate matter in the atmosphere in some previous studies (1, 20). However, the extensive three dimensional view of the distribution of pollutants provided by the present LARPP data makes evident another strong candidate, nitrogen dioxide, for a major source of the observed attenuation in this case at least. There is a relatively large concentration of NO_2 present during much of the day, and the depth of the polluted layer is great. As a first attempt to rationalize the attenuation we may assume that it is due entirely to absorption by NO_2 within the polluted layer. With this model the intensity of the direct radiation transmitted through the polluted layer to the ground level ($I_{dt\lambda}$) and that of the scattered radiation transmitted to ground level ($I_{st\lambda}$) should be given approximately by Equations VII and VIII:

$$I_{dt\lambda} = I_{d\lambda} 10^{-\alpha c l \sec Z} \quad (\text{VII})$$

$$I_{st\lambda} = I_{s\lambda} 10^{-\alpha c l} \quad (\text{VIII})$$

Here l is the average depth of the polluted layer in which there is an average concentration of $\text{NO}_2 = c$; α is the extinction coefficient for NO_2 at λ ; il , the average path length of the scattered radiation within the polluted layer of depth l , may be taken as $2l$ following the approximate theoretical treatment of this problem as outlined by Leighton (1). The total uv light (2900–3900 Å) received at ground

level then may be estimated from the summation in Equation IX of the intensities over the incremental values estimated from Equations VII and VIII:

$$I_{dt} + I_{st} = \Sigma(I_{dt\lambda} + I_{st\lambda}) \quad (\text{IX})$$

We have carried out such calculations assuming various values for the product of impurity concentration times path length (cl) in Equations VII and VIII. The results of two such calculations for choices of $cl = 5.3 \times 10^{-4}$ and $7.5 \times 10^{-4} \text{ mol}\cdot\text{l}^{-1}\cdot\text{cm}$, are shown in Figure 14 (solid lines) together with the experimentally measured intensities of uv light at the downtown Los Angeles and the El Monte stations, the two which should be most representative of that received within the air mass followed in Operation #33. The data are described reasonably well by this model. It is important to note as well that the size of the cl product which fits the data well is realistic in terms of the actual measurements of Operation #33. About 0.20 ppm ($8 \times 10^{-9} \text{ mol/l}$) of NO_2 is present near midday. A depth of polluted layer of about 660 m at this concentration would account entirely for the observed attenuation at midday. This depth is the correct order of magnitude for the conditions of Operation #33; a mixing depth of about 600 m was observed at LAX in the 1130-hour radiosonde measurement. Flights were commonly made at elevations of 800 ft and below; those few flight patterns made at about 1400 hour showed fairly uniform mixing of the NO_2 impurity from ground level to the maximum height flown, 1522 ft (464 m) above ground level. Although it is unlikely that NO_2 is the only impurity which causes the uv attenuation here, it is probable that it accounts for a large share of it. Thus the assumed form of the attenuation law employed will at least form a good empirical basis for us to correct the solar irradiation for attenuation at various observation times and elevations within the polluted layer. Unfortunately uv measurements were made only at ground level, so that the necessary correction of the data to the observation points above the earth is somewhat tedious and involved.

After the 0900 hour there was a reasonably good mixing

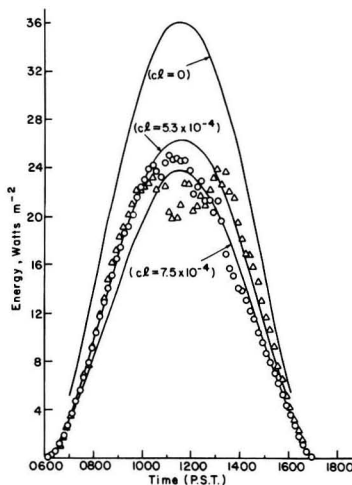


Figure 14. Comparison of theoretical ultraviolet energy (2900–3900 Å) from light received on a horizontal surface within the atmosphere as function of time for Los Angeles on November 5, 1973, and for different assumed attenuations due to NO_2 absorption. Open circles and triangles represent the experimental values measured at ground level at El Monte and downtown Los Angeles stations, respectively.

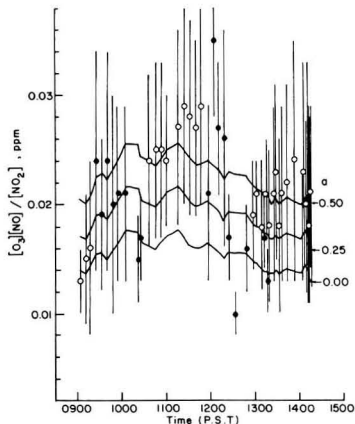


Figure 15. Plot of function $[O_3][NO]/[NO_2]$ as estimated from experimental data from operation #33

Open circles and darkened circles are data from Smog #2 and Smog #3, respectively; lengths of vertical lines indicate range of standard deviation of average over the four legs of the given constant elevation run; the solid curves give the theoretically expected values of k_1/k_3 for three different assumed values of the surface albedo, $a = 0, 0.25, \text{ and } 0.50$. Theoretical model in this case includes attenuation of ultraviolet within the polluted layer

of the NO_2 within the polluted layer sampled, so that we may estimate accurately the product of $[NO_2]$ times the elevation of the observation point above ground level for each run of the aircraft flights at each elevation. A series of calculations was made in which $I_{dt} + I_{st}$ was estimated for various Z angles and cl products, assuming the form of the attenuation given by Equations VII and VIII; these were used to prepare a family of curves relating the three variables. Then from the difference between the total cl product which accounted for the observed attenuation at ground level and the ch product of the measured concentration of NO_2 and the height, h , of the given observation above ground, an effective attenuation for the actual height of each experimental run was estimated. In this case the average of the four legs of a flight at a given elevation was used to minimize the calculation time.

One additional feature must be included in this more complete model. An account must be taken of the light reflected from the earth's surface to the air parcel under study. Unfortunately there are not experimental data related directly to the Los Angeles albedo in the ultraviolet along the Operation #33 track which we can draw on now. Thus we have assumed various average albedos (a) for the ultraviolet reflection from the surface of Los Angeles to achieve a match between experiment and theory. We have corrected for the attenuation of this reflected light in transmission from the earth's surface to the particular elevation where product analysis was made at each time period. It has been assumed that the reflected ray will be about twice the vertical distance, h , of the observation point above the surface, the expected theoretical value for scattered light. The reflected ray intensity (I_r) was calculated from the summation of $I_{r\lambda}$ values estimated for the 2900–3900 Å region using Equation IX:

$$I_{r\lambda} = (I_{d\lambda} + I_{st\lambda})(a)(10^{-\alpha_{sc}2h}) \quad (IX)$$

Now the total of the $I_{dt} + I_{st} + I_r$ was obtained for each observation series and used together with k_1 estimates of Figure 10 to estimate "true" k_1' values, corrected for impurity

attenuation and surface reflection of the ultraviolet component of the sunlight using Equation X:

$$k_1' = k_1(I_{dt} + I_{st} + I_r)/(I_d + I_s) \quad (X)$$

I_d and I_s represent the intensities of the sunlight as calculated from Equations VII and VIII and which correspond to that received within the atmosphere but just outside the polluted layer (such as Mt. Disappointment).

The values of k_3 were calculated as before for the particular temperature which represented the average over the four legs of a given constant elevation flight, and the ratios of k_1'/k_3 were determined. The final results of these calculations are summarized in Figure 15 for three different choices of albedo for the Los Angeles surface under the air path followed in Operation #33, $a = 0, 0.25, \text{ and } 0.50$. The fine structure seen in the theoretical curves is a result of the regular change in attenuation expected as elevation was changed. It appears that a choice of a equal to approximately 0.25 does lead to theoretical estimates consistent with the experimental data. Further tests of the theoretical models of ozone production must await the determination of experimental values of the albedo for the appropriate surface of Los Angeles. However, it is clear that the magnitude of the albedo assumed here is in general accord with the ratio of the outgoing to incoming radiation in the 3000–3800 Å range measured in Los Angeles on a smogless day, October 16, 1965 (21).

Although there are obvious problems in fitting the LARPP Operation #33 $[O_3]$, $[NO]$, and $[NO_2]$ results to theory, the treatment presented here shows clearly that the essential features of ozone formation mechanism are correct, and useful predictive modeling of O_3 levels seems to be possible with a knowledge of only the $[NO]/[NO_2]$ ratios, the solar irradiance in the NO_2 absorption region, and reasonable estimates of the surface albedo for ultraviolet light. Present information and theory are not adequate to explain the results of the early morning observations, and suitable methods such as that of Hilst (22) must be developed further so that proper account can be made of the inhomogeneous interactions of parcels of O_3 -rich and NO-rich air.

Acknowledgment

The author is grateful to the Coordinating Research Council and its LARPP Project Committee for access to the data of Operation #33 prior to archiving, and to Drs. K. L. Demerjian (EPA), J. Peterson (NOAA), and P. Monson (General Motors Corp.), for making available to him other useful data related to the project. He also thanks his son, R. J. Calvert, for his help with many of the detailed calculations.

Literature Cited

- Leighton, P. A., "Photochemistry of Air Pollution", Academic Press, New York, N.Y., 1961.
- Demerjian, K. L. Kerr, J. A., Calvert, J. G., Chap. 1 in *Adv. Environ. Sci. Technol.*, 4, 1 (1974).
- Niki, H., Daby, E. E., Weinstock, B., Chap. 2 in "Photochemical Smog and Ozone Reactions", *Adv. Chem. Series 113*, p 16, American Chemical Society, Washington, D.C., 1972.
- Stedman, D. H., Niki, H., *Environ. Sci. Technol.*, 7, 735 (1973).
- Westberg, K., Cohen, N., Wilson, K. W., *Science*, 171, 1013 (1971).
- (a) Stedman, D. H., Jackson, J. O., *Int. J. Chem. Kinet., Symp No. 1*, 493 (1975); (b) Calvert, J. G., McQuigg, R. D. *ibid.*, p 113.
- Johnson, F. S., *J. Meteorol.*, 11, 431 (1954).
- Ackerman, M., *Inst. Aeron. Spatials Belg. Brussels, A-77*, 149 (1970); data also available in the CIAP documents.
- Arvesen, J. C., Griffin, R. N., Jr., Pearson, B. D., Jr., *App. Optics*, 8, 2215 (1969).
- Thekaekara, M. P., *J. Environ. Sci.*, 6 (Sept.–Oct. 1970).

- (11) Dütsch, H. U., *Adv. Geophys.*, **15**, 219 (1971).
- (12) Nautical Almanac for the Year 1973, U.S. Government Printing Office, Washington, D.C., 1971.
- (13) Hall, T. C., Jr., Blacet, F. E., *J. Chem. Phys.*, **20**, 1745 (1952).
- (14) Pitts, J. N., Jr., Sharp, J. H., Chan, S. I., *ibid.*, **39**, 238 (1964).
- (15) Jones, I. T. N., Bayes, K. D., *Chem. Phys. Lett.* **11**, 163 (1971); paper at Informal Conference on Photochemistry, Oklahoma State University, Stillwater, Okla., May 1972.
- (16) Clyne, M. A. A., Thrush, B. A., Wayne, R. P., *Trans. Faraday Soc.*, **60**, 359 (1964).
- (17) Eschenroeder, A. Q., Martinez, J. R., Nordsieck, R. A., "Evaluation of a Diffusion Model for Photochemical Smog Simulation", Final Report of General Research Corp., Santa Barbara, Calif., to EPA Contract No. 68-02-0336, October 1972.
- (18) Winer, A. M., Peters, J. W., Smith, J. P., Pitts, J. N., Jr., *Environ. Sci. Technol.*, **8**, 118 (1974).
- (19) Joints tests conducted by the California Air Resources Board (ARB), the Environmental Protection Agency (EPA), and the Los Angeles Air Pollution Control District (W. B. DeMore, Calif. Air Res. Board Bull., December 1974), indicate that the EPA and ARB oxidant calibration procedures, which employ buffered KI solutions, give ozone readings considerably higher than either photometric or gas phase titration values. Other factors, such as humidity, seem to influence the magnitude of the discrepancy (J. N. Pitts, Jr., private communication to the author). In view of the present continued confusion on the appropriate correction, no definitive conclusion as to the possible error can be drawn at this time.
- (20) Stair, R., *Proc. Natl. Air Pollut. Symp., 3rd Symp.*, p 48, Pasadena, Calif., 1955.
- (21) Altshuller, A. P., Bufalini, J. J., *Environ. Sci. Technol.*, **5**, 39 (1971).
- (22) Hilst, G., "A Coupled Two Dimensional Diffusion and Chemistry Model for Turbulent and Inhomogeneously Mixed Reaction Systems", Report from Aeronautical Research Associates of Princeton, Inc., Princeton, N.J., 1973, Contract R4-73-016C to the Office of Research and Monitoring, U.S. EPA.

Received for review May 6, 1975. Accepted October 2, 1975.

Hydrocarbon Involvement in Photochemical Smog Formation in Los Angeles Atmosphere

Jack G. Calvert

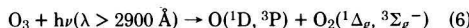
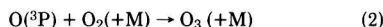
Department of Chemistry, The Ohio State University, Columbus, Ohio 43210

■ The extensive chemical and physical measurements of the Los Angeles Reactive Pollutant Program (LARPP), made during one day of the studies, November 5, 1973, are analyzed to test current theories of hydrocarbon involvement in photochemical smog formation. It is noted that the ratio of the concentration of a reactive hydrocarbon to that for acetylene decreases regularly throughout the day. Indirect estimates are made of the average ambient concentration of the HO-radical from the observed rates of removal of the hydrocarbons, C_2H_4 , C_3H_6 , $1-C_4H_8$, *iso*- C_4H_8 , *t*- $2-C_4H_8$, *n*- C_5H_{12} , and *iso*- C_5H_{12} , and estimated rates of O_3 -alkene and $O(^3P)$ -alkene reactions. Similar estimates are made using the change in $[NO_x]/[CH_4]$ and $[NO_x]/[C_2H_2]$ ratios with time. All of these results suggest that the average ambient level of HO-radical in the morning hours of November 5, 1973, in Los Angeles was in the range $(1.0 \pm 0.8) \times 10^{-7}$ ppm. Considerations of pollutant concentrations and rates show that realistic models of photochemical smog formation must involve all classes of hydrocarbons, as well as CO and the aldehydes, as important reactants.

Recently extensive new chemical and physical data of interest to the atmospheric scientists has become available through the LARPP study of the Los Angeles atmosphere. This study was designed to measure the chemical changes occurring in well-defined parcels of polluted air as they moved about the Los Angeles Basin under the influence of the prevailing winds. The concentrations of several pollutants (NO , NO_x , O_3 , CO , hydrocarbons) were measured as a function of time within the designated air parcel at selected elevations by instrumented aircraft (Smog #2 and Smog #3) and at ground level by mobile vans positioned under the air mass. In a previous publication we have employed the analytical data from a selected single day's operation #33 of November 5, 1973, to test the current theory of ozone generation in the lower atmosphere (1). In the present paper, a study of the extent and the nature of the

hydrocarbon involvement in smog formation is made employing the analytical data collected in the same operation. Reference to the earlier paper will provide the reader with supplementary information not included here on NO , NO_2 , and O_3 concentration trends, physical data related to the path of the air mass studied, and solar ultraviolet light intensities monitored during the day of this operation.

In the previous study (1) it was observed that the $[O_3]$ is controlled largely by the simple sequence of Reactions 1-6:



For the atmospheric conditions and the pollutant concentrations encountered in this particular study, between 0930 and 1430 and at elevations of 200-800 ft (AGL), the reactions 1, 2, and 3 dominate, and to a first approximation the $[O_3]$ is determined largely by the ratio of $[NO_2]/[NO]$ and the solar irradiance as indicated in the Relationship I:

$$[O_3] \approx \frac{[NO_2]k_1}{[NO]k_3} \quad (I)$$

However the fraction of the total NO and NO_2 (NO_x), which is present as NO_2 , increases dramatically as the day progresses; for the conditions of this LARPP operation, the result is seen in the data of Figure 1. Obviously the chemical conversion of NO to NO_2 that these data reflect is not the result of the reactions 1-6; their occurrence alone would result only in a depletion of the initial $[NO_2]$ and a slight increase in $[NO]$ as O_3 was formed. Smog chamber studies, laboratory experiments, and atmospheric studies have shown that the hydrocarbons, carbon monoxide, aldehydes,

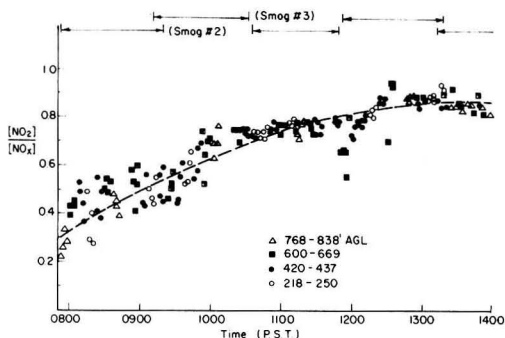
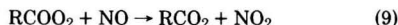


Figure 1. Plot of the $[NO_2]/[NO_x]$ ratio vs. time for data collected at several elevations in the LARPP Operation #33; the operation cycles of the sampling helicopters, Smog #2 and Smog #3, are shown at the top of the Figure

and other oxidation products of the hydrocarbons, are important participants in the reactions which convert NO to NO_2 . In particular, the hydroperoxy (HO_2), alkylperoxy (RO_2), and acylperoxy ($RCOO_2$) radicals derived from the reactions of these compounds are thought to be the important reactants which effect this change (2).



We may treat the present rather extensive hydrocarbon, CO, NO, and NO_x concentration-time data of this LARPP operation to test theories of the hydrocarbon involvement in these atmospheric reactions and to provide a more extensive scientific base needed in the development of more realistic atmospheric models of photochemical smog formation.

Results and Discussion

Considerations of the Reactivity and Rates of Chemical Transformation of the Hydrocarbons. The concentrations of the reactive hydrocarbons in a polluted atmosphere change with time, not only because of the chemical reactions which they undergo, but because of the turbulent diffusion, mixing, and dilution which occur in the atmosphere. One may isolate somewhat effectively the effects of reaction and diffusion/dilution by using the concentration of some relatively inert compound as a normalizing factor (3-5). It appears to the author that acetylene is the best such tracer gas to employ here in an attempt to separate these factors, since it appears to have the same pollution source as the olefinic hydrocarbons, namely the automobile, and its reactivity toward the common reactive species of smog [O_3 , $O(^3P)$, HO] is very low compared to that of the alkenes.

Thus the ratio of the rate constants for O_3 attack on C_2H_2 compared to that for C_3H_6 is 0.0049 at 298 °K (6, 7) that for the $O(^3P)$ reactions with C_2H_2 and C_3H_6 is 0.049 (8-11), while that for the HO reactions with C_2H_2 and C_3H_6 is 0.0011 (12-14). The other simple alkenes show similar enhanced reactivities compared to acetylene; with C_2H_4 the difference is somewhat less than that with C_3H_6 , while with 1- C_4H_8 , *iso*- C_4H_8 , and *t*- C_4H_8 , the difference is greater. Thus the acetylene does constitute a good tracer gas for our purposes. The hydrocarbon analyses of the bag samples collected in this operation have been used to derive the time variation of the ratios (concentrations in

pphm carbon) of $[C_2H_4]/[C_2H_2]$, $[C_3H_6]/[C_2H_2]$, $[1-C_4H_8]/[C_2H_2]$, and $([t-C_4H_8] + [iso-C_4H_8])/[C_2H_2]$ (Figures 2-5 respectively). The data collected at different elevations are noted by the characteristic symbols shown on each Figure. Observe that in each case there is a regular decrease in the ratio of reactive alkene to C_2H_2 that occurs for data collected at each altitude. This results directly from the chemistry involving the alkenes preferentially.

We can gain some useful insight into the mechanism of the alkene removal reactions and firm up some ideas important for model development using these data. We may illustrate the reasoning and calculations using the $[C_3H_6]/[C_2H_2]$ data for 420-457 ft (AGL) in Figure 3. The fractional removal rate of C_3H_6 can be shown to be about $8.3\% h^{-1}$ near the 0800 to 1000 period. (We assume for simplification

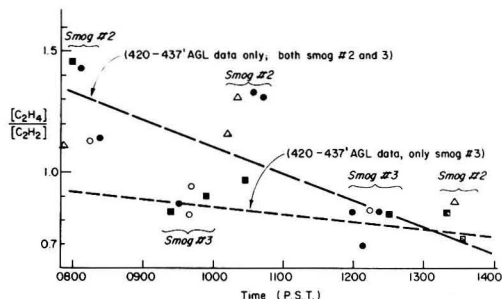


Figure 2. Plot of the ratio $[C_2H_4]/[C_2H_2]$ vs. time for the LARPP Operation #33; in this case the two sets of data from Smog #2 and Smog #3 are not consistent with one another, so the data from each helicopter was treated separately; legend for elevations is as in Figure 1

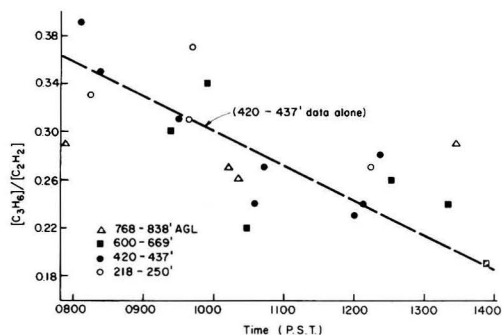


Figure 3. Plot of the ratio $[C_3H_6]/[C_2H_2]$ vs. time for the LARPP Operation #33 data

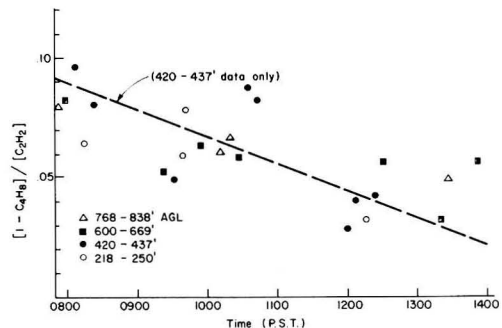


Figure 4. Plot of the ratio $[1-C_4H_8]/[C_2H_2]$ vs. time for the LARPP Operation #33 data

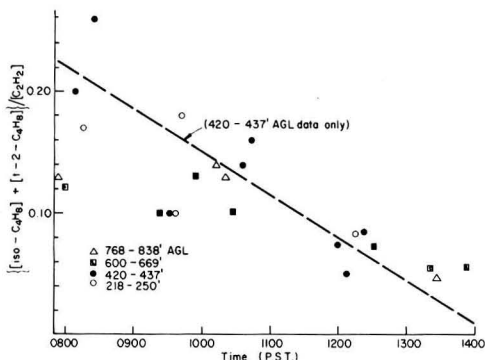
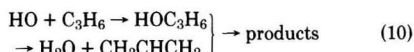


Figure 5. Plot of the ratio $([iso-C_4H_8] + t-2-C_4H_8)/[C_2H_2]$ vs. time for the LARPP Operation #33 data

in this calculation that the parcel of air we are studying does not receive a new supply of alkenes and acetylene of greatly different composition in ratios during the time period studied; that is, dilution of the reacting mixture with air of approximately equal age is assumed.) We may estimate fairly accurately from our previous considerations of the NO_2 photolysis rate (1), the analytical data of this operation, and well-established rate constants (7, 9, 10), that the fractional rate of removal of C_3H_6 by $O(^3P)$ for conditions of the Operation #33 in the 0800–1000 period is about $0.32\% h^{-1}$, while that for O_3 is $3.2\% h^{-1}$ (12–14). Thus about $4.8\% h^{-1}$ of the C_3H_6 is removed by reactants other than O_3 and $O(^3P)$. In view of the many recent experimental and theoretical considerations of the smog mechanism, it is reasonable to assign the extra removal to the action of the HO-radical (2, 15, 16) With this postulate we can estimate the necessary average $[OH]$ to cause the observed rate.



$$\frac{d[C_3H_6](100)}{dt[C_3H_6]} \approx 4.8\% h^{-1} = \frac{[HO][C_3H_6]k_{10}(6 \times 10^3)}{[C_3H_6]}$$

Table I. Summary of Estimates of the Average Hydroxyl Radical Concentrations in the Morning Hours of November 5, 1973, in Los Angeles (LARPP, Operation #33)

Impurity ratio employed	Flight elevation, ft, AGL	$[HO], \times 10^7, ppm^a$
$[1-C_4H_8]/[C_2H_2]$	420–437	0.28 ± 0.09
$[iso-C_4H_8 + t-2-C_4H_8]/[C_2H_2]$	420–437	0.21 ± 0.06
$[C_3H_6]/[C_2H_2]$	420–437	0.32 ± 0.08
$[C_2H_4]/[C_2H_2]$	420–437 (Smog #3)	1.8 ± 2.1
	420–437 (Smog #2)	1.5 ± 1.7
$[n-C_5H_{12}]/[C_2H_2]$	218–250	1.1 ± 2.5
	420–437	1.9 ± 2.2
	584–640	1.7 ± 1.8
$[iso-C_5H_{12}]/[C_2H_2]$	218–250	0.56 ± 0.47
	420–437	1.7 ± 1.2
	584–640	1.0 ± 1.2
$[NO_x]/[C_2H_2]$	218–250	0.79 ± 1.1
	420–437	1.2 ± 0.5
	584–669	0.80 ± 0.22
$[NO_x]/[CH_4]$	188–291 (Smog #3)	1.3 ± 0.3
	225–277 (Smog #2)	1.6 ± 0.2
	386–487 (Smog #3)	1.0 ± 0.4
	386–487 (Smog #2)	1.0 ± 0.3
	577–669 (Smog #3)	1.0 ± 0.3
	559–685 (Smog #2)	1.1 ± 0.2

^a The error limits shown are derived from the standard deviation of the slopes in Figures 2–8 and reflect only random errors in the data. Estimates for the reactive olefins, 1-C₄H₈, iso-C₄H₈, t-2-C₄H₈, and C₃H₆ are minimum values in view of the possible attenuation of the alkene content of bag samples during the ARB storage and analysis procedures. The estimates from the NO_x data are maximum values since other NO_x removal processes than the HO Reaction 11 may be significant.

Here $k_{10} = 2.5 \times 10^4 ppm^{-1} min^{-1}$ (13) and 6×10^3 converts min^{-1} to $\% h^{-1}$ units. Thus $[HO] = (3.2 \pm 0.08) \times 10^{-8} ppm$; the error limits are derived from the standard deviation of the slope in Figure 3 and reflect only random errors in the data.

Similar calculations have been made for the other alkenes using the data for the 420–437-ft (AGL) elevation, the elevation for which the greatest number of samples were taken. These data are summarized in Table I. There is reasonable accord between the $[HO]$ values estimated from the different reactive olefinic hydrocarbons. [The data for the $[C_2H_4]/[C_2H_2]$ ratios are least reliable since there is a very large scatter and an unexplained inconsistency exists between the results from Smog #2 and Smog #3 for this case (Figure 2). The results were calculated in this case using the data from the two helicopters as separate inputs.] The magnitude of the $[HO]$ levels is also in the range of those anticipated from computer simulation studies of photochemical smog analogues. Thus Calvert and McQuigg (16) estimate that $[HO]$ values will be in the range $(4–14) \times 10^{-8} ppm$ for a wide range of $[CO]$, $[RH]$, $[NO]$, $[NO_2]$, and $[aldehyde]$ in simulated smog mixtures using solar irradiances equivalent to those present near ground level for a relatively clean atmosphere and a solar zenith angle of 40° .

There is an uncertainty in the accuracy of the alkene concentrations reported in the LARPP study which should be noted by potential users of the data. The concentrations of the reactive alkenes may have been inadvertently attenuated as a result of the collection and storage processes employed by the California Air Resources Board (ARB) laboratories handling this phase of the operation. Although the bag samples were collected in a fashion to remove the O_3 at the instant of collection, transfer of the bags from the helicopter to the van in sunlight, and the usual period of storage of the bags in the artificially lighted area prior to analysis, both must lead to the regeneration of ozone at some reduced level characteristic of the intensity of the ultraviolet component of the light present. Thus if the intensity were only $1/10$ th of that of the sunlight, the $[O_3]$ would quickly rise during storage to a level about $1/10$ th of that present in sunlight for a given $[NO_2]/[NO]$ ratio. Although rates of reaction of O_3 and alkene are relatively slow for these concentrations, a period of several hours of storage is sufficient to

Table II. Hydrocarbon Concentration Ratios Calculated from Samples Collected at Ground Level by ARB Van in LARPP Operation #33, November 5, 1973

Location of Van: Time:	ARB Downey 0745	Paramount 0945	Compton 1045	Cerritos 1145	Sante Fe, S.P. 1245
Ratio ^a					
$[C_2H_4]/[C_2H_2]$	0.77	0.96	0.94	0.99	1.00
$[C_3H_6]/[C_2H_2]$	0.36	0.42	0.31	0.34	0.32
$[1-C_4H_8]/[C_2H_2]$	0.063	0.085	0.053	0.033	0.053
$([iso-C_4H_8] + [t-2-C_4H_8])/[C_2H_2]$	0.16	0.18	0.13	0.092	0.13
$([C_3H_4] + [1-C_4H_8] + [iso-C_4H_8] + [t-2-C_4H_8])/[C_2H_2]$	0.59	0.69	0.50	0.52	0.52

^a Based on peaks measured in ppm carbon.

Table III. Ratios of Concentrations of Hydrocarbons from Analyses of Data Collected in General Motors Corp. Van in West Covina, October 5, 1973

Time:	0800	0900	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000	2100	2200	2300
Ratio ^a															
$[C_2H_4]/[C_2H_2]$	0.80	0.73	0.78	0.64	0.62	0.44	0.35	0.52	0.41	0.54	0.93	0.64	0.44	0.56	0.55
$[C_3H_6]/[C_2H_2]$	0.56	0.43	0.48	0.32	0.33	0.47	0.40	0.43	0.55	0.57	0.68	0.50	0.56	0.62	0.73
$[1-C_4H_8]/[C_2H_2]$	0.15	0.07	0.06	0.09	0.09	0.24	0.10	0.10	<0.05	0.07	0.21	<0.05	0.19	0.19	0.18
$([iso-C_4H_8] + [t-2-C_4H_8])/[C_2H_2]$	0.61	0.45	0.57	0.55	0.56	0.56	1.10	0.95	0.75	0.75	1.10	1.43	1.43	1.31	2.09
$([C_3H_4] + [1-C_4H_8] + [iso-C_4H_8] + [t-2-C_4H_8])/[C_2H_2]$	1.33	0.95	1.11	0.95	0.98	1.26	1.60	1.48	1.54	1.39	2.00	1.41	2.63	2.13	3.00

^a Based on peaks measured in ppm carbon.

alter the alkene distribution significantly. Thus removal of the O₃ initially on collection of the samples is no guarantee of its absence during storage.

Unfortunately there were no independent analyses made using different delay times before analyses of the samples collected by the aircraft. However a qualitative test for the potential storage problem can be made comparing ground level analyses in the ARB van (storage with the delay prior to analyses as with the aircraft samples) and in the van of the General Motors Corp. in which analyses were performed without significant delay. Unfortunately, the operation of the GMC van was terminated before the November 5, 1973, timing of this operation under consideration. Typical data from the GMC van showed no great variations in the reactive alkene to acetylene ratios obtained from day to day during October 1973, so such a comparison should be qualitatively significant. Compare the [alkene]/[C₂H₂] ratios derived from the ARB van data for this operation in Table II with those in Table III from the GMC van as collected at various times during October 5, 1973 in West Covina. There are only rather small differences between the given [alkene]/[C₂H₂] ratios for most of the alkenes shown.

However, the most sensitive test for possible alkene concentration alteration in the ARB samples is given in the last row of the Tables II and III. Here the ratio of the sum of the concentrations of the reactive hydrocarbons, C₃H₆, 1-C₄H₈, t-2-C₄H₈, and iso-C₄H₈ to that for C₂H₂ is shown. There appears to be a significant difference between the ARB and the GMC van data in this case. On the basis of this limited comparison, no firm conclusion can be made as to the reliability of the ARB reactive alkene analyses, although there is some indication of the inadvertent attenuation of the alkene concentrations. Any error introduced as a result of this storage problem would be most serious for the analyses of the early morning samples that presumably would have the longest storage period. Thus the estimates of [HO] derived in Table I from the alkene data may be somewhat lower than those actually present in the atmosphere. The potential problem of the alteration of the reactive hydrocarbon concentrations is of sufficient importance to the future modeling of the LARPP hydrocarbon data that the ARB collection procedure should be evaluated in further direct and indirect tests.

The saturated hydrocarbons are not reactive to O₃ so delays in hydrocarbon analysis should not alter significantly their concentrations. Thus we may apply the same hydrocarbon ratio-time treatment to the alkanes to obtain independent [HO] estimates and check further on the possible alkene attenuation during storage. However, the ethane, propane, and the butanes may originate in part from the leakage of natural gas sources which may be quite variable in character over the path of the air parcel; these components need not correlate with the acetylene and are not suitable for the test desired. The hydrocarbons n-pentane and isopentane do not suffer from this complication and may be used to estimate the HO-radical concentration in the atmosphere.

Since the alkanes are less reactive than the alkenes, lower conversions and less accuracy in the estimates are expected. The ratios of [n-C₅H₁₂]/[C₂H₂] and [iso-C₅H₁₂]/[C₂H₂] are shown as a function of time for measurements at one elevation in Figure 6. There is an insignificant correction to the measured percentage reacted per minute in these cases for the O₃ and O-atom attack. The [HO] levels which account for the observed rates of removal for experi-

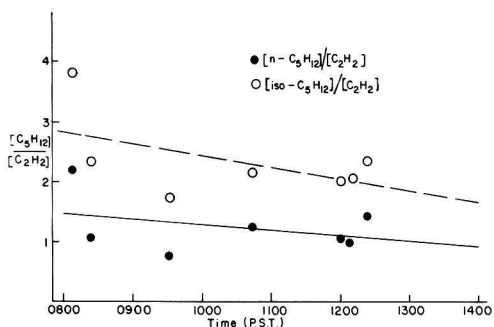


Figure 6. Plot of the ratios of $[n-C_5H_{12}]/[C_2H_2]$ and $[iso-C_5H_{12}]/[C_2H_2]$ vs. time for the LARPP Operation #33 data from the 420-437-ft elevation (AGL) flights; similar data (not shown here) were found from runs at other elevations

ments at several elevations are also summarized in Table I. The estimates are comparable to those found for the least reactive alkene, C_2H_4 , and are somewhat higher than those calculated from the reactive alkene data. This result also is consistent with the inadvertent attenuation of the reactive alkene concentrations in the ARB bag analysis procedures.

A further independent estimate of the $[HO]$ can be derived from the NO_x measurements. The relatively inert gases CH_4 and C_2H_2 were used to normalize the NO_x concentration data in an attempt to separate atmospheric dilution processes from chemical effects. Typical data from measurements at one elevation are shown for the $[NO_x]/[CH_4]$ ratios as a function of time in Figure 7. The $[NO_x]/[C_2H_2]$ data are given in Figure 8. In each case there is an obvious decrease in the ratio throughout the day, suggesting a loss of NO_x . The method of NO and NO_x analysis used in the aircraft assures us that any PAN or organic nitrates formed will be counted as NO_x since these compounds reduced quantitatively to NO during the NO_x cycle (17). Then the "removal" of NO_x must imply formation of species other than these which are detected. Perhaps $HONO_2$ and inorganic nitrate salts formed from $HONO_2$ would fall in this category. If we assume the NO_x detector does not respond well to $HONO_2$ and nitrate salts, two possible mechanisms for NO_x loss may be considered:

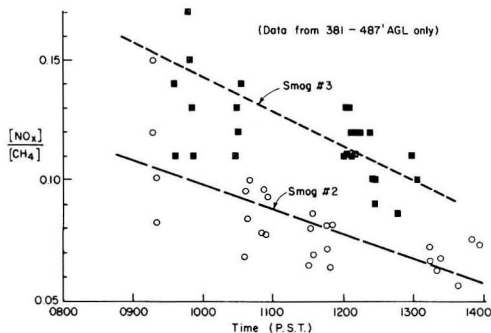
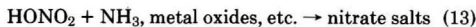
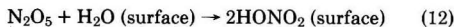


Figure 7. Plot of $[NO_x]/[CH_4]$ ratio vs. time for the LARPP Operation #33 data from the 381–487-ft elevation (AGL) flights; the $[CH_4]$ data from the two helicopters were incompatible so each set was treated independently in this case. Very similar data (not shown here) were found from runs at other elevations

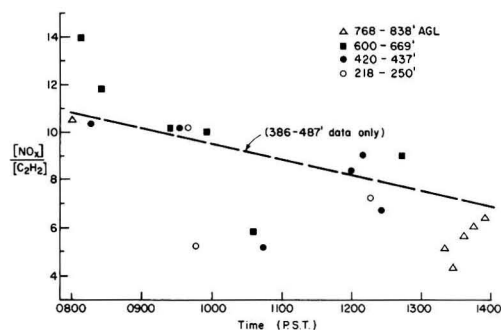


Figure 8. Plot of $[NO_x]/[C_2H_2]$ ratio vs. time for the LARPP Operation #33 data

Reaction 11 must be important; however, the rate of the homogeneous reaction of N_2O_5 with H_2O is small and its significant occurrence in the atmosphere is open to question (2, 16, 18). The rate of the heterogeneous NO_x "loss" reaction (12) is uncertain, but it may be significant for some conditions such as high atmospheric aerosol loading and high humidity.

If we assume that the NO_x "removal" occurs only through Reaction 11, then we may estimate the maximum $[HO]$ level which must be present to cause the observed NO_x removal rates. The two helicopters, Smog #2 and Smog #3, gave incompatible results for CH_4 analysis in the flights of November 5, 1973, so the two sets of data were treated separately in the plots of Figure 7. Both sets of data for $[NO_x]/[CH_4]$ and $[NO_x]/[C_2H_2]$ lead to very similar estimates for $[HO]_{max}$; these are summarized along with the other estimates for $[HO]$ in Table I. The rate of $HONO_2$ (and nitrate salt) formation, predicted to occur in Reaction 11 (and 13) for the conditions of this operation ($3.0 \pm 2.4 \times 10^{-4}$ ppm min^{-1}), is somewhat higher but compatible with the measured rates of $HONO_2$ formation in the Los Angeles atmosphere reported by Miller and Spicer during the LARPP study period (19). The estimates of $[HO]$ are again in the range expected in theory from simulation studies (2, 16), $[HO] = (0.4 - 1.4) \times 10^{-7}$ ppm; they are nearly equal to those derived from the least reactive alkene, C_2H_4 , and the alkanes, $n-C_5H_{12}$ and *iso*- C_5H_{12} .

All of the data from this operation suggest that the ambient HO-radical concentration present in the atmosphere of Los Angeles on November 5, 1973, is somewhat below that reported originally by Wang and Davis ($\sim 6 \times 10^{-6}$ ppm) who have carried out the first direct measurement of $[HO]$ in ambient Detroit air (20). Calvert and McQuigg have questioned the magnitude of the $[HO]$ estimated by Wang and Davis on other grounds (16). Perhaps the method as employed in the ambient air measurement was complicated by the direct formation of HO through water photolysis induced by the two-photon absorption of light from the analyzing laser beam; Wang and Davis observed this effect in subsequent laboratory studies (21).

The intense laser pulse at 2835.8 Å employed to excite the 3060 Å fluorescence of HO in the ambient air may also form HO through the direct single quantum photolysis of HONO ($HONO + h\nu \rightarrow HO + NO$) and/or O_3 ($O_3 + h\nu \rightarrow O(^1D) + O_2$; $O(^1D) + H_2O \rightarrow 2HO$). However, the reported laser intensity effects on the observed ambient HO signal do not seem to support this hypothesis. The present data are in better accord with the most recent direct estimates of $[HO]$ in ambient Detroit air reported by Wang et al. (22); they estimated values of $[HO] \approx 4 \times 10^{-7}$ ppm in the morning hours, increasing to a maximum of 2.4×10^{-6} ppm later in the day, and decreasing to the detection limit ($\sim 2 \times 10^{-7}$ ppm) in the late afternoon. Both the continued addition of freshly formed pollutants to the air mass under study and the possible attenuation of alkenes in ARB hydrocarbon analysis procedures require that our present estimates represent the minimum $[HO]$ present in the Los Angeles atmosphere on November 5, 1973. In view of the large uncertainties inherent in all of the present methods of $[HO]$ estimation, the degree of agreement between the recent results of Wang et al. (22) and those derived in this work is as good as can be expected.

Nature of the Hydrocarbons That Carry the HO— HO_2 and HO— RO_2 Chain Steps in the Oxidation of NO to NO_2 . It is instructive to note the distribution of the hydrocarbons in the samples collected during the operation of November 5, 1973, and to determine the extent to which each of these species is expected to participate in the reactions with HO and in the chain-carrying reactions that, in

Table IV. Estimated Relative Rates of HO-Radical Attack on Hydrocarbons and CO Present in the 0823 sample, LARPP Operation #33, Smog #2, 425-ft (AGL) Flight^a

Compound	[RH], ppm, mol basis	Rel. rate, HO reaction	Compound	[RH], ppm, mol basis	Rel. rate, HO reaction
CH ₄	2.01	2.8	3-Methylhexane	0.0063	5.8
C ₂ H ₆	0.049	2.2	1-Heptene	0.0044	~25.9
C ₂ H ₄	0.043	11.6	<i>n</i> -C ₇ H ₁₆	0.0043	3.8
C ₂ H ₂	0.038	1.0	Methylcyclohexane	0.0037	4.7
C ₃ H ₈	0.037	4.4	2,2,3- and 2,3,3-Trimethylpentane	0.0019	1.4
C ₃ H ₆	0.0087	21.8	2,2,4-Trimethylpentane	0.0025	1.8
<i>iso</i> -C ₄ H ₁₀	0.012	4.2	Toluene	0.020	17.6
<i>n</i> -C ₄ H ₁₀	0.037	13.3	1-Methylcyclohexene	0.0047	~6.0
1-C ₄ H ₈	0.0015	8.9	2,2,5-Trimethylhexane	0.0010	0.9
<i>iso</i> -C ₄ H ₈	0.0030	27.9	<i>n</i> -C ₈ H ₁₈	0.0021	2.2
<i>iso</i> -C ₅ H ₁₂	0.0443	29.2	EtC ₆ H ₅	0.0041	~4.2
<i>n</i> -C ₅ H ₁₂	0.0162	8.9	<i>p,m</i> -Xylenes	0.014	~32.1
Cyclo-C ₅ H ₁₀	0.0026	2.1	<i>o</i> -Xylene	0.0060	11.3
1-C ₅ H ₁₀	0.004	~2.4	<i>n</i> -C ₉ H ₂₀	0.0013	1.6
2-Methylbutene	0.0008	~7.4	<i>n</i> -PrC ₆ H ₅	0.0010	~1.2
2,2-Dimethylbutene	0.0008	~4.7	<i>sec</i> -BuC ₆ H ₅	0.0050	~7.0
2-Methylpentane	0.0110	9.1	<i>n</i> -C ₁₀ H ₂₂	0.0011	1.5
3-Methylpentane	0.0100	8.3	<i>n</i> -C ₁₁ H ₂₄	0.0010	1.5
1-Hexene	0.0017	~10.0	<i>n</i> -C ₁₂ H ₂₆	0.0003	0.5
<i>n</i> -Hexane	0.0100	7.1	CO	1.91	47.8 (12.1%)
Cyclohexene	0.0107	~10.7	<u>Total alkane</u>		<u>128.0 (32.5%)</u>
2,2,3-Trimethylbutane	0.0077	4.4	<u>Total alkene</u>		<u>138.3 (35.1%)</u>
C ₆ H ₆	0.0082	6.3	<u>Total aromatic hydrocarbons</u>		<u>79.7 (20.2%)</u>
2-Methylhexane	0.0069	6.3	<u>Grand total</u>		<u>393.8</u>

^a Data for the C₆-C₁₂ hydrocarbons were estimated from typical data from the General Motors Corp. van and ratios of the light hydrocarbons common to both the ARB and GMC van analyses. Identified hydrocarbons comprise about 85% of the total carbon atoms detected in the chromatographic analyses in the GMC van.

theory, control a large part of the NO → NO₂ conversion. The concentrations of the various hydrocarbons in Bag #5 of Smog #2 collected at 0823 and their appropriate relative rates for reaction with HO are shown in Table IV. We have employed the published HO-hydrocarbon rate constants available for these compounds (12-14, 23-25) and extrapolated the appropriate data for similar compounds to estimate the constants for those compounds not studied as yet. The relative rate for the HO-C₂H₂ reaction was taken as unity in the table. The detailed product analysis data for the higher hydrocarbons (C₆-C₁₂) were obtained from the analyses of the General Motors Research Laboratory group obtained during this LARPP study period in the GMC van (26). The ratios of the lighter hydrocarbons common to both analyses were used to normalize the concentrations for each species above the hexanes, so that the resulting total mixture should be comparable to that present in Bag #5 of this operation. Some interesting conclusions concerning model development result from the data of Table IV:

(1) Even though the compounds such as CH₄ and C₂H₄ are usually considered to be relatively unimportant reactants in smog development in the lower atmosphere, the rates of HO attack on them are not insignificant. Thus methane is attacked at a rate which is greater than that for C₂H₆, C₂H₂, *cyclo*-C₅H₁₀, and many of the higher paraffinic hydrocarbons. Of course this results from the relative high concentrations of CH₄ and C₂H₄ present in the polluted ambient air.

(2) The alkanes and the aromatic hydrocarbons are very important reactants in the smog mixture even in the early morning hours. Note that of the HO-radicals reacting in the chain-carrying steps, about 33% react with alkanes, 35% with alkenes, 20% with aromatics, and 12% with CO. Of

course the efficiencies of HO₂ and RO₂ formation following the HO attack step and subsequent reaction with NO to form NO₂ are not the same for the various hydrocarbons; thus the comparison is not a quantitative test of the effective contribution of each species. However it is evident that a realistic model of the role of the hydrocarbons in NO → NO₂ conversion will require that account be taken of every class of hydrocarbon (if not each individual RH) as well as CO, since each group is important. Other classes of organic molecules not included here, the aldehydes and ketones, should also become significant reactants as they are among the major products of the oxidation of the hydrocarbons. Unfortunately there are no analytical data for these species, so modelers of the LARPP data will have a degree of flexibility and uncertainty in their treatment which is unfortunate.

The nature of the primary interaction of HO with olefinic and aromatic hydrocarbons remains uncertain; both radical abstraction of H-atoms and addition to the olefinic bond have been suggested to occur with the alkenes, although the importance of each is obscure at this time. The secondary steps of radical oxidation are also uncertain in most cases. Obviously chemical models developed to rationalize the LARPP data will require scientists with good chemical intuition as well as scientific ability at this stage of our knowledge.

We may conclude in summary that the present results, derived from the measured time dependence of impurity concentrations within a tagged parcel of polluted air, confirm the general conclusions formulated in many previous, less direct studies of photochemical smog formation (3, 4, 27-30). Of course the full significance of the LARPP data cannot be gleaned from this chemical study of the results of a single day's operation. It is the author's hope that the

present study will serve to stimulate the interest of the scientific community in continued further study of this important set of data available to all who desire it.

Acknowledgment

The author is grateful to the Coordinating Research Council and its LARPP Project Committee for access to the data of Operation #33 prior to arriving, and to Drs. K. L. Demerjian and J. Peterson (Environmental Protection Agency), and Drs. P. Monson and C. S. Tuesday (General Motors Research Laboratory), for making available to him other useful data related to the project, and for helpful discussions during the course of this study.

Literature Cited

- (1) Calvert, J. G., *Environ. Sci. Technol.*, **10**, 248 (1976).
- (2) For a general review of the extensive literature related to these reactions see: Demerjian, K. L., Kerr, J. A., Calvert, J. G., *Adv. Environ. Sci. Technol.*, **4**, 1 (1974).
- (3) Stephens, E. R., Burselson, F. R., *J. Air Pollut. Control Assoc.*, **17**, 147 (1967).
- (4) Stephens, E. R., Burselson, F. R., *ibid.*, **19**, 929 (1969).
- (5) Altschuler, A. P., Lonneman, W. A., Sutterfield, F. D., Kopczynski, S. L., *Environ. Sci. Technol.*, **5**, 1009 (1971).
- (6) DeMore, W. B., *Int. J. Chem. Kinet.*, **1**, 209 (1969).
- (7) Japar, S. M., Wu, C. H., Niki, H., *J. Phys. Chem.*, **78**, 2318 (1974).
- (8) Stuhl, F., Niki, H., *J. Chem. Phys.*, **55**, 3954 (1971).
- (9) Atkinson, R., Pitts, J. N., Jr., *J. Phys. Chem.*, **78**, 1780 (1974).
- (10) Atkinson, R., Cvetanovic, R. J., *J. Chem. Phys.*, **56**, 432 (1972).
- (11) Cvetanovic, R. J., *ibid.*, **30**, 19 (1959).
- (12) Breen, J. E., Glass, G. P., *Int. J. Chem. Kinet.*, **3**, 145 (1970).
- (13) Morris, E. D., Jr., Stedman, D. H., Niki, H., *J. Am. Chem. Soc.*, **93**, 3570 (1971).
- (14) Morris, E. D., Jr., Niki, H., *J. Phys. Chem.*, **75**, 3640 (1971).
- (15) Niki, H., Daby, E. E., Weinstock, B., Chapter 2 in "Photo-

- chemical Smog and Ozone Reactions", R. F. Gould, Ed., *Adv. Chem. Ser.*, **113**, 16 (1972).
- (16) Calvert, J. G., McQuigg, R. D., paper in Symposium on "Chemical Kinetics Data for the Lower and Upper Atmosphere", Airlie House, Va., September 1974; *Int. J. Chem. Kinet.*, *Symp. 1*, 113 (1975).
- (17) Winer, A. M., Peters, J. W., Smith, J. P., Pitts, J. N., Jr., *Environ. Sci. Technol.*, **8**, 1118 (1974).
- (18) Morris, E. D., Jr., Niki, H., *J. Phys. Chem.*, **77**, 1929 (1973).
- (19) Miller, D. P., Spicer, C. W., *J. Air Pollut. Control Assoc.*, **25**, 940 (1975).
- (20) Wang, C. C., Davis, L. I., Jr., *Phys. Rev. Lett.*, **32**, 349 (1974).
- (21) Wang, C. C., Davis, L. I., Jr., *J. Chem. Phys.*, **62**, 53 (1975).
- (22) Wang, C. C., Davis, L. I., Jr., Wu, C. H., Japar, S., Niki, H., Weinstock, B., *Science*, **189**, 797 (1975).
- (23) Greiner, N. R., *J. Chem. Phys.*, **53**, 1070 (1970).
- (24) Davis, D. D., Bollinger, W., Fischer, S., *J. Phys. Chem.*, **79**, 293 (1975).
- (25) Doyle, G. J., Lloyd, A. C., Darnall, K. R., Winer, A. M., Pitts, J. N., Jr., *Environ. Sci. Technol.*, **9**, 237 (1975).
- (26) We are grateful to Drs. Paul Monson and Charles Tuesday of the General Motors Research Laboratories for access to these data before publication.
- (27) Altschuler, A. P., Cohen, I. R., *Int. J. Air Water Pollut.*, **7**, 787 (1963).
- (28) Glasson, W. A., Tuesday, C. S., *Environ. Sci. Technol.*, **4**, 916 (1970).
- (29) Altschuler, A. P., Bufalini, J. J., *ibid.*, **5**, 39 (1971).
- (30) Dimitriadis, B., *ibid.*, **6**, 253 (1972).

Received for review July 28, 1975. Accepted November 24, 1975. [The Los Angeles Reactive Pollutant Program (LARPP) was carried out in Los Angeles during the period September through November 1973. It was jointly sponsored by the Coordinating Research Council and the Environmental Protection Agency with participation of several other research groups. All basic data from the 35 days of successful operations have been archived on magnetic tape at the National Technical Information Service, Washington, D.C., and they are available to all who wish access to them.]

Kinetics of Limestone Neutralization of Acid Waters

Paul Barton* and Terdthai Vatanatham¹

Department of Chemical Engineering, The Pennsylvania State University, University Park, Pa. 16802

■ The rate of neutralization of sulfuric acid by limestone particles is shown to be controlled by hydrogen diffusion in the pH range of 2–6. The first-order rate constant is 10^{-4} l/(cm)² (s) at 298 K for a limestone containing 87 wt % carbonates, using as a driving force the hydrogen concentration in the bulk phase minus that at equilibrium at the end of the neutralization. A shrinking particle model physically described dissolution of the limestone. Particle sizes investigated vary from 0.037–0.044 mm to 0.500–0.595 mm. Effects of temperature (274–348 K), stoichiometry, turbulence, and carbon dioxide pressure are analyzed.

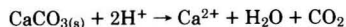
Limestone is the least expensive neutralizing agent for metal-acid wastewaters, particularly if it doesn't have to be ground into powder form. When present in excess of the stoichiometric amount, it automatically buffers the effluent to a pH of about 8 and provides a compact granular base for retaining flocculent precipitates. Concern is expressed about relatively slow reaction rates, possible coating of the limestone surface with flocculent metal precipitates, and an equilibrium pH too low to precipitate certain

metal ions. The objectives of this work are to investigate the kinetics and equilibria of limestone treatment of metal-acid wastewaters and to devise a kinetic expression for designing neutralization reactors. Applicable wastes include those from coal and ore mine facilities, metal-cleaning facilities, and plating shops.

Background

For extensive literature surveys concerning treatment of metal-acid wastes, the theses of Wentzler (1) and Powell (2) are recommended.

The neutralization process can be described as the replacement of the undesirable cation components (H⁺, Fe²⁺, Fe³⁺, Al³⁺) by a more acceptable cation, which is Ca²⁺ in the limestone neutralization process. The overall reaction can be written as follows:



Wentzler and Aplan (3) reported the investigation of the kinetics of limestone dissolution in acidic solutions of nitric acid at constant pH by the rotating disk method. This work covered a wide pH range. They suggested that the dissolution mechanism is transport rate controlled and that the applicable equation is in the form

$$dw/dt = kA(C_0 - C_i)$$

¹ Present address, Department of Chemical Engineering, College of Engineering, Prince of Songkla University, Haad Yai, Thailand.

where k is the rate constant, C_0 and C_i are concentrations in the bulk and at the interface, respectively, and du is the quantity dissolved that diffuses through cross-sectional area, A , in time, dt . From their data, they concluded that the rate-controlling species is hydrogen and that a first-order relationship with the bulk hydrogen concentration is followed. However, they did not evaluate the concentrations that are necessary for strictly evaluating the above equation and they did not employ activity coefficients to convert pH values to concentrations. In the rotating disk method, additional acid is added during reaction to maintain a constant pH (activity), but this does not correspond to constant hydrogen ion concentration inasmuch as the ionic strength is increasing.

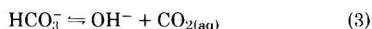
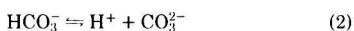
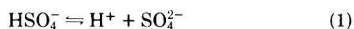
Pearson and McDonnell (4) had simulated the neutralization of acid streams by barriers of crushed limestone, using particles of 2½–4-in. diameter. The tests were all made at ambient temperature, both in the absence and presence of metal ions. They found that a rate mechanism based on coupled hydrogen diffusion and carbonate surface reaction successfully modeled the data. They concluded that the surface reaction resistance becomes increasingly significant above a pH of about 5.

Wentzler (1) reacted calcite crystals with 0.02-M ferric sulfate at constant pH and examined the solid product. By using an electron microscope and x-ray diffraction, he found that precipitated calcium sulfate was present on the limestone and that it was in the form of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). The formation of a reaction-inhibiting film of calcium sulfate on limestone particles in a metal-acid neutralization reactor is thus a possibility, especially at high sulfate concentrations.

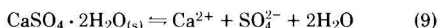
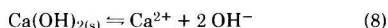
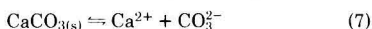
In our work, models such as the above are tested over a much wider range of reaction conditions involving the varying of particle size, stoichiometry, temperature, carbon dioxide concentration, and anion and metal ion concentrations. The effect of temperature is especially important in evaluating the contribution of a chemical reaction rate controlling step.

Solid CaCO_3 -Sulfuric Acid System

Bulk Phase Concentrations. In the bulk liquid phase it is assumed that all reactions are in equilibrium and dissolved CO_2 is in equilibrium with the gas above the solution. With these assumptions, the following equilibrium equations as presented by Butler (5) can be applied:



The following chemical reactions can be applied also. These three reactions are first tested to determine whether they are applicable and whether they are at equilibrium.



At equilibrium the chemical activity of each species can be related through the equilibrium constants of the above reactions. In addition, an electrical neutrality equation and a mass balance on sulfate groups are applied.

Consider the case where no calcium hydroxide or calcium sulfate precipitates, and equilibrium is not established with the solid calcium carbonate. When we know all the reaction equilibrium constants as well as $[\text{H}^+]$, $[\text{CO}_{2(\text{aq})}]$, and total sulfate, 8 unknowns with 8 relationship equations will exist. Thus the activity of each species can be calculated with a minimum of experimental measurements at any given time during a neutralization reaction.

The concentration of each ionic species is related to the activities by use of activity coefficients correlated with ionic strength using the modified Davies equation presented by Butler (5).

From the assumption that aqueous CO_2 is in equilibrium with the gas evolved from the solution, the concentration of aqueous CO_2 can be related to the partial pressure of CO_2 in the gas by using Henry's law.

Reaction Rate. The kinetic equation representing a reaction rate that approaches first order with respect to hydrogen ion can be given by:

$$-\frac{d(\text{CaCO}_{3(\text{s})})}{(\text{CaCO}_{3(\text{s})})^{2/3} dt} = \frac{kM (\text{CaCO}_{3(\text{s})})}{6\rho_p D_0} [(\text{H}^+)_i - (\text{H}^+)_e] \quad (10)$$

The depletion of reaction surface with time is accounted for by assuming the particles are uniformly shrinking spheres. The reaction is presumed to be controlled by diffusion of hydrogen ions. The driving force is the difference between the hydrogen concentration in the bulk liquid and at the solid interface. Since the surface hydrogen ion concentration is not measurable, it is assumed to be equal to that in equilibrated $\text{CaCO}_{3(\text{s})}$ -sulfuric acid mixtures—i.e., the hydrogen ion concentration at the end of the experiments whenever an excess of CaCO_3 is present.

Experimental Procedures

To get a uniform concentration, all sizes of limestone were crushed from a single batch of rock from Oak Hall, Pa. This limestone contains 87 wt % carbonates, only a few percent being magnesium carbonate. The particles were sieved into narrow-size ranges, while wet with isopentane to wash fine particles from the larger ones and to reduce agglomeration of the fines.

The batch reactor used was a vigorously agitated, partly sealed beaker immersed in a constant temperature bath. The solution was continuously purged with gas presaturated with water vapor at the solution temperature. The initial acidity of the solution was determined by titration of an aliquot with hot sodium hydroxide. Limestone was dumped into the 1-l. charge of acid solution and the pH of the solution was monitored with time. Samples of the effluent gas were taken at various times and analyzed for carbon dioxide content by gas chromatography or Kitagawa gas detector tubes.

The recycle downflow reactor system consisted of an acid feed tank, diaphragm pump, thermostatic bath, and a 3.8-cm diameter cylindrical reactor chamber supported on filter cloth. The limestone charge was placed in the chamber and aerated acid solution pumped down through the bed of particles. The pH of the recycled solution and the carbon dioxide content of the effluent gas were monitored with time.

Experimental Results

Twenty tests on the neutralization of sulfuric acid and sulfuric acid-metal solutions with limestone particles were made. Detailed results can be obtained (6). The limestone was present in twice the stoichiometric amount needed to balance the acidity in all but one of the experiments.

The effect of particle size, ranging from 0.037–0.044 mm to 0.500–0.595 mm, on the reaction of limestone with sulfuric acid in the agitated batch reactor is shown in Figure 1. A neutral solution (pH = 7) is reached in 13 min with the finest particles, but takes 3 h with the largest particles. The effect of temperature, ranging from 274–348 K, on the reaction of 0.250–0.297-mm particles is presented in Figure 2. The curves in these figures represent direct tracings between experimental pH values vs. time.

The effect of various metal ions in sulfuric acid solution on neutralization with limestone particles can be seen in

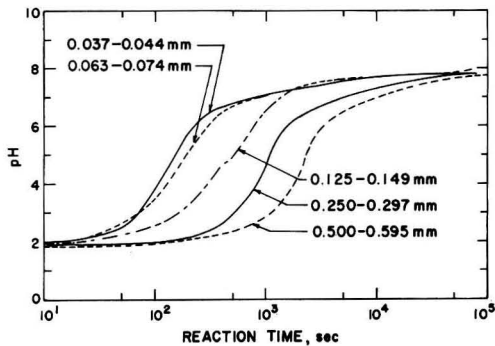


Figure 1. Effect of initial limestone size on neutralization rate of sulfuric acid

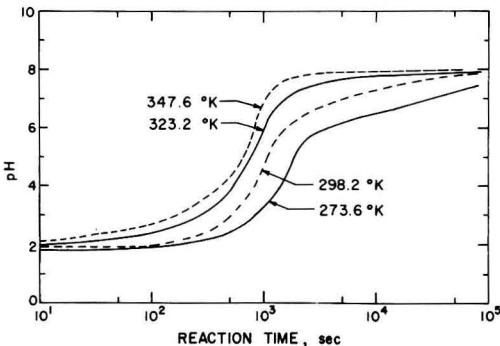


Figure 2. Effect of temperature on neutralization rate of sulfuric acid with 0.250–0.297-mm limestone

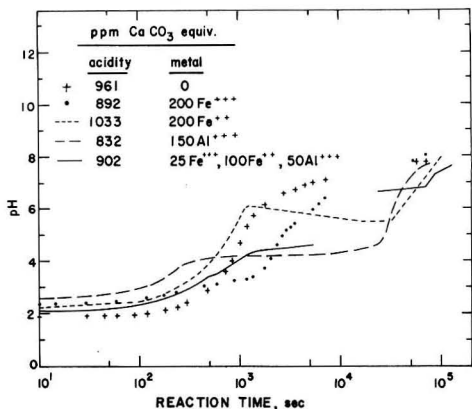
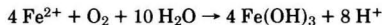


Figure 3. Effect of metal ions on neutralization rate of sulfuric acid with 0.250–0.297 mm of limestone at 298.2 K

Figure 3, starting with solutions of comparable acidity. The mixture containing Fe^{2+} , Fe^{3+} , and Al^{3+} is typical of strong acid coal mine drainage. The metals are seen to slow down its neutralization rate by a factor of 10. For the mixture containing Fe^{2+} , the pH rises sharply to above 6 and then drops down and rises again to above 6 toward the end point. This can be explained by considering the oxidation of ferrous to ferric ion by oxygen in the purge gas according to the reaction (7):



The oxidation proceeds faster at higher pH, producing hydrogen ions which require additional base for neutralization.

Kinetic Modeling

The reaction rate data for the metal-free sulfuric acid feeds were tested with the following models: zero-order reaction controls; carbon dioxide diffusion controls; surface reaction controls; and first order with respect to hydrogen ion. A calcium ion-diffusion-controlled model would somewhat parallel the carbon dioxide-diffusion-controlled model. The hydrogen ion-first-order model best fit the data.

A graph of the hydrogen ion-first-order rate constant (k of Equation 10) as a function of hydrogen ion concentration is shown in Figure 4 for the neutralization of sulfuric acid with 0.250–0.297-mm limestone particles at 298 K. The fit is excellent in the pH range of 2.5–6, representing a 3000-fold change in hydrogen ion concentration in the bulk liquid. Apparently experimental error or other transport or kinetic mechanisms became important at $\text{pH} < 2.5$ and $\text{pH} > 6$. The low pH region is where the concentration of CO_2 in the aqueous phase is difficult to ascertain, particularly since the reaction is just starting and carbon dioxide is being generated profusely, causing a rapid rise in CO_2 concentration. The largest errors in measuring the hydrogen ion concentration also occur at low pH in our experiments. In the high pH region, the end point is being approached, and the equilibrium concentration of hydrogen ion assigned as the surface concentration sensitively affects modeling with Equation 10.

The hydrogen ion-first-order rate constant is seen in Table I to be unaffected by particle size in the pH range of 2–6. This is a good indication that the shrinking sphere model adequately describes physical dissolution of the particles and the amount of surface available. With a micro-

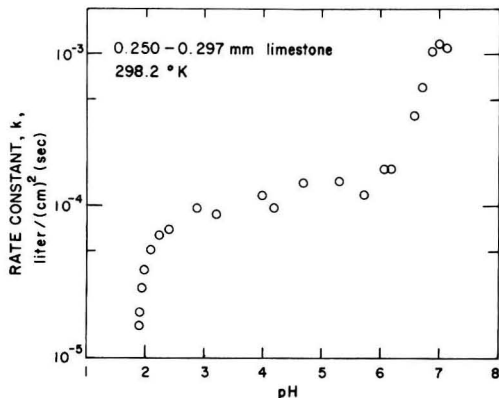


Figure 4. Variation of rate constant with pH for hydrogen ion first order

scope, the ratio of average diameter of reacted to unreacted limestone particles was 0.64, as compared to 0.72 from calculations, for the 0.250–0.297 mm limestone.

Modeling with Equation 10 can be viewed as hydrogen diffusion controlled with the surface concentration of hydrogen ion taken to be the concentration at the end point. In this way, the rate constant, k , is a function of the diffusivity of hydrogen ion or

$$k = \frac{D}{\Delta x}$$

where Δx is the film thickness. Film thickness can be expected not to vary widely in the stirred batch experiments.

If we use the equation of Chapman (8) to calculate the limiting diffusivity of ions, based on limiting ionic conductance, with data in Perry et al. (9) to correct for changes in temperature, the apparent film thickness was calculated at several temperature levels. The results are shown in Table II.

The value of 0.0095 mm for the average film thickness appears low, yet represents 4% of the particle diameter of 0.250–0.297 mm. It is noteworthy that the value of film thickness stays constant despite the quadrupling of the rate constant as the temperature increases. The hydrogen diffusion-controlled model satisfactorily accounts for temperature change.

If the dependency of hydrogen ion concentration is instead chemical reaction controlled, the variation of the rate constant in Table II is expected to be greater. The apparent activation energy calculated from these rate constants is 1.5×10^4 J/mol, which is rather small for chemical-reaction controlled situations.

In the recycle downflow experiments, the flow over the particles can be well characterized compared to the stirred batch experiments. In the two downflow experiments, the rate constant for 0.250–0.297-mm limestone at 298 K is 3.5×10^{-5} l/(cm)²(s) over a flow rate range of 0.01–0.03 l/s. The calculated film thickness is 0.027 mm, or 10% of the particle diameter. This appears quite reasonable.

In one stirred batch experiment at 298 K, the amount of 0.250–0.297-mm limestone used was slightly less than the stoichiometric amount. The average rate constant is 10^{-5} l/(cm)²(s) in the pH range of 2–3. The start of the reaction conformed to the curve in Figure 4 for twice the stoichiometric limestone, but fell off toward the end. This might be attributable to interference of diffusion by the 12 wt % residual solid inerts in the limestone.

The effect of varying the partial pressure of carbon dioxide in the purge gas on the neutralization of sulfuric acid with limestone is shown in Table III. A 50% increase in the hydrogen ion–first-order rate constant occurs with increasing carbon dioxide level from 0–3 to 712 mm Hg. This increase in rate is small compared to the several orders of magnitude increase in the carbon dioxide concentration, indicating that carbon dioxide transport does not control the neutralization rate. In calculating the equilibrium concentrations between experimental pH data points, the partial pressures of carbon dioxide were linearly interpolated and extrapolated on log-log graphs of P_{CO_2}/P_{CO_2} (equil) vs. a_{H^+}/a_{H^+} (equil). The error limit in this procedure is $\pm 30\%$, which is not enough to affect significantly the modeling results.

Calculation of concentrations of various species in the solution revealed that no gypsum precipitated. This is the case for low sulfate concentrations. Also, examination of the residual limestone with a microscope showed no apparent white coating of gypsum.

The solutions were in equilibrium with solid calcium carbonate at the end of the tests at 323 and 348 K. The prod-

Table I. Rate Constants for Hydrogen Ion First Order at Different Limestone Particle Sizes (Temperature, 298.2 K)

Particle size, mm	pH range	k , l/(cm) ² (s)
0.037–0.044	2.00–5.85	1.01×10^{-4}
0.063–0.074	2.09–6.00	1.36×10^{-4}
0.125–0.149	2.00–5.31	9.31×10^{-5}
0.250–0.297	1.92–6.18	9.78×10^{-5}
0.500–0.595	1.92–6.15	1.13×10^{-4}

Table II. Effect of Temperature on Rate Constant for Hydrogen Ion First Order (0.250–0.297 mm of limestone)

Temp., K	pH range	k , l/(cm) ² (s)	Apparent film thickness, mm
273.6	1.90–6.51	4.64×10^{-5}	0.0113
298.2	1.92–6.18	9.78×10^{-5}	0.0086
323.2	2.05–5.85	1.59×10^{-4}	0.0085
347.6	2.34–5.60	1.90×10^{-4}	0.0096
			Av 0.0095

Table III. Effect of Carbon Dioxide Partial Pressure on Rate Constant for Hydrogen Ion First Order (Temperature, 298.2 K; 0.250–0.297 mm limestone)

\bar{P}_{CO_2} , mm Hg	pH range	k , l/(cm) ² (s)
0–3	2.03–6.28	1.01×10^{-4}
170–188	2.02–5.10	1.03×10^{-4}
712	1.92–5.22	1.55×10^{-4}

ucts of calcium ion concentrations and carbonate ion concentrations at 274 and 298 K were approximately 60% of the solubility product of calcium carbonate, which is within experimental error.

In conclusion, this work has shown that the reaction of sulfuric acid with limestone is controlled by hydrogen diffusion in the pH range of 2.5–6. One explanation is that the hydrogen ion, despite its small size, is the only species that diffuses toward the solid surface, while other species such as CO_2 , Ca^{2+} , CO_3^{2-} , and HCO_3^- are all diffusing out. The hydrogen ion is in essence diffusing upstream against bulk convective flow of materials. The apparent rate constant increases from the start to the end of the reaction, indicating that accumulation of calcium ions is not strongly hindering the diffusion of H^+ . Additional modeling work is needed to describe how the presence of iron and aluminum ions slows down the reaction.

Nomenclature

- a = activity
- A = surface area
- C = concentration
- $[CaCO_3(s)]_t$ = moles of solid $CaCO_3$ at time t
- $[CaCO_3(s)]_0$ = moles of initial solid $CaCO_3$
- D = diffusivity
- D_0 = initial particle diameter
- $(H^+)_e$ = molar hydrogen ion concentration in bulk solution at equilibrium
- $(H^+)_t$ = molar hydrogen ion concentration in bulk solution at time t
- k = rate constant
- M = molecular weight of $CaCO_3$
- P_{CO_2} = partial pressure of carbon dioxide
- Δx = apparent film thickness
- ρ_p = density of limestone

Literature Cited

- (1) Wentzler, T. H., "A Study of the Interactions of Limestone in Acid Solutions", MS Thesis in Mine Processing, The Pennsylvania State University, University Park, Pa., 1971.
- (2) Powell, R. W., "Hydrocarbon Extraction of Acid Mine Drainage", MS Thesis in Chemical Engineering, The Pennsylvania State University, University Park, Pa., 1972.
- (3) Wentzler, T. H., Aplan, F. F., "Kinetics of Limestone Dissolution by Acid Waste Waters", Environmental Control, *Proc. Symposium AIME 1972*, The Metallurgical Society, AIME, New York, N.Y., 1972.
- (4) Pearson, F. H., McDonnell, A. J., "Neutralization of Acidic Wastes by Crushed Limestone", Res. Publ. No. 79, Inst. for Land and Water Resources, The Pennsylvania State University, University Park, Pa., 1974.
- (5) Butler, J. N., "Ionic Equilibrium, A Mathematical Approach", Addison Wesley Publishing Co., Inc., Reading, Mass., 1964.
- (6) Vatanatham, Terdthai, "Kinetics of Limestone Neutralization of Mine Drainage", MS Thesis in Chemical Engineering, The Pennsylvania State University, University Park, Pa., 1975.
- (7) Lovell, H. L., "An Appraisal of Neutralization Process of Mine Drainage", Rep. No. EPA 670/2-73-093, U.S. Environmental Protection Agency, 1973.
- (8) Bird, R. B., Stewart, W. E., Lightfoot, E. N., Chapman, T. W., "Lectures in Transport Phenomena", AIChE Continuing Education Series No. 4, American Institute of Chemical Engineers, New York, N.Y., 1969.
- (9) Perry, R. H., Chilton, C. H., Kirkpatrick, S. D., "Chemical Engineers Handbook", 3rd ed., pp 14-23, McGraw-Hill, New York, N.Y., 1963.

Received for review July 21, 1975. Accepted November 12, 1975. Microfilm of the theses listed as references may be obtained, free of charge for specified periods, on interlibrary loan from Pattee Library, The Pennsylvania State University, University Park, Pa., 16802.

Records of Lead Deposition in Lake Michigan Sediments Since 1800

David N. Edgington*

Radiological and Environmental Research Division, Argonne National Laboratory, Argonne, Ill. 60439

John A. Robbins

Great Lakes Research Division, The University of Michigan, Ann Arbor, Mich. 48105

■ The distribution of stable lead has been determined in several Lake Michigan cores that have been dated using the ^{210}Pb technique. A mathematical model, based on records of national and regional fuel use, is developed that accounts for the effect of aquatic residence time, processes of sedimentation, compaction, postdepositional redistribution of sediment solids, and the effect of finite core sectioning. The model gives an excellent quantitative description of the data, indicating that the lead profiles reflect the history of lead input from the burning of coal and leaded gasoline since about 1830 and 1920, respectively. The model is applied to obtain the sedimentation and lead deposition rates from stable lead distributions in undated sediment cores measured previously by others. The 1972 anthropogenic lead flux into the southern basin of the lake is determined to be $1.3 \mu\text{g cm}^{-2} \text{ yr}^{-1}$ in comparison to the natural (pre-cultural) flux of $\sim 0.16 \mu\text{g cm}^{-2} \text{ yr}^{-1}$. The anthropogenic lead deposited in the southern basin in 1972 is estimated to be ~ 240 metric tons as compared with an estimate of ~ 230 metric tons from air pollution fallout originating in the Chicago-Gary urban-industrial area. The measurement of both lead and lead-210 fluxes in the same core may allow contributions of atmospheric lead to be distinguished from terrigenous pollution inputs.

Several studies have shown that the sedimentary deposits of coastal basins and freshwater lakes may contain the historical records of the cultural usage of lead. Lead concentration profiles in several dated sediment cores from the inner basin region off the coast of Southern California have features consistent with the increase in use of leaded gasoline since 1940 (1) and the concentration of lead in rainfall noted by Bruland et al. (2). In the sediments of Lake Washington, Crecelius and Piper demonstrated a qualitative correspondence between the concentration of lead and the history of local lead pollution sources (3). High surficial concentrations of lead have been observed in Lake Michigan sediments by Shimp et al. (4) and Lineback and Gross (5), but evidence for an anthropogenic component is cir-

cumstantial because the cores were neither dated nor was the isotopic composition determined.

The southern basin of Lake Michigan is an ideal location for the determination of anthropogenic lead deposition rates. Along the southwestern shore of the lake is a heavily industrialized and urban area (Chicago, Gary, Milwaukee) that constitutes a major source of atmospheric lead. Patterns of postglacial deposition are comparatively well-known from the work of Lineback and Gross (5, 6) and Robbins and Edgington who have reported the modern sedimentation rates to be of the order of a few millimeters per year based on ^{210}Pb dating (7). From the work of Shimp et al. there are excellent data available concerning the distribution of lead and other trace elements in the sediments (4).

The objectives of the present study are to determine whether the increased concentration of lead in the upper few centimeters of the surficial sediments can be accounted for in terms of cultural additions, and to determine the history of lead deposition rates in Lake Michigan.

Methods

The 3-in. diameter gravity cores studied were taken aboard the University of Michigan Research Vessel, *Inland Seas*, at the locations in Lake Michigan shown in Figure 1. Cores showing any appreciable disturbance of surface sediment were rejected. Suitable ones were sectioned aboard ship using a hydraulic extrusion system that facilitated careful control of section thickness. Subsamples were frozen for return to the laboratory.

For each of these cores, the porosity, ^{210}Pb , and ^{137}Cs activity distributions have been measured previously, and sedimentation rates and mixing depths calculated (7). The stable lead concentration was measured by atomic adsorption spectrophotometry (AAS) using aliquots of the same acidified solutions as had been used for the determination of ^{210}Pb . The ^{210}Pb and stable lead were extracted from oven-dried sediment samples by prolonged boiling in a mixture of concentrated nitric and hydrochloric acids. Approximately 80% by weight of the bulk sediment was dissolved by this method and there was no appreciable variation in this percentage over the length of each core studied

(7). To check for matrix interferences, several of the AAS analyses were performed by the method of standard addition. The extractable lead concentrations are expressed as $\mu\text{g/g}$ dry weight and appear in Figure 2a-d. It is assumed

that the fraction of unextracted lead is insignificant. Analytical errors in the concentrations are generally $<15\%$.

Discussion

Lead Profiles and Historical Lead Usage. The profiles (Figure 2A-D) are all roughly exponential, decreasing to an apparently constant value of about $23 \mu\text{g/g}$ in all cores. The concentration at the top of the cores is more variable, ranging from about $100\text{--}160 \mu\text{g/g}$.

In Figure 2A-D, a time scale has been associated with sediment depth based on the previously reported ^{210}Pb dating of these cores (7). It can be seen that in each case, the lead in "excess" of the $23 \mu\text{g/g}$ "background" is found primarily within the interval corresponding to the period (1930-72) in which the combustion of leaded gasoline has been assumed to be the major source of lead in the environment. This correspondence suggests qualitatively that the excess lead appears to be of cultural origin. It is clear from Figure 2A-D, however, that there were considerable inputs of excess lead into the lake sediments even in the late 1800's, although the major increase has occurred within the last 60 years. The lead distributions are very different from core to core, but have a similar shape when time equivalent concentrations are compared. The "flattening-out" of the lead profiles near the sediment/water interface in cores 29 and 31 is attributable to vertical mixing effects discussed elsewhere (7) and in the Appendix.

The similarity in the shapes of the profiles at widely spaced locations suggests that the annual rate of deposition

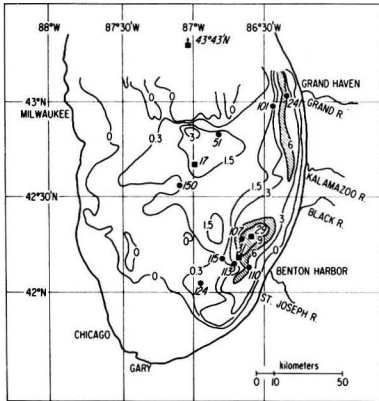


Figure 1. Study area in southern Lake Michigan. The contours (in meters) indicate the thickness of the Waukegan Member (5). The shaded area shows the region of greatest recent sediment accumulation and anomalously high values of the anthropogenic lead deposition rate. ■ This study (labeled UMAN in Table I). ● Data taken from Ref. 4 (labeled IGS in Table I)

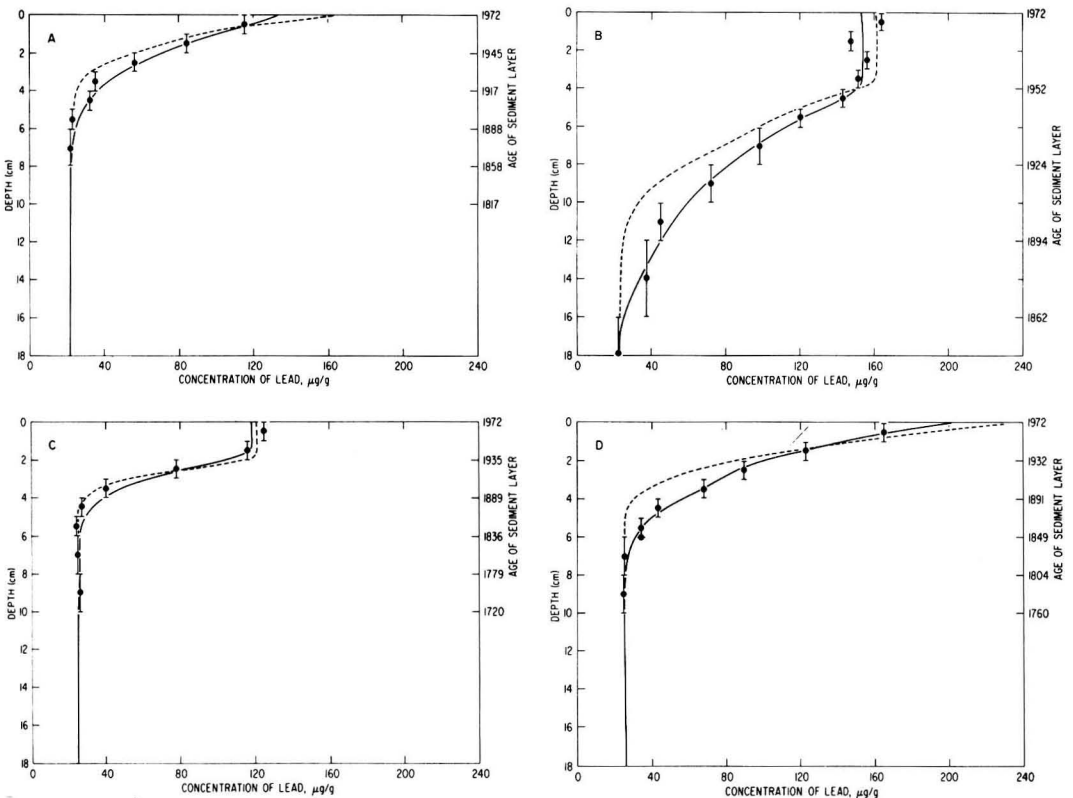


Figure 2. Lead distributions and model fits in lead-210-dated sediment cores. For the solid line fit, only two parameters are allowed to vary: the surficial concentration, C_s , and the proportion of coal-derived lead, k . The dashed line represents the least squares fit assuming contributions from gasoline only. Values of the parameters are given in Table I. (A) Station 72-17; (B) Station 72-29; (C) Station 72-31; (D) Station 72-105

Table I. Anthropogenic Lead Fluxes at $z = 0$ (1972) in Individual Cores

Core	Figure	Sedimentation rate		Mixing depth, cm, S	Anthropogenic lead		k	
		\bar{R}^a , cm/yr	ω , g/cm ² /yr		$C_s - C_{bg}^b$, $\mu\text{g/g}$	F^b , $\mu\text{g/cm}^2/\text{yr}$		
UMAN								
LM-72	17	1-A	0.06	0.012	0	123.	1.5	1.4
	29	1-B	0.15	0.094	4.0	243.	23.0	1.6
	31	1-C	0.04	0.018	2.0	246.	4.4	1.4
	105	1-D	0.07	0.015	0	180.	2.8	1.6
IGSc	51-3	2-A	0.12	0.029	4.0	294.	9.0	
	101-3		0.12	0.029	0	182.	5.0	
	107-2	2-B	0.32	0.078	0	197.	15.0	
	110-3		0.15	0.036	5.0	112.	4.0	
	113-3		0.18	0.044	0	154.	7.0	
	115-3		0.07	0.017	0	197.	3.0	
	124-3		0.04	0.010	0	283.	3.0	
	150-3	2-C	0.20	0.049	0	140.	7.0	
	241-3	2-D	0.15	0.036	0	119.	4.0	

^a \bar{R} is the average sedimentation rate, since the value of R varies as a function of the porosity, ϕ . ^b $F = (C_s - C_{bg})\omega = fJ_a(272)\omega$ (see Equation 11a). ^c For all IGS cores, the porosity, ϕ , is taken to be 0.9 and the mean density of sediment solids, ρ_s , equal to 2.45 g/cm³. The mass sedimentation rate, ω , is then given by:

$$\omega = (1 - \phi)\rho_s R = (1 - \phi_o)\rho_s R_o \approx (1 - \phi_o)\rho_s \bar{R}$$

of lead in a given core is proportional to some universal source function, and that variations from core to core would be taken care of by a variable factor of proportionality. Such a source function could be reconstructed from the distribution of lead in dated cores or by the development of an inventory for the input of lead to the lake over the last 100 years or so. The latter approach will be developed further here.

The occurrence of "excess" lead in sediments deposited prior to 1920 may be primarily due to atmospheric inputs from the combustion of coal. Winchester and Nifong reported that the burning of coal and gasoline in the Chicago-Northwestern Indiana area accounted for more than 95% of the total atmospheric emissions of lead (8). Their inventory included such sources as the burning of coal, coke, fuel oil, and leaded gasoline, and the production of cement, iron, and steel. They suggested that the major proportion (>95%) of the total cultural lead input to the lake originates via deposition of suspended particulates from the atmosphere.

To arrive at a quantitative prediction of the distribution of lead, it is assumed that the annual input of excess lead to the sediments is proportional to a linear combination of the yearly atmospheric emissions from the burning of coal and gasoline in the Chicago area. For this first approximation, the contributions of lead from other sources such as rivers and direct discharges are taken implicitly to be proportional to the atmospheric lead emission rate. This is reasonable and will not cause serious error because of the apparent unimportance of this route of entry.

The estimated annual input, in terms of tons of lead emitted to the atmosphere for both fuels separately, may be calculated from national coal and gasoline production statistics released by the U.S. Department of Commerce (9, 10). Total production figures were prorated by the fraction of the population residing in the Gary-Chicago-Milwaukee area (~4%). The absolute magnitudes of the inputs were determined by normalization to the emission inventory values for 1967 reported by Winchester and Nifong (8). However, the 1967 estimate of the quantity of fly ash emitted to the atmosphere is probably appreciably lower than the total amounts of solids emitted before the major clean-up brought about by the Clean Air Acts of 1963 and 1967.

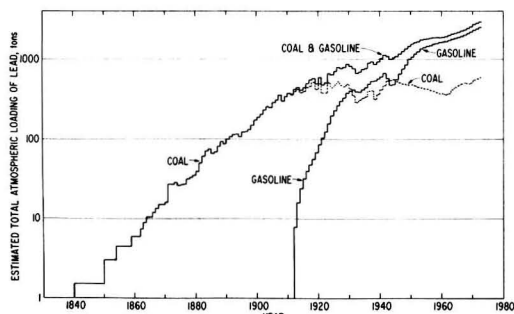


Figure 3. Estimated annual atmospheric emissions of lead from the combustion of coal and leaded gasoline in the Milwaukee-Chicago-Gary area since 1830. The sum of coal and gasoline histograms is the source function which represents the time dependence of lead inputs to the sediments. The proportion of coal-derived lead prior to 1960 includes the factor of $k = 1.5$ (see text)

Therefore, the contribution of lead to the total inventory from the burning of coal before 1963 may be considerably underestimated. According to Harrison, the concentration of total suspended particulates in the air in Chicago has decreased by a factor of two in the last 10 years due to a reduction in stack emissions (11).

Therefore, the source function is taken to be a linear combination of coal and leaded gasoline emission rates where the post-1960 ratio of these two components is fixed but where the pre-1960 coal component is allowed to vary to take account of this decrease in emission of particulates in the 1960's.

A model has been developed to describe the distribution of lead in sediment cores utilizing such a source term. Details and definitions are given in the Appendix. Since the sedimentation rate (R) and mixing depth (S) (see Appendix) have been determined from lead-210 measurements, there are only three adjustable parameters in the model (Equation 18a): the time-independent factor, f , relating the lead source function to the distribution of lead in sediments, the background lead concentration, and the pre-1960 proportion of coal-derived lead, k . However, of these

three parameters, only one, f , is expected to vary significantly from core to core. The precultural concentration shows negligible variation in the cores and the factor, k , is a characteristic of the source term, and in principle, should be constant from core to core.

The lines shown in Figure 2A-D are the least square fits to this model where both f and k have been allowed to vary. Continuous fits are shown only for ease of visualization inasmuch as the model provides values for depth intervals. The line has been extrapolated to $z = 0$ to allow the prediction of the concentration of lead deposited in 1972, provided there is no surficial mixing ($S = 0$). When there is surficial mixing ($S > 0$), the concentration of lead at the surface will be the average of several years deposition. At each station, the solid curve is in excellent agreement with the measured distribution, and the value of k remains essentially constant from core to core. The best values of the sedimentation rate (\bar{R}, ω), mixing depth (S), flux of lead at sediment/water interface, and k are given in Table I. The dashed lines represent least square fits based on inputs from gasoline only. It can be seen that the fits are considerably improved by the inclusion of coal-derived lead except in the case of the station 31 core where the difference is indistinguishable. The average value of 1.5 for k is consistent with the estimated effect of reducing stack emissions in the 1960's. The increasing lead concentration in the sediments from 1830 onward is in marked contrast to the distribution found by Chow et al. in the sediments off the southern California coast where increased concentrations occur primari-

ly after 1940 (1). This difference presumably reflects the negligible use of coal in Los Angeles area for heating or industrial activity and the tremendous increase in the use of automobiles since 1930. It should be pointed out that the effect of molecular diffusion of lead would tend to broaden the distribution and produce a "tail" which might be reproduced by the model for values of k greater than one. In organic rich muds of the Great Lakes, the chemical/diffusional mobility of lead is thought to be insignificant due to the formation of lead sulfides or orthophosphates which have very low solubility, but studies of these specific sediments are needed to definitively rule out this possibility (12, 13). In the present model, the broadening of the distribution is attributed entirely to coal-derived lead.

Therefore, it would seem that Equation 1a with $k = 1.5$ is a reasonable representation for the input of lead to undisturbed sediments throughout the lake. The resulting source function is shown in Figure 3 and can be used to infer the sedimentation rate, mixing depth, and anthropogenic lead flux in undated sediments where the vertical distribution of lead is known. The model has been applied to the data of Shimp et al. (4) (IGS cores). The results are shown in Figure 4A-D. In each case, k was taken as 1.5, while R , S , and f were allowed to vary. The best values of the parameters for these cores are given in Table I, with corresponding locations shown in Figure 1. The fits to the data are satisfactory in each case. The values of R given in Table I for the UMAN cores are computed by allowing R as well as k and f to vary and by not making corrections for

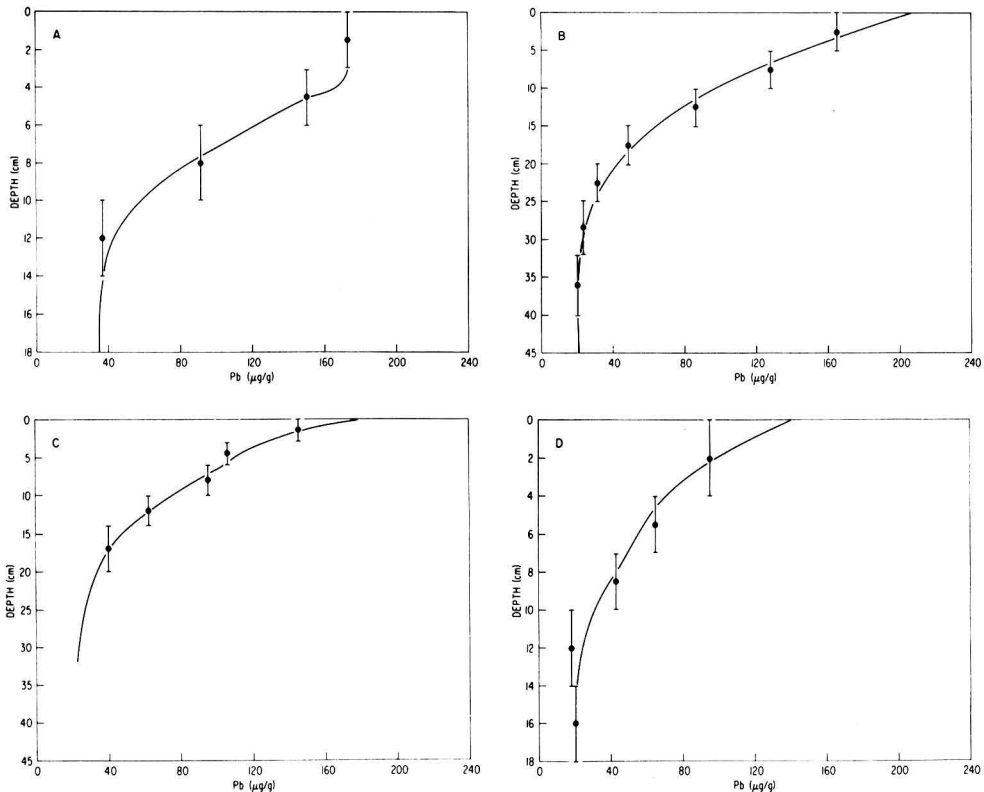


Figure 4. Model fit to several lead distributions in undated sediment cores (4) using anthropogenic lead source function in Figure 3

In these cases the mean sedimentation rate, mixing depth, and surficial lead concentration were allowed to vary. The values of the parameters are given in Table I. (A) Station 51-3; (B) Station 107-2; (C) Station 150-3; (D) Station 241-3

Table II. Estimated Average and Total Lead Deposition Rate in Southern Basin of Lake Michigan

Postglacial sediment thickness, m	Mean mass sedimentation rate, g/cm ² /yr	Anthropogenic lead flux at z = 0 (1972) ^a , μg/cm ² /yr	Area within sediment thickness interval, cm ² × 10 ¹³	Total flux (μg/yr) × 10 ¹³
0.0	0.0	0.0	5.6	0.0
0.0-0.3	0.0	0.0	5.0	0.0
0.0-3.0	0.01	1.9	0.5	0.95
0.3-1.5	0.006	1.1	3.5	3.9
1.5-3.0	0.015	2.9	1.6	4.45
3.0-6.0	0.030	5.7	1.2	6.6
6.0-9.0	0.050	9.5	0.5	4.8
9.0-12.0	0.070	13.5	0.2	2.7
		Total 18.1		24.

Mean sedimentation rate over the southern basin, 7.0 mg/cm²/yr. Mean anthropogenic lead flux, 1.3 μg/cm²/yr. Natural flux, 0.16 μg/cm²/yr. Total anthropogenic lead deposition rate in 1972, 240 metric tons/yr. Natural lead deposition rate 30 metric tons/yr.

^aBased on an average concentration of 190 μg/g.

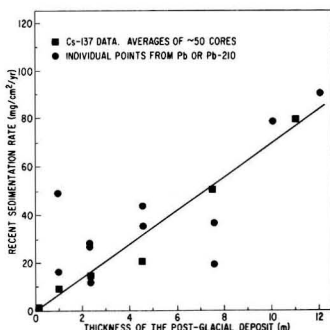


Figure 5. Correspondence between thickness of postglacial deposits and modern sedimentation rates inferred from either radioactivity measurements or stable lead distributions

compaction. The values derived are lower than the sedimentation rate at $z = 0$ since the mean over the upper several centimeters will reflect the sharp decrease in porosity. The values of R so obtained are comparable to those inferred from analysis of the distribution of lead in the IGS cores where the compaction corrections cannot be made with confidence.

Total Lead Deposition in Sediments. It is difficult to arrive at a reliable estimate of the total lead deposition in the southern part of the lake from the cores analyzed. Both the surficial concentration and the flux are highly variable. The surficial concentration varies by a factor of 2.5, and the estimate of the flux by a factor of 10. This illustrates the dangers inherent in attempting to calculate pollution loading on the basis of one or two cores, unless the properties of the lake are well known.

If the concentration of lead in any material deposited in 1972 is assumed to be constant, then the total annual deposition may be calculated if the sedimentation rates are known for the whole area of the southern basin. These rates may be estimated from the seismic profiles measured by Lineback and Gross (5), assuming that the total deposition over the last 7000 years is proportional to the present rate of sedimentation. Contours representing the thickness of the uppermost postglacial deposits (Waukegan Member) are shown in Figure 1. The relationship between the thick-

ness of these deposits and the recent sedimentation rates based on our measurement of ²¹⁰Pb or ¹³⁷Cs in over 50 sediment cores is shown in Figure 5. The mean mass sedimentation rate corresponding to the mean Waukegan member thickness within a specified contour interval, given in Table II, is based on the value of 6.7 mg/cm²/yr/meter derived from a least squares fit to the data shown in Figure 5. The average mass sedimentation rate in the southern part of the lake (below 43°N) is about 7 mg/cm²/yr (Table II). If we take the natural background to be 23 μg/g, the mean natural lead flux is approximately 0.16 μg/cm²/yr which corresponds to a total input of about 30 metric tons/yr. If the mean surficial anthropogenic lead concentration is taken to be 190 μg/g, then the average deposition rate over the southern basin is 1.3 μg/cm²/yr, which corresponds to about 240 metric tons/yr in 1972.

Inputs of Lead to Lake Michigan. Atmospheric. The values calculated above may be compared to other estimates of the inputs of natural and anthropogenic sources of lead to the lake. The emissions inventory (Figure 3) indicates about 2900 metric tons of lead originated from Chicago-Gary in 1972, but the fraction which enters the lake is uncertain. Our source function, Equation 3a, implies a time-dependence of the total loading, but does not provide an absolute magnitude. Winchester and Nifong assumed a total deposition of velocity (V_d) of 0.5 cm/s and arrived at an estimate of 10% for the fraction of emissions from Chicago-Gary entering the lake (8). Both Robbins et al. (14) and Skibin (15) have pointed out that this value is too low. Sehmel has shown that the dry deposition velocity (V_d) of nuclear fallout on smooth surfaces comparable to undisturbed water is ~0.4 cm/s for a mean wind speed of 5 m/s, which is the average for the lake (16). This is almost the same as the 0.3 cm/s reported for lead in the English Lake District by Cawse (17). It has been shown also from measurements of radioactive fallout by Hicks (18) that dry deposition accounts for approximately 25% of the total removal. Therefore, the total deposition velocity (V_d) would be between 1.2 and 1.0 cm s⁻¹.

As the average height of the mixing layer around Chicago is about 500 m (19), the atmospheric residence time of lead over the lake will be $5 \times 10^4/V_d$ s, or approximately 10 h. Robbins et al. have calculated the fraction transferred from the Gary-Chicago region to the lake as a function of residence time (14). The calculation assumes straight wind trajectories and makes use of long-term windrose data for the Chicago area. The dependence is shown in Figure 6. For very short residence times, the fraction of emissions entering the lake is essentially equal to the fraction of time the wind blows over the lake. The fraction begins to decrease significantly when the residence time approaches the mean transit time of an air parcel across the lake. For a residence time of 10 h, the efficiency is about 25%. Since our estimate of the 1972 lead emissions is 2900 metric tons, and assuming, as before, that the total atmospheric input is uniformly distributed in the water and the rate of deposition in the upper two-thirds of the lake is the same as in the southern part, the atmospheric contribution to the sediments would be $0.31 \times 2900 \times 0.25 = 225$ metric tons. This value is in remarkable agreement with our estimate of the amount of lead deposited in the sediments in 1972, considering the many approximations involved.

There is an alternative means of estimating the flux from the atmosphere by examining the concentration in rain water and air. The flux of lead in precipitation in the Chicago area (~100 μg cm⁻² yr⁻¹) as reported by Lazrus is predictably much higher than expected over the lake because the collection sites were within the metropolitan area (20). Similarly, the concentrations in aerosols collected by high-

volume air samplers in and around Chicago and northwestern Indiana by Harrison undoubtedly do not represent mean concentrations over the lake. The concentration of lead in urban air averaged about $2 \mu\text{g}/\text{m}^3$, while the lowest value of lead observed in outlying rural areas was $0.1 \mu\text{g}/\text{m}^3$ (21). These values are consistent with the range of lead concentrations measured over Lake Michigan by Gillette (downwind $0.2\text{--}1.4 \mu\text{g}/\text{m}^3$, and upwind $0.01\text{--}0.6 \mu\text{g}/\text{m}^3$) (22). Hesse measured the atmospheric concentration of lead along the eastern shore of Lake Michigan, and found a mean concentration of $\sim 0.03 \mu\text{g}/\text{m}^3$ (23). If this can be taken as the average atmospheric concentration of lead over the lake, it would correspond to a mean flux of

$$V_t \times 0.03 \times 3.17 \times 10^7 \approx 1.5 \mu\text{g cm}^{-2} \text{yr}^{-1}$$

comparable to the average value estimated from the lead found in the sediments.

Nonatmospheric Inputs. We have not considered so far in this inventory inputs of anthropogenic lead from sewers, storm runoff, or rivers. The magnitude of the inputs of lead from unpolluted streams has been calculated by Winchester and Nifong (8) from the data summarized by Turekian (24) to be 100 metric tons/yr. If this loading is uniformly mixed in the water column and deposited over the whole lake, the natural loading of lead in the southern basin is about 30 tons/yr, which is in agreement with our estimate.

Because the flow of the Chicago River was diverted away from the lake in about 1900, a potentially considerable source of nonatmospheric anthropogenic lead was eliminated. However, there are undoubtedly significant contributions of lead from three major, relatively polluted rivers, the Grand, Kalamazoo, and St. Joseph, which flow into the southern basin (14).

River-borne contributions of anthropogenic lead to freshwater environments will have a more localized pattern of deposition than atmospheric contributions. Koide and Goldberg have shown that heavy metals, such as lead and mercury entering ocean waters from rivers or sewer outfalls, are quickly removed and associate with the sediments within several kilometers of the discharge site (25). Tierney has found that the concentrations of several trace elements (Fe, Zn, Cu, Cr) in Lake Michigan surface waters 1 mi out from the mouth of the Grand and St. Joseph Rivers (Figure 1) are markedly higher than in water 10 mi offshore (26). In contrast, corresponding inshore-offshore concen-

Table III. Comparison of Stable Lead and Lead-210 Fluxes at $z = 0$ (1972)

Core	Anthropogenic stable lead		Unsupported lead-210			
	Mass sedimentation rate, $\text{g}/\text{cm}^2/\text{yr}$	Concentration, $\mu\text{g}/\text{g}$	Flux, $\mu\text{g}/\text{cm}^2/\text{yr}$	Activity, pCi/g	Flux, $\text{pCi}/\text{cm}^2/\text{yr}$	Ratio, $F_{\text{Pb-210}}/F_{\text{Pb}}$
17	0.012	123.	1.5	15.4	0.19	8
29	0.094	243.	23	14.7	1.4	17
31	0.018	246.	4.4	11.1	0.20	22
105	0.015	180.	2.7	17.7	0.26	10

tration differences are not seen in northern Lake Michigan around Charlevoix, presumably because of the lack of significant discharges from polluted rivers into inshore waters in that area (26). Since the zone of high postglacial sediment accumulation shown in Figure 1 is clearly a sink for river-borne sediments, elevated fluxes of lead would be expected where the polluted river waters enter the lake. The calculated fluxes to the lake in 1972 at stations IGS-107 and UMAN-29 $\sim 20 \mu\text{g}/\text{cm}^2/\text{yr}$, both located within the 9-m contour, are higher by about a factor of four than the flux averaged over the remaining stations, $\sim 5 \mu\text{g}/\text{cm}^2/\text{yr}$, (Figure 1 and Table I). This difference in flux of $\sim 15 \mu\text{g}/\text{cm}^2/\text{yr}$ corresponds to a total of 30 tons/yr within the 9-m contour, compared with the expected 3 metric tons/yr due to "natural" inputs. The ratio of "excess" anthropogenic lead loading to natural lead, ~ 10 , compares favorably with the ratio of lead on "settleable" solids in polluted rivers to that expected in natural waters. The mean concentration of lead in "settleable" solids in three polluted rivers, the Grand, Kalamazoo, and St. Joseph, is about $170 \mu\text{g}/\text{g}$ (26). The expected concentration of lead in suspended solids from unpolluted water may be assumed to be the same as the preculculation concentration measured in the sediments ($23 \mu\text{g}/\text{g}$) which gives a ratio of $170/23 \approx 7$.

Comparison of ^{210}Pb and Stable Lead Fluxes. Further evidence of river-borne lead contributions can be seen from a comparison of lead and lead-210 fluxes. The atmospheric flux of lead-210 is known to be essentially constant in this latitude band (27).

Because of the high affinity of soils for lead, a minor fraction of the ^{210}Pb deposited over land will be eroded or washed into streams and then enter the lake via runoff. In contrast, a large proportion of the stable lead emitted to the atmosphere, particularly from automobiles (75% or 6000 tons/yr), is deposited on paved areas after rainstorms. This is readily transported to streams after rainfall because of very efficient surface drainage along highways to prevent flooding. Since lead used in the manufacture of tetraethyllead contains very low concentrations of ^{210}Pb (28) and the concentration of ^{210}Pb in soil is $\sim 1 \text{ pCi}/\text{g}$, runoff of lead from streams would not be expected to contribute a significant concentration of unsupported ^{210}Pb to the sediments. Consequently, higher values of the ratio of lead to lead-210 fluxes would be expected in those areas where there is a significant input of terrigenous material via stream runoff, particularly if the stable lead entering the basin is associated with heavy particles which settle out readily in the inshore region where the rate of sedimentation is greatest. This effect can be seen from the data given in Table III. In two widely spaced offshore locations, UMAN-17 and 105, the lead to lead-210 flux ratio is about 10. Each location is normal with respect to the flux of lead-210, in the sense that the flux to the sediments is very nearly equal to the estimated flux to the lake surface ($\sim 0.2 \text{ pCi}/\text{cm}^2/\text{yr}$). The two

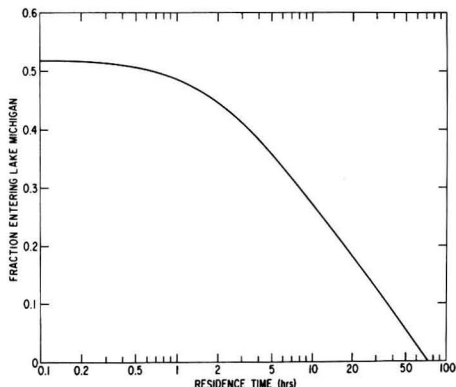


Figure 6. Fraction of emissions from Chicago-Gary which enter Lake Michigan as function of atmospheric residence time

inshore locations, UMAN-29 and 31, are very different in terms of their annual flux of lead-210. The flux of lead-210 at station 31 (0.2 pCi/cm²/yr) is not significantly different from fluxes found offshore, but at station 29 is considerably higher indicating preferential scavenging and deposition in the area of this latter station. In contrast, the lead to lead-210 flux ratios at these two locations are quite comparable and are about a factor or two higher than the offshore ratios.

If the lead and lead-210 derived from the atmosphere are chemically indistinguishable and have the same history of transport and deposition in the water column, the normal values of the flux of lead-210 at offshore stations suggest that most of the anthropogenic lead at these offshore locations originates also from the atmosphere. In this case, the atmospheric lead contribution at stations possessing significant terrigenous lead may be inferred from the data given in Table III. The stable lead flux to the sediments from atmospheric inputs is approximately nine times the unsupported flux of Pb-210 to the sediments in 1972. Table IV shows the total lead flux to the sediments separated into background, atmospheric, and nonatmospheric parts according to the above relation. It can be seen that the nonatmospheric part at station UMAN-29 (10 μg/cm²/yr) is very comparable to the value of 12 μg/cm²/yr derived from our previous consideration of the "excess" flux at this station. Thus, the measurement of both lead and lead-210 in the same cores seems to provide a means of distinguishing atmospheric and nonatmospheric inputs. Therefore, Pb-210 is a tracer for that part of the lead in the aquatic system which originates from atmospheric inputs. It must be recognized that these results are quite speculative and will require confirmation by taking additional cores to delineate the inshore and offshore patterns of deposition more accurately.

Appendix

Details of the Mathematical Model. In this model, we assume that neither lead nor lead-210 has a significant diffusional mobility in the sediments, although we shall allow for the effects of redistribution of lead associated with sediment solids through mechanical mixing. Let the time parameter, t , arbitrarily be set to zero at some convenient preindustrial date, say 1700. If $J_a^c(t)$ is the total atmospheric emissions rate and $J_a^g(t)$ is the corresponding rate for combustion of leaded gasoline, then the expected total atmospheric emission rate (tons/year) would be:

$$J_a(t) = k J_a^c(t) + J_a^g(t) \quad t \leq 260 \text{ years}$$

and

$$J_a(t) = J_a^c(t) + J_a^g(t) \quad 260 < t \leq 272 \text{ years} \quad (1a)$$

where k is the proportion of coal-derived lead before 1960. In view of our previous discussion, we expect that k should be greater than unity.

The total lead loading of the lake then should be proportional to the atmospheric emissions rate plus several other time-dependent terms: $J_s(t)$, the anthropogenic lead loading by all tributaries; $J_d(t)$, the anthropogenic lead loading by all direct discharges; and $J_o(t)$, the natural component of the loading from all tributaries and the atmosphere. Each term is expressed in tons/year. The total loading of the lake is then given by:

$$J(t) = \beta' J_a(t) + J_s(t) + J_d(t) + J_o(t) \quad (2a)$$

where β' is the proportion of atmospheric lead emissions that enter the lake.

Table IV. Sources of Lead in Lake Michigan Sediments
Flux to the Sediments in 1972, μg/cm²/yr

Station	Total	Anthropogenic		Back-ground
		Atmospheric	Nonatmospheric	
17	2.0	1.7	~0	0.3
29	25	13	10	2
31	4.8	1.8	2.6	0.4
105	2.7	2.3	~0	0.4

If it is assumed that the anthropogenic lead loading from direct discharges and stream runoff are also proportional to $J_a(t)$, and that $J_o(t)$ is a constant = J_o , then:

$$J(t) = \beta J_a(t) + J_o \quad (3a)$$

where β is a constant of proportionality taking account of the fraction of atmospheric, tributary, and direct discharge sources of lead entering the lake.

To calculate the effect of the residence time of lead in the water column on its distribution in the sedimentary column, we assume instantaneous, uniform mixing (29) of the input within the volume of the lake, V . If Q is the outflow rate, then the concentration, C , of lead in the water column is given by:

$$V \frac{dc}{dt} = J(t) - QC - J_{sed}(t) = \beta J_a(t) + J_o - QC - J_{sed}(t) \quad (4a)$$

where $J_{sed}(t)$ is the total flux of lead to the sediments [cf. Robbins and Edgington (30)]. If the lead is removed from the water column through attachment to settling particles, we may reasonably expect that the flux is proportional to the concentration, or:

$$J_{sed}(t) = Q'C \quad (5a)$$

where Q' is the "flow rate" to the sediment. In this case, Equation 4a has the solution (31):

$$C = C_o + \frac{\beta}{V} \int_0^t e^{\alpha(t-\varphi)} J_a(\varphi) d\varphi \quad (6a)$$

where:

$$\alpha = (Q + Q')/V \text{ and } C_o = J_o/\alpha V$$

and α^{-1} is the residence time. Since the residence time of lead in natural waters is very short, of the order of a year (25), for all practical purposes Equation 6a may be replaced by:

$$C = C_o + \beta J_a(t)/\alpha V \quad (7a)$$

and the mean flux of lead to the sediments is given by:

$$\bar{F}_{Pb} \equiv \frac{J_{sed}(t)}{A} \equiv \left[\frac{Q}{Q + Q'} \right] \left[\frac{J_o + \beta J_a(t)}{A} \right] \quad (8a)$$

where A is the area of the lake. Since $V/Q \approx 100$ years while V/Q' is the order of a few years, $Q' \gg Q$ and the mean flux may be written as:

$$\bar{F}_{Pb} = \frac{1}{A} [J_o + \beta J_a(t)]$$

We now assume that the flux of lead to a given location in the basin is proportional to the mean flux. This allows us to separate spatial and time variables. The expected lead concentration in the sediment (μg/g) is given by:

$$C(t) = f'[\beta J_a(t) + J_o] = f J_a(t) + C_{bg} \quad (10a)$$

where f' is a function of coring location and C_{bg} is the pre-culcational concentration of lead. The concentration in surface sediment will be:

$$C_s = fJ_a(272) + C_{bg} \quad (11a)$$

if R is the sedimentation rate (cm/yr), then at depth z :

$$C_{Pb}(z) = fJ_a \left(\frac{272R - z}{R} \right) + C_{bg} \quad (12a)$$

provided the sedimentation rate is uniform and there is no sediment compaction. The correspondence between R and t when there is significant compaction, was developed in a previous paper by Robbins and Edgington (7). There it was shown that the age vs. depth relationship is given by:

$$T = \frac{\rho_s}{\omega} \int_0^z [1 - \phi(\xi)] d\xi \quad (13a)$$

where ϕ is the porosity and ρ_s is the mean density of sediment solids. Such compensation for the effects of compaction are included in the application of the model below to the lead distributions.

However, comparison of the ^{210}Pb and ^{137}Cs distributions has shown (7) that in some cases there are vertical mixing effects. The stable lead distribution at stations 29 and 31 show the same patterns as were observed for ^{210}Pb and ^{137}Cs —viz., an almost constant concentration of lead within the upper 4 or 2 cm respectively. This pattern is found, as well, for many other elements strongly associated with sediment solids (32). The redistribution of sediment in the upper few centimeters, which may be due to bioturbation and microturbulence, has the effect of distributing the lead deeper into the core than would be expected in undisturbed sediments [cf. Davis (33)].

We derive here an integral form of the model developed previously by Robbins and Edgington (7) in terms of a finite sum. Let S (cm) be the thickness of the mixing zone at the top of the sedimentary column. At time t (yr) the concentration ($\mu\text{g/g}$) within this zone is $C_m(t)$. At time $t + \delta t$ new sediment having a concentration $C(t + \delta t)$ is added at the top of the core. This material is assumed to be instantly distributed throughout the mixing zone which has moved upward by an amount $R\delta t$. The new concentration within the zone is then

$$C_m(t + \delta t) = \frac{C(t + \delta t) \cdot R\delta t + C_m(t) \cdot (S - R\delta t)}{S} \quad (14a)$$

the rate of change of C_m is then

$$\frac{\delta C_m}{\delta t} = \frac{C_m(t + \delta t) - C_m(t)}{\delta t} = \gamma [C(t + \delta t) - C_m(t)] \quad (15a)$$

passing to the limit as $\delta t \rightarrow 0$ and integrating, the solution is (31)

$$C_m(t) = \gamma \int_0^t e^{\gamma(t-\tau)} C(\tau) d\tau \quad (16a)$$

where $\gamma = R/S$.

Thus the concentration of lead will be

$$C_{Pb}^{\text{mix}}(t) = f\gamma \int_0^t e^{\gamma(t-\tau)} J_a(\tau) d\tau + C_{bg} \quad (17a)$$

for $t < \gamma^{-1}$ and

$$C_{Pb}^{\text{mix}}(t) = C_{Pb}(1/\gamma) \text{ for } t \geq 1/\gamma$$

At time t , the base of the mixing zone will be located at $R(272 - t) + S$ centimeters. So for $z > S$

$$C_{Pb}^{\text{mix}}(z) = C_{Pb}^{\text{mix}} \left(272 - \frac{(z - S)}{R} \right)$$

and for $z \leq S$

$$C_{Pb}^{\text{mix}}(z) = C_{Pb}^{\text{mix}}(272) \quad (18a)$$

Note that the effects of residence time and vertical mixing are not mathematically distinguishable except for the zone of constant concentration as can be seen from comparison of Equations 6a and 17a. This is built into the linear model, which makes no distinction between mixing within a zone at the top of the sediments or in the overlying column of water.

The effect of sectioning the cores in finite intervals has been included by integrating Equation 18a over the appropriate depth interval.

Acknowledgments

We would like to express our appreciation to Capt. R. Thibault and the crew of the University of Michigan R/V *Inland Seas* for their invaluable help in obtaining cores for this study; to M. M. Thommes and K. Johansen for their assistance in the field work; and to J. O. Karttunen for the analytical effort.

Literature Cited

- (1) Chow, T. J., Bruland, K. W., Bertine, K., Soutar, A., Koide, M., Goldberg, E. D., *Science*, **181**, 581-2 (1973).
- (2) Bruland, K. W., Bertine, K., Koide, M., Goldberg, E. D., *Environ. Sci. Technol.*, **8**, 425-32 (1974).
- (3) Crecelius, E. A., Piper, D. Z., *ibid.*, **7**, 1053-5 (1973).
- (4) Shimp, N. F., Schleicher, J. A., Ruch, R. R., Heck, D. B., Leland, H. V., *Ill. Geol. Survey, Environ. Geol. Note*, **41**, (1971).
- (5) Lineback, J. A., Gross, D. L., *ibid.*, **58**, 1-25 (1972).
- (6) Lineback, J. A., Gross, D. L., Meyer, R. P., *ibid.*, **54** (1972).
- (7) Robbins, J. A., Edgington, D. N., *Geochim. Cosmochim. Acta*, **39**, 285-304 (1975).
- (8) Winchester, J. W., Nifong, G. D., *Water, Air, Soil Pollut.*, **1**, 50-64 (1971).
- (9) U.S. Department of Commerce, "Historical statistics of the United States 1789-1945", Bureau of the Census, Washington, D.C., 1952.
- (10) U.S. Department of Commerce, "Statistical Abstract of the United States, 1974", 1974.
- (11) Harrison, P. R., Chicago Department of Environmental Quality, personal communication.
- (12) Leland, H. V., Shukla, S. S., Shimp, N. F., "Factors affecting distribution of lead and other trace elements in sediments of southern Lake Michigan", "Trace Metal and Metal-Organic Interactions in Natural Waters", P. C. Singer, Ed., pp 89-129, Ann Arbor Science, Ann Arbor, Mich., 1973.
- (13) Nriagu, J. O., *Geochim. Cosmochim. Acta*, **37**, 367-7 (1973).
- (14) Robbins, J. A., Landstrom, E., Wahlgren, M. A., *Proc. 15th Conf. Great Lakes Res.*, pp 270-90, Int. Assoc. Great Lakes Res., Ann Arbor, Mich., 1972.
- (15) Skibin, D., *Water, Air, Soil Pollut.*, **2**, 405-7 (1973).
- (16) Sehmel, G. A., Sutter, S. L., Pacific Northwest Laboratory Annual Report for 1973, BNWL (Part 3) 171-4, 1974.
- (17) Cawse, P. A., "A Survey of Atmospheric Trace Elements in the U.K. (1972-1973)", United Kingdom Atomic Energy Authority Report, AERE R7669, 1974.
- (18) Hicks, B., Argonne National Laboratory, personal communication.
- (19) Moses, H., Gatz, D. F., Strong, A. C., Zerbe, G. A., Argonne National Laboratory Radiological Physics Division Annual Report, Environmental Studies, ANL-7760 (Part III) 84-108, 1970.
- (20) Lazrus, A. L., Lorange, E., Lodge, J. P., Jr., *Environ. Sci. Technol.*, **4**, 55-8 (1970).
- (21) Harrison, P. R., "Area-Wide Distribution of Lead, Copper, Cadmium and Bismuth in Atmospheric Particles in Chicago and Northwest Indiana: a Multisample Application and Anodic Shipping Voltammetry", PhD Thesis, University of Michigan, Report 01173-4-T, 1970.
- (22) Gillette, D. A., "A study of aging of lead aerosols", *ibid.*, Report 01173-3-T (1970).
- (23) Hesse, J. L., "Heavy Metals in the Atmospheric Samples along Michigan's Shoreline of Lake Michigan, Lake Michigan Toxic Substances Com. Report, Michigan Water Resources Commission, Bureau of Water Management, Department of Natural Resources, State of Michigan, 1973.
- (24) Turekian, K. K., "Elements, Hydrosphere Distribution. 1969

- Yearbook of Science and Technology", McGraw-Hill, New York, N.Y., 1969.
- (25) Koide, M., Goldberg, E. D., *Science*, 134, 98-9 (1961).
- (26) Tierney, D. P., In "Lake Michigan Toxic Substances Committee Report", Michigan Water Resources Commission, Bureau of Water Management, Department of Natural Resources, State of Michigan, 1973.
- (27) Jaworowski, Z., *Nature*, 212, 886-9 (1966).
- (28) Weller, R. I., Anderson, E. C., Baker, J. L., Jr., *ibid.*, 206, 1211-12 (1965).
- (29) Rainey, R. H., *Science*, 155, 1242-3 (1967).
- (30) Robbins, J. A., Edgington, D. N., "Radiological and Environmental Research Division Annual Report (Part III) January-December 1972", pp 31-53, Argonne National Laboratory, ANL-7960, 1973.
- (31) Agnew, R. P., "Differential Equations", 180 pp, McGraw-Hill, New York, N.Y., 1942.
- (32) Edgington, D. N., Robbins, J. A., unpublished data.
- (33) Davis, R. B., In "Quaternary Paleoecology", E. J. Cushing and H. E. Wright, Eds., pp 153-7, Yale University Press, New Haven, Conn., 1967.

Received for review June 30, 1975. Accepted November 12, 1975. Work supported by the U.S. Energy Research and Development Administration.

Diffusive Collection of Aerosol Particles on Nuclepore Membrane Filter

Terence N. Smith¹, Colin R. Phillips*, and Octavio T. Melo²

Department of Chemical Engineering and Applied Chemistry, University of Toronto, Ont., M5S 1A4, Canada

Recoveries of aerosol particles on a Nuclepore filter with pores of 3.0- μm diameter are measured using a condensation nuclei counter. Substantially larger values than those expected for capture by diffusion to the walls of the pores are found, and it is concluded that diffusion to the face of the filter is the dominant mechanism for recovery of particles in this filter geometry. Experimental results are presented, and a means of generalization to filters with pores having length-to-diameter ratios different from that of the 3.0- μm filter is suggested.

Because of its availability in pore diameters ranging down to 0.03 μm , the Nuclepore membrane filter has commanded much interest in its potential application to the sampling and, possibly, to the size analysis of aerosols. In its standard form, it is a polycarbonate film, 10 μm in thickness, through which parallel, straight pores of uniform, circular section have been etched following sensitization by irradiation. A full description of the filter and its properties is available from the manufacturer, Nuclepore Corp., Pleasanton, Calif. 94566.

The mechanisms by which particles are arrested in the Nuclepore filter have been identified by Spurny and Pich (1). Efficiencies for the separate processes of inertia, interception, and diffusion have been defined and related to the governing variables such as particle size, aerosol approach velocity, and filter pore size in further work by Spurny and Pich (2) and by Spurny et al. (3). Exploitation of the dependence of collection efficiency of a given particle size on filter pore size and aerosol velocity in the determination of particle size distributions in aerosols has been suggested by Spurny et al. (4) and pursued by Melo and Phillips (5). For such purposes, it is essential that the relationship between particle size and collection efficiency be closely defined.

An improved estimate of the recovery of particles (collection efficiency) by the inertial mechanism is the subject of a recent study by Smith and Phillips (6). Computations of the flow pattern of a real fluid entering a pore and of the

trajectories of particles through this flow are used to derive the collection efficiency of the filter.

Interception is also considered in the same work. The flow profile of the aerosol at the entrance to a pore is almost completely developed to that for laminar flow in a tube. Recoveries by interception should, accordingly, be reckoned from this profile rather than from the rectangular profile sometimes assumed. Because there is comparatively little flow near the wall of the pore, recovery by interception in the laminar profile is much smaller than in the rectangular profile. Figure 1 shows the respective recoveries as functions of the ratio of particle diameter to pore diameter, derived from

$$1 - \eta_P = \left(1 - \frac{d}{D}\right)^2 \quad (1)$$

for the rectangular profile and from

$$1 - \eta_P = \left(1 - \frac{d}{D}\right)^2 \left[2 - \left(1 - \frac{d}{D}\right)^2\right] \quad (2)$$

for the laminar profile.

The differences in recoveries are large enough to explain the necessity for Spurny et al. (3) to introduce a modifying factor of 0.15 and for Spurny and Madelaine (7) to refine the factor further when inserting interception recoveries based on the rectangular profile into an expression for total recovery by a Nuclepore filter.

Diffusive recovery is usually estimated from a solution to the equation for the diffusion of particles across the laminar fluid flow profile to the wall of the pore. The approximate result of Twomey (8)

$$\begin{aligned} \eta_D = 1 - & 0.81904 \exp(-7.3136 X D) \\ & - 0.0972 \exp(-44.609 X D) \\ & - 0.03248 \exp(-113.9 X D) \\ & - 0.0157 \exp(-215.2 X D) \end{aligned} \quad (3)$$

is used for this purpose. In this equation, the product $X D$ is the term $2e(L/D)/(UD/D)$. Certainly this is a proper means of accounting for diffusion to the walls but it appears from the experiments discussed subsequently that there can also be a considerable contribution to recovery of particles by diffusion from the approaching aerosol to the face of the filter.

¹ Present address, Department of Chemical Engineering, University of Adelaide, Adelaide, 5001, Australia.

² Present address, Ontario Hydro, 800 Kipling Ave., Toronto, Ont., Canada.

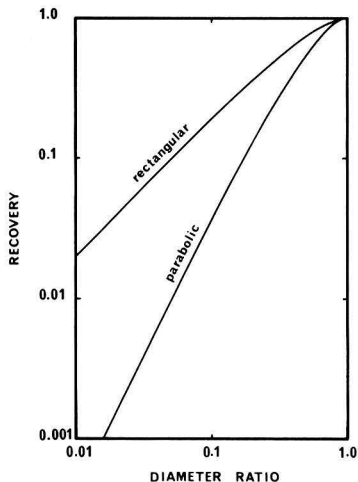


Figure 1. Comparison of recoveries by interception from laminar and rectangular flow profiles

Experiments on Diffusive Recovery

Some experiments on the recovery of particles of uranine dye in Nuclepore filters with 3.0- μm pores are reported below. Over the ranges of the variables examined, the dominant mechanism for recovery is diffusion since the ratio of particle diameter to pore diameter is small and the particle Stokes number, which is an index of its propensity for inertial recovery, is small.

The apparatus used in the tests is shown schematically in Figure 2. A solution of uranine dye in methanol is atomized with nitrogen and passes to a cyclone which eliminates the larger droplets. A pump takes some of the aerosol to a tee where it joins a stream of dry nitrogen and then passes to a reservoir. Dry aerosol leaving the reservoir is exposed to radiation from a β -source (phosphorus 32) to dissipate any electrostatic charge before entering the filter train. The train consists of a preparation filter with a pore size chosen to limit the maximum size of the aerosol particles followed by a series of four filters each having the pore size under test. Because passage through each filter tends to sharpen the size distribution, the aerosol reaching the last test filter is nearly monodisperse. Flows through the preparation filter and the main filter train are regulated by venting or dilution and are measured using flow meters or, where necessary, readings of pressure drop across calibrated filters. Control of aerosol particle size is exercised primarily by varying the concentration of dye in solution and subsequently by the pore size of and the velocity through the preparation filter.

Particle concentrations entering and leaving the test filter are measured using a condensation nuclei counter, Model Rich 100, Environment One Corp., Schenectady, N.Y. Efficiencies are, in consequence, based on particle number rather than particle mass.

Particle size is determined from electron microscopy either of filter surfaces or of samples of particles collected electrostatically from the stream passing the test filter.

Details of the atomizer and of the electrostatic sampler are given by Melo (9).

It is worth remarking that, though provided for in the apparatus, β -irradiation to disperse electrostatic charge is unnecessary. There is no difference between the performances of the filters with and without the irradiation.

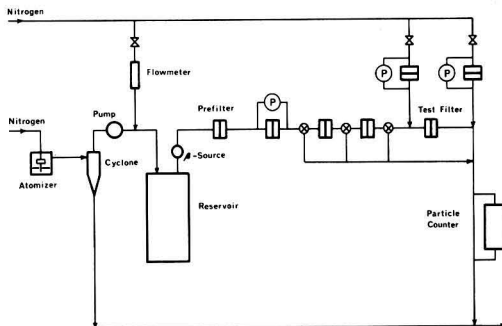


Figure 2. Scheme of apparatus

Results

Some results for aerosols ranging in diameter from 0.12–0.23 μm are shown in Figure 3 where a comparison is made with recoveries by diffusion to the walls of the pore calculated from Equation 3.

The Nuclepore filter is evidently much more effective in removing particles than it would be if diffusion to the walls of the pores were the only mechanism of collection. The possible scale of errors arising in measurements of the particle size and estimates of its diffusivity according to the usual formula

$$D = \frac{kT}{3\pi\mu d} \left(1 + 2A \frac{\lambda}{d}\right) \quad (4)$$

where A , the Cunningham correction factor, is much too small to raise doubt concerning the reality of the effect.

It can be inferred from the results that mechanism of collection is a diffusive process because recovery remains correlated with the ratio UD/D which is the determining parameter in solutions of the diffusion equation.

The most ready explanation is that there must be diffusion of particles to the face of the filter from the approach-

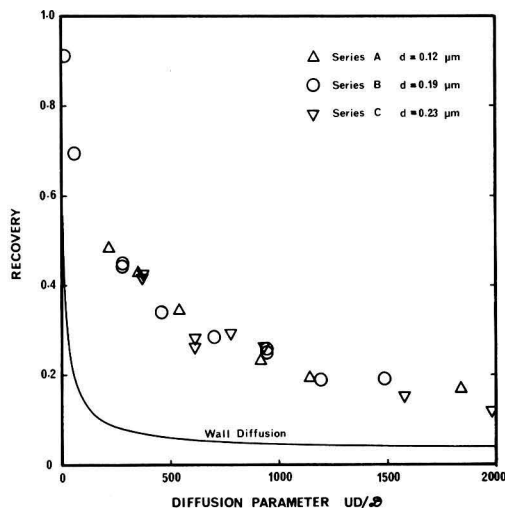


Figure 3. Recoveries of aerosols in 3.0 μm filter

ing aerosol. Indeed, under the conditions of operation in these tests, this should be the principal mechanism. Almost as much area is offered by the face of the filter with porosity 0.11 as by its 3- μm diameter, 10- μm long pores. With convection toward the face and a relatively long exposure time by comparison with the transit time through the pores, much more diffusion to the face than to the walls of the pores must be expected. In thinner filters or those with larger pores, the effect would be even more pronounced. Only in filters with large ratios of pore length to pore diameter would collection at the wall predominate, giving efficiencies as expected from Equation 3.

Diffusion to the face of the filter has been reported previously by Kirsch and Spurny (10) using NaCl aerosol of diameter less than 0.04 μ , in which case 23–37% of the particles were deposited on the face of the filter. The mechanism was also noted subsequently by Spurny (11).

Proper analysis of the efficiency of collection by diffusion requires a solution of the convection and diffusion equations in the geometry of the filter face and pore wall system. Such a solution is not easily obtained. A correlation of measured efficiencies in a system of fixed geometry can, however, be made using the parameter UD/D which is effectively a ratio of convective effects to diffusive effects. Figure 3 is just such a correlation. It may be used to estimate efficiencies of recovery by diffusion in all filters with the same porosity and the same ratio of pore length to pore diameter as in the test filter.

Results that can be applied to filters with, again, the same porosity but with various length-to-diameter ratios can be obtained by separating the face and wall effects. This can be done by choosing a level of efficiency on Figure 3 and reading the corresponding values of UD/D for both the wall diffusion line and the experimental line. If the increased experimental efficiency owing to the effect of the face is regarded as having been obtainable alternatively by an equivalent additional length of pore, the ratio $(UD/D)_{\text{total}} : (UD/D)_{\text{wall}}$ is the appropriate multiple of the actual L/D of the pores of the test filter. To estimate the recovery of a filter with any combination of pore length and diameter, the L/D inserted into Equation 3 is increased by adding the value of this multiple, minus 1.

For applications of the recovery by diffusion in aerosol particle size analysis, it is especially useful if a simple expression can be developed to represent the relationship between efficiency and its governing variables. If the efficiencies presented in Figure 3 are plotted against a function of the form $K/(K + UD/D)$, where K is a constant, rather than against the parameter UD/D directly, linear relationships can be obtained with proper choices of the values of K . Figure 4 shows the results of correlating the efficiencies in this way. Best fits to the data are obtained with values of K of 280 for the measured efficiency and 11 for efficiency of collection by diffusion to the wall. The relationships between efficiency and the parameter UD/D are then

$$\eta_D = \frac{280}{280 + UD/D} \quad (5)$$

for measured efficiency and

$$\eta_D = \frac{11}{11 + UD/D} \quad (6)$$

for diffusion to the wall.

An incidental advantage of this form of representation is that it is easy to force the result for wall diffusion alone to

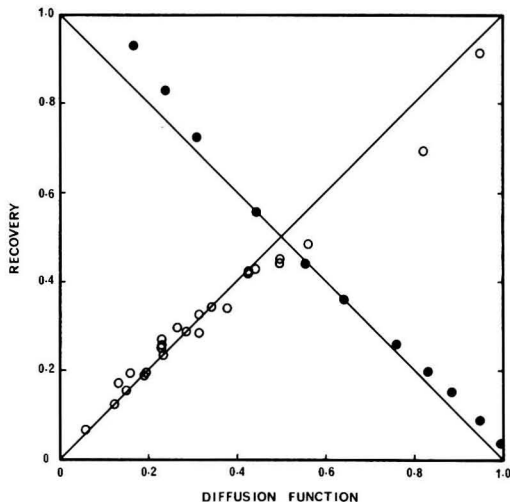


Figure 4. Approximate correlation of experimental particle recoveries using functions $280/(280 + UD/D)$ for whole filter (open circles) and $11/(11 + UD/D)$ for wall diffusion (full circles). For clarity, values of $(1 - \eta_D)$ rather than of η_D have been plotted for the wall diffusion results

pass to zero as UD/D nears infinity. This is a physical requirement which is not met by Equation 3 because it is a truncation of a series solution to the diffusion equation.

It must be remarked that the efficiencies found in this study are substantially greater than those reported for similar membrane filters by Spurny et al. (3). Perhaps the explanation lies in the different means of determination of particle concentration. Number concentrations measured with the condensation nuclei counter are used in this work whereas mass concentrations are found by Spurny et al. For a truly monodisperse aerosol, there is, of course, no reason for different concentrations to be found. If there is some spread of particle size, however, serious differences could appear. The filter collects the finest particles most completely and the largest particles least well. The fine particles, which are "overcollected" in relation to the main body of aerosol, contribute fully to numbers but add little to mass. The large particles are "undercollected" and diminish the number accordingly but cause a large deficit in mass. Mass-based efficiencies must therefore be smaller than number-based efficiencies. It is not possible to be specific about the sizes of the variations without some definition of the actual size distributions of the aerosols under consideration.

Because the test aerosols in these experiments could not be completely monodisperse, there remains some uncertainty about the measured efficiencies. This is regarded as minimal, however, because of the precaution to have a series arrangement in the filter tests. Such a system tends to truncate the fine end of the size spectrum, to which efficiencies based on particle count are sensitive. Numerous electron micrographs, taken during the B-series tests, showed a uniform particle diameter.

Conclusion

Recovery of aerosol particles by diffusion in Nuclepore filters of 3.0 μm or in other membrane filters with the same proportions should be reckoned from the relationship shown in Figure 3.

If the ratio of pore length to pore diameter is smaller or

larger than in this filter, an allowance as noted in the Discussion must be applied.

Together with the recovery by the mechanism of inertia and interception, for which the results of Smith and Phillips (6) can be used, these results give the total recovery for a specific size of aerosol particle in a Nuclepore filter. The response of overall recovery to particle size is easily determined and can be applied to equipment using this principle for the determination of particle size distribution in an aerosol.

In the range of very fine particle size where diffusion is the dominant mechanism, the recovery is defined conveniently by the approximation to the experimental data expressed in Equation 5.

Acknowledgment

Ida P-C Fok assisted in the experimental work.

Nomenclature

- d = particle diameter
 e = filter porosity
 k = Boltzmann constant
 A = Cunningham correction factor for particle resistance
 D = filter pore diameter
 K = experimental constant
 L = filter pore length
 T = temperature
 U = aerosol approach velocity

- X = parameter in Equation 3, equal to $2eL/D^2U$
 λ = molecular mean free path in gas
 η_D = efficiency of particle collection by diffusion
 η_P = efficiency of particle collection by interception
 μ = gas viscosity
 \mathcal{D} = particle diffusivity

Literature Cited

- (1) Spurny, K. R., Pich, J., *Collect. Czech. Chem. Commun.*, **28**, 2886 (1963).
- (2) Spurny, K. R., Pich, J., *ibid.*, **30**, 2276 (1965).
- (3) Spurny, K. R., Lodge, J. P., Frank, E. R., Sheesley, D. C., *Environ. Sci. Technol.*, **3**, 453 (1969).
- (4) Spurny, K. R., Lodge, J. P., Frank, E. R., Sheesley, D. C., *ibid.*, p 464.
- (5) Melo, O. T., Phillips, C. R., *ibid.*, **8**, 67 (1974); *ibid.*, **9**, 560-4 (1975).
- (6) Smith, T. N., Phillips, C. R., *ibid.*, **9**, pp 564-8.
- (7) Melo, O. T., Madelaine, G., *Collect. Czech. Chem. Commun.*, **36**, 2857 (1971).
- (8) Twomey, S., *Bull. Observ. Puy Dome*, **10**, 173 (1962).
- (9) Melo, O. T., M. Appl. Sc. Thesis, Department of Chemical Engineering, University of Toronto, 1972.
- (10) Kirsch, A. A., Spurny, K. R., *J. Appl. Mech. Tech. Phys.* (Russ.), **3**, 109-112 (1969).
- (11) Spurny, K. R., Aerosol "Filtration by Means of Analytical Pore Filters", "Assessment of Airborne Particles", p 60, T. T. Mercer, D. E. Morrow, and W. Stober, Eds., published by Charles C Thomas, Illinois, 1972.

Received for review September 23, 1974. Accepted October 13, 1975. Work supported by the Atmospheric Environment Service, Environment Canada.

Continuous Determination of Free Cyanide in Effluents Using Silver Ion Selective Electrode

M. Hofton

British Steel Corp., Research Centre, Skippers Lane, Middlesbrough, Cleveland, England

■ This report describes the development of a monitor for the continuous determination of free cyanide in effluents and rivers at concentration levels between 0.01 and 1 $\mu\text{g ml}^{-1}$. The report describes the equipment required by the monitor based upon a silver ion selective electrode and discusses the effect of potential interferents likely to be found in complex steelworks effluents. Details of an on-line trial monitoring free cyanide in a steelworks effluent over a two-week period is also presented in the report with the results being compared with manual, daily check analysis.

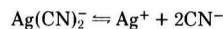
The highly toxic cyanide ion is one of the most difficult species to determine in complex liquors, particularly at levels below 0.05 $\mu\text{g ml}^{-1}$, a common-consent-to-discharge concentration imposed by Water Authorities.

The ion-selective electrodes already available and devised primarily to determine cyanide down to 0.03 $\mu\text{g ml}^{-1}$ (1) suffer from numerous disadvantages including erosion of the membrane and interference from other ions such as chloride. These electrodes are based on silver iodide or mixed silver iodide/silver sulfide membranes. Frant et al. (2), however, have described the use of a silver sulfide crystal membrane electrode coupled with a standard addition technique for the indirect determination of cyanide. The method can be used at levels below 0.03 $\mu\text{g ml}^{-1}$ without

the associated disadvantages of the other type of electrode. Because of the need for "standard addition", however, the method developed by Frant et al. cannot be easily adapted for the continuous determination of free cyanide in effluents. The present paper describes the use of this measurement system adapted for continuous monitoring.

Theory

In the method of Frant et al. a $K\text{Ag}(\text{CN})_2$ indicator solution is added to the test solution where any cyanide ions present disturbs the equilibrium:

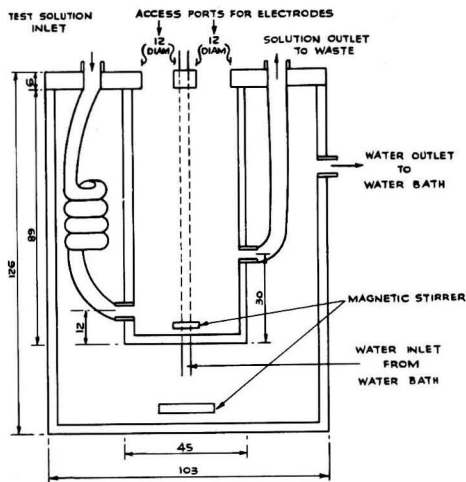


in favor of the removal of free silver ions from the solution. The formation constant (K) for the equilibrium is given by

$$K = \frac{[\text{Ag}(\text{CN})_2^-]}{[\text{Ag}^+][\text{CN}^-]^2} \quad (1)$$

As K is a constant and the concentration of $[\text{Ag}(\text{CN})_2^-]$ will remain virtually unchanged throughout the reaction if present in excess over cyanide, the concentration of silver liberated on addition of cyanide will be given by;

$$[\text{Ag}^+] = \frac{B}{[\text{CN}^-]^2} \quad (2)$$



ALL DIMENSIONS IN mm

Figure 1. Sectional details of cell

$$\text{where } B = \frac{[Ag(CN)_2]}{K}$$

The inverse proportionality between the cyanide present in the test solution and the concentration of silver ions released provides an indirect method of measuring the concentration of cyanide present. This change in silver and cyanide concentration is followed by a silver ion-selective electrode, the response of which is given by the Peters-Nernst equation

$$E = E^0 + \frac{RT}{nF} \text{Log}_e a \quad (3)$$

which in terms of the silver ion-selective electrode, the electrode slope (S) and the activity coefficient (γ) may be presented as

$$E = E^0 + S \log \gamma + S \log Ag^+ \quad (4)$$

where $S = 2.303 RT/nF$ and $\gamma = a/[Ag^+]$
Combining Equations 2 and 4 and rearranging yield

$$E = E^0 + S \log \gamma + S \log B - 2S \log [CN^-]$$

or, as E^0 , γ , S , and B are all constants

$$E = Q - 2S \log [CN^-]$$

where $Q = E^0 + S \log \gamma + S \log B$

Rearranging and taking antilogs give

$$[CN^-] = \text{antilog} \frac{Q}{2S} - \text{antilog} \frac{E}{2S}$$

A plot of the concentration of cyanide, $[CN^-]$, vs. the antilog ($E/2S$) will yield a straight line with a linear concentration axis. More conveniently, Gran's Plot papers (Orion Cat. No. 90-00-92) may be used where the vertical antilog axis is scaled in units of E/S .

Experimental

All potentiometric measurements were made with an Orion silver ion-selective electrode (Model No. 84-16) and

a Corning (No. 476109) reference electrode containing 4-M potassium chloride. The cell potential was measured on a Corning-EEL Model 12 pH Meter and displayed on a Pye-Unicam AR45 potentiometric recorder.

The silver indicator solution was prepared by dissolving 0.625 g of Analar potassium cyanide in 2 l. of water. Silver nitrate solution [0.6% (w/v)] was added until a permanent precipitate was observed. A solution of potassium cyanide ($100 \mu\text{g ml}^{-1}$) was added to the indicator solution in a dropwise manner until the precipitate just dissolved. A further 2.5 ml of potassium cyanide solution ($100 \mu\text{g ml}^{-1}$) was added to the indicator solution before it was finally diluted to 2.5 l. with water. The indicator solution once prepared was stable for several months.

The measurement cell used for the continuous determination of cyanide (Figure 1) was made from Perspex and was immersed in a constant temperature water jacket held at 30°C to ensure that all measurements were made at the same temperature. Both the cell and water jacket were equipped with magnetic stirrers driven by one motor placed underneath the cell. A Technicon AutoAnalyzer Pump and Manifold was used to pump and mix the reagents prior to the continuous analysis and also to supply water from a thermostatic water bath to the water jacket.

The flow diagram of the complete system (Figure 2) includes two solenoid valves and an associated timer permitting the introduction of a standard cyanide solution to restandardize the monitor at preselected time periods (every 12 h) throughout a monitoring exercise. Initial calibration was accomplished by introducing standard cyanide solutions directly into the pump manifold allowing time for a steady-state response to be recorded from each.

The manual determination of cyanide used in the check analysis was accomplished by following the method of Frant et al. (2).

Results and Discussions

The general response and limit of detection of the silver ion-selective electrode to cyanide are directly ascribable to the concentration of the indicator solution added to the test solution, a high flow rate immediately saturates the

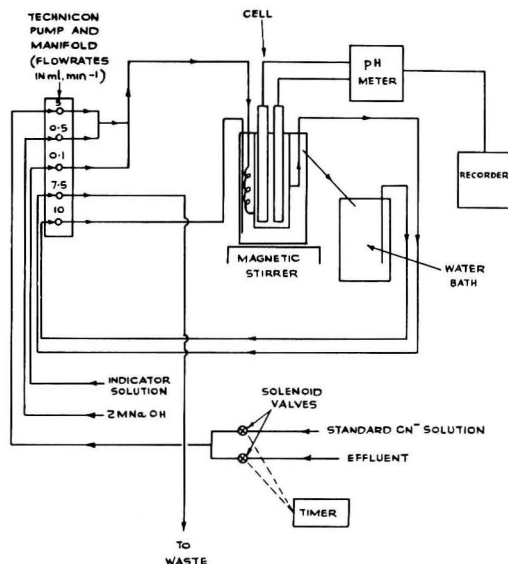


Figure 2. Flow diagram of cyanide monitor

test solution with cyanide, masking the effect of trace amounts of cyanide in the test solution. On the other hand, too little indicator proves insufficient for a stable reaction to occur and the subsequent response to cyanide is limited.

In general, the concentrations and flow rates of the various reagents used in the monitor and the flow rate of the sample, shown in Figure 2, ensured a stable and fast response from the electrodes to changes in the concentration of cyanide and provided a relatively constant ionic strength in which potential interferences would be minimal. The flow rates selected ensured the minimum in sample and reagent requirements.

The emf developed by any ion-selective electrode system is temperature dependent, as this affects the slope of the calibration line. For this reason the temperature was maintained at $30 \pm 1^\circ\text{C}$ so fluctuations in the electrode response due to temperature were minimal while, at the same time, ensuring a small but consistently higher temperature over ambient when the heat losses through the interconnecting tubing were small.

The calibration of the monitor was linear from 0 to at least $1\ \mu\text{g ml}^{-1}$ of cyanide with $0.01\ \mu\text{g ml}^{-1}$ marking the lowest practical limit of detection (Figure 3). The time taken for a change in the concentration of cyanide to be recorded was 10 min (Figure 4), the time being virtually inde-

pendent of both the concentration of cyanide and whether ascending or descending concentrations were sampled.

Drifting of the electrode response to a $0.05\ \mu\text{g ml}^{-1}$ cyanide solution over a 4-day period was only about $1\ \text{mV day}^{-1}$ toward a more positive potential, and consequently the calibration line could easily be reconstructed or the emf backed off from the emf of one standard solution of cyanide sampled every 12 h for a 30-min period. Figure 3 also shows the calibration line after 1 week's monitoring where, although the slope is different because of the antilogarithmic plot, the drift in response is uniform over the whole range of calibration points.

The determination of cyanide relies on the formation of the very stable $\text{Ag}(\text{CN})_2^-$ complex. Consequently, the only ions likely to interfere with the determination are those forming more stable complexes with silver or those which interfere with the electrode response to silver—e.g., sulfide. Indeed, of the ions likely to be found in complex steelworks effluents, sulfide was the only one which caused interference (Table I) with the determination and therefore the only criterion applicable to the type of effluents analyzed is that it should be sulfide free—i.e., biologically or chemically pretreated.

The determination of cyanide in the presence of a known amount of Fe^{3+} as complexant gave an analysis which cor-

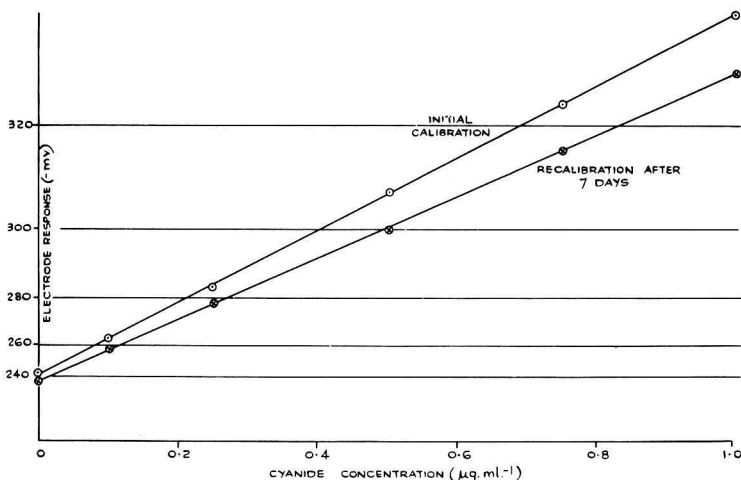


Figure 3. Calibration of cyanide monitor, 30°C

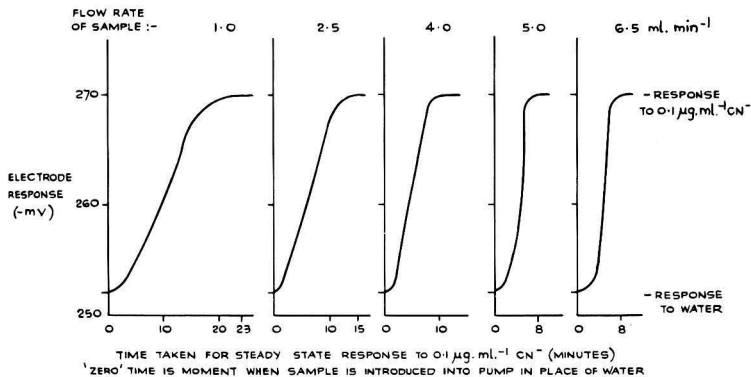
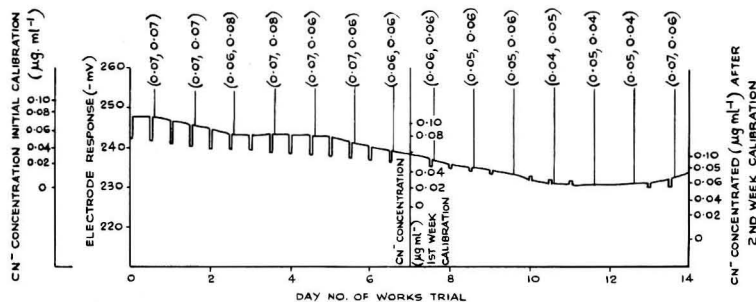


Figure 4. Response times of cyanide monitor



THE FIGURES SHOWN IN(BRACKETS) ARE THE CN⁻ CONCENTRATIONS AT THE MANUAL SAMPLING TIME AND REPRESENT THAT DETERMINED (IN μg.ml⁻¹) BY (MONITOR, STANDARD ADDITION) RESPECTIVELY

Figure 5. Determination of cyanide in steelwork's effluent

Table I. Interferences

Interferent	Concentration of Interferent, μg ml ⁻¹	Concentration of CN found, ^a μg ml ⁻¹
Cl ⁻	5000	0.050
SO ₄ ²⁻	1000	0.050
SCN ⁻	500	0.060
S ₂ O ₃ ²⁻	100	0.055
NO ₃ ⁻	500	0.045
S ²⁻	50	>1
Ca ²⁺	1000	0.055
NH ₄ ⁺	5000	0.050
Fe ³⁺	1-μ mole ^b	0.040
Phenol	1000	0.050

^a In each case, except Fe³⁺, the test solution contained 0.05 μg ml⁻¹ CN⁻. ^b The initial CN⁻ concentration was 0.2 μg ml⁻¹ (1-μ mole Fe³⁺ theoretically complexes 0.156 μg ml⁻¹ CN⁻ and the detectable CN⁻ concentration was, therefore, 0.044 μg ml⁻¹).

Table II. The Analysis of Effluents

Effluents	Cyanide Standard addition	Content, ^a μg ml ⁻¹	
		Colorimetry	Monitor
Coke oven No. 1	0.146	0.15	0.150
No. 2	0.257	0.28	0.250
Blast furnace			
No. 1	0.086	0.10	0.095
No. 2	0.125	0.10	0.120
River water No. 1	0.070	0.10	0.070
No. 2	0.065	0.10	0.060

^a In each case potassium cyanide was added to each effluent before analysis.

responded to the concentration of free cyanide in the solution (0.04 μg ml⁻¹) and not the total amount added (0.2 μg ml⁻¹), confirming the applicability of the procedure to the toxic-free cyanide ion and not to any complexed form of the ion.

The analysis of a series of coke oven and blast furnace effluents (Table II) to which cyanide had been added showed excellent agreement with the values obtained by the manual method of Frant et al., and the usual colorimetric method (3).

Figure 5 shows the results of applying the monitor to the continuous determination of cyanide in a steelworks effluent.

The effluent contained a high concentration of potentially interfering ions (e.g., 3500 μg ml⁻¹ Cl⁻, 1500 μg ml⁻¹ NH₃, 30 μg ml⁻¹ SCN⁻). The trial was carried out over a two-week period where the overall drift in electrode response to the restandardizing cyanide solution was 12 mV. at the 0.05-μg ml⁻¹ level. Check analysis of the cyanide content of the effluent, using the manual method of Frant et al. was carried out once per day (Figure 5) and agreement between the two procedures was within 95%. Check analysis using distillation/colorimetry (3) was not carried out as, in the past, the analysis had been unreliable at these low concentrations.

The membrane of the silver electrode was inspected for wear after the work's trial. Apart from a few solid particles which had adhered to the membrane, the crystal still retained its bright appearance and had suffered no abrasion at all. During the work's trial the tubing and cell gradually gained a coating of CaCO₃ from the hard water. This produced no noticeable side effects during the trial, but longer trials might require treatment of the tubing and parts to remove the coating. A general maintenance program was invoked at the start of the trials to ensure the smooth running of the monitor.

Conclusion

A monitor is described for the determination of free cyanide and is based upon a silver ion-selective electrode. The monitor is responsive to cyanide down to 0.01 μg ml⁻¹ and has been applied to its determination in river waters and numerous steelworks effluents. The technique has been shown to be as accurate as the conventional colorimetric method, rapid, and free from interference by a wide range of ions present in complex steelworks effluents.

Acknowledgments

The author wishes to thank Dr. H. Hughes, Head of Chemical Services Section at the Teesside Research Centre of British Steel Corp., for his interest and constant encouragement throughout the work and in the preparation of this paper.

Literature Cited

- "Analytical Methods Guide," 6th ed., Orion Research Inc., 1973.
- Frant, M. S., Ross, J. W. Jr., Riseman, J. H., *Anal. Chem.*, **44**, 2227 (1972).
- "Analysis of Raw, Potable and Waste Waters," p 228, HMSO, 1972.

Received for review July 17, 1975. Accepted November 24, 1975.

Transport of Atmospheric Sea Salt in Coastal Zone

S. A. Hsu* and Thomas Whelan III

Coastal Studies Institute, Louisiana State University, Baton Rouge, La. 70803

■ Experiments on the vertical distribution of sea salt below 5 m above beaches were conducted on Padre Island, Tex., and Barbados, W.I. These sites are under the influence of diurnal sea breezes and yearly trade winds, respectively. A model is developed to explain the distribution of aerosols. The model is supported by independent measurements below 20 m above a windward beach in Hawaii by Duce and Woodcock (1) and Hoffman and Duce (2).

Atmospheric sea salts have become an increasingly important subject for investigation in recent years. Sea salt aerosols are a significant source of condensation nuclei (3). The quantity and quality of sea salt particles deposited on land may also be important in determining the physical and chemical characteristics of coastal soils and plants (4, 5). Evaporation of droplets of seawater ejected into the atmosphere when bubbles burst at the sea surface in the surf and whitecap zones adds a net positive space charge to the air (6).

At least two types of atmospheric sea salt particles exist which can affect the coastal zone: Surf-produced sea spray generated by breaking waves and aerosols generated in the open ocean by bursting bubbles (1, 7). Airborne sea salts range in size from about 0.5μ (8) to 100μ (9). Toba (10) concluded, from theoretical considerations, that oceanic aerosol mass concentration generally decreased exponentially with height and that below 1 km the concentration was independent of particle size. Simpson (11) reported an increase in Na concentration above the trade wind inversion during periods of diurnal change in temperature and humidity.

Experimental Methods

Two field experiments were conducted, the first on Padre Island National Seashore near Corpus Christi, Tex., during September 1972 and the second at Barbados, W.I., during August 1973. The sampling apparatus at Padre Island was located at the high tide mark. Breaking waves were observed from 10–150 m offshore, and sea state, wind speed, and wind direction were variable. The sampling apparatus at Barbados was located on the northeastern coast at Conset Bay. Breaking waves were filtered from the mainland by a fringing reef approximately 200 m offshore. Sea state, wind speed, and wind direction were relatively constant.

Three air samplers, 1.55, 3.1, and 4.6 m high, were placed approximately 3 m apart on the beach and parallel to the high tide mark (Figure 1). Air samples containing gases and particles of all sizes were collected by a method similar to that described by Tsunogai et al. (12). Air was drawn through 250 ml of double-distilled water in Greenburg-Smith glass samplers by vacuum pumps operated from a gasoline generator placed 100 m downwind from the sampling site. Flow rates were calibrated in the laboratory and set with a purge meter at 12 l./min, or $0.75 \text{ m}^3/\text{h}$. Total air

volumes of 1.5–2.3 m^3 were obtained for individual determinations of Na and Mg by atomic absorption spectrophotometry. The Mg concentration was determined in each sample as an internal check for Na inasmuch as the Mg/Na ratio in worldwide air samples is the least fractionated of the major atmospheric cations with respect to seawater. The average fractionation or E value ($E_{\text{Mg}} = [(\text{Mg}/\text{Na})_{\text{air}}/(\text{Mg}/\text{Na})_{\text{seawater}}] - 1$) for Mg was +0.065. However, E_{Mg} ranged from +0.98 during an offshore wind period to -0.30 during a persistent onshore wind period (13). All positive E_{Mg} values occurred during periods of offshore winds, a fact which suggests that a terrestrial source of Mg was introduced into the sample. The most negative E_{Mg} value occurred during persistent onshore winds above 5 m/s.

Two aerosol samplers set at 1.55 m above the beach were run simultaneously for several 3- to 6-h periods to measure the overall analytical precision of the method. A difference of 8.1% in Na concentrations was observed between duplicate samples when the aerosol concentrations were above $100 \mu\text{g Na}/\text{m}^3$. There was less than 2% difference between duplicate samples which had concentrations less than $100 \mu\text{g Na}/\text{m}^3$.

The Model

The generation of aerosols depends upon many meteorological and oceanographic factors (14). Among those in the coastal region are wind speed, direction, duration, and fetch (which govern the sea state and whitecap distribution), and subaqueous bathymetry (which controls the breaking wave condition in the surf zone) (Figure 2). Therefore, aerosols occur neither as point sources (for whitecaps) nor as line sources (for surf zone) from an atmo-



Figure 1. Aerosol samplers at three elevations along a Padre Island beach

spheric diffusion viewpoint. The best approach to estimating the aerosol concentration may be to assume a distributed area source which simply treats the offshore and nearshore area contributions as coming from a continuous distribution of infinitesimal sources.

Because the coastline constitutes a discontinuity in terms of the roughness of the underlying surface, as well as of heat and moisture, the wind must readjust as it passes such areas. The flow does not immediately adapt itself at all levels to the local surface roughness but does so only in the layer adjacent to the surface. The height of the layer in which the influence of the new roughness is felt, the so-called internal boundary layer (Figure 2), increases with distance downwind from the point of change in roughness (15). Measurements of this boundary layer have been made by Hsu (16) on a beach and by Panofsky and Peterson (17) on a narrow peninsula surrounded by bays of varying widths. The thickness of the internal boundary layer is greater under the influence of a sea breeze, owing to stronger solar radiation (18), than under synoptic onshore winds (e.g., gradient winds). Thus, over land influenced by onshore wind, such as a beach-dune complex, mixing depths are considerably reduced but highly variable and thus act as a sink.

Irregular terrain such as a nearshore cliff or dunes will act as another source or sink, but which condition prevails depends upon where the separation of airflow occurs (19). Turbulent vortices commonly induced by obstacles should be taken into account. In addition, gravitational settling should be considered as a possible aerosol sink.

For areas where there is no internal boundary layer effect, there are many area source formulas for modeling urban air pollution, but a simple and effective one has recently been developed by Gifford and Hanna (20). Given the equation

$$\chi = CQ/U \quad (1)$$

where χ is the volume concentration of a pollutant emitted from an area source of strength Q , and U is the average wind speed, according to their model the parameter C is given by

$$C = (2/\pi)^{1/2} X^{1-b} [a(1-b)]^{-1} \quad (2)$$

where X is the distance from a receptor point to the upwind edge of the area source. The constants a and b are defined by the vertical atmospheric diffusion length, $\sigma_z = aX^b$. Values of a and b for different atmospheric dispersion conditions can be found in various texts and handbooks (21).

For Equation 1 to be useful, it must be verified by available data. Chesselet et al. (22) have measured sea salt aerosols over the open ocean where $\chi = 2.0 \mu\text{g}/\text{m}^3$ and $U = 5 \text{ m/s}$. The value of C may be calculated by Equation 2. For the neutral stability condition, which is prevalent in most oceanic regions (23), the value of C ranges from 100 for X

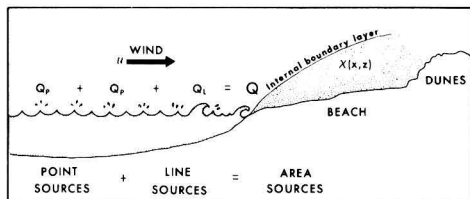


Figure 2. Schematic representation of point and line sources for sea salt and the effect of the internal boundary layer (see text for explanation)

= 5 m to 133 for $X = 50 \text{ m}$, assuming $a = 0.080$ and $b = 0.881$ (21). These values indicate that on the open ocean whitecaps would be observable within an upwind distance of 5–50 m. This assumption is reasonable because for fully developed seas whitecaps are distributed in such a way that the most common distance between two caps ranges from 10–100 m (24). Substituting values of χ , U , and C into Equation 1, $Q \approx 0.1 \mu\text{g}/\text{m}^2/\text{s}$.

The validity of Q may be examined from another viewpoint. Since the production of atmospheric sea salts from the ocean surface must equal the input from both precipitation and dry fallout, one can follow the data provided by Eriksson (25) for calculating the input of sea salt into the ocean. If Q is a reasonable number, then the annual input should equal the production as calculated from Q . Given $Q = 0.1 \mu\text{g}/\text{m}^2/\text{s}$ and the area of the ocean surface is $3.6 \times 10^{14} \text{ m}^2$, then the annual production of sea salts is $1.1 \times 10^{15} \text{ g/yr}$. If the fallout rate [from data provided by Eriksson (25) from two trade wind stations (6 m/s)] is $5.5 \times 10^{-6} \mu\text{g}/\text{cm}^2/\text{s}$ or $540 \times 10^6 \text{ tons/yr}$, and assuming that sea salts are equally removed by dry fallout and precipitation, then the removal rate of sea salts from the atmosphere to the oceans is $1.8 \times 10^{15} \text{ g/yr}$. Thus, Q appears to be a valid number on the basis of the geochemical balance of the world's oceans.

We now examine the estimation of vertical distribution of aerosols in the coastal zone. First, because atmospheric stability in the coastal area plays an important role in the vertical structure of horizontal winds, for a given beach (18) where the roughness parameter is known (26), the power law relationship with stability characteristics (21) is adapted:

$$U/U_1 = (Z/Z_1)^P \quad (3)$$

where U_1 is the wind speed at some reference level Z_1 . The exponent, P , depends on the stability class. Substituting Equation 3 into Equation 1,

$$\chi = CQ/[U_1(Z/Z_1)^P] \quad (4)$$

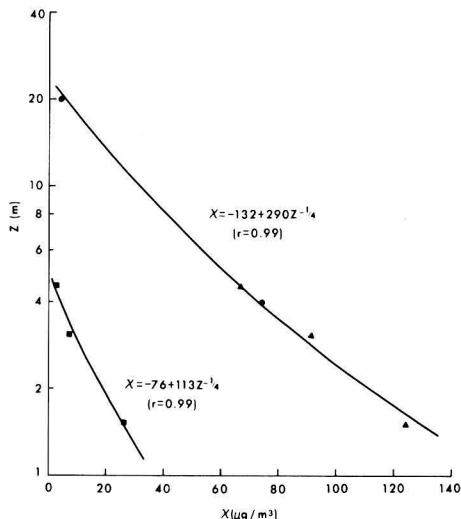


Figure 3. Model verification by available data obtained on open coasts in Texas and Hawaii and a protected coast on Barbados. Note that the tower top in Duce and Woodcock (1) was 24 m above sea level and that of Hoffman and Duce (2) was 20 m above sea level.

● Hawaii (1, 2); ▲ Texas, 1972; ■ Barbados, 1973

As discussed previously, the internal boundary layer, gravitational settling, and terrain-induced vortices will act as a source or as a sink, depending upon the aerodynamic roughness over the area in question. Equation 4 should be modified as follows:

$$\chi = (CQZ_1^P/U_1)Z^{-P} \pm S \quad (5)$$

where S represents source (positive) and sink (negative).

For a given location on the beach, the values of C , Q , U_1 , and Z_1 can be estimated from known meteorological and oceanographic conditions. Therefore, the vertical distribution from a given region (such as a beach face) toward the open ocean is

$$\chi = \pm S + BZ^{-1/4} \quad (6)$$

where $B = CQZ_1^{1/4}/U_1$ from Equation 5, in which $1/4$ is substituted for P to represent neutral stability conditions of an average day and night (21).

Figure 3, in which data from Texas, Hawaii, and Barbados are incorporated, accurately supports Equation 6. Note that the concentration downwind from a pollution source should also depend on the obliqueness of the wind. However, a recent numerical experiment by Calder (27) shows that although the concentrations increase as the wind more closely parallels the direction of a line source, the increase is only slight and, for many practical purposes, may be disregarded.

Remarks

It should be noted that the study presented here is preliminary. However, it is felt that the model is useful as a first approximation. Certainly much more data are needed to improve the model. Particularly, similar experiments deploying three vertical levels and three onshore stations, extending landward, should be conducted under several meteorological and oceanographic conditions. Atmospheric systems such as migratory storms, monsoons, and other localized coastal winds should be studied because they can induce variable offshore whitecapping and surf zone breaking conditions. Structures of the internal boundary layer and the effect of terrain on the airflow in the coastal zone under various wind systems should also be studied in more detail.

Acknowledgment

Comments by Hans Dolezalek of the Office of Naval Research and the journal's reviewers are appreciated.

Literature Cited

- (1) Duce, R. A., Woodcock, A. H., *Tellus*, **23**, 427-35 (1971).
- (2) Hoffman, G. L., Duce, R. A., *J. Geophys. Res.*, **77**, 5161-9 (1972).
- (3) Dinger, J. E., Howell, H. B., Wajciechowski, T. A., *J. Atmos. Sci.*, **27**, 791-7 (1970).
- (4) El Swaify, S. A., Swindale, L. D., Uehara, G., "Salinity Tolerances of Certain Tropical Soils and Relationship between Sodium Ion Activities and Soil Physical Properties", 49 pp, Hawaii Inst. Geophys., Univ. of Hawaii, HG-68-12, 1968.
- (5) James, N. P., *J. Sediment. Petrology*, **42**, 817-36 (1972).
- (6) Blanchard, D. C., *J. Atmos. Sci.*, **23**, 507-15 (1966).
- (7) Junge, C. E., *J. Geophys. Res.*, **77**, 5183-5200 (1972).
- (8) Durbin, W. G., White, G. D., *Tellus*, **13**, 260-75 (1961).
- (9) Junge, C. E., Jaenicke, R., *Aerosol Sci.*, **2**, 305-14 (1971).
- (10) Toba, Y., *Tellus*, **17**, 131-45 (1965).
- (11) Simpson, H. J., *J. Geophys. Res.*, **77**, 5266-77 (1972).
- (12) Tsunogai, S., Saito, O., Yamada, K., Nakaya, S., *ibid.*, pp 5283-92.
- (13) Whelan, T. III, *Contributions in Marine Science* (Univ. of Texas at Austin), **19**, 3-11 (1975).
- (14) Roll, H. U., "Physics of the Marine Atmosphere", 426 pp, Academic Press, N.Y., 1965.
- (15) Blom, J., Wartena, L., *J. Atmos. Sci.*, **26**, 255-65 (1969).
- (16) Hsu, S. A., *J. Geophys. Res.*, **76**, 2880-5 (1971).
- (17) Panofsky, H. A., Peterson, E. L., *Quart. J. Roy. Meteor. Soc.*, **98**, 845-54 (1972).
- (18) Hsu, S. A., *Mon. Weather Rev.*, **101**, 187-94 (1973).
- (19) Scorer, R. S., "Natural Aerodynamics", 312 pp, Pergamon Press, N.Y., 1958.
- (20) Gifford, F. A., Hanna, S. R., *Atmos. Environ.*, **7**, 131-6 (1973).
- (21) Environmental Protection Agency, National Environmental Research Center, Research Triangle Park, N.C., "User's Guide for the Climatological Dispersion Model", 131 pp, 1973.
- (22) Chesselet, R., Morelli, J., Burt-Menrad, P., *J. Geophys. Res.*, **77**, 5116-31 (1972).
- (23) Hsu, S. A., *Boundary-Layer Meteorol.*, **6**, 509-14 (1974a).
- (24) Neumann, G., Pierson, W. J., Jr., "Principles of Physical Oceanography", 545 pp, Prentice-Hall, Englewood Cliffs, N.J., 1966.
- (25) Eriksson, E., *Tellus*, **11**, 375-403 (1959).
- (26) Hsu, S. A., *Boundary-Layer Meteorol.*, **6**, 505-7 (1974b).
- (27) Calder, K. L., *Atmos. Environ.*, **7**, 863-8 (1973).

Received for review March 28, 1975. Accepted October 9, 1975. Work supported by Geography Programs, Office of Naval Research, under Contract N00014-69-A-0211-0003, Project NR 388 002.

CORRESPONDENCE

SIR: I found the paper by Jackson, Judges, and Powell [*Environ. Sci. Technol.*, **9**, 656 (1975)] of considerable interest since the authors describe a procedure similar to the one recently standardized by the U.K. Institute of Petroleum (I.P. method 318/74 T). The main difference between the two methods is that I.P. 318 T specifies a GC column of higher resolving power than the one used by Jackson et al. so that the pristane and phytane peaks are almost completely separated from the adjacent normal paraffins (n -C₁₇ and n -C₁₈).

This difference in resolution has an important practical result if numerical values of peak height ratios are to be quoted as in Table I of the paper. If other laboratories wish to reproduce the ratios listed they must achieve the same degree of partial resolution since otherwise the peak height ratios obtained will be different from the published ones. It is difficult to reproduce a partial resolution exactly and it is for this reason that the I.P. method specifies almost complete resolution of the peaks of interest. Complete resolution would have been better but with the type of column employed (50 m × 0.5 mm stainless steel coated with silicone fluid OV 101), it was found in correlation trials that the ratios n -C₁₇/pristane, n -C₁₈/phytane could be reproduced to about ±10%.

It was felt that this reproducibility was sufficient for characterization if the method were used in conjunction with other analytical techniques. Chromatograms obtained by the IP method are shown in Figures 1 and 2.

I write this letter to draw attention to the I.P. method so

Figure 1. Chromatogram of <343 °C fraction of Light Nigerian crude oil

Stainless steel column, 50 m × 0.50 mm, coated with OV 101. Column temperature, 100–220 °C at 5 °C/min. He carrier gas at 4 ml/min. Sample size, 0.9 μl

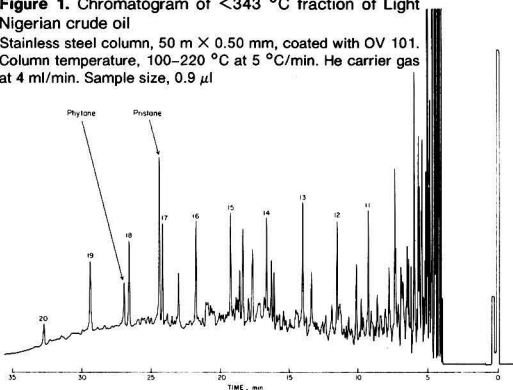
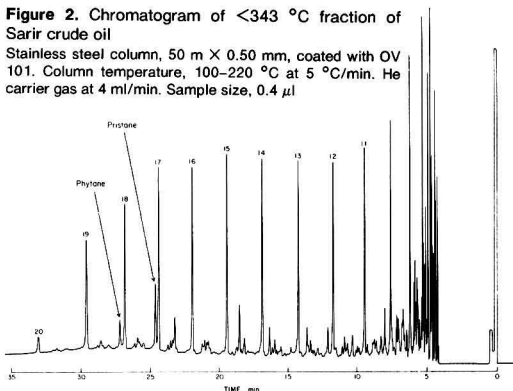


Figure 2. Chromatogram of <343 °C fraction of Sarir crude oil

Stainless steel column, 50 m × 0.50 mm, coated with OV 101. Column temperature, 100–220 °C at 5 °C/min. He carrier gas at 4 ml/min. Sample size, 0.4 μl



that laboratories engaged in oil characterization will use it in future thereby enhancing the value of their work.

E. R. Adlard

Chairman IP Panel ST-G-6
c/o Thornton Research Centre
P.O. Box 1
Chester CH1 3SH England

SIR: The comment of Dr. Adlard on the desirability of obtaining more efficient separation of pristane and phytane from their neighboring normal paraffins is most certainly a valid one. However, there are some points regarding the accuracy of our method I feel should be advanced.

First, studies performed in this laboratory over 15 consecutive runs show that, although only partially resolved, the n -C₁₇/pristane and n -C₁₈/phytane ratios have a repeatability of ±2.5% and ±3.1% respectively.

Furthermore, comparative trials utilizing a number of identically prepared 10-m w.c.o.t. columns revealed a % relative standard deviation of the above ratios of ±3.2% and ±5.1% respectively. Both of these relative standard deviations are considerably lower than the figure Adlard has quoted using 50-m w.c.o.t. columns with almost complete resolution of the pertinent doublet peaks.

These values are of a similar order of magnitude to those quoted by Zafiriou et al. ["Correlation of Oils and Oil Products by Gas Chromatography," Woods Hole Oceanographic Institution, Tech. Rep. WHOI-72-55 (unpublished manuscript)] whose analyses using SCOT columns were also based on partial resolution of the pristane and phytane pairs.

After further studies involving all three types of columns mentioned, it would appear that no matter what degree of component resolution is achieved, the limiting factor in determining the accuracy of the characteristic ratios is the reproducibility and stability of the analytical conditions—e.g., carrier flow rate, column temperature, and programming rate.

The aim of the paper was to demonstrate the viability of our method as a differential and identification technique when applied to oil pollution and geological formation delineation, rather than to provide an academic tabulation of characteristic ratios for comparative purposes between laboratories.

Since the method's ability to differentiate and identify is based upon the *consequential* analysis of two or more samples under identical conditions, it would appear that the above-mentioned repeatabilities of the characteristic ratios are most satisfactory for this purpose.

J. L. POWELL

Hematite Oil and Gas Laboratory
BHP Research Laboratories
Clayton, Victoria 3168, Australia

SIR: I would like to comment on the Note, "Trace Elements in Corn Grown on Long-Term Sludge Disposal Site" (1).

1. A contribution on this important topic should contain such essential information as the pH and the organic content of the treated soil.

2. Also the amounts of metals added and found in soils.

(a) Table IV, which shows how the (unknown) total weight of sludge added has been indirectly estimated by analyzing for several elements present today in the soil, is back to front and therefore confuses the reader who is not familiar with this method of estimation.

(b) The reader is not told what an "extractable" metal is (Table II), but is left to guess that perhaps an ammonium acetate solution was used.

(c) The comparison with Chaney's recommendations (2) is very puzzling. Taking Cd first, Chaney recommends (his Table 14) that the Zn/Cd ratio be at least 200. The actual ratio recorded in the sludge is 10 (Table I) and in the soil is 30 (Table II)—that is, 20 times and 7 times as much Cd as Chaney recommends, not 100 times as stated in the Note. When we consider the content of the sludge in other metals, Table I has values 6, 4, 5, and 5 times as high as Chaney's recommendations for Cu, Ni, Pb, and Zn respectively—not 40–50 times as stated in the Note.

3. Also when we consider crops and contents of heavy metals:

(a) The reader is told nothing of the health of the corn crop, only that the corn of the control plot might have been P-deficient. But as evidence for this possibility there is no report of symptoms, only an indirect inference from the high Fe, Al, and (perhaps) Cd content of the leaves. Now if this inference is correct, the sludged plants must have been even more P-deficient because their contents in these three metals are higher. But this is most improbable for plants treated with sludge containing 2% P. This section of the Note might have been prudently omitted.

(b) It is reassuring to see that the Cd content of grain is probably not significantly higher in the treated plots (0.9, 1.0 ppm) than in the controls (0.8 ppm), and this similarity fits other unpublished findings that I know of. But it is rash to imply, as in the Note, that this content is normal for corn grain.

Literature Cited

- (1) Kirkham, M. B., *Environ. Sci. Technol.*, 9, 765–8 (1975).
- (2) Chaney, R. L., in "Proceedings of the Joint Conference on Recycling Municipal Sludges and Effluents on Land", pp 129–41, Nat. Assoc. State Univ. and Land-Grant Coll., Washington, D.C., 1973.

G. W. Leeper

Flat E6, 89 O'Shanassy St.
N. Melbourne
Victoria 3051, Australia

SIR: I appreciate Professor Leeper's comments. I have found his treatise on heavy metals in soils a valuable reference (1).

In response to his points:

1. I agree that pH and organic content of the treated soil are important to know. Unfortunately, I did not measure them. Because the study was not a thorough one, I wrote a "Note". I felt that the results I did have were significant to publish.

2. (a) This "back-to-front" method was the only way I could estimate the unknown total weight of sludge added. I regret that the paper "confuses the reader" on this point. In the abstract, I should have said that the amount of sludge added was an *estimated* amount.

(b) In the original manuscript submitted to *Environ. Sci. Technol.*, I described the techniques used to analyze sludge, plant, and soil samples. In the review process, it was suggested that I omit the detailed procedures and only give the references.

(c) In my calculations, I used Equation 1 developed by Chaney (2), a cation-exchange capacity of 15 (on the low side), and the maximum values for metals in sludge he sets forth (2, 3) which are, in ppm: Zn, 2000; Cu, 1000; Ni, 200; Cd, 10; Pb, 1000.

According to that Equation 1, the total quantity of sludge, in tons per acre, equals:

$$\text{C.E.C. (meq/100 g unamended soil)} \times 1.63 \times 10^4 =$$

$$1 \left(\frac{\text{mg Zn}}{\text{kg sludge}} - 50 \right) + 2 \left(\frac{\text{mg Cu}}{\text{kg sludge}} - 25 \right) + 8 \left(\frac{\text{mg Ni}}{\text{kg sludge}} - 25 \right)$$

46 T/A (105 metric tons/ha)

Using the maximum concentrations for metals in sludge, I obtained the following:

Element	Permissible loading, metric tons/ha
Zn	0.207
Cu	0.103
Ni	0.021
Cd	0.001
Pb	0.103

These values are 40–50 times lower for Zn, Cu, Ni, and Pb, and more than 100 times lower for Cd, than those in Table IV. I did not cite Chaney's work in the Environmental Protection Agency reference (2) because it is not published. I should have been more explicit in describing how I compared the metal loadings on the soil at the Dayton, Ohio, site to those recommended by Chaney.

3. (a) The plants on the treated plots looked as healthy as those grown on the control plots. Phosphorus availability in sludge-treated soils is important to know, as Professor Leeper (1) and Chaney (3) have pointed out. Hence, I included the discussion on phosphorus. Since I published this study, I have analyzed the corn samples for phosphorus content. They are as follows:

Plant part	%		
	Control	Supernatant	Sludge
Roots	0.09	0.31	0.14
Leaves	0.13	0.25	0.16
Grain	0.42	0.39	0.44

Plants grown on the sludge-treated soil had a higher phosphorus content than those grown on the control soil. But the phosphorus contents of both control and sludge-treated plants were low. Chapman (4) reports the normal concentration ranges for phosphorus in corn leaves and grain are 0.12–0.52% and 0.43–0.80% respectively. A high phosphorus content in the sludge-treated plants, therefore, cannot explain "minimal transport of the elements to the grain", as I postulated in the note.

(b) Because there is little *published* information on cadmium content of grain, it is hard to know what "normal" contents are.

Literature Cited

- (1) Leeper, G. W., "Reactions of Heavy Metals with Soils with Special Regard to Their Application in Sewage Wastes", Prepared for Department of the Army, Corps of Engineers, Contract No. DACW73-73-C-0026, 70 pp, 1972.
- (2) United States Environmental Protection Agency, "Policy Statement on Acceptable Methods for the Utilization or Disposal of Sludges", Appendix I, 23 pp, Environmental Protection Agency, Office of Air and Water Programs, Washington, D.C., 20460, 1974.
- (3) Chaney, R. L., in "Proceedings of the Joint Conference on Recycling Municipal Sludges and Effluents on Land", pp 129–41, Nat. Assoc. State Univ. and Land-Grant Coll., Washington, D.C., 1973.
- (4) Chapman, H. D., Ed., "Diagnostic Criteria for Plants and Soils", 2d Printing, 1973, 793 pp, Quality Printing Co., Inc., Abilene, Tex., 1966.

M. B. Kirkham

Department of Plant and Soil Sciences
University of Massachusetts
Amherst, Mass. 01002

INDUSTRY TRENDS

U.S. Rubber Reclaiming Co. (Vicksburg, Miss.) announced that rubberized asphalt developed by the company, and Arizona Refining Co. (Phoenix), is being tested on city streets by the City of Phoenix. Reclaimed rubber is used in the asphalt.

The MRM Division of **Ecodyne Corp.** has made plans for construction of a multi-million dollar manufacturing and office complex to be in operation at Conroe, Tex., by the middle of this year.

WAHLCO, Inc. (Santa Ana, Calif.) will design and construct a proprietary flue gas conditioning system for Detroit Edison Co. to assure air pollution control compliance. Cost: More than \$1 million.

A **Lockheed Marine Biology Laboratory** (Carlsbad, Calif.), to make coastal area environmental surveys and perform sea life and electrochemistry research, opened in early January.

Smith, Hinchman & Grylls Associates Inc. (Detroit, Mich.) has begun construction of a 1000-ft² solar energy collector on the roof of its downtown Detroit headquarters building.

UOP Inc. has been recommended by the Commonwealth of Massachusetts to design, construct, and operate for 20 yrs the world's largest integrated solid waste processing and energy recovery facility. Contract value could be \$95 million.

United International Research Inc. (Hauppauge, N.Y.) is seeking to buy 100 000 gpd of crude alcohols for production of its gasoline-conserving "HydroFuel", in which up to 50% of gasoline can be replaced with alcohols, water, and "Hydrelate".

Varian Data Machines (Irvine, Calif.) said that its Series 620 minicomputers cut costs, boost throughput, and overcome pollution control problems at three vinyl chloride plants.

Ionics, Inc. received two orders totalling more than \$3 million for ELECTROMAT electrochemical processing systems for air pollution control and food product manufacture.

PPG Industries has been granted five U.S. patents for an automotive emission control system to replace the conventional muffler and remove lead and particulate matter from exhausts.

A **Dynalactor Corp.** (McLean, Va.) subsidiary, **AFB Contractors, Inc.**, is now U.S. licensee for Lucas cyclonic furnaces designed specifically for waste disposal with simultaneous re-

covery of energy. Lucas systems are now working in England and Japan.

Rust Engineering Co., a **Wheelabrator-Frye Inc.** subsidiary, has a \$4 million contract for design and construction of two 1000-foot tall steel-reinforced concrete chimney shafts and their liners. Potomac Edison, West Penn Power, and Monongahela Power Cos. are the customers.

Betz Environmental Engineers, Inc. (Plymouth Meeting, Pa.) was awarded Phase I of a two-phase EPA R&D contract to evaluate usefulness and practicality of land-use planning methods with respect to water pollution.

Smith, Hinchman & Grylls Associates Inc. will be consultants on a 6000-ft² solar collector system for the Terraset Elementary School, Fairfax County, Va. The school should be completed in January 1977.

Envirex Inc. will build a 1.3 million-bbl facility to treat oil tanker ballast water discharged at Valdez, Alaska. Oil will be recycled to the crude oil storage tank terminal.

Peter F. Loftus Corp. (Pittsburgh, Pa.) has acquired the firm of Gurnham and Associates, Inc. (Chicago, Ill.). Gurnham is a consulting and conceptual design firm working in industrial wastewater treatment.

Season-All Industries, Inc. (Indiana, Pa.) has installed a "torture chamber" facility to test replacement windows, storm windows, and storm doors, often used for better home insulation, against the most hostile environmental extremes.

Research-Cottrell, Inc. has received a \$20 million commitment from Texas Utilities Services Inc., agent for three Texas utilities, for design and materials of two electrostatic precipitators.

Envirotech Corp. announced that agreement has been reached in principle with Chemical Construction Corp. (Chemico) for acquisition of Chemico's Air Pollution Control Company.

Scott Environmental Technology Inc. (Plumsteadville, Pa.) will supply ACUBLEND calibration gas mixtures and accessory equipment to the State of New Jersey Department of Environmental Conservation.

The **Electric Power Research Institute** (Palo Alto, Calif.) has let a \$90 000 contract to The Johns Hopkins University for a study of biological effects of exposure to high-intensity electric fields.

Davy Powergas, Inc. (Lakeland, Fla.) announced that a formaldehyde plant, which uses absorber tail gases for part of its import steam requirements, has been accepted by its customer, Chem-bond Corp., for use at Springfield, Ore.

Parsons Brinckerhoff Quade & Douglas, Inc., in joint venture with Lawler, Matusky & Skelly, Engineers, and Frank & Haefeli Associates, P.A., have started the planning study for areawide waste treatment management for Middlesex County, N.J., under P.L. 92-500, Sec. 208.

TEC Systems Inc. (De Pere, Wis.) has begun a new program to provide improved sales coverage and expedite introduction of its drying systems to the paper and textile industries.

International Energy Associates Ltd. has been formed at Washington, D.C., to assist governments, industries, and the financial community in solving major energy problems.

IBM has recently won an "excellent" citation from the Federal Energy Administration (FEA) for better than 35% savings over 1972-1973 at its General Products Division at San Jose, Calif.

Camp Dresser & McKee Inc. has acquired Limnetics, Inc. (Milwaukee, Wis.), which is now CDM/Limnetics. Limnetics has done much environmental assessment work for land and water developments, power plant sitings, and energy source development.

J. F. Pritchard and Co. (Kansas City, Mo.) has received a contract for installation of an NO_x abatement unit from Cominco, for Cominco's 420-tpd nitric acid plant at Beatrice, Neb.

Regenerative Environmental Equipment Co., Inc. (REECO, Morris Plains, N.J.) will install a RE-THERM fume and odor control system for Champion Spark Plug Co., at New Burlington, Iowa. Cost: over \$100 000.

Air Pollution Technology, Inc. (San Diego, Calif.) has an EPA contract to continue preparation of design criteria for scrubbing systems to control emissions from solid rocket test motors at Edwards Air Force Base, Calif.

The **American Boiler Manufacturers Association** (Arlington, Va.) foresees electric utility orders of 23 000 MW of new generating capacity in 1976.

Normandeau Associates, Inc. (Bedford, N.H.) is developing fisheries inventories and assessing related environmental impacts associated with the proposed Dickey-Lincoln School Lakes hydroelectric project, in Northern Maine, for the U.S. Army Corps of Engineers.

NEW PRODUCTS

Pump control panels

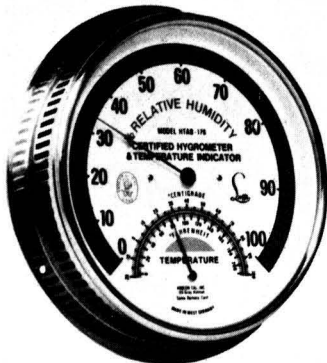
Designed for use with the company's electric submersible pumps. Panel enclosure construction material can be varied to meet environmental severity. Panel relays are hermetically sealed and of solid-state design. Flygt Corp. **101**

Screw pump

These pumps are designed to pump raw sewage in sewage plants and can be used to pump return activated sludge. By design, capacity is variable, but capacities in excess of 40 000 gal/min on low-head applications are possible. A bar screen is optional. Gray Engineering Company, Ltd. **102**

Flue gas conditioning system

Allows power plants to burn low-sulfur coal to reduce SO₂ emissions and still maintain the collection efficiency of electrostatic precipitators. Wahloco, Inc. **103**



Humidity/temperature sensor

This indicator reads temperature in Centigrade and Fahrenheit simultaneously. The hygrometer indicates relative humidity as a percent of saturation from 0-100%. Abbeon Cal, Inc. **104**

Baghouse

Newly designed felt material allows system to handle constant operating temperatures from 650-750 °F. AVT Corp. **105**

Pumping system

The automated system is said to save 35% or more of water and thereby reduces the usage of heated water and

sewer load. All eliminated faucets are replaced with non-mechanical spouts. Ultraflo Corp. **106**



Gas sensing electrode

Can be used to selectively measure carbon dioxide, ammonia, sulfur dioxide, nitrogen oxide or hydrogen sulfide. The electrode is designed to be used with pH/millivolt meters. Lazaar Research Laboratories **107**

Sewage and air pump

The immersible pump features an impeller that draws outside air through the motor drive, mixes the air with the pumped liquid and discharges a liquid/air mixture with a high level of dissolved oxygen. The pump can stimulate bacterial activity for aerobic sewage treatment. Oberdorfer Pump Division **117**

Scrubber

The pilot electrostatic scrubber uses charged water droplets to collect fine particulate emissions. Features include gas pressure drops of less than 1-in. water gauge, water pressure of less than 50 psig and water to gas flow rates of less than 5 gal/1000 acf. Pollution Control Systems Corp. **108**

Timesharing computer system

The single functional unit includes the central processing unit, core memory, controllers and a front-end PDP-11 processor. The system features a full complement of languages. Digital Equipment Corp. **109**

SO₂ stack monitor

Electroconductivity, using acidified hydrogen peroxide as the standard reagent, is the basic principle for this continuous monitor. Depending upon the model, measuring ranges are 0-200 ppm (high), 0-100 ppm (low) or 0-0.4 ppm (high), 0-0.2 ppm (low). Scientific Glass & Instruments, Inc. **111**

Atomizing nozzles

These are available in standard sizes to handle a flow range of 6-2400 gal/h. They find application in fuel oil combustion, dust suppression, hot gas cooling, and insecticide fogging. Fluid Kinetics Inc. **112**

Digitizer/microprocessor

Input is via the alpha numeric keyboard or the electronic digitizer. Input data from these two sources go directly to the microprocessor, which "outputs" to a 15-digit display. Numonics Corp. **113**

Fossil fuel catalytic system

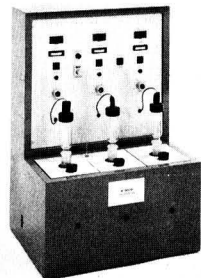
The catalyst, introduced to the combustion air, increases the burning rate of fossil fuels. The system increases flame temperature, lowers stack temperature, increases CO₂ and lowers other emissions. Vaporpak International Corp. **114**

Level monitor

The non-contact ultrasonic level monitor can measure liquids up to 33 ft away, and solids up to 25 ft away. Accuracy is within 1%, according to the manufacturer. Wesmar **115**

Chlorine analyzer/recorder

Automatically measures chlorine residual levels. Signal is drift-free. Data are recorded on a circular chart recorder. Capital Controls Co. **116**



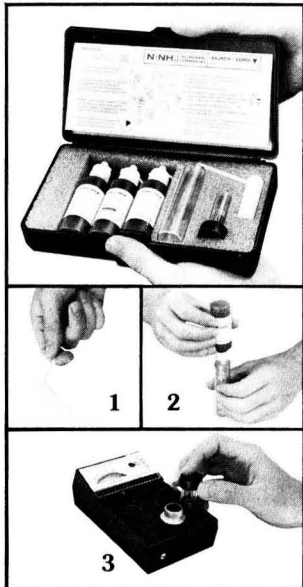
Computer interfaced BOD

The output from the continuous measurement of BOD (biochemical oxygen demand) is interfaced with computers. The computer interface requires only an 8-bit simplex input/output board. The output format is 4-bit numeric characters. Oceanography International **118**

The Easiest Way to test Water

...SpectroKit™ Reagent Systems

Now you can be sure of reliable, on-the-spot results. Fully illustrated instructions and unique chemical packaging make Bausch & Lomb SpectroKit™ Reagent Systems easy, accurate, dependable to use. Compact for the lab—perfect for the field.



Just sample, react and read . . . as easy as 1-2-3

Test for:

Alkalinity	Hardness (EDTA)
Carbon Dioxide	Iron
Chloride	Nitrogen (Ammonia)
Chlorine	Nitrogen Nitrate
(Free and Total)	Nitrogen Nitrite
Chromium	Phosphate
(Hexavalent)	Sulfate
Copper	Turbidity
Dissolved Oxygen	

Ask for information on our other water testing systems—

- Laboratory Reagents and Standards
- Portable and Laboratory Spectrophotometers (15 models)
- Applications Laboratory Assistance
- Water Technology Manual

For complete information contact Bausch & Lomb, Analytical Systems Division.

BAUSCH & LOMB 

ANALYTICAL SYSTEMS DIVISION

25-03-28 Linden Avenue, Rochester, N.Y. 14625.

Sold in U.S.A. only by
Fisher Scientific and VWR Scientific.

See us at the WWEMA Show
March 30-April 1, Booth 107

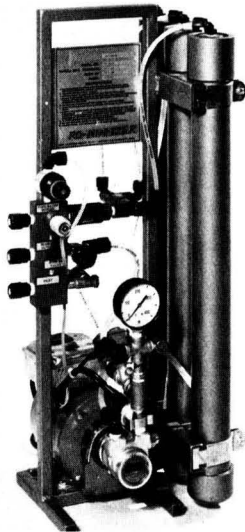
CIRCLE 17 ON READER SERVICE CARD

Tertiary filters

Remove suspended solids from domestic effluents of secondary wastewater treatment plants. At a rate of 2 gpm/ft², suspended solids removal is 85% or better. Flow rate capacity ranges from 5000–500 000 gpd. Can-Tex Industries 119

Filter bags

The filter medium is a microporous membrane of polytetrafluoroethylene laminated to a fabric backing. The inert membrane, designed for use in the chemical industry, resists corrosive chemicals and withstands temperature up to 550 °F. W. L. Gore & Associates, Inc. 120



RO unit

This reverse osmosis system consists of a prefilter rotary vane pump, RO modules, pressure gauges and conductivity lights. Four sizes are available and salt rejection is 90–98% of the total dissolved solids. Ion Exchange Products, Inc. 121

Fiberglass pipe

Available in incremental diameters from 18–48 in. with pressure ratings of 25–150 psi, these pipes find application in wastewater treatment, chemical and power plants. A. O. Smith-Inland Inc. 122

Biodegradable material

The plastic, a mixture of alpha-olefin polymer and para-alkanolyaminophenols, may be used in foodstuff-pharmaceutical-feeds packaging and in grocery and garbage bags. David W. Young & Associates, Inc. 123

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



NO_x monitor

Portable unit may be used to monitor ambient air for OSHA compliance and to measure stack gas emissions. It features dual ranges of 0–200 and 0–1000 ppm, has a response time of 90% in 3 min and an accuracy ≥2%. Joy Manufacturing Co. 124

Exhaust fume hood

This hood system was designed for performing tests with perchloric acid. The stainless steel hood, duct system and exhaust blower are designed to permit no condensation of acid vapors. Spray systems for periodic "washdowns" are included. Lab Fabricators Co. 125

Chromatography data system

System allows up to 8 users to develop and edit analytical programs while it automatically evaluates real-time data from up to 30 remote instrument interfaces. Hewlett-Packard Co. 126



Sulfur dioxide probe

The probe can be fitted in a continuous-flow system to analyze 30 samples/h. Concentrations between 0.3 mg/l to 3 g/l can be measured. Electronic Instruments Ltd. 127

Dust collection test systems

Portable units permit collection and analysis of data at the plant site. The units, of varying types and sizes, are

available on a rental or lease basis.
Griffin Environmental, Inc. 128

Debris swabber

The swab, made of polyurethane with spiral straps, removes debris left in water and wastewater lines during construction. The swab can be hand launched and retrieved from open pipe ends. Girard Polly-Pig, Inc. 129

Air quality monitor

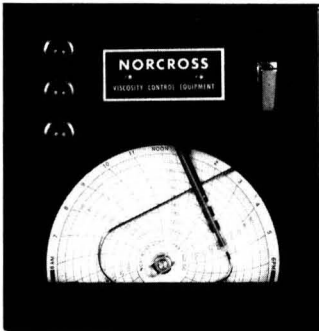
The unit is a self-contained, portable ambient air sampler, programmed to collect 8-24 samples, at preselected times, over 1-4 days. The filled sample bags are taken to a central location for analysis. Environmental Measurements, Inc. 130

Trash compactor

The 7 yd³ compactor can be truck mounted or trailer towed. The unit can haul up to 3000 lb of compacted trash in one operation. A 10-gal bladder accumulator provides stored energy for the compaction cycle and a compaction ratio of 6:1. Greer Hydraulics, Inc. 131

Dissolved oxygen meter

Portable unit is designed for determining dissolved oxygen in the field. The manufacturer claims laboratory titration-type accuracy. InterOcean Systems, Inc. 132



Viscosity recorder

The semi-circular recorder, designed to minimize panel space without compromising the circular chart, may be used with any of the company's measuring elements. The recorder converts the viscosity signal to a viscosity reading. Norcross Corp. 133

Conductance probe

The explosion-proof probe and electronics are in one package that can be mounted on the side or top of any tank. A built-in time delay ensures that a splashing liquid will not trigger falsely. ASI Systems International, Inc. 134

Thermocouples

These refractory sheathed instruments are designed for thermal cycling applications and extended use at temperatures up to 5000 °F. Nanmac Corp. 135

NEED ON-THE-SPOT OIL-IN-WATER MEASUREMENTS?

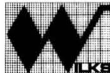
WILKS has the answer for under \$2,000 with 1/2 ppm accuracy!



The Wilks MIRAN-I Hydrocarbon-In-Water Analyzer is compact and portable. It can be used in the laboratory or in the field for rapid, accurate determinations.

The MIRAN-I Analyzer is ideal for the infrared analysis of dissolved hydrocarbons in water by solvent extraction based on the API Method #733-58.

Call or write today for a free copy of our Application Report, "Infrared Determination of Hydrocarbons In Water" and further information on the MIRAN-I Analyzer.



WILKS SCIENTIFIC CORPORATION

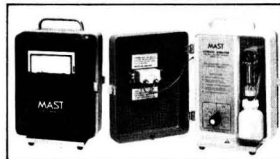
P. O. Box 449 • S. Norwalk, Ct. 06856
203/853-1616

CIRCLE 2 ON READER SERVICE CARD

NEW! 'Anywhere' Continuous Ozone (Oxidant) Measurements



- Immediate and reliable Ozone measurements read directly in ppm/vol. from front panel meter. Four selectable ranges (0-0.1, 0-0.2, 0-0.5, and 0-1.0 ppm).
- Factory calibrated for Ozone. Can also be calibrated to measure chlorine, bromine, and fluorine.
- Completely portable for field and factory Ozone surveys. Designed to NIOSH recommendations for direct reading compliance monitors.
- Linear recorder output in all ranges. Simple zero and span adjustments.
- Powered by 20-hour rechargeable battery pack (optional battery charger/AC adapter available).



Model 724-4 Battery Powered Oxidant Monitor
7 1/2" x 6" x 11" high — 12 lbs.

For complete data write



AIR MONITORING DIVISION

Dept. ES3, 2212 East 12th St.
Davenport, Iowa 52803

CIRCLE 1 ON READER SERVICE CARD

NEW LITERATURE

- Sanitary sewer pipe.** A 20-page manual answers technical questions about ABS composite pipe asked by owners and specifiers of sewage collection systems. Armco Steel Corp. 151
- Aerators.** Bulletin 200 describes the Aqua-Jet Axial Flow Aerator with applications to situations in which influent concentration and BOD levels fluctuate. Complete specifications are given. Aqua-Aerobic Systems 152
- Dust collector bags.** Catalog describes filter fabrics and replacement dust bags, and gives information about efficiency and resistance to abrasion, heat, and chemical attack. National Filter Media Corp. 153
- Screen separator.** Updated bulletin VS-75 describes and gives specifications for different sizes of screen separators (18-100 in. diameter) for chemicals, ceramics, food, pulp, and wastes. Kason Corp. 154
- Water management.** Illustrated brochure, "Water Resource Development and Water Quality Management", describes company capabilities and services in water supply, power, recreation, and many other areas, including water protection. Michael Baker, Jr., Inc. 155
- Control valve sizing.** Control Valve Pocket Handbook offers a condensed guide to control valve sizing, with formulas applicable to gas, liquid, or steam. DeZURIK 156
- Steelmaking emission control.** Brochure, "Steelmaking and Ironmaking with MIDREX Reduced Iron", shows how steelmaking can be done with less noise and dust emission, time savings, increased yield, and other advantages. Midrex Corp. 157
- Microscopy immersion oil.** Technical reprint describes immersion oil with non-drying formulations free of PCB content. R. P. Cargille Laboratories, Inc. 158
- Invention marketing.** Booklet, "The Link Between The Inventor and Industry", describes industry's search for new products to develop. Lawrence Peska Associates, Inc. 159
- Vapor recovery.** Bulletin No. 129 describes petroleum vapor recovery system, and how it removes vapors from the air-gas stream. Components are explosion-proof, and electrical system meets stringent safety requirements. Tenney Engineering, Inc. 160
- Laundry wastewater recycle.** Report explains how the LECTRO CLEAR process clears water sufficiently for recycling in laundries, and saves heat and surfactant. Swift Environmental Systems Co. 161
- Marine ventilators.** Bulletin 194R describes ventilators and exhaustors usable aboard ships and in other confined areas. Coppus Engineering Corp. 162
- Chlorination.** Four bulletins, Nos. 3001, 3005, 3006, and 3007 describe use of recirculated water in chlorinator operation, chlorination of well water, and chlorine gas feed techniques. Capital Controls Co. 163
- Air cleanup.** Latest issue of *Air Journal* emphasizes new air pollution control technology, and discusses costs, coal desulfurization, and boiler efficiencies. Peabody Air Pollution Control Group 164
- Safety in gas handling.** Quick-reference wall chart gives a guide to safe handling of the company's Isotron compressed gas cylinders in refrigerant, air conditioning, and propellant applications. Pennwalt Corp. 165
- Solar energy use.** Brochure lists books covering space heating of homes, water heaters, technology, do-it-yourself systems, components, building designs, and many other topics of solar energy. J. C. Young Co. 166
- Activated carbon.** Pamphlet, "Questions and Answers About Taste and Odor Control in Potable Water with Filtrasorb® Granular Activated Carbon", answers frequently-asked questions concerning organics removal with granular activated carbon. Calgon Corp. 167
- Instrumentation.** "Environmental Instruments News", periodically published, describes company's latest environmental monitoring instrumentation. Thermo Electron Corp. 168
- Combustion systems.** Brochure describes heat recovery systems, heat recovery media, fuel-oil atomizers, combustion control systems, and similar products. CEA Combustion, Inc. 169
- Audiometric testing.** Bulletin 5.1112.0, "Recommended Techniques for Accurate Audiometric Tests", describes the best ways of testing workers to protect them from noise effects and ascertain these effects. Test controls are suggested. Industrial Acoustics Co., Inc. 170
- Flow monitors.** Information on the UMM-12, a non-contact portable wastewater monitoring instrument for measuring wastewater level in sewage lines, is available. Device is battery-powered and almost maintenance-free. Environmental Measurement Systems 171
- Measuring dissolved solids.** Brochure lists and specifies over ten models of portable, battery-operated conductivity instruments for dissolved solids measurement. Myron L Co. 172
- Pneumatic ejectors.** Bulletin CPC 100 describes pneumatic ejector systems for transporting sludge, grit, and screenings. CPC Engineering Corp. 173
- Fiberglass pumps.** Bulletin 10B1/20B1 describes high-performance fiberglass horizontal pumps, especially useful in corrosive chemical atmospheres. Fybroc, Inc. 174
- X-ray spectrometers.** A 16-page brochure describes the SPECTRACE 440 series of X-ray spectrometers for analysis systems which are totally automated. Nuclear Semiconductor 175
- Waste treating equipment.** A 32-page catalog describes water-treating items, including demineralizers, reverse osmosis systems, filters, water softeners, and accessories. Ion Exchange Products, Inc. 176
- Laboratory supplies.** January 1976 catalog lists line of laboratory supplies for nuclear, biological, chemical, environmental, and radiological work. Interex Corp. 177
- Water conditioning.** Bulletin 335-200 describes operating principles of company's water conditioning systems, and tells where they can be used. Envirex 178
- Infrared spectrophotometers.** Brochure DB-10/75 20 details Models 735B, 727B, and 710B infrared spectrophotometers with scanning ranges of 4000-400 cm⁻¹, and sample spectra. Perkin-Elmer 179
- Oxygen measurement.** Brochure exclusively describes oxygen measurement,

and covers several dissolved oxygen meters and accessories in detail. The Horizon Bio-Oxidation System for pilot municipal and industrial waste studies is also described. Horizon Ecology Co. **180**

Hydrocarbon analyzer. January 1976 issue of *Infrared News* discusses relationship between the firm's hydrocarbon in-water analyzer and EPA alternate-approved testing methods. Wilks Scientific Corp. **181**

Corrosion-resistant motors. Complete specification for variable-speed, corrosion-resistant Motodrives, 1/4-50 hp, suitable for pollution control and wastewater systems, is available. Reliance Electric Co. **182**

Sludge/slurry readouts. Bulletin PDS-4102 describes the company's Sensall Model 4940 Sludge Density Transmitter with linear readouts of solids and sludge conditions in slurries. National Sonics Division, Envirotech Corp. **183**

Dissolved solids. Bulletin describes problem of dissolved solids in recirculating water systems in cooling towers, boiler controllers, test equipment, and other situations. Cambridge Scientific Industries **184**

Wet scrubber. Brochure describes wet scrubber system attaining high efficiency in dust control and stack emission abatement. Data for actual installations are given. Josam Manufacturing Co. **185**

Gas flow calibration. Bulletin DS-1052 describes a series of gas flow rate calibrators with $\pm 0.2\%$ accuracy and range of 1-24 000 cm³/min. Brooks Instrument Division, Emerson Electric Canada Ltd. **186**

pH electrodes. Bulletin S200 describes new Sensorex polymer and glass body pH electrodes, and gives selection criteria for electrode types. Sensorex **187**

Oil skimmer. Bulletin OS-5 describes the Series 7000 oil skimmer that removes floating oils from wastewater, especially in sumps, pits, tanks, or ponds. Met-Pro Systems, Inc. **188**

Liquid membrane electrodes. New 93 Series liquid membrane electrodes, for water hardness, calcium, chloride, fluoroborate, nitrate, perchlorate, and potassium determination, are described in brochure. They are insensitive to bubbles and static. Orion Research Inc. **189**

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

Thermocouple technology. General Bulletin GB-308 describes the development of vastly expanded capabilities in the production of advanced, high-grade thermocouples. Claud S. Gordon Co. **190**

Chromatography. Publication, *Current Peaks*, gives analytical chromatograms for sulfurous flue gas, trace CO, natural gas, and other materials. Carle Instruments, Inc. **191**

Noise control. IAC Case History No. 92875 tells how a "Simulated Open Field" anechoic chamber was used to design quieter fork-lift trucks. Industrial Acoustics Co., Inc. **192**

Sulfur gas analysis. Application Note ANGC 5-75 (Pub. No. 5952-5687) tells how SO₂, H₂S, and carbonyl sulfide are determined in the sub ppm range with an 18-in. Teflon column. Hewlett-Packard. **193**

Flammable gas indicators. Data Sheet 08-00-06 describes indicators for measuring flammable gases and vapors in a wide range of industrial applications. Mine Safety Appliances Co. **194**

Dust collectors. Brochure describes industrial dust collectors with expected efficiencies of over 99.9%, even for particles of sub-micron size. Alcar Metals, Inc. **195**

Butterfly valves. Bulletin 760 describes five complete lines of butterfly valves for types of service ranging from general industrial to severely corrosive. Garlock Inc. **196**

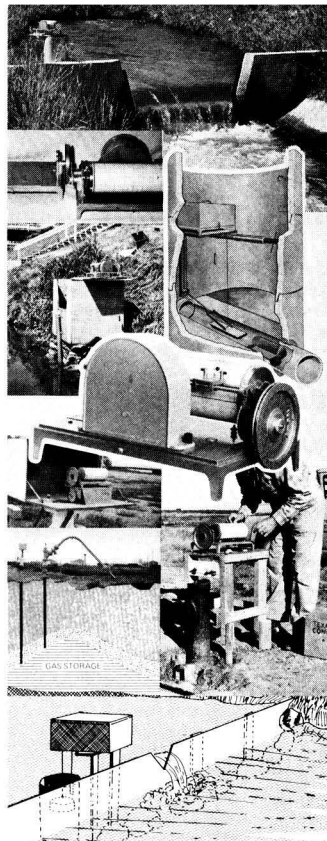
Energy cost reduction. Brochure describes a computer program aimed at minimizing total energy costs for industrial utility systems with numerous boilers, turbine-generators, fuels, and pressure levels. Profimatrics, Inc. **197**

Activated carbon. Article tells how use of powdered and granular activated carbon is effective in treatment of refinery wastewater. ICI United States Inc. **198**

"Federal Materials Research and Development: Modernizing Institutions and Management". OSP-76-9. Comptroller General of the United States, Washington, DC 20548 (write direct).

"Residential Paper Recovery, A Municipal Implementation Guide". Publication SW-155, by Penelope Hansen. U.S. Environmental Protection Agency, Washington, DC 20460 (write direct).

Waste paper recycle. Booklet, "Waste Paper Recycling", describes need and advantages of waste paper recycling. Single copies free; additional copies, \$1 each. American Paper Institute, 260 Madison Ave., New York, NY 10016 (write direct).



Where can YOU use this versatile*, simple, low cost chart recorder?

* Stevens Type F Recorder with float input has been used for over 40 years for various water measurement applications such as stream gaging, irrigation, open channel flows over weirs and flumes, manhole installations, and ground water levels in small diameter wells.

The simplicity of operation, low cost and reliability of the Type F appealed to many Stevens customers who adapted it for many unforeseen uses — for example — ice cap settlement, snow ablation, ground settling, fault line creep, natural gas storage, telemetering, precipitation measurement and other applications where an inexpensive record of movement is needed. Where can you use it?

Write for free product bulletin and Application Note — this may just be the recorder for your application.



STEVENS
Instruments since 1907
Leupold & Stevens, Inc.

P.O. Box 688 Dept. C-51 Beaverton, Ore. 97005 USA

CIRCLE 16 ON READER SERVICE CARD

BOOKS

The Measurement of Airborne Particles. Richard D. Cadle. xi + 342 pages. John Wiley & Sons, Inc., 605 Third Ave., New York, NY 10016. 1975. \$22.50, hard cover.

The measurement of airborne particles has become a high specialty. This text is devoted entirely to that specialty, and presents advantages and disadvantages of various techniques and devices for such measurement. It discusses commercially available equipment, as well as that treated only in literature. Isokinetic sampling and statistical treatment of particle-size data are also covered.

Herbicides: Chemistry, Degradation, and Mode of Action, Volume I. Philip C. Kearney and Donald D. Kaufman, Eds. 512 pages. Marcel Dekker, Inc., 270 Madison Ave., New York, NY 10016. 1975. \$39.50, hard cover.

This volume represents findings of 20 years of research. Among its subjects are substituted ureas, 5-triazines, and substituted uracil herbicides. Also included are articles on thiocarbamates, chlorinated aliphatic acids, benzoic acid herbicides, and herbicide photodecomposition.

Sources of Information in Water Resources. Gerald J. Giefer. 290 pages. Water Information Center, Inc., 14 Vandeventer Ave., Port Washington, NY 11050. 1976. \$23.50, cloth.

Literature searches are often highly time-consuming. This book is designed to save valuable time by citing and annotating more than 1100 sources. These are arranged under 62 subject subdivisions in a comprehensive list.

Pesticide Handbook—Entoma. 26th ed. Samuel C. Billings, Ed. 290 pages. Entomological Society of America, 4603 Calvert Rd., Box AJ, College Park, MD 20740. 1975. \$6, paper; \$7.50, cloth-bound.

This work comprises a 1975–1976 edition. It lists poison control centers, and gives complete data concerning insecticides, fungicides, rodenticides, fumigants, and other biocides. Environmental implications are discussed, and EPA regional pesticide contacts are list-

ed. Insect pheromones and growth regulators are also discussed.

Resource Recovery and Recycling Handbook of Industrial Wastes. Marshall Sittig. xvi + 427 pages. Noyes Data Corp., Mill Rd. at Grand Ave., Park Ridge, NJ 07656. 1975. \$36, hard cover.

One of the Environmental Technology Handbook series, this work explains the conversion of industrial wastes into resources. It emphasizes process technology. Complex waste products, ferrous metals, inorganic materials, glass and ceramics, non-ferrous metals, natural products, and food and beverage industry wastes and their beneficiation are among the many subjects exhaustively discussed.

Non-Nuclear Futures: The Case for an Ethical Energy Strategy. Amory B. Lovins and John H. Price. xxxii + 223 pages. Ballinger Publishing Co., c/o John B. Lippincott Co., East Washington Square, Philadelphia, PA 19105. 1975. \$11.95, cloth; \$5.95, paper.

The authors present a conceptual basis for energy policies that can meet long-range goals without what they feel is a risk of enormous costs and irreversible commitments of nuclear power in exchange for uncertain benefits. The choice and social differences between high- and lower-energy development paths are discussed.

Studies in Ecology, Vol. 2. River Ecology. B. A. Whitton, Ed. x + 726 pages. University of California Press, 2223 Fulton St., Berkeley, CA 94720. 1975. \$40, hard cover.

This volume provides a comprehensive treatment of river ecology and a fundamental framework for the subject. Designed for the more advanced student and professional, it covers hydrology, algae, heavy metals, bacteria and fungi, fish, biological indicators, river management, and many other relevant topics.

The Changing Dream. John V. Tunney. 120 pages. Doubleday & Co., Inc., Garden City, NY 11530. 1975. \$5.95, hard cover.

In this book, Senator Tunney (D-Calif.) outlines some of the practical steps that must be taken now, if a brighter future is to be realized. He explains what tough decisions need to be made concerning the twin threats of inflation and recession, spiraling population growth, environmental problems, and dwindling resources. He warns that expanding technologies—solar, geothermal, and nuclear—are not developed enough to meet expected demands. However, Sen. Tunney believes that with comprehensive planning, Americans can still redeem their future.

Air Pollution Control: A Welfare Economic Interpretation. Robert E. Kohn. xxi + 155 pages. Lexington Books, D.C. Heath and Co., 125 Spring St., Lexington, MA 02173. 1975. \$16.50, hard cover.

The interface between welfare economics and air pollution control involves a clear definition of the requirements for efficient allocations of inputs and outputs when air pollution occurs. It also comprises a distinct separation of efficiency and equity considerations. The author discusses the technology of abatement in these contexts, and uses models to amplify his points.

Birds of the Antarctic and Sub-Antarctic. George E. Watson. 350 pages. American Geophysical Union, 1909 K St., N.W., Washington, DC 20006. 1975. \$12.

This book is a definitive work on the bird life of the world's most southerly regions. It covers more than 140 species of these birds, and illustrates them in black-and-white or full color plates. English and Latin synonyms and French and Spanish vernacular names are given. The book can be a reference work and a field guide.

The Liquid Metal Fast Breeder Reactor: An Economic Analysis. Brian G. Chow. 76 pages. American Enterprise Institute for Public Policy Research, 1150 17th St., N.W., Washington, DC 20036. 1975. \$3, paper.

Has the government atomic energy establishment overestimated the projected benefits of the LMFBR program? Chow states that some of these bene-

fits may never come into existence. He gives many reasons, including overestimates of future energy demands, high capital and plant costs, and cost overruns for a recommendation that some LMFBR funding resources be dedicated to other efforts.

Standard Reference Materials: Standardization of pH Measurements. 48 pages. National Technical Information Center, Springfield, VA 22151. 1975. \$1.05.

The National Bureau of Standards has adopted an operational scale of pH defined in terms of pH of a series of standard buffer solutions. The bureau explains how these solutions are to be prepared, what types of electrodes should be used, and how instruments should be calibrated. Ask for NTIS No. SP-260-53.

Photochemical Oxidant Air Pollution. 94 pages. OECD Publications Center, Suite 1207, 1750 Pennsylvania Ave., N.W., Washington, DC 20006. 1975. \$3.75.

This report examines the problems and policies involved in preventing Los Angeles-type smog. It assesses comparative experience in Australia, Japan, and the U.S. It also stresses the need for a strong scientific basis for use in the development of abatement strategies.

Pioneers of Conservation in America. 15 pages. Soil Conservation Society of America, 7515 N.E. Ankeny Road, Ankeny, IA 50021. 1975. \$0.30, paper.

This booklet is a cartoon version of the history of conservation in America, and a story of the statesmen and thinkers who propounded conservation. A Bicentennial project, it is suited to young and old alike.

Handbook of Environmental Control, Volume V, Hospital and Health Care Facilities. Conrad P. Straub, Ed. 426 pages. CRC Press, Inc., 18901 Cranwood Parkway, Cleveland, OH 44128. 1975. \$37.95, hard cover.

Unlike its predecessor volumes, this book deals with microenvironmental control. It covers pathogens in health care areas, types of care facilities, environmental hygiene, toxic agents, radiological health, waste disposal, and other very relevant topics. About 95% of the book consists of tabular data.

Water Supply and Wastewater in Coastal Areas. 187 pages. Water Resources Research Institute of the University of North Carolina, 124 Riddick Building, N.C. State University, Raleigh, NC 27607. 1975. \$8, prepaid; \$10, if billed.

Coastal lands and waters are among the most valuable resources of the southeastern U.S. This book contains

the presentations at a conference that was devoted to review the state-of-the-art of proper planning and management of water supply and wastewater handling in this area.

Geothermal Energy Technology Assessment. Paul N. Chermisnoff and Angelo C. Morresi. 183 pages. Technomic Publishing Co., Inc., 265 W. State St., Westport, CT 06880. 1976. \$20.

The National Science Foundation has estimated that by 1985, geothermal sources could account for 137 000 MW of power production. This book tells engineers, businessmen, economists, and government officials how this prophecy could be fulfilled. It covers exploration and drilling future plans; work done so far; and many other related subjects.

Toxicology Research Projects Directory. Periodical. Toxicology Document and Data Depository, National Technical Information Service, Springfield, VA 22151. \$50/yr; \$15, single issue (\$65 and \$20, foreign).

To be issued quarterly, this periodical contains descriptions of 2500 on-going toxicology research projects. It covers agricultural, industrial, household, pharmaceutical, food, and cosmetic materials; biotoxins, trace elements; minerals; and environmental problems. Ask for Publication No. NTISUB/B/021-76/001.

DIRECTOR of ENVIRONMENTAL RELATIONS SAN FRANCISCO BAY AREA

Corporate growth and expansion have created an excellent opportunity for an Environmentalist to join the Corporate staff of our International Fortune 500 Company, headquartered in SAN FRANCISCO.

You will have primary responsibility for developing and implementing Corporate programs dealing with EPA/OSHA/Consumer complaints and other state and federal compliance programs. You will develop and implement programs that assure the Corporation of compliance.

The professional we seek will have a BS in Engineering or the Sciences with an MS in Environmental Sciences—MBA highly desirable. You should have at least 5 years in direct environmental matters and in-depth experience with regulatory agencies required. Must be able to interface with many inter-company departments.

This career position offers an attractive salary and an excellent opportunity for personal and professional growth. If you would like to pursue this situation, please communicate a complete profile of your qualifications with salary history, in full confidence, to Box 3761, ACS, 1155 16th St., N.W., Washington, D.C. 20036.

An equal opportunity employer M/F

Portable gas monitors


Models for SO₂, H₂S, O₂, CO, NO_x, NO₂

Lightweight, rugged unit is excellent for both OSHA and stack sampling requirements.

- For OSHA—accurate sensor ($\pm 2\%$), plus self-contained sample pump and power pack. Terminals for an accessory recorder are built in.

- For checking stacks—use our efficient, built-in sample preconditioner.

Dosimeter option available for ppm-hour integration. Low cost. Send for details.

 Under 10 lbs.



World-Wide Response / Ability

**WESTERN
PRECIPITATION
DIVISION**



Joy Manufacturing Company
P.O. Box 2744, Terminal Annex
Los Angeles, California 90051

CIRCLE 28 ON READER SERVICE CARD

CHEMICAL CARCINOGENS

A tape recorded in-depth look at the problem of hazardous substances in the environment.

5 Speakers
Length: 164 Minutes
14 Figures

The Speakers:

- H.H. Fawcett**—Purpose of Symposium
B. Carroll (N.I.O.S.H.)—Toxic Substances List—What, Why, How, For Whom
W.F. Malone (Nat'l. Cancer Inst.)—Occupational Cancer Control and Prevention
N. Meade (EPA)—Actual vs. Acceptable Risks from Asbestos
W.S. Wood (Wood Assoc.)—Engineering Approach to Control of Chemical Carcinogen Exposure

PRICE: \$18.00 (Cassettes Only)

(Postpaid, includes printed copies of slides used)

Order From: American Chemical Society
1155 Sixteenth Street, N.W.
Washington, D.C. 20036
ATTN: Dept. AP

Name _____

Address _____

City _____

State _____ Zip _____

(allow 4 to 6 weeks for delivery)

PROGRESS IN CANCER CHEMOTHERAPY

Tape recorded discussions about new drugs that look promising in the battle against cancer.

5 Speakers/167 Minutes/85 Figures

The Speakers:

- A.C. Sartorelli** (Yale U.)—Optimization of the Antineoplastic Potential of α -(N)-Heterocyclic Carboxaldehyde Thiosemicarbazones (HCT)
D.W. Henry (Stanford Res. Inst.)—Adriamycin
N.R. Bachur (Nat'l Cancer Inst.)—Biochemical Pharmacology of the Anthracycline Antibiotics
A.J. Lin (Yale U.)—Potential Bioreductive Alkylating Agents
G.P. Wheeler (Southern Res. Inst.)—Review of Studies on the Mechanism of Action of Nitrosoureas

PRICE: \$18.00 (Cassettes Only)

(Postpaid, includes printed copies of slides used)

Order From: American Chemical Society
1155 Sixteenth Street, N.W.
Washington, D.C. 20036
ATTN: Dept. AP

Name _____

Address _____

City _____

State _____ Zip _____

(allow 4 to 6 weeks for delivery)

CONTROL OF ATHEROSCLEROSIS

A tape recorded symposium detailing the latest advances toward controlling atherosclerosis and reducing coronary heart disease which kills 600,000 Americans each year.

6 Speakers/210 Minutes/125 Figures

The Speakers:

- R.I. Levy** (Nat'l Heart & Lung Inst.)—Lipids in Atherosclerosis
G.F. Holland (Pfizer)—Recent Advances in the Discovery & Development of Antihyperlipidemic Agents
R.M. Tomarelli (Wyeth)—Antihypercholesterolemic Activity of WY 14,643, a 2-Pyrimidinylthioacetic Acid Derivative
R.A. Parker (Merrell-National)—5-(Tetradecyloxy)-2-Furancarboxylic Acid (RMI 14,514) & Related Hypolipidemic Fatty Acid-like Alkylaryloxy-carboxylic Acids
L.R. Mandel (Merck)—Studies of the Mode of Action of Halofenate
L.A. Kolly (Sandoz)—Studies of a Series of Compounds which Reduce Serum Cholesterol With and Without Accumulation of Sterol Precursors of Cholesterol

PRICE: \$18.00 (Cassettes Only)

(Postpaid, includes printed copies of slides used)

Order From: ACS / 1155 16th Street, N.W., Wash., D.C. 20036/Attn: Dept. AP

Name _____

Address _____

City _____

State _____ Zip _____

(allow 4 to 6 weeks for delivery)

INTERFERON

Interferon may play an important role in protecting against virus infections, cancer, and other diseases. The potential for interferon is examined in this tape recorded symposium.

4 Speakers
Length: 143 Minutes
44 Figures

The Speakers:

- S. Baron** (Nat'l. Inst. Allergy, Infect. Dis.)—Biological Aspects of the Interferon System
H.B. Levy (N.I.A.I.D.)—Mechanism of Antiviral Action of Interferon
J. Vilcek (New York U.)—Interferon Induction with Polynucleotides and Viruses
J.F. Niblack (Pfizer)—Synthetic Inducers of Interferon

PRICE: \$18.00 (Cassettes Only)

(Postpaid, includes printed copies of slides used)

Order From: American Chemical Society
1155 Sixteenth Street, N.W.
Washington, D.C. 20036
ATTN: Dept. AP

Name _____

Address _____

City _____

State _____ Zip _____

(allow 4 to 6 weeks for delivery)

Selective Insect Control

Tape recorded symposium examines the potential of growth regulating chemicals as selective insect control agents.

3 Speakers
Length: 135 Minutes
95 Figures

The Speakers:

- L.I. Gilbert** (Northwestern U.)—Biochemical and Physiological Aspects of Insect Growth and Development
J.H. Law (U. Chicago)—Juvenile Hormone Synthesis and Action in Insects
J.W. Barnett (Ciba-Geigy)—Recent Developments in Insect Growth Regulators

PRICE: \$18.00 (Cassettes Only)

(Postpaid, includes printed copies of slides used)

Order From: American Chemical Society
1155 Sixteenth Street, N.W.
Washington, D.C. 20036
ATTN: Dept. AP

Name _____

Address _____

City _____

State _____ Zip _____

(allow 4 to 6 weeks for delivery)

Progress Toward Synthetic Oils

Shale, coal, oil-bearing sands all offer an opportunity to add to our energy reserves. The potential for each is examined in this tape recorded symposium.

4 Speakers
Length: 125 Minutes
47 Figures

The Speakers:

- H.W. Sternberg** (Lawrence Livermore Lab.)—The Nature of Coal Liquefaction Products
S.K. Kunchal (Paraho Oil Shale Demo.)—Energy and Dollar Requirements in an Oil Shale Industry—Based on the Paraho Process
G.A. Myers (Atlantic-Richfield)—Prerrefining of Shale Oil
R.H. Fischer (Mobil)—Non-Hydrogenative Demetallation of Residua Using Manganese Nodules

PRICE: \$18.00 (Cassettes Only)

(Postpaid, includes printed copies of slides used)

Order From: American Chemical Society
1155 Sixteenth Street, N.W.
Washington, D.C. 20036
ATTN: Dept. AP

Name _____

Address _____

City _____

State _____ Zip _____

(allow 4 to 6 weeks for delivery)

MEETING GUIDE

March 17 Hoboken, N.J.

The Electrochemistry of the Three E's: Energy, Environment and the Economy. Electrochemical Society/Metropolitan New York Local Section

Write: Palmer H. Langdon, Secretary/Treasurer, Metropolitan New York Local Section, Electrochemical Society, One University Plaza, Hackensack, N.J. 07601

March 21-25 Washington, D.C.

41st North American Wildlife and Natural Resources Conference. The Wildlife Management Institute

Write: Wildlife Management Institute, 1000 Vermont Ave., N.W., 709 Wire Building, Washington, D.C. 20005

March 22 Orlando, Fla.

ASTM Conference on the Ozone Problem—Real or Imaginary? American Society for Testing and Materials' (ASTM) Committee D-22 on Methods of Sampling and Analysis of Atmospheres

Write: Richard C. Barras, Conference Committee Chairman, Atlantic Richfield Co., 400 E. Sibley Blvd., Harvey, Ill. 60426

March 22-23 Newark, N.J.

Industrial Pollution Control Measurement and Instrumentation Conference. New Jersey Institute of Technology

Write: Division of Continuing Education, New Jersey Institute of Technology, 323 High St., Newark, N.J. 07102

March 22-26 Salt Lake City, Utah

International Symposium on Toxicity and Physiology of Combustion Products. Committee on Fire Research of the National Academy of Sciences and the Flammability Research Center of the University of Utah

Write: I. N. Einhorn, Flammability Research Center, University of Utah, P.O. Box 8089, Salt Lake City, Utah 84108

March 25 Washington, D.C.

Public Hearing on the Biological and Ecological Impact of Project Seafarer. National Research Council

Write: Samuel Abramson, staff officer, National Research Council, 2101 Constitution Ave., N.W., Washington, D.C. 20418

March 25-27 Santa Maria, Calif.

Alternate Fuel Sources Symposium. California Polytechnic State University

Write: Dr. Hendel, School of Engineering & Technology, California Polytechnic State University, San Luis Obispo, Calif. 93407

March 28-30 San Antonio, Tex.

Annual Meeting. National Petroleum Refiners Association (NPRA)

Write: NPRA, Suite 802, 1725 DeSales St., N.W., Washington, D.C. 20036

March 28-31 Chicago, Ill.

First International Electric Vehicle Exposition and Conference. Electric Vehicle Council

Write: Robert Black, President, The Show Company International, 1605 Cahuenga Blvd., Los Angeles, Calif. 90028

March 29-31 Urbana, Ill.

18th Public Water Supply Engineers Conference: Water Treatment-Part I. American Water Works Association, the Illinois Environmental Protection Agency and the University of Illinois

Write: Michael J. Semmens, Assistant Professor, Environmental Engineering, 3207 Civil Engineering Building, University of Illinois, Urbana, Ill. 61801

March 29-31 Washington, D.C.

3rd Energy Technology Conference/Exposition. *Research/Development, Power Engineering and Pollution Engineering*

Write: Energy Technology Conference, c/o Government Institutes, Inc., 4733 Bethesda Ave., N.W., Washington, D.C. 20014

March 29-31 New York, N.Y.

NOISEXPO '76: The National Noise and Vibration Control Conference. *Sound and Vibration*

Write: NOISEXPO, 27101 E. Oviatt Rd., Bay Village, Ohio 44140

March 30-April 1 Houston, Tex.

Annual Pollution Conference and Exposition. Water and Wastewater Equipment Manufacturers Association (WWEMA)

Write: WWEMA, 7900 Westpark Drive, Suite 304, McLean, Va. 22101

March 31-April 2 Washington, D.C.

1976 International Synthetic Pulps and Papers Symposium. Technical Association of the Pulp and Paper Industry (TAPPI)

Write: W. B. Manning, TAPPI, One Dunwoody Park, Atlanta, Ga. 30341

April 1-2 Pittsburgh, Pa.

Stack Sampling Procedures. Research Appliance Co.

Write: Ralph J. Bulger, vice president, marketing, Research Appliance Co., Route 8, Gibsonsia, Pa. 15044

April 4-April 9 New York, N.Y.

American Chemical Society's Centennial Meeting

Write: A. T. Winstead, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036

April 5-8 San Diego, Calif.

National Water Resources and Ocean Engineering Convention and Exposition. American Society of Civil Engineers

Write: American Society of Civil Engineers, 345 E. 47th St., New York, N.Y. 10017

April 7-8 Washington, D.C.

4th Annual APCA Government Affairs Seminar. Air Pollution Control Association (APCA)

Write: Public Relations Dept., APCA, 4400 Fifth Ave., Pittsburgh, Pa. 15213

April 7-9 Atlanta, Ga.

Seventh National Symposium on Food Processing Wastes. U.S. Environmental Protection Agency, National Canners Association, and others

Write: Kenneth Dostal, U.S. EPA, 200 SW 35th St., Corvallis, Ore. 97330

April 11-14 New Orleans, La.

1976 Noise Control Seminar. Technical Association of the Pulp and Paper Industry (TAPPI)

Preregistration is mandatory. *Write:* W. B. Manning, TAPPI, One Dunwoody Park, Atlanta, Ga. 30341

April 13-14 Chicago, Ill.

Fifth Mineral Waste Utilization Symposium. U.S. Bureau of Mines and IIT Research Institute

Write: S. A. Bortz, IIT Research Institute, 10 W. 35th St., Chicago, Ill. 60616

April 19-21 San Antonio, Tex.

ASTM Committee E-33 on Environmental Acoustics

Write: C. W. Rodman, Battelle Memorial Institute, 505 King Ave., Columbus, Ohio 43201

April 19-22 Palm Springs, Calif.

National Geothermal Conference. The Geothermal Energy Association (GEA)

Theme is "Geothermal Energy—'76 The Year of Decision." *Write:* Sam M. Dermegian, GEA, Box 752, Azusa, Calif. 91702

April 20-22 Cincinnati, Ohio

Conference on Environmental Modeling and Simulation. U.S. Environmental Protection Agency (EPA)

Write: Elijah Poole (PM-218), Management Information & Data Systems Division, U.S. EPA, 401 M St., S.W., Washington, D.C. 20460

April 20-22 Hawthorne, Nev.

The Demilitarization of Conventional Munitions. American Defense Preparedness Association (ADPA)

Environmental topics will be discussed. *Write:* ADPA, 819 Union Trust Building, 740 15th St., N.W., Washington, D.C. 20005

(continued on page 296)

environmental professionals

IF YOU WANT TO DO SOMETHING
SPECIAL — FOR YOUR CAREER
and THE WORLD AROUND YOU ...

envirosphere could be your most productive environment.

A division of Ebasco Services, Inc., ENVIROSPHERE specializes in problem-solving assessment of environmental impacts involved with the construction and operation of electric power generation and other industrial facilities.

Both supervisory and senior-level positions are now available as follows; all offering a highly competitive salary, and requiring one or more degrees in the appropriate engineering or scientific discipline, plus several years of pertinent experience.

supervising geologist (HYDROGEOLOGIST)

To direct a staff concentrating on geophysical analysis, emphasizing environmental factors such as geology, beach erosion, hydrology, and ground water relating to site selection and assessment for power plants and other large building projects.

supervising terrestrial ecologist

To direct a staff engaged in terrestrial ecology programs for industrial clients and electric utilities. Responsibility will cover proposing, designing, managing and evaluating all terrestrial studies.

supervising hydrothermologist (OCEANOGRAPHER)

To head up a staff conducting near-shore field work involving diffusion studies, current and temperature monitoring, plus providing in-house data analysis and numerical predictions of heat dispersal from power plant cooling water.

senior air quality engineer

To assess the potential impact on air quality of alternative configurations for smoke stacks, scrubbers, reheaters and cooling towers/ponds at proposed power plants; and, in accordance with air quality standards, recommending the most appropriate air quality control systems.

senior water & waste management engineer

Based on evaluation of water and waste systems, must present alternative courses of action for treatment and re-use of industrial wastes. Will also develop conceptual design and recommend suitable waste processing equipment.

environmental project leader

To supervise and coordinate projects, including report preparation, by in-house multi-discipline teams performing environmental and site selection studies. Responsibilities also include client contact, liaison with regulatory agencies, coordination of sub-contractor input and expert testimony at hearings.

Functions of senior-level positions as shown above will include preparation of environmental reports, plus liaison with regulatory agencies and including expert testimony in Federal and State hearings.

Interested and qualified candidates, please send your resume with salary requirement, in confidence, to: Peter Domingo, Professional Employment, Dept. 302



envirosphere company

A Division of
Ebasco Services Incorporated
Two Rector Street
New York, N.Y. 10006
A HALLIBURTON Company

An equal opportunity, affirmative action employer

MEETING GUIDE

(continued)

April 21-22 Pittsburgh, Pa.
Annual Technical Meeting. Western Pennsylvania Section of the Air Pollution Control Association (APCA)

Theme is "Coal Utilization and Air Pollution Control." Write: Dr. Paul E. Fredette, Environmental Engineering Division, Aluminum Company of America, Alcoa Building, Pittsburgh, Pa. 15219

Courses

March 15-19 Athens, Ga.
Pesticide Ecology Seminar, Course No. 103.3. U.S. Environmental Protection Agency (EPA)

Fee: \$110. Write: Training, U.S. EPA, Region IV, Environmental Research Lab, College Station Road, Athens, Ga. 30601

March 15-19 New Brunswick, N.J.
Stack Testing Short Course. Rutgers, the State University

Fee: \$275. Write: Donald A. Deieso, Cook College, P.O. Box 231, Department of Environmental Science, Rutgers, the State University, New Brunswick, N.J. 08903

March 16-17 Madison, Wis.
Industrial Wastes. University of Wisconsin-Extension

Fee: \$100. Write: John T. Quigley, Program Director, Department of Engineering, University of Wisconsin-Extension, 432 N. Lake St., Madison, Wis. 53706

March 22-24 Los Angeles, Calif.
5th Annual Gas Chromatography Short Course. Occidental College

Fee: \$200. Write: R. L. Amey, Dept. of Chemistry, Occidental College, Los Angeles, Calif. 90041

March 22-26 Austin, Tex.
Advanced Water Pollution Control: Physical and Chemical Waste Treatment. The University of Texas at Austin

Fee: \$300. Write: Engineering Institutes, Cockrell Hall 2.102, The University of Texas at Austin, Austin, Tex. 78712

March 24-26 Davis, Calif.
Assessment of the Impact of Transportation Systems on Air Quality. University of California-Davis

Fee: \$150. Write: University of California-Davis, University Extension, Davis, Calif. 95616

March 28-31 Nashville, Tenn.
Development of Design Criteria for Wastewater Treatment Processes: Biological Waste Treatment. Vanderbilt University

Fee: \$225. Write: Prof. W. Wesley Eckenfelder, Jr., Vanderbilt University, Box 6222, Station B, Nashville, Tenn. 37235

March 29-30 Philadelphia, Pa.
Applied G.C.—Intermediate. Sadtler Research Laboratories Inc./Education Division

Fee: \$235. Write: Sadtler Research Laboratories Inc., Education Division, 3316 Spring Garden St., Philadelphia, Pa. 19104

(continued on page 297)

MEETING GUIDE

(continued)

March 29-31 Cleveland, Ohio
Polyvinyl Chloride Technology. New York University

Fee: \$425. Write: Ms. Heidi Kaplan, Information Services Manager, New York Management Center, Inc., Department 14NR, 360 Lexington Ave., New York, N.Y. 10017

March 29-31 Madison, Wis.
Gas and Leachate Generation and Control in Landfills. University of Wisconsin-Extension

Fee: \$150. Write: John Reindl, Department of Engineering, University of Wisconsin-Extension, 432 N. Lake St., Madison, Wis. 53706

April 5-9 Research Triangle Park, N.C.

Air Quality Monitoring Systems, Course No. 463. Air Pollution Training Institute

Fee: \$150. Write: Registrar, Air Pollution Training Institute, MD 17, National Environmental Research Center, Research Triangle Park, N.C. 27711

April 5-15 Arlington, Tex.

Sewage Works Operation (Unit 1). North Central Texas Council of Governments

Fee: \$40. Write: North Central Texas Council of Governments, P.O. Drawer COG, Arlington, Tex. 76011

April 5-16 New York, N.Y.

Environmental Health. New York University Post-Graduate Medical School and the Institute of Environmental Medicine

Fee: \$600. Write: Office of the Associate Dean, New York University Post-Graduate Medical School, 550 First Ave., New York, N.Y. 10016

April 6-8 Sewickley, Pa.

The Fundamentals and Needs of Industrial Hygiene. Industrial Health Foundation and the American Industrial Hygiene Association/Pittsburgh Section

Fee: \$150 (member companies); \$225 (nonmember companies). Write: George Reilly, Director of Safety and Training, Industrial Health Foundation, 5231 Centre Ave., Pittsburgh, Pa. 15232

April 7-8 Newark, N.J.

Wastewater Treatment Update. New Jersey Institute of Technology

Fee: \$120. Write: Director Continuing Education, New Jersey Institute of Technology, 323 High St., Newark, N.J. 07102

April 19-20 Chicago, Ill.

Slurry Wall Design and Construction. Resource Management Products (RMP)

Fee: \$265. Write: Dave Lager, RMP, Suite 1432, 30 W. Washington, Chicago, Ill. 60602

April 19-23 Washington, D.C.

Environmental Law. The George Washington University

Fee: \$425. Write: Director, Continuing Engineering Education, The George Washington University, Washington, D.C. 20052

(continued on page 300)

CLASSIFIED SECTION ■ POSITIONS OPEN

LABORATORY DIRECTOR: To supervise laboratory involved in analysis of water, plant and soils samples for primarily inorganic constituents. Must have good knowledge of analytical water chemistry and experience in supervision, data processing and quality control. Minimum requirements master's degree in analytical chemistry with two years supervisory experience in analytical (water) chemistry laboratory. Send resume to **Personnel Dept., C & S Flood Control District, P. O. Box V, West Palm Beach, Fla. 33402.**

AIR POLLUTION EXPERT

The New York City office of WAPORA, Inc. is looking for an individual with experience in the field of air pollution. The position is in environmental impact work and requires a knowledge of sampling techniques, modeling, meteorology, etc. Please forward resume to: **Director, Northeastern Office, WAPORA, Inc., 211 East 43rd Street, New York, New York 10017.**

AA/E/O.E. EMPLOYER

ENVIRONMENTAL ENGINEERING FACULTY POSITION.

Duties include teaching at undergraduate and graduate levels and research. Background in industrial water and wastewater and/or industrial air pollution preferred. Rank and salary open depending on qualifications of candidates. Reply to **Dr. David Hansen, Chairman, Department of Chemical and Environmental Engineering, Rensselaer Polytechnic Institute, Troy, New York 12181.**

An equal opportunity employer.

ENVIRONMENTAL ENGINEERS

We have many position openings in U.S. for professionals experienced in the design, application and/or sale of air, water or waste pollution control equipment, chemicals and systems. Client companies pay fees. Send resume & salary history in confidence to **Roger M. Hoffman,**

ESSEX PLACEMENT ASSOCIATES

2 North Main Ipswich, Mass. 01938

IMPORTANT NOTICE

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

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	\$55	\$53	\$51	\$49	\$47

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

SHIPPING INSTRUCTIONS:

Send all material to

Environmental Science & Technology Classified Advertising Department
50 West State St.
Westport, Ct. 06880

A new position as Professor of Ecology and Environmental Science is open for applications at the Technical University of Denmark.

This newly-established chair involves teaching and research, on a biological basis, concerning ecosystems, the impact of technological activity on ecosystems and possibilities of forecasting the consequences of said impact. The teaching of pollution abatement is not included. Applicants are requested to document research experience within this area.

The chair will be assigned to a new department, which, depending on future developments, may later be merged with other departments. A close cooperation on teaching and research with related departments in the university is expected.

Further information may be obtained from the Dean of Chemistry and Chemical Engineering, Professor, Dr. Anders Björkman, Building 227, The Technical University of Denmark, DK-2800 Lyngby.

The present yearly salary is Danish Crowns 206,511.

Applicants are asked to submit their curriculum vitae and to state their background in the fields of ecology and environmental science. They should also document their competence in teaching and enclose copies of relevant publications.

The selection committee, which will be composed of highly qualified scientists, will produce a final report, a copy of which will be sent to each applicant. This report will summarize the considerations on which the committee's final selection is based, and it will include an adjudication of each individual application.

Applications should be addressed to **Her Majesty the Queen** and submitted to the **Rector, Building 101, The Technical University of Denmark, DK-2800 Lyngby, not later than 3 May 1976.**

ENGINEERS

Positions are available for experienced engineers for the performance of government and industrial environmental studies. Applicants must be prepared to demonstrate proficiency in communication skills and have had extensive involvement in:

- Operation/technology of emission controls
- Engineering and cost analysis
- Environmental sampling and testing
- Measurement systems and instrumentation
- Environmental effects of energy use/conservation/extraction

Candidates most likely to qualify for these positions will be experienced chemical or instrument engineers. To be considered for a professionally challenging career in Environmental Engineering, and a wide spectrum of environmental tasks associated with Energy Systems, send resume and salary requirements to:

TRW Environmental Engineering Division
800 Follin Lane, S.E.
Vienna, Virginia 22180
Attention: Mrs. Jones

SENIOR PROJECT ENGINEER

Theford Corporation, Ann Arbor, Michigan has outstanding opportunity for individual to demonstrate technical competence, intelligence and project management ability. Opening requires the complete supervision of chemical laboratory and wastewater treatment product development program of a recycling toilet called Cycle-Let®. Individual will have two to four individuals reporting to him initially.

Opening requires a biochemical engineer, chemical engineer or biochemist with experience or educational training in wastewater treatment kinetics. A thorough understanding of chemistry, microbiology and biochemistry is required. Individual should have experience in designing or working with wastewater treatment equipment. Individual should be broad enough in order to be able to communicate effectively with other engineers concerning hardware components such as pumps, carbon filters, etc. Candidate should be shirtsleeve oriented, aggressive, analytical, mature and objective.

Send resume and salary requirements to: **Allan Coviello, Theford Corporation, Waste Treatment Equipment Division, P.O. Box 1285, Ann Arbor, Michigan.**

professional consulting services directory

ENVIRONMENTAL SPECIALIST
WATER POLLUTION
MONITORING & PURIFICATION SYSTEMS



9625 COZYCROFT AVE.
UNIT J
CHATSWORTH, CA 91311
(213) 341-6130

CLIFF OVERTON
PRESIDENT
GEN. MANAGER

Laboratory and Process Development
Industrial Waste Water Control
Liquid and Solid Incineration
Air Pollution Control
In-plant Control and Process Modifications
Desalination

CATALYTIC INC.

Consultants • Engineers • Constructors
Environmental Systems Division
Centre Square West, 1500 Market Street
Philadelphia, Pa. 19102, 215-864-8000
Charlotte, N.C. 28209, 704-525-8220

BUCK, SEIFERT & JOST
INCORPORATED



Consulting Engineers
201-567-8990

WATER SUPPLY • SEWAGE •
INDUSTRIAL WASTE TREATMENT •
TREATABILITY STUDIES •
HYDRAULIC DEVELOPMENTS • REPORTS •
INVESTIGATIONS • VALUATIONS •
RATES • DESIGN • CONSTRUCTION •
OPERATION MANAGEMENT •
CHEMICAL AND BIOLOGICAL LABORATORIES

140 Sylvan Avenue, Englewood Cliffs, New Jersey 07632

CUT REGULATORY PROBLEMS WITH PLANNED ENVIRONMENTAL PROGRAMS



50 years of technical
service to industry

- Water Pollution Measurement
- Stack Testing
- Ambient Air Sampling
- OSHA Compliance
- Solid Waste Management
- Energy Planning

FOSTER D. SNELL, INC. Subsidiary of
BOOZ • ALLEN & HAMILTON INC.
Hanover Road, Florham Park
New Jersey 07932 (201) 377-6700

Lawler, Matusky & Skelly Engineers

ENVIRONMENTAL
SCIENCE &
ENGINEERING
CONSULTANTS

Environmental assessment reports
Water body modeling
Water resources development
Municipal and industrial wastes disposal
Aquatic and marine biology
Plant siting
Air and water pollution control

TREATMENT PLANT DESIGN
ANALYTICAL LABORATORY
COMPUTER SERVICES
(914) 359-2100

415 Route 303, Tappan, New York 10983

JOHN G. REUTER ASSOCIATES

ENVIRONMENTAL ENGINEERS

- Water Quality Planning
- Water Resources & Supply
- Wastewater Management
- Solid Waste Management
- Resource Recovery
- Air Pollution Control
- Testing & Monitoring Services
- Analytical Laboratory

Ninth & Cooper Streets
Camden, New Jersey 08101
609-541-7700



CAMP DRESSER & MCKEE INC.

ONE CENTER PLAZA, BOSTON, MA 02108

ENVIRONMENTAL ENGINEERS

NEW YORK • WASHINGTON • DENVER • PASADENA
FT. LAUDERDALE • ORLANDO • ATLANTA • AUSTIN
WALNUT CREEK, CA • SPRINGFIELD, VA
MILWAUKEE • NEW ORLEANS



BLACK & VEATCH / CONSULTING ENGINEERS

COMPLETE ENGINEERING SERVICES FOR POLLUTION CONTROL

AIR • WATER • WASTEWATER • INDUSTRIAL WASTES
SOLID WASTES • ENVIRONMENTAL PLANNING

1500 MEADOW LAKE PARKWAY, KANSAS CITY, MISSOURI 64114

DALLAS • DENVER • ORLANDO • NEW YORK • SAN FRANCISCO • WASHINGTON D.C.



HENNINGSON, DURHAM & RICHARDSON

ENGINEERING • SYSTEMS • PLANNING • ECOSYSTEMS

Complete Services in Planning and
Design of Pollution Control Facilities

Atlanta • Charlotte • Chicago • Dallas • Denver • Helena • Los Angeles • Minneapolis
Norfolk • Pensacola • Phoenix • Santa Barbara • Seattle • Washington, D.C.

8404 INDIAN HILLS DRIVE

Omaha, Nebraska 68114 (402) 399-1000



YORK RESEARCH CORP.

TESTING - EVALUATION - CONSULTING

- Source Testing & Monitoring Systems
- Combustion & Energy Engineering
- Meteorological & Ambient Air Surveys
- Environmental Impact Statements
- Analytical & Fuels Laboratory
- Engineering Feasibility Studies
- Waste Management
- Certified Water Analysis Laboratory

AIR - WATER - WASTE - NOISE

One Research Drive - Stamford, Conn. 06906 (203) 325-1371
7100 Broadway - Denver, Colorado 80221 (303) 426-1582

Stearns-Roger

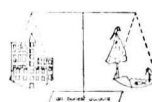


COMPLETE ENVIRONMENTAL SERVICES:

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

ENVIRONMENTAL SCIENCES DIVISION
(303) 758-1122

P. O. Box 5888
Denver, Colorado 80217



draft Environmental Impact
Reports Statements
Ecologic Assays Monitoring
Archeology... Botany... Zoology
SCIENTIFIC COUNSELING
BIOmedic-engineering-chemic
agricultural, educational
Interregional-International!

Joe GORMAN PhD ASSOCIATES

1333 Mountain, Claremont California 91711; 714 626-9929

professional consulting services directory

ENVIRONMENTAL ENGINEERS
24 HOUR EMERGENCY RESPONSE
 314/569-0991

D. W. Ryckman & Associates, Inc.
 689 Craig Road
 St. Louis, MO 63141

Judith H. Clausen, Ph.D.
 CONSULTING CHEMIST

- Pollution Analysis and Monitoring
- Treatability and Impact Studies
- Product Liability
- Safety and Hygiene
- Complete Laboratory Services

P. O. Box 203
 Lexington, Mass. 02173
 (617) 646-0220

SAMPLING & ANALYSIS
 Source • Water • Ambient Air
 fast, accurate service

Coors Spectro-Chemical Laboratory
 P. O. Box 500 • Golden, Colo. 80401
 (303) 279-6565

Pyrolysis
 Waste Gasification/Combustion
 Waste-to-Energy Systems

K. T. Lear Associates, Inc.
 P. O. Box 1431—Manchester, CT 06040
 (203) 647-9795

DUPONT ANALYTICAL & PHYSICAL
 MEASUREMENT SERVICE

We offer:

- Measurements
- Method Development
- Research

 Relating to:

- OSHA Compliance
- Air Analyses
- General Air Quality Measurements

 Du Pont Co.
 Experimental Station-269
 Wilmington, DE 19898 (302) 772-2821

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

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

Complete Analytical Services for
 Environmental Studies & Pollution Control

MANCHESTER LABORATORIES, INC.

WATER POLLUTION CONTROL
 AIR POLLUTION CONTROL
 CHEMICAL PROCESS ENGINEERING
 CHEMICAL ANALYSIS

105 North Franklin St. Manchester, Iowa 52057
 Post Office Box 65 (319) 927-5115

BURGESS ANALYTICAL LABORATORY

Chemical Analyses
 For Environmental Studies
 And Pollution Control

525 Ashland St., North Adams, MA 01247
 Tel. 413/663-6769

ENVIRONMENTAL QUALITY ANALYSTS
A Division of Brown and Caldwell

- Water Quality and Marine Investigations • Chemical and Biological Laboratories • Environmental Studies

150 So. Arroyo Pkwy. • Pasadena, CA 91109
 943 Newhall St. • Costa Mesa, CA 92627
 428 Jervis St. • San Francisco, CA 94103

ENTROPY ENVIRONMENTALISTS, INC.
 SPECIALISTS IN
 GROUND SAMPLING

Walter S. Smith President
 P. O. Box 12291, RTP
 Durham, N.C. 27709
 919/781-3550

53 South Broadway
 Yonkers, New York 10701
 914/423-8721

Environmental Engineering
 Industrial—Municipal • Water—Sewage
 Solid Wastes Management
 Air Pollution Control • Power Engineering

Gibbs & Hill, Inc.
 ENGINEERS. DESIGNERS. CONSTRUCTORS
 393 Seventh Avenue, New York, N.Y. 10001
 A Subsidiary of Dravo Corporation

PENNONI ASSOCIATES
 INCORPORATED
 CONSULTING ENGINEERS

2006 WALNUT ST. PHILADELPHIA, PA 19103
 (215) 561-0460

SMALL PARTICLE ANALYSIS
 BY ELECTRON MICROSCOPY

ERNEST F. FULLAM, INC.
 P. O. BOX 444 • SCHENECTADY, N. Y. 12301
 TELEPHONE 518-785-5533

SUPPLIER OF
ACCESSORIES FOR MICROSCOPY
 WRITE FOR CATALOG

Are your horizons clouded by NO_x?
 Call (518) 783-9002 for insight.

Chemical and Environmental Processes Department, of
 BRC International, Inc. / 24 Wade Road / Latham, NY 12110

CHARLES R VELZY ASSOCIATES, INC.
 CONSULTING ENGINEERS

WATER POLLUTION CONTROL • SOLID WASTE DISPOSAL • AIR POLLUTION CONTROL • INDUSTRIAL WASTES • DRAINAGE • WATER SUPPLY

350 Executive Boulevard
 Elmsford, New York 10523
 Mineola, New York Babylon, New York

J. E. SIRRINE COMPANY

Engineers Since 1902 An Employee Owned Company

Complete Design of
 Environmental Facilities

Greenville, South Carolina 29606 • Houston, Texas 77027
 Raleigh, North Carolina 27607

MVTL MINNESOTA VALLEY TESTING LABORATORIES, INC.

Specialists in Water and Wastewater

- Municipal/Industrial Waste Surveys
- Routine Monitoring Services
- Complete Laboratory Services

New Ulm, Minn 56073
 Phone 507-354-8517

GREELEY AND HANSEN ENGINEERS

STUDIES, DESIGNS AND CONSTRUCTION SERVICES FOR WATER, WASTEWATER AND SOLID WASTES

222 S. Riverside Plaza • Chicago, IL 60606 • (312) 648-1155
 New York 10007 Philadelphia 19103
 Richmond 23230 Tampa 33607

ENPROX™ SERVICE AND CHEMICAL SYSTEMS

industrial water treatment
 pollution control

ENVIRONMENTAL PRODUCTS DIVISION OF
 working with industrial water 62 years

OAKITE.
OAKITE PRODUCTS, INC.
 BERKELEY HEIGHTS, N.J. 07922 • TLX 138661

Environmental Studies, Design and Construction Management

Gilbert/Commonwealth

Engineers / Consultants
 Reading, Pennsylvania / Jackson, Michigan

AIR & WATER STACK & EXHAUST TESTS CONSULTING • LABORATORY

Particulates • Aerosols • Odor • Smoke
 Organics • Fumes • Acids • Foundries
 G. C. Chemical Analyses/O.S.H.A.
 "TEST IT FIRST SO YOU REALLY KNOW WHAT THE PROBLEM IS"

ROSSNAGEL & ASSOC.

Engineering & Testing Consultants
 1999 Rt. 70, Cherry Hill, N.J. 08003
 (609) 424-4440
 250 Arizona Ave., N.E. Atlanta, Ga. 30307
 (404) 377-4248, 4249

STRUCTURE PROBE, INC.

Specialists in Materials Research

Small Particle Analysis

- Scanning Electron Microscopy
- Transmission Electron Microscopy
- Electron Probe Micro Analysis
- Optical Microscopy
- Quantitative Image Analysis
 Quantimet Image Analyzing Computer

New York Area
 230 Forrest Street Metuchen, NJ 08840 • 201 549 9350

Philadelphia Area
 535 E. Gay Street West Chester, PA 19380 • 215 436 5400

HAVENS AND EMERSON LTD.
 Environmental Engineers

700 Bond Ct. Bldg. 299 Market Street 150 Technology Park
 Cleveland, OH Saddle Brook, NJ Atlanta, GA

INDEX TO ADVERTISERS IN THIS ISSUE

Balston, Inc. 212 Levy Advertising Assoc., Inc.	Western Precipitation 293 Reeds & Farris
Bausch & Lomb 288 Wolff Associates, Inc.	Whatman, Inc. 205 J. S. Lanza & Associates
Burdick & Jackson Lab., Inc. ... 223 Studio 5 Advertising, Inc.	Wilks Scientific Laboratory 289 WILSCI Advertising
Calgon Corporation 214 Ketchum, MacLeod, & Grove, Inc.	CLASSIFIED SECTION 297
Energetics Science, Inc. 210 J. M. Ferrazza Assoc., Inc.	PROFESSIONAL CONSULTING SERVICES DIRECTOR 298-299 Advertising management for the American Chemical Society Publications
Envirosphere Company, A Div. of EBASCO Services Incorporated 216 Hartel, Catalano, & Gornick, Inc.	CENTCOM, LTD. Thomas N. J. Koerwer, President; Clay S. Holden, Vice President; Benjamin W. Jones, Vice President; Robert L. Voepel, Vice President; C. Douglas Wallach, Vice President; 50 West State Street, Westport, Connecticut 06880 (Area Code 203) 226-7131
Envirosphere Company, A Div. of EBASCO Services Incorporated 296 McFrank & Williams Advertising Agency, Inc.	
Ethyl Intertech Corporation 206 Gaynor & Ducas Advertising	ADVERTISING SALES MANAGER Thomas N. J. Koerwer SALES REPRESENTATIVES
Fluid-Ionic Systems 225 Robert A. Mullen Advertising	Atlanta ... Richard L. Going, CENTCOM, LTD., Phone WX 2586
Leupold & Stevens, Inc. 291 Tualatin Advertising	Chicago 60093 ... Eugene Eldridge, CENTCOM, LTD., 540 Frontage Rd., Northfield, Ill. (Area Code 312) 441-6383
Martek Instruments, Inc. 238 Tekmar Marketing Services	Cleveland ... Michael Hayes, CENTCOM, LTD., 20340 Center Ridge Rd., Rocky River, Ohio 44116. (Area Code 216) 331-2324
Mast Development Company ... 289 Warren & Litzenberger, Inc.	Denver ... Clay S. Holden, CENTCOM, LTD., (Area Code 213) 776-0552
Matheson OBC Kenyon Hoag Associates	Houston ... Michael Hayes, CENTCOM, LTD., (Area Code 216) 331-2324
Meloy Labs. IBC Pallace, Incorporated	Los Angeles 90045 ... Clay S. Holden, CENTCOM LTD., Airport Arcade Bldg., 8820 S. Sepulveda Blvd., Suite 215, (Area Code 213) 776-0552
National Sanitation Foundation . 213 The Connelly Co., Advertising	New York 10017 ... Anthony J. Glamanco, CENTCOM, LTD., 60 E. 42nd Street, (Area Code 212) 972-9660
Philips Industries 218 C. J. Nicholl & Assoc., Ltd.	Philadelphia ... Anthony J. Glamanco, CENTCOM, LTD., 113 Essex Ave., Narberth, Pa. 19072, (Area Code 215) 677-9666
Raytheon Company 223 Provan die Eastwood & Lombardi Inc.	San Francisco ... Clay S. Holden, CENTCOM, LTD., (Area Code 213) 776-0552
Research Appliance Co. IFC W. F. Minnick & Assoc., Inc.	Westport, Ct. 06880 ... Anthony J. Glamanco, CENTCOM, LTD., 50 West State Street, (Area Code 203) 226-7131
Supelco 223 Supelco Park Advertising	Manchester, England ... Jill E. Loney, Technomedia Ltd., 218, Longhurst Lane, Mellor, Stockport, SK6 5PW Telephone: 061-427-5660
Taylor Chemicals Inc. 225 Emery Advertising Corp.	Reading, England ... Malcolm Thiele, Technomedia Ltd., Wood Cottage, Shurlock Row, Reading, RG10 0QE. Telephone: 073-581-302
Technical Heaters, Inc. 233 Gilbert & Benton Advertising	Paris, France ... Jack Anderson, Patric Hale, Technomedia Ltd., 18 Rue Gounod, 92 Saint-Cloud, Paris. Telephone: 602-24-79
Technicon Industrial Systems ... 209 Mediad, Incorporated	Tokyo, Japan ... Haruo Moribayashi, International Media Representatives Ltd., 1, Shiba-Kotohiracho, Minato-ku, Tokyo. Telephone: 502-0658
Teledyne Energy Systems 225 Emery Advertising Corp.	
	PRODUCTION DIRECTOR Joseph P. Stenza PRODUCTION ASSISTANT Ailce M. Hansen

MEETING GUIDE

(continued)

April 22-23 Madison, Wis.
Esthetic Considerations in Highway and Bridge Design. University of Wisconsin-Extension

Fee: \$110. *Write:* Lawrence A. Soltis, Associate Professor-Engineering, Department of Engineering, University of Wisconsin-Extension, 432 N. Lake St., Madison, Wis. 53706

April 26-30 Madison, Wis.
Wastewater Collection and Treatment Facility Planning. University of Wisconsin-Extension

Fee: \$350. *Write:* John T. Quigley, Program director, Department of Engineering, University of Wisconsin-Extension, 432 N. Lake St., Madison, Wis. 53706

April 29-30 Las Vegas, Nev.
Environmental Law. Government Institutes, Inc.

Fee: \$265 (early registration). *Write:* Nancy C. McNerney, Government Institutes, Inc., 4733 Bethesda Ave., N.W., Washington, D.C. 20014

Call for Papers

March 31 deadline
14th Biennial Mechanisms Conference. American Society of Mechanical Engineers

Conference will be held on September 26-29 in Montreal, Quebec, Canada. *Write:* Papers Review Chairman (U.S.A., South America, Australia, Japan), Dr. Frederick R. Tepper, U.S. Army Picatinny Arsenal, Fuze Development Branch, Bldg. 62-H, Dover, N.J. 07801; or (Canada, Europe, Asia, Africa), Dr. T. S. Sankar, Dept. of Mechanical Engineering, Concordia University, 1455 de Maisonneuve Blvd. W., H-929, Montreal, Quebec, Canada H3G 1M8

March 31 deadline
Twelfth American Water Resources Conference. American Water Resources Association

Conference will be held on September 20-23 in Chicago, Ill. *Write:* John E. Priest, chairman, technical program committee, Associate & Head Environmental Sciences and Hydrology Division, Harza Engineering Co., 150 S. Wacker Dr., Chicago, Ill. 60606

April 1 deadline
Annual Combined Meeting. American Academy of Clinical Toxicology, the American Association of Poison Control Centers, and the Canadian Academy of Clinical Toxicology

Conference will be held on August 4-6 in Seattle, Washington. *Write:* Barry H. Rumack, M.D., General Chairman, Rocky Mountain Poison Center, W. 8th & Cherokee St., Denver, Colo. 80204

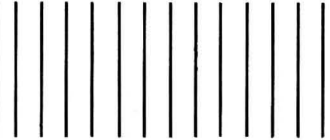
Environmental Science & Technology

QuickSearch!

To get fast, free data on whole groups of products, scan this list and circle numbers in the *QuickSearch* section on the reply card. Literature from advertisers in the previous issue will be sent to you.

No.	Product
201	Air Pollution Instruments
202	Air Purification Equipment
203	Auto Emission Instruments
204	Books, Journals, Publications
205	Construction Services
206	Consulting Services
207	Chemicals & Gases
208	Noise Measuring Instruments
209	Residue Analysis Instruments
210	Solid Waste Equipment
211	Telemetry & Data Acquisition
212	Waste Disposal Services
213	Water Pollution Instruments
214	Water Purification Equipment

FIRST CLASS
Permit No. 25682
Philadelphia,
Pa. 19101



BUSINESS REPLY MAIL

no stamp necessary if mailed in the United States

will be paid by

ronmental
science & Technology

P. O. BOX 8639
PHILADELPHIA, PA. 19101

ENVIRONMENTAL Science & Technology

MARCH 1976

**VALID THROUGH
JULY 1976**

ADVERTISED PRODUCTS:

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

NEW PRODUCTS, NEW LITERATURE:

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

QuickSearch:

201	202	203	204	205	206	207	208	209	210	211	212	213	214
-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----

NAME _____

TITLE _____

FIRM _____

STREET _____

CITY _____

STATE _____ ZIP _____

TELEPHONE _____

PLEASE CHECK: ACS MEMBER NONMEMBER

ADVERTISED PRODUCTS:

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

NEW PRODUCTS, NEW LITERATURE:

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

QuickSearch:

201	202	203	204	205	206	207	208	209	210	211	212	213	214
-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----

NAME _____

TITLE _____

FIRM _____

STREET _____

CITY _____

STATE _____ ZIP _____

TELEPHONE _____

PLEASE CHECK ACS MEMBER NONMEMBER

Environmental Science & Technology

QuickSearch!

To get fast, free data on whole groups of products, scan this list and circle numbers in the *QuickSearch* section on the reply card. Literature from advertisers in the previous issue will be sent to you.

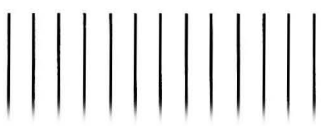
No.	Product
201	Air Pollution Instruments
202	Air Purification Equipment
203	Auto Emission Instruments
204	Books, Journals, Publications
205	Construction Services
206	Consulting Services
207	Chemicals & Gases
208	Noise Measuring Instruments
209	Residue Analysis Instruments
210	Solid Waste Equipment
211	Telemetry & Data Acquisition
212	Waste Disposal Services
213	Water Pollution Instruments
214	Water Purification Equipment

Environmental
Science & Technology
P. O. BOX 8639
PHILADELPHIA, PA. 19101

postage will be paid by

BUSINESS REPLY MAIL
No postage stamp necessary if mailed in the United States

FIRST CLASS
Permit No. 2568
Philadelphia
Pa. 19101



IT'S MELOY AGAIN!

In November It Was Our Ozone Analyzers

NOW OUR SO₂ ANALYZERS ARE EPA DESIGNATED AS EQUIVALENT METHODS

TUESDAY, JANUARY 27, 1976



federal register

Federal Register Tuesday, January 27, 1976, Page 3893 . . . Wilson K. Talley, Environmental Protection Agency Assistant Administrator for Research and Development, gave notice that the EPA, in accordance with 40 CFR Part 53, has designated the MELOY Model SA185-2A Analyzer as an equivalent method for the measurement of ambient concentrations of sulfur dioxide. This method is an automated analyzer utilizing the "flame photometric detection" measurement principle operated with a scale range of 0 to 0.5 ppm, with or without any of the following options:

- S-1. Linearized Output
- S-2. Modified Recorder Output
- S-6A. Re-ignite Timer Circuit
- S-7. Press to Read
- S-11A. Manual Zero and Span
- S-11B. Automatic Zero and Span
- S-14. Output Booster Amplifier
- S-18. Rack Mount Conversion
- S-18A. Rack Mount Conversion

**MELOY MODEL SA185-2A
SULFUR DIOXIDE ANALYZER**

As an equivalent method, the MELOY Model SA185-2A Sulfur Dioxide Analyzer is acceptable for use by States and other control agencies for purposes of ¶51.17(a) of 40 CFR Part 51 ("Requirements for Preparation, Adoption, and Submittal of Implementation Plans") as amended on February 18, 1975 (40 FR 7042). Mr. Talley's designation of this equivalent method will provide assistance to the States in establishing and operating their air quality surveillance systems under 40 CFR ¶51.17(a).

Note: EPA regulations require that after February 18, 1976 new purchases of sulfur dioxide and ozone monitors must be EPA designated reference methods and/or equivalent methods when used to be in compliance with state implementation plan requirements. (Reference 40 CFR ¶51.17(a)).



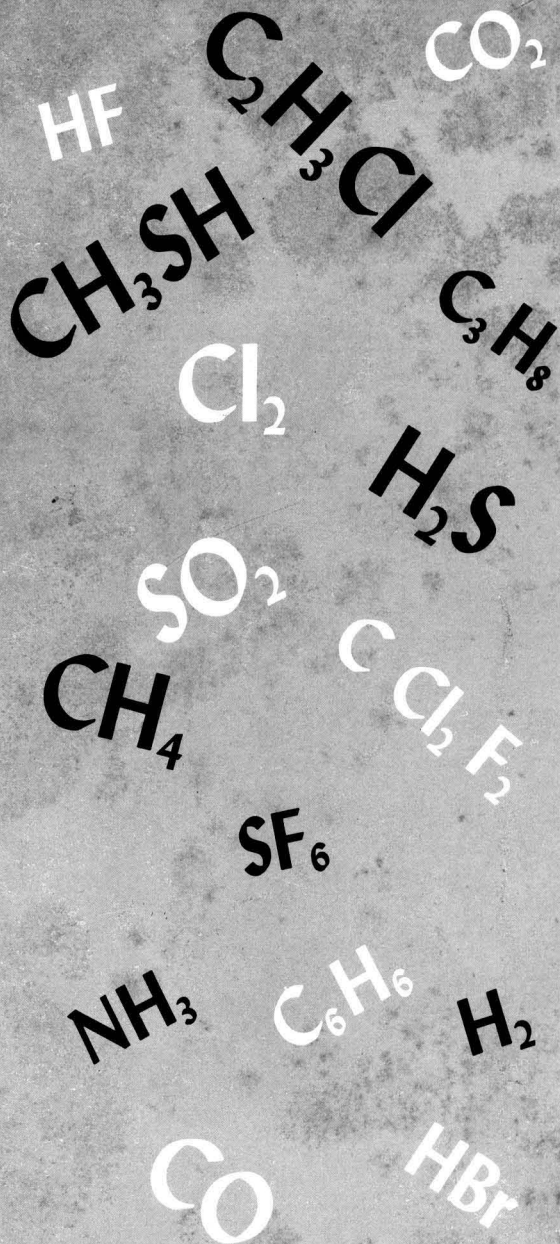
Meloy Laboratories, Inc.

INSTRUMENTS & SYSTEMS DIVISION

SULFUR ANALYZERS • OZONE ANALYZERS • NO_x ANALYZERS
HYDROCARBONS ANALYZERS • PHOSPHORUS ANALYZERS • CALIBRATION SOURCES

6715 Electronic Drive
Springfield, Virginia 22151
Phone: (703) 354-2600
TELEX 899-440

MATHESON SUPPLIES SPAN GASES FOR MOST TOXIC VAPORS... AND THE EQUIPMENT TO MAKE IT WORK



To test or monitor for toxic gases and vapors is a vital and difficult job, whatever the instrument that you use.

The accuracy of your measurements is critical . . . health and life itself are often in the balance. To ensure this vital accuracy you need a suitable zero gas and an accurate span gas to calibrate your instrument.

Matheson supplies both zero gases and the widest variety of span gases. We offer both Primary and Certified Standards, or will custom blend to your requirements.

But, an accurate mixture and high quality zero gas are not enough. Without the proper transfer system to carry the gas from the cylinder to your instrument you jeopardize the value of your work. A good regulator like Matheson's 3104 or 3800 — constant pressure, metal diaphragm — combined with the proper clean metal tubing is a must.

More important, Matheson supplies experience that **you** can draw upon to keep your instrument working at peak efficiency, or to help you select the proper equipment for a new instrument.

To improve your operation send for "Gas Mixtures, Facts and Fables." We discuss all this in detail and more.

 **MATHESON**
Lyndhurst, NJ 07071

Plants and Offices

East Rutherford, NJ 07073	Cucamonga, California 91730
Morrow, Georgia 30260	Newark, California 94560
Gloucester, Massachusetts 01930	Whitby, Ontario, Canada L1N 5R9
Joliet, Illinois 60430	Edmonton, Alberta, Canada T5B 4K6
La Porte, Texas 77571	B 2431 Oevel, Belgium