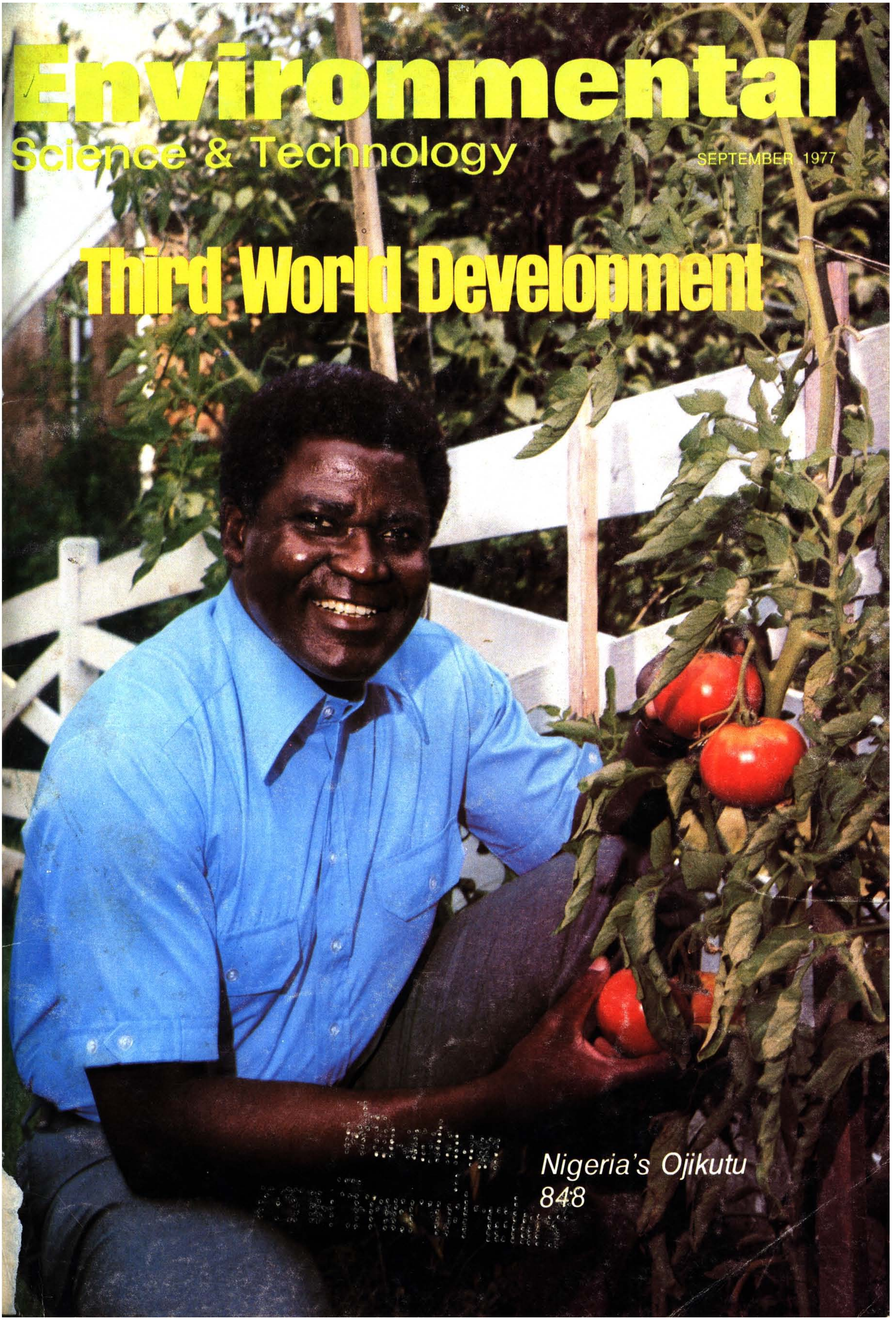
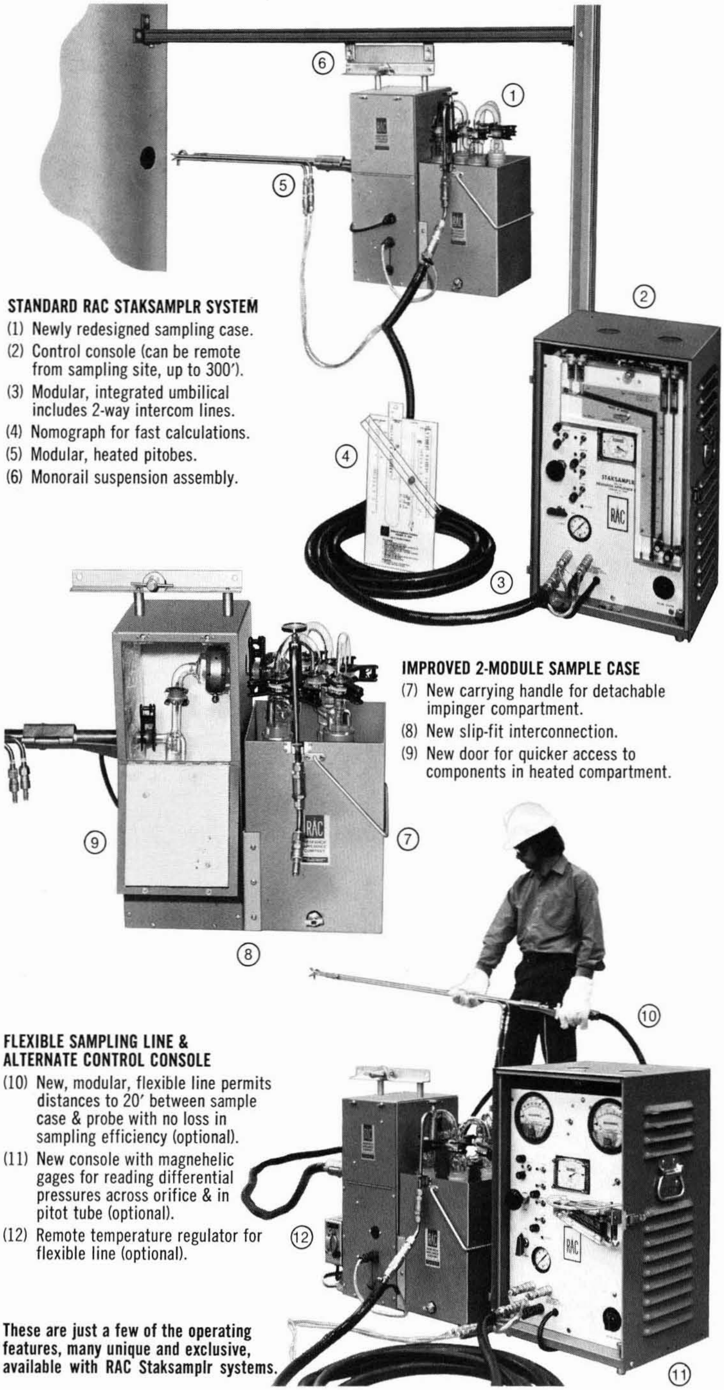
Environmental
Science & Technology

SEPTEMBER 1977

Third World Development



Nigeria's Ojikutu
848


⑥
①
⑤
②
④
③
⑨
⑦
⑧
⑩
⑫
⑪

You know how much you're putting into environmental control.

We can tell you how much you're getting out of it.

We can because that's our job at the Rockwell International Air Monitoring Center. Helping you with every phase of environmental monitoring: air, water, radiation and meteorological.

Our prime emphasis: valid, reliable data on your environmental position to help you show factual results — and prove exactly what you've accomplished.

In addition to monitoring, we offer a broad range of capabilities: Program definition. Consultation. Meteorology. Modeling. Operation and maintenance. Data processing. Telemetry. Stack sampling. Analytical chemistry. Instrumented stations. Mobile laboratories. Integrated, automated monitoring networks.

Our extensive background and involvement in major federal and state programs has given us broad knowledge of regulatory requirements and proposed environmental quality standards. This experience as a full service contractor has proven extremely valuable in serving all sections of industry — electric utilities, metals, petroleum, chemicals.

As part of Rockwell's Atomics International Division and working with the company's Science Center, we are expanding industry knowledge through extensive contractor and company funded R&D programs.

With major efforts in meteorology/modeling, analytical chemistry and measurement science, we are attacking the problems underlying the key issues — sulfates, metal emissions, atmospheric reactions, pollutant transport, predictive models.

Conducting programs throughout the country, we have major operations in the Raleigh-Durham, St. Louis and Los Angeles areas. We welcome the opportunity to serve you. For more information, call or write: Alton Schmitt, Manager, Business Development, Air Monitoring Center, Rockwell International, 2421 W. Hillcrest Drive, Newbury Park, CA 91320. Telephone: 805/498-6771.

Rockwell International

...where science gets down to business

CIRCLE 17 ON READER SERVICE CARD

Down the drain?

Process water isn't cheap any more. It's expensive to acquire. To use. Even to throw away.

A sensible solution is to re-cycle it. Use it over and over again. But to do this you must control its quality. Especially its organic pollution load. Otherwise, forget it.

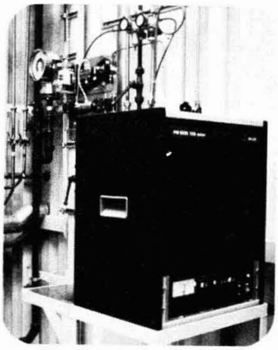
Control, of course, means measurement. Conventional BOD and COD methods are too slow. Too expensive in manpower. Intermittent. So they miss the quick changes in oxygen demand.

The only practical way is to use a Philips Automatic TOD (Total Oxygen Demand) Monitor.

Automatically measures for oxygen demand every 5 or 10 minutes. No reagents. No calibration. No operator! No waste! Get the full story.

Please direct all enquiries to:
Philips Electronic Instruments, Inc.,
85 McKee Drive,
Mahwah, New Jersey 07430

...enquiries outside USA, to:
Philips Industries,
Pollution Measuring Department,
Building TQIII-2, Eindhoven, The Netherlands.



Water is money...
save it continuously...
with Philips

PHILIPS

Scientific &
Analytical Equipment

PHILIPS

CIRCLE 8 ON READER SERVICE CARD

Environmental
Science & Technology
Volume 11, Number 9, September 1977

ESTHAG 11 (9) 833–938 (1977)
ISSN 0013 936X

CONTENTS

Special report

PAT report

Outlook

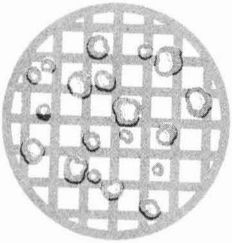
Features

Departments

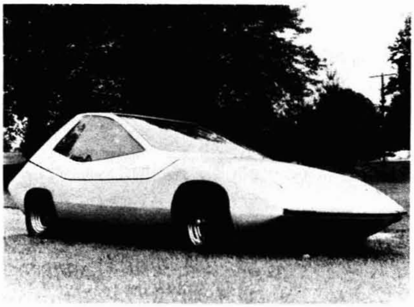
Current research

848

843



856



858

Published monthly, with additional issue 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: 25 Sylvan Road South, Westport, Conn. 06880. Second-class postage paid at Washington, D.C., and at additional mailing offices.

***ES&T* IN MICROFORM:** Available on microfilm or microfiche. For information, write to: Special Issues Sales, ACS, 1155 16th St., N.W., Washington, D.C. 20036, or call (202) 872-4554.

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 1977: 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, $4.50 per year; Canada and others, $5.00 per year. Air freight rates per year available on request. Single copies: current issues, $3.50; Environmental Control Issue, $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 data; 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.

CURRENT RESEARCH

Effect of environmental variables on collection of atmospheric sulfate 873

Robert W. Coutant

Principal operational parameters and atmospheric variables are investigated, and their effects on the collection of ambient sulfates are determined.

Quantity and relative desorption rates of air-strippable organics in industrial wastewater 879

Louis J. Thibodeaux* and Jerry D. Millican

A desorption experiment is developed to aid in determining the maximum quantity of organic material in wastewater that can be volatilized.

Effect of chronic exposure of brook trout to sublethal concentrations of hydrogen cyanide 883

Walter M. Koenst, Lloyd L. Smith, Jr.*, and Steven J. Broderius

Brook trout are exposed to various concentrations of hydrogen cyanide to determine the effects of continuous exposure on survival, growth, and reproduction.

Heavy metals from waste disposal in Central Puget Sound 887

William R. Schell* and Ahmad Nevissi

The concentrations of heavy metals measured in water, biota, and sediment samples collected near a domestic sewage outfall in Central Puget Sound are presented.

Photochemical production of chlorinated organics in aqueous solutions containing chlorine 893

Barry G. Oliver* and John H. Carey

The photochlorination of ethanol, *n*-butanol, and benzoic acid is studied to demonstrate that chlorinated organics can be produced photochemically by sunlight in waters being disinfected with chlorine.

Photochemical ozone in smoke from prescribed burning of forests 896

Leslie F. Evans*, Ian A. Weeks, Anthony J. Eccleston, and David R. Packham

Parameters relating to the photochemical generation of ozone in the smoke plume of a burning forest are discussed, and ozone measurements are updated.

Thermal decomposition of peroxyacetylnitrate in the presence of nitric oxide 900

Richard A. Cox* and Michael J. Roffey

Thermal reactions occurring in mixtures containing peroxyacetylnitrate and nitric oxide at part-per-million concentrations in synthetic air are investigated.

Isotopic organic and inorganic mercury exchange in river water 907

Akira Kudo*, Hirokatsu Akagi, D. C. Mortimer, and Donald R. Miller

Isotopic exchange reactions between methylmercuric and mercuric chloride are observed for Ottawa River water. Concentrations of mercury in river water are investigated.

Physical model of marine phytoplankton chlorination at coastal power plants 908

Joel C. Goldman* and John A. Davidson

A physical model of the impact of coastal power plant chlorination on marine phytoplankton is developed. The gross impact of chlorine on phytoplankton is assessed.

NOTES

Algae removal by high gradient magnetic filtration 913

Ruth Yadidia, Aharon Abeliovich, and Georges Belfort*

High gradient magnetic filtration is used to study the removal efficiency of laboratory and high-rate oxidation pond-grown *Scenedesmus obliquus* from dilute solutions.

Heavy-metal pollution from automotive emissions and its effect on roadside soils and pasture species in New Zealand 917

Neil I. Ward, Robert R. Brooks*, Edward Roberts, and Colin R. Boswell

Heavy-metal concentrations are determined in soils and pasture species along a major motorway in New Zealand by atomic absorption spectrophotometry.

CORRESPONDENCE

Oxidant control strategies. Part I. Urban oxidant control strategy derived from existing smog chamber data 920

Donald H. Stedman
Harry H. Hovey, Jr.
James W. Ford
Basil Dimitriades

* To whom correspondence should be addressed.

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

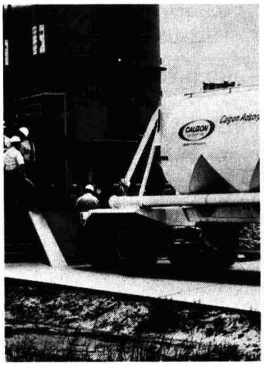
Credits: 844, 849 (2 photos), *ES&T*'s Julian Josephson; 848, 851, Alan Kahan; 850, Diane Reich
Cover: Barry Baron, Photo Optik (Washington, D.C.)

Nine questions about removing toxic organics from wastewater that Calgon® carbon can answer.

1. Is it broadly effective against organics?

A comprehensive study showed that carbon adsorption successfully removed dissolved organics from 327 different wastewater samples drawn from 104 manufacturing operations. Tests on the toxic organics toxaphene, DDT, DDD, DDE, aldrin, dieldrin and endrin showed that carbon effectively removed them.

2. Are Calgon carbon systems for industrial water treatment operating commercially?



Industrial wastewater treatment systems using Calgon® granular activated carbon are in daily use in 25 states in the U.S., and in a number of foreign countries.

3. Is it cost competitive?

The high efficiency and accurate design parameters of carbon adsorption systems, plus Calgon expertise in applying and handling carbon, make this approach the most cost-effective one for removing toxic and refractory organics. Point-source treatment and recycling of reactivated carbon can contribute to the overall system economics.

4. Can it be tailored to any size waste stream?

Yes. Calgon carbon systems for industrial wastewater treatment have been supplied in sizes ranging from five gallons per minute to more than 20 million gpd. If wastewater volumes or levels of treatment change, Calgon systems can be readily expanded. In all cases, system design is based on type of contaminant, concentration and rate of adsorption.

5. Can I get a toxic-organic removal system operating in less than a year?

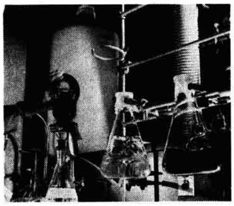
With Calgon's Carbon Adsorption Service℠ you can be operating within 45 to 90 DAYS after terms are agreed on. This compact, shop-assembled system is tailored to your specific needs, then skid-mounted and delivered to your prepared site. Calgon installs and starts up the units, trains your operator, monitors effluent and maintains the equipment.

6. Do I have a choice of carbon treatment systems?

In addition to the Carbon Adsorption Service (see answer to Question 5) where Calgon supplies the system plus removal and reactivation of spent carbon, we can help you with a custom-designed adsorption system with on-site reactivation or supply high-grade Calgon carbon for existing facilities.

7. Can I be sure in advance that carbon will remove my organics?

Careful analysis of your wastewater samples in the Calgon Laboratories (among the nation's largest water labs) will confirm the effectiveness and rate of removal by carbon adsorption. Once we agree the process will work, dynamic pilot-plant studies are used to confirm details. And all contracts for Calgon's Carbon Adsorption Service systems include an agreed-on level of effluent quality which can be maintained.



8. Is the process environmentally "clean"?

With the Carbon Adsorption Service, concern over air pollution is eliminated, since Calgon removes used carbon from the customer's plant site for reactivation in its own furnaces. Processing in high-temperature reactivation equipment completely destroys toxic organics, converting them to carbon dioxide and water. Unlike activated sludge plants which produce an odorous secondary sludge that must be disposed of, carbon plants produce no secondary sludge, and there is no sludge disposal problem.

Most important, the Calgon carbon adsorption process is effective in meeting clean-streams and Best Practicable Technology guidelines for effluents; in most cases, the carbon treatment process also qualifies as the Best Available Technology.

9. Can I talk with someone who can help right now?

Just call one of the numbers listed below and talk with an experienced pollution control specialist from Calgon. For a copy of the study referred to in the answer to Question 1 and a descriptive brochure on carbon systems, write to Calgon Environmental Systems Division, Calgon Center, Pittsburgh, Pa. 15230.

Get more details. Call:
(412) 923-2345 in Pittsburgh
(201) 526-4646 in Bridgewater, N.J.
(713) 682-1301 in Houston
(314) 863-3201 in St. Louis
(415) 369-4684 in Redwood City, Calif.
In Europe: Chemviron, Brussels—375.24.20

The Water Managers

CALGON
CORPORATION

SUBSIDIARY OF MERCK & CO., INC.

CIRCLE 22 ON READER SERVICE CARD

MSA INSTRUMENTS in the NEWS

COMBUSTION CONTROL • HEALTH & SAFETY • ENVIRONMENTAL • PROCESS

Accurate combustion control with MSA Oxygen Analyzer helps industry save scarce fuel.

Since its introduction in 1975, the Model 803 Oxygen Analyzer from MSA has received a warm welcome from combustion engineers across industry. Wherever fuel is burned for process heat, power generation or manufacturing, fine tuning of excess air in the combustion process pays big dividends. It used to be difficult to get reliable readings in the hot, dirty conditions in the stack. But the Model 803 O_2 Analyzer is changing all that.

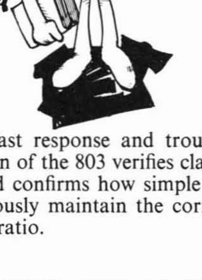
Located right on the stack, the Model 803 gives you the shortest possible sampling line. It operates hot so that gases are kept above their dewpoint. That minimizes plugging problems and increases time on line without shutdown. The analyzer measures oxygen directly—not just an effect of oxygen. So it produces a high-level signal. And its sensitivity holds through the full 0.1% to 21% O_2 range.

Many users have commented on the 803's speed of response when furnace operating conditions vary. Prompt corrective action saves them fuel and avoids pollution incidents.

MSA Oxygen Analyzer goes to "energy college."

The engineering department of a southern college conducts seminars to help industry improve their boiler operating efficiency. During the lecture portion, the Model 803 Oxygen Analyzer demonstrates the theory of excess air control; then the professor takes the group of boiler operators and superintendents to a nearby industrial plant to observe this combustion control theory in operation.

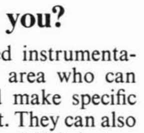
The class analyzes the combustion gases from the boiler with the Model 803 and correlates the analysis to Orsat tests. Conditions are deliberately varied, and effect on excess air and efficiency noted.



The fast response and trouble-free operation of the 803 verifies classroom data and confirms how simple it is to continuously maintain the correct excess air ratio.

Flue gas analysis goes portable.

The popular Model 803 is now also available as the 803-P Portable O_2 Analyzer. The 20-pound unit is complete in a single case with handle. It offers the same high levels of accuracy, measuring O_2 from 0.1% to 21%. The logarithmic scale provides highest accuracy at the lowest concentration levels.

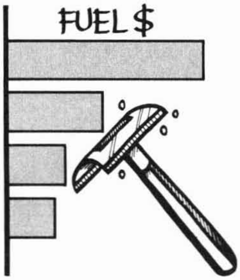


While measuring flue gas excess oxygen is a major application, inert gas generators, heat-treating atmospheres and other combustion processes can all benefit from its use. You just plug it in at the test location, and within 20 minutes you're ready for accurate analysis of combustion oxygen level. Adjustments in ratios are recorded in seconds for fast correction of fuel/air imbalances.

Multi-plant air analysis shows how to shave fuel costs.

In the dim, dark past when fuel was cheaper than controls, boiler operators didn't mind losing a little heat in the form of excess air. It was heated and then carried its Btu's right out the stack, but it didn't bother the burning rate or the operation.

Now, that "little heat" can add up to a loss of thousands of dollars *every month*. More and more industrial boiler operators are turning to oxygen monitoring and control as a cost-efficient way to reduce fuel consumption.



One multi-plant company studied the effect of increasing boiler efficiency from 1% to 5% for four classes of boilers. The figures showed, for example, that a 2% improvement for a 100,000-lb boiler would offer savings of $3,000 *per month* when fuel was 26¢ a gallon. At that rate, the cost of controls could be paid off in a matter of months.

Today, saving fuel is not just a matter of economics—it can be the difference between operating or shutting down in cold weather.

As a bonus, efficient combustion processes are less likely to create air pollution problems from the stack.

How can we help you?

MSA has experienced instrumentation engineers in your area who can review your needs and make specific proposals for your plant. They can also provide details on other MSA instruments for stack emission monitoring, health and safety analysis systems and air quality monitoring. Check the Yellow Pages for the nearest MSA office or write MSA Instrument Division, 600 Penn Center Blvd., Pittsburgh, Pa. 15235.

Make sure/check MSA

CIRCLE 7 ON READER SERVICE CARD

EDITORIAL

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

ADVERTISING MANAGEMENT
Centcom, Ltd.

For offices and advertisers, see page 936

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

For author's guide and editorial policy, see June 1977 issue, page 575, or write Katherine I. Biggs, Manuscript Reviewing Office *ES&T*

Carter and the Environment

President Carter's environmental message to Congress has received relatively little attention by the national press. Comments that have been made are generally critical of the lack of new and extensive legislative programs in the President's environmental package.

Actually, Carter's message is the most encouraging and thoughtful one we have had in some time, and is worthy of much closer attention from its critics. Its central theme is that our primary need is not for sweeping new programs but for intelligent, orderly, and sensitive administration of the ones we have. It recognizes that Congress has already (a) outlawed water pollution by 1983, (b) strained the technical capability of Detroit in meeting auto emissions standards that do not enjoy consensus in the scientific community, (c) mandated the provision of safe drinking water to an estimated 240 000 public water supplies, (d) brought the use of toxic materials under scrutiny and control, and (e) issued numerous other federal directives controlling the quality of the work place, wilderness, urban and agricultural environments, and the rate and mechanisms of energy development. Most importantly, the legislation emphasizes the need to reduce the burdensome bureaucratic regulations resulting from presently uncoordinated administration of these many statutes.

But is the message really the word? Looking beyond the formal statements to Congress, the President has attempted, and partially succeeded, the cancellation of 19 pork-barrel water projects, and made two excellent selections to head Interior and EPA. Under Cecil Andrus, the Department of the Interior is showing definite signs of environmental renewal, and Mr. Costle of EPA has indicated that his agency will receive the benefit of additional staff that it has been denied since 1975. Most encouraging of all are reports that the Office of Management and Budget is studying the reorganization of EPA, Interior, the Corps of Engineers, and the Forest Service into a single administrative unit at the Cabinet level.

It's comforting to see evidence that the President recognizes the wisdom of preventing the environmental movement from becoming legislatively top-heavy. His goal seems to be the provision of simpler and manageable procedures, which is entirely consistent with his pre-election rhetoric.

R F Christman

LETTERS

Air monitoring networks

Dear Sir: I have just finished the excellent article on Air Monitoring Networks (*ES&T*, June 1977, pp 544–549). Unfortunately, the article leaves the reader with the impression that there are only three domestic and one international firms seriously engaged in the construction of network systems. I wish to point out that Monitor Labs has built eighteen (18) telemetry network systems. Installations include:

- California Air Resources Board statewide network.
- Department of Public Health, Commonwealth of Massachusetts.
- Georgia Power Company, Atlanta, Georgia.
- State of Victoria, Melbourne, Victoria, Australia.
- Department of Environment, State of Washington.
- Department of Environmental Quality, State of Wisconsin.

Each of these networks consists of more than ten (10) remote sites with air quality and meteorological sensors telemetered to a central site with a computer to control telemetry, validate the data, and perform data reduction.

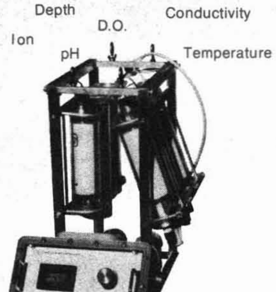
With our System 7000 measurement system and System 5000 ADAM network software, we offer a complete package with most of the equipment of our own manufacture. The major distinction between Monitor Labs and others in the field is that we specialize in hardware and computer software, leaving the data interpretation to the consultants.

Allan L. Budd
Vice President, Marketing
Monitor Labs, Inc.
San Diego, Calif. 92121

More on air monitoring networks

Dear Sir: I was delighted to see your June issue with the article on building air monitoring networks. I noticed in the article errors that are rather important from our point of view. At the top of page 548 column 3, the figure for the total number of people employed in Philips should be of course 400 000. In the same column, paragraph 4, the sentence "The NO, NO_2, and O_3 instruments were purchased from Bendix." has been added. We are very puzzled about this because these instruments were in fact supplied by Philips.

A. S. Lodder
N.V. Philips Gloeilampenfabrieken
Eindhoven, The Netherlands



Also in the air monitoring business

Dear Sir: We would like to call readership attention to another company in the business of designing, constructing, installing and operating air monitoring networks (see *ES&T* Special Report, *Building Air Monitoring Networks,* June 1977, p 544).

The Environmental Systems Division of Xonics, Inc., based in Van Nuys, California, recently secured the EPA contract for data management and collection, and operation of the entire CHAMP network, having a cumulative value of approximately $5 million. Prior to this award, Xonics designed and delivered the air quality instrumentation systems under subcontract to Rockwell for use in the EPA-funded CHAMP and RAMS programs. Xonics' portion of the total contracts amounted to approximately $2.5 million.

Xonics also is delivering air and water-quality monitoring systems under contract with the U.S. Army. Value of these orders exceeds $4 million. And, on the international scene, Xonics has delivered about $400 000 worth of monitoring equipment overseas, and has recently booked an additional $500 000.

Xonics' engineering innovations led to many system hardware improvements, now considered standard practice in the industry, such as automatic dynamic gas calibration, accurate data conditioning, logging, integration, and display of air quality parameters, centralized ambient air-processing equipment, accurate temperature control of sensitive calibration components, meteorological monitoring equipment, and many others.

Daniel L. Esau
Director of Marketing
Xonics
Van Nuys, Calif. 91406

Air monitoring networks (cont.)

Dear Sir: I was disappointed to see that the special report on air pollution monitoring (*ES&T*, June 1977, p 544) gave the impression that there are only three major companies providing total contractor services in the building and operation of air pollution monitoring networks (p 545, col. 3).

The facts are that several other companies are major factors in this field. Enviroplan, for example, has designed, installed, and has been operating air pollution and meteorological monitoring networks at more than forty site locations for several of our more than forty-five government and industrial clients.

It is precisely because there now are a substantial and growing number of experienced and qualified companies providing these monitoring services that the electric

Enjoy *your own* monthly copy of 1977

ENVIRONMENTAL SCIENCE & TECHNOLOGY

Start my subscription as follows:

	U.S.	PUAS*	Canada & Other Countries**
ACS Members*	☐ $10.00	☐ $14.50	☐ $15.00
Nonmembers (Personal)	☐ $15.00	☐ $19.50	☐ $20.00
Institutions	☐ $30.00	☐ $34.50	☐ $35.00

☐ Bill Me ☐ Bill Company ☐ Payment Enclosed

(Make payable: American Chemical Society)

Name

Position

Your Employer

Address ☐ Home ☐ Business

City State ZIP

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

If manufacturer, type of products produced

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

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

Mail this postage-free card today

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

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.

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

utility, industrial, and government customers for these services have benefited in terms of improved quality of the monitoring data, increased percentages of valid data collection, and a host of other specialized monitoring program services provided at the minimum possible cost.

Howard M. Ellis, President
Enviroplan, Inc.
Rutherford, N.J. 07070

Water monitoring

Dear Sir: We just completed a multiclient study, "Instrumentation and Process Control for Analysis and Control of Water Quality". We forecasted that the markets for instrumentation and process control systems for the analysis and control of water quality will total over $4 billion during the 1976–85 period. The forecasts were made for (1) analytical instruments, (2) conventional instruments and control systems, (3) final control devices, and (4) computers and telemetry. In addition, markets were forecasted for various individual analytical and specialty instruments, as well as for other product categories.

Seven market sectors relating to water quality were evaluated and market projections were made for each sector. These included: (1) municipal water treatment, (2) municipal water distribution, (3) industrial water treatment, (4) municipal wastewater collection, (5) industrial wastewater treatment, (6) municipal wastewater treatment, and (7) water quality monitoring. The markets for the various instruments and process control systems will vary, but will average about 11%/y during the 1976–85 period.

In addition to the above study, we conducted a multiclient study entitled, "Industrial Water Pollution Control—U.S. Markets and Technology," last year. The price of the instrument study is $1200 per client.

Robert E. De La Rue, President
Robert E. De La Rue Associates
P.O. Box 2370
Santa Clara, Calif. 95051

Opacity correction

Dear Sir: I would like to correct one of the sketches used to illustrate the feature, "Clearing the Opacity Issue" (*ES&T*, June 1977, pp 561–563) in order to clear up any confusion. The caption under the sketch labeled Altitude states, "Due to sunlight scattering, visual opacity increases as the sun's altitude increases. In summer, the altitude of the sun at noon is 79°; in winter, 33°; spring 56° and fall 34°." The last clause is in error, the altitude of the sun at noon in the fall (at the autumnal equinox) is *not* 34°. In the caption I submitted I stated "In spring and fall, the sun's altitude at noon is 56° at 34° *North Latitude.*" Therefore, in the sketch itself, the label "fall" should not have been attached to "winter sun" but to the "spring sun." The relationship of the sun's altitude to opacity is quite significant. A perfect observer who read 56% opacity at noon in winter, would read 75% opacity in

spring or fall and 85% opacity in summer, all other factors being constant.

A minor error was also observed in Table 1. The heading of the third column should read "No. with*in* 7.5% opacity of meter reading", rather than "No. with 7.5% opacity. . .". Thus, in only 17 times out of 94 were EPA observer's opacity readings within 7.5% opacity of the transmissometer reading.

Alex Weir, Jr.
Southern California Edison Co.
Rosemead, Calif. 91770

Opacity controversy

Dear Sir: I am deeply disturbed by the continuing controversy in your magazine concerning plume opacity and visual effects. In my opinion, the two feature articles by Dr. Alexander Weir, Jr. ("Factors Influencing Plume Opacity," June 1976, p 539; "Clearing The Opacity Issue", June 1977, p 561) serve no constructive purpose in the dissemination of information on the subject, but through misconception and misrepresentation attempt an indictment of visual opacity as a regulatory option.

The primary misconception in the June 1977 feature is that an industry's failure to meet NSPS opacity standards while complying with mass emission standards will result in the expenditure of millions of dollars in additional control equipment to meet the opacity limit. Perhaps the author should read 40 CFR 60.11, which specifies the procedure to be followed in appealing to the EPA Administrator for an adjusted opacity standard, which will be established upon demonstration of the source operator that control equipment was being properly maintained and operated at the time of the opacity excursion. A new opacity standard will be established that the source will be able to meet *all times* during which the source meets the applicable mass emission standard. The author's emotional appeal to consumers that opacity regulation will increase prices of concrete, steel, and electricity because of additional controls to meet a visual standard is simply not valid, as the *Federal Register* will indicate to all who will read it.

Dr. Weir's statements on the effect of sun angle or altitude on visual opacity can be refuted by data collected by the Texas Air Control Board during Visible Emissions Evaluation courses, which are given twice yearly at each of six locations across Texas. For example, the Corpus Christi course is held in December and June, so an observer training in December should be reading higher opacities on the same plume in June because of the higher sun angle. Since most observers requalify in June on the first set of readings, apparently no bias exists because of sun altitude. The field experience of hundreds of Method 9 opacity evaluators simply does not support his supposition.

The examples cited here are but two of the many mistaken and misleading assertions made by the author in the cited articles. I believe your magazine is remiss in sponsoring the publication of these articles, which unfortunately by their very publication in a prestigious journal such as *ES&T* gain unwarranted credence. I would hope that the EPA will be *invited* to submit a feature article in which any damage done by Dr. Weir might be repaired.

John W. Key
Texas Air Control Board
Austin, Tex. 78758

Financing pollution control

Dear Sir: In the April issue (*ES&T*, April 1977, p 329) you incorrectly say that the Small Business Administration (SBA) will guarantee tax-free municipal bonds. The SBA will guarantee the payment of the financing contracts, which are the security for the bonds. There is an important difference that will be noted by your more sophisticated readers. California expects to shortly sell about $5 million worth of bonds for its pilot program.

James H. McCall
California Pollution Control
Financing Authority
Sacramento, Calif. 95814

Nuclear radiation

Dear Sir: The letter by Andrew P. Hull (*ES&T*, April 1977, p 326) regarding our reply (*ES&T*, December 1976, p 1185) to the Currents (*ES&T*, August 1976, p 730) report of our atmospheric tellurium-132 research fails to recognize the significant points of the communication. The purpose of our earlier reply was to state that our data showed no evidence of the Hanford nuclear facilities being the source of the tellurium-132, as was inadvertently implied in the Currents report. The concentrations of ^{132}Te were mentioned in the reply solely for clarification and were not reported as research results since there is no space for concomitant data interpretations. However, a detailed technical report concerning this research project is available upon request from the authors.

S. O. Farwell
S. J. Fernandez
Washington State University
Pullman, Wash. 99163

NO_x in boilers

Dear Sir: In your informative article on Exxon's Thermal Denox Process (*ES&T*, March 1977, p 226), it is stated that the sulfuric acid dewpoint in boilers is generally around 180 °F. Hopefully, this is just a typographical error on your part. Actually, you meant to say 180 °C. This corrected value would agree with the fact that the sulfuric acid dewpoints generally range between 130–180 °C for residual oil or coal-fired boilers. The exact dewpoint is dependent on the SO_3 and water vapor in the flue gas.

Richard C. Diehl
Calgon Corp.
Pittsburgh, Pa. 15230

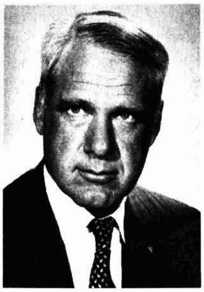
CURRENTS

INTERNATIONAL

Poland has embarked on an ambitious environmental program. Its many facets will include water pollution control for 3000 major, and 10 000 minor dischargers. Also, about 1000 chemical and power plants will be under air pollution controls. Moreover, at least 3 million hectares of eroded and industry-devastated land will be restored; all this by 1990.

WASHINGTON

A bill creating the cabinet-level Dept. of Energy was signed by President Carter. James R. Schlesinger, Jr., Carter's energy advisor, becomes the new department's first secretary. The Dept. of Energy will have a staff of 20 000 and a budget of $10 billion, both inherited from existing agencies, which will be pulled together to form the new department. These agencies are the Federal Energy Administration, the Energy Research and Development Administration, the Federal Power Commission, and various organizations in the Dept. of the Interior. An independent 5-member commission within the Dept. of Energy will have the power to set the price of natural gas.



Secretary Schlesinger

The 1977 Clean Air Act Amendments were finally signed into law. The new law extends the deadline for meeting tailpipe emission standards from 1978 to 1980 model-year cars. In signing the bill into law, President Carter said: "This new timetable will be enforced." Also required by the law are a 2-year or 24 000-mi performance warranty that a vehicle will meet emission standards, and a 5-year or 50 000-mi warranty on the pollution control equipment. Mandatory inspection/ maintenance programs are established for five cities that are now violating federal air quality standards.

Citizen and state lawsuits against the TVA for violating federal/state SO_x standards have been joined by the EPA. After a 7-year battle against the TVA, a major SO_x polluter, the EPA, through the Dept. of Justice, filed an intervening motion on July 25 in one (Ala.) of 6 U.S. District Courts in Ala., Ky., and Tenn. In announcing the suit, EPA's deputy administrator Barbara Blum called it "a showcase for energy and environmental coexistence." The suits allege that 10 of 12 TWA power plants violate state implementation plans and standards for SO_x. TVA has continued to resist scrubber installation on these plants, contending that as a federal agency, it does not have to comply as rapidly as private industry. Alabama filed suit on June 13, and the citizen suits were filed on June 22.

EPA's latest Water Quality Inventory report to Congress cites control of toxic pollutants as a major problem facing the states. Thirty-five states reported the presence of heavy metals—arsenic, cadmium, chromium, lead, mercury, and zinc. Eastern states reported the sources of excess toxic metal concentrations as industrial discharges, urban stormwater runoff and atmospheric fallout of air pollutants. Western states traced the sources to mining operations and to "natural conditions." In the matter of safe drinking water, the EPA proposes a maximum contaminant level of 0.10 mg/L for total trihalomethanes in drinking water supplied by systems serving more than 75 000 people. Included under this regulation is chloroform, a possible human carcinogen.

A conference report on strip mining legislation passed both houses of Congress, and has been signed by President Carter. The bill is supported by environmentalists and generally opposed by the coal industry. It requires that the coal industry restore strip-mined land to nearly its original contour, and sets up an Abandoned Mine Reclamation Fund, supported by a fee on coal, to reclaim abandoned mines from past operations. The Secretary of the Interior will be permitted to designate areas unsuitable for mining and will be able to restrict mining from alluvial valley floors and prime farm lands. Citizens will be allowed to participate in the review process by which state agencies decide land areas to be strip mined.

A recent NRC report says that increased reliance on fossil fuels as an energy source may have adverse climatic effects. A National Research Council committee states, "The climatic effects of carbon dioxide (CO_2) release may be the primary limiting factor on energy production from fossil fuels over the next few centuries." By the end of the 22nd century, CO_2 could increase four- to eightfold with a corresponding average world temperature increase of more than 6 °C. But the committee cautions that the study "should not lead to panic or complacency," but to "a lively sense of urgency in getting on with the work [to resolve] the scientific uncertainties that remain. The committee also said that the report should not be taken as an endorsement of any other energy source.

STATES

Connecticut has ended its indirect source control program with the exception of major airports and highways. Being the only state in the U.S. with extensive controls on indirect sources of air pollution, with permits required for shopping centers, race tracks, and other large developments, Connecticut found itself at an economic disadvantage. State environmental commissioner S. J. Pac reportedly told the Regulations Review Committee that the state would lose development opportunities if the program was retained. Under the old program, developments that attracted large volumes of cars were required to obtain a permit and to renew this permit every five years. Under the new ruling, corporations would be required to undergo an initial inspection and obtain a permit, but reapplication for another permit would not be mandatory.

Cleanup of Morgan Lake in the Four Corners, New Mexico area, is under way. The Arizona Public Service Co. will spend $6 million to bring its Farmington facility into compliance with federal water requirements. The utility, under its NPDES permit, must control all its waste discharges to Morgan Lake and the San Juan River. Morgan Lake's restoration is important because the lake flows into the San Juan River, which then empties into the Colorado River system.

CARB chairman Quinn

California takes action to lower NO_x emissions from autos and light-duty trucks by 1980. Terming it a "giant stride forward," Tom Quinn, chairman of California Air Resources Board (CARB), announced the board's unanimously adopted resolution to lower nitrogen oxide emissions to 1.0 g/mi in 1980 model vehicles and to 0.4 g/mi in 1982 models. The present state standard is 1.5 g/mi. According to Quinn, the new NO_x standard will reduce NO_x emissions in the state by 10% by 1990.

Illinois reports no violations of its ambient sulfur dioxide standards for the preceding year, the first time this has occurred since the state EPA began statewide air monitoring in 1970. In its 1976 Air Quality Report, the Ill. EPA also reports slightly higher particulate matter levels, slightly lower statewide ozone levels, relatively constant nitrogen dioxide levels that are well below the federal standard, relatively high concentrations of hydrocarbons and relatively constant carbon monoxide levels, except in Chicago, where CO violations decreased drastically. The Ohio EPA, on the other hand, reports that seven counties in the state will require sulfur oxide emission reductions to meet federal regulations. The seven counties are Lucas, Lorain, Cuyahoga, Lake, Mahoning, Columbiana and Jefferson. New state regulations are under development.

Because of high mercury levels in fish, another 160 mi of Virginia rivers were closed to fishing for human consumption. Gov. Mills E. Godwin, Jr. announced the ban, which applies to the South River and South Fork, and the Shenandoah River, which is formed from the confluence of the first two rivers. There is no indication that the water is unsafe for drinking. Also, the Michigan Dept. of Natural Resources reports that fish in Great Lakes waters surrounding the state are variously contaminated with toxicants that make them unfit for human consumption. In Lake Michigan, chubs and trout show levels of the pesticide dieldrin exceeding federal guidelines. Trout contain high levels of DDT, and Lake St. Clair walleye have mercury in excess of maximum safe level.

At present, 70% of 1200 community water systems in Oregon fail to meet new federal standards under the Safe Drinking Water Act. Art Goodman, assistant director of the Oregon Health Division said that state officials feel that half of the systems not meeting federal standards will require only minor improvements. Any system requiring major construction to correct a violation can seek financial assistance from the state. A recently enacted measure provides Oregon with a $200 million bonding authority to make loans to water districts and cities.

California's first reported infestation by gypsy moths, the first known infestation by this pest west of Iowa, was successfully halted, according to USDA officials. Two aerial sprayings, at a cost of $90 000, took place over more than 3000 acres in south San Jose. The aerial sprayings of the insecticide Dimilin supplemented ground spraying throughout an 18-square block area in the Willow Glen district of San Jose. Dimilin is a new EPA-registered biological growth regulator that inhibits the development of chitin. Dimilin is claimed to have a low toxicity to humans, animals, plants, and beneficial insects. The costs of the sprayings were shared equally by California's Dept. of Food and Agriculture and the USDA. Santa Clara County provided $50 000 for 1000 moth traps that will be used to monitor the success of the program through 1980.

MONITORING

NO analyzers can measure NO_x accurately by chemiluminescent analysis, and inaccuracies caused by the presence of carbon monoxide (CO) can be eliminated. The instrument is specific for NO (nitric oxide), but is upgraded by addition of a NO_x-to-NO converter accessory. According to NASA's Lewis Research Center (Cleveland, Ohio), where the technique was developed, NO_x in the sample is the difference between the amount of NO measured with sample gas bypassing the converter, and the amount of NO measured with sample gas flowing through the converter. CO problems were obviated through use of a chemiluminescent analyzer equipped with a molybdenum converter, and use of an air purge.

TECHNOLOGY

Instead of disposing of aqueous chemical wastes, convert them to energy. That is what Union Carbide's petrochemical plant (Brownsville, Tex.) does to make process steam for plant use in a $1.3 million boiler. That boiler blends 80% chemical wastes with 20% fuel oil to provide an 8000-Btu "fuel". The wastes and oil are mixed in an 8000-rpm pump homogenizer, and are then fed to the burners at 30 ft/s. Equipment is designed to withstand corrosive effects of high-velocity transfer of wastes. This boiler, together with conventional boilers, helps the plant to use 97% of its wastes as fuel. The remaining 3% is treated in a recently-completed zero-discharge solar evaporation waste treatment system.

The world's largest closed system for wastewater treatment (wwt) will purify 100 tpd of wastewater. Centrifugation and other means will be used. Also, 5000–7000 tpd of cooling water will be cycled. No water will be discharged from the new Onomichi plant of Yokohama Rubber Co., Ltd. (Japan), which makes jumbo-sized tires for heavy equipment. The only water loss will be 150 tpd by evaporation, to be replenished by Numata River water. So far, no problems with scale, slime, or erosion are evident. The closed wwt system was designed and constructed by Mitsubishi Heavy Industries, Ltd. (Tokyo).

A vinyl chloride monomer (VCM) recovery system can save energy and meet EPA's proposed new limit of 5 ppm. Research-Cottrell, Inc., developed

CARLO ERBA STRUMENTAZIONE

20 years applying gas chromatography to the pollution field

in hazardous areas too, with environmental gas chromatographs, total hydrocarbon and total sulphur monitors, and tailored sampling systems

4 years successfully selling the

TOTAL CARBON MONITOR

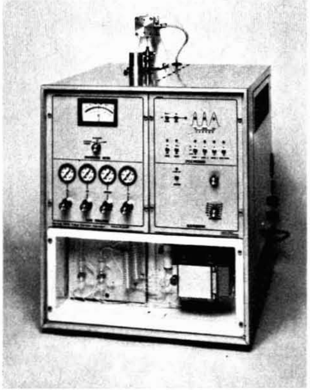
☐ Completely automatic
☐ Direct measure of TOC
☐ 0.1-600 ppm range
with 9 attenuation steps

as well as chemical photometric automatic analyzers to monitor organic and inorganic pollutants in water and air, i.e., formaldehyde.

For your enquiries please contact:

SUBSIDIARY OFFICES
Austria - Erba Science G.m.b.H.
Karlsplatz 1 - 1010 Wien
Brasil - Montedison Farmaceutica
Av. Ver. Jose Diniz 3465
Sao Paulo
France - Erba Science S.A.R.L.
4 Rue F. Mistral - 75015 Paris
Germany - DBR Erba Science
Wilhelmstrasse 2 B
6238 Hofheim/Taunus
Spain - Montedison Farmaceutica
Infanta Carlotta 36 - 9° - Barcelona
United Kingdom
Erba Science U.K. Ltd.
14 Bath Road
Swindon Wiltshire - England

DEALERS - REPRESENTATIVES
Belgium - Vel S.A. - Louvain
Finland - Prolab - Kauniainen
Netherlands - Van Hengel
Instrument bv - Breda
Norway - Instrument - Teknikk
A/S - Oslo 6
Sweden - Instrument - Teknikk
Svenska AB - Göteborg
Switzerland - Brechbuehler AG
Urdorf



GRUPPO MONTEDISON
CARLO ERBA

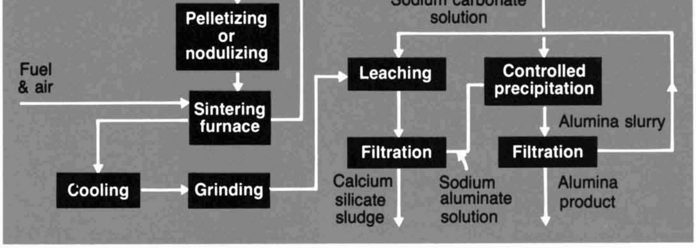
CARLO ERBA
STRUMENTAZIONE
P.O. Box 4342 I - 20100 MILANO

CIRCLE 27 ON READER SERVICE CARD

the system by which VCM-laden gas is adsorbed on activated carbon. The carbon is regenerated by stripping off the VCM, which is salvaged and returned to the polyvinyl chloride manufacturing process. What is new is that the VCM is stripped off the carbon under vacuum, rather than by steam, as is normally done. According to the company, the vacuum stripping of the carbon is what assures compliance with the 5-ppm VCM limit.

Power plant emission control techniques can be tested at a new $4.5 million facility built at Public Service Co. of Colorado under the auspices of the Electric Power Research Institute (Palo Alto, Calif.). Tests can be made under actual utility conditions at 300–750 °F, at flow rates of 5000–50 000 cfm. Different grades of coal can be used. All particulate, and some gaseous effluent control devices can be tried. The facility's aim is to help to devise smaller, less expensive, more efficient and reliable collection systems, and save utilities and consumers capital costs of over $1 billion, and maintenance/outage costs of up to $50 million/y over the next 7 years. Another task is to lower costs of increasing particulate collection efficiency to 99.5%, to comply with recent regulations.

A process to recover over 95% of the alumina in fly ash was devised by Mike Murtha and George Burnet of Iowa State University. It is a modification of one used in Hungary and Poland. First, iron is magnetically removed. Normally, limestone is ground into the remaining non-magnetic portion, but the Iowa State engineers found that sodium carbonate works much better. Not only is alumina recovery enhanced, but sintering can be done at 1250 °C, instead of 1380 °C, before aluminate leaching. Removal of excess sodium from the residual calcium silicate sludge—possibly by improving the leaching process—would make that sludge suitable for use in concrete.



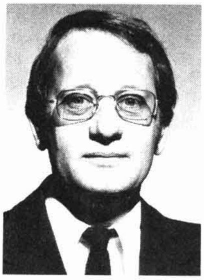
INDUSTRY

Pollution and noise control could consume 30% of Du Pont's $10 billion, 10-year capital budget, assuming that existing or anticipated environmental laws and regulations do not change. The company foresees that 75% of that outlay will yield no practical benefit. Moreover, water cleanup beyond "fishable-swimmable" would cost $785 million, and control of industrial air pollutants, insignificant in comparison with natural or other man-made ones, could cost $685 million. Also, by 1985, Du Pont would have to spend $1 billion/y to meet environmental requirements. These conclusions grew out of a 200-man-day plant-by-plant survey done by the company.

Hollytex Carpet Mills (City of Industry, Calif.) found that reclaimed wastewater is better for dye processes than is regular tap water. The company uses a closed water system for 70% of its water needs, and is aiming for 90%. Hollytex is licensing its water reclamation technology to other firms.

The chemical industry has generally met July 1 "best practicable" water cleanup requirements, the Manufacturing Chemists Association (MCA, Washington, D.C.) said. The MCA advocated keeping 1983 "best available" standards only to achieve "fishable-swimmable" water goals, or to control toxic pollutants.

The contract for the first fabric filter fume abatement system in the U.S., for a top-blown oxygen converter went to the Buell Emission Control Division of Envirotech Corp. It will be installed at the Crucible, Inc., Division of Colt Industries (Midland, Pa.). Steelmaking emissions are collected in existing water-cooled hoods, but will be carried by new ductwork to an evaporative cooler. Fugitive emissions will be collected. Three fans will exhaust the fumes (475 000 acfm, 475 °F), which will be cleaned in more than 2300 fiberglass bags, each 12 in. in diameter by 31 ft long. Startup is scheduled for the second half of 1978.


Davy Powergas' Earl

"Only flue gas desulfurization can achieve emission limitation standards in the time frame mandated by present or proposed changes to the Clean Air Act," Christopher Earl, senior process engineer for Davy Powergas Inc. (Lakeland, Fla.), told an editorial forum. Earl does not expect alternative technologies to be competitive sooner than the early 1980s, and even then, "the economics will still have to be proved." He also said that Davy Powergas has the only proven system (Wellman-Lord) offering regeneration of the SO_2 scrubbing medium (sodium sulfite); 90+% SO_2 removal efficiency; and a way to make marketable sulfuric acid or sulfur. Earl noted that a Wellman-Lord system recently started up at Northern Indiana Public Service Co.

Con Edison is strongly contesting an EPA requirement to build expensive new cooling towers at its Hudson River (N.Y.) power plants. So are three other New York utilities. These utilities argue that backfitting these towers could cost a cool $350 million, not to mention $100 million/y in operating expenses that would be reflected in ratepayers' bills. The companies say that their present once-through cooling towers would not cause great harm to fish populations, according to results of a $27 million, 7-year study. They do expect an 8% reduction in the river's striped bass population over the next 40 years, but do not foresee any significant economic or social losses because of that.

ONE SOURCE KEEPS YOU UP-TO-DATE ON ENVIRONMENTAL DECISION-MAKING.

The international awakening of concern for the environment has brought with it a large, increasingly complex variety of organizations whose recommendations strongly influence the decisions that government officials in each country, and businessmen in international markets, must live with day-by-day.

Until now, corporate and government planners have had to seek out documents from a bewildering array of official sources. The search takes time, and often brings the discovery that the wrong organization has been approached, or the documents obtained are outdated and no longer useful. A clear need has emerged for a single, comprehensive source to cut through the tangle of organizations, and give current information on international environmental issues, organizations and treaties.

This source is now available for the first time. It is a loose-leaf publication, Environmental Programs of Intergovernmental Organizations, a "living book," issued by Martinus Nijhoff Publishers. In two parts it gives the most complete and up-to-date data now available on organizations and treaties. To ensure that the information will stay up to date, readers are also offered a subscription service which will bring fresh pages for loose-leaf insertion twice each year.

Part I is a ready reference guide to the who, the what and the where of these and other key organizations shaping environmental policies of governments:

- Intergovernmental Oceanographic Commission (IOC).
- United Nations Educational, Scientific and Cultural Organization (UNESCO).
- Organization for Economic Cooperation and Development (OECD).
- North Atlantic Treaty Organization (NATO).
- Council of Europe.
- Nordic Council.
- Inter-Governmental Maritime Consultative Organization (IMCO).
- International Council for the Exploration of the Sea (ICES).
- United Nations Economic Commission for Europe (ECE).
- European Economic Community (EEC)
- Food and Agriculture Organization of the United Nations (FAO).
- Joint Group of Experts on the Scientific Aspects of Marine Pollution (GESAMP).
- United Nations Environment Program (UNEP).
- World Meteorological Organization (WMO).
- International Labor Organisation (ILO).
- International Agency for Research on Cancer (IARC).
- World Health Organization (WHO).

For each organization, Part I gives clear and systematic information on addresses, membership, aims, activities and publications in the environmental field; the names of officers responsible for environmental policy; and lists of environmental reports and publications issued by the organization. For quick reference, a specially compiled table relates specific subject areas to the relevant organizations.

Part II presents the official texts of recent important multilateral treaties of environmental interest, such as the Conventions of Oslo, London, Paris and the Rhine Conventions. Additional notes update the status of each convention and explain the apparatus for its implementation.

You can also reserve now the semi-annual supplements that will keep you in the know on organizational changes and new developments, and will present the official texts of important new treaties as they occur. The volume of pages of each supplement will of course vary with the developments to be covered. The present estimate is 300 - 400 pages per year; actual billing will be determined at the rate US $0.12 per page. The subscription can be cancelled at any time.

To order your copy of Environmental Programs of Intergovernmental Organizations (Parts I and II – approx. 700 loose-leaf pages into one binder), simply fill in the coupon below. Individual orders should enclose payment of the cost, US $80 postpaid. (Institutional orders will be billed by the publishers if requested.)

US - 1 - 1/1

I wish to order:

___ copies of Environmental Programs of Intergovernmental Organizations ($80 postpaid)

___ subscriptions to the semi-annual updating service (to be billed at $0.12 per page postpaid when mailed).

I enclose: ☐ personal check ☐ money order ☐ unesco coupons
☐ please bill my organization

name ____________________

title and organization ____________________

address ____________________

city, state, zip code ____________________

date ____________________ signature ____________________

Martinus Nijhoff Publishers P.O. Box 442 The Hague, The Netherlands

CIRCLE 13 ON READER SERVICE CARD

SPECIAL REPORT

Building the Third World

ES&T's Julian Josephson takes a look at some practical problems, prospects and efforts for reducing adverse environmental impacts of development in LDC's

The Less Developed Countries (LDC's) of the world aspire to catch up to the Developed World in terms of standards of living and quality of life. To do so, however, they must undertake a massive program of agricultural, industrial, and technological development. This development can be done in such a way as to minimize environmental disruption; and perhaps utilize previously unthought of or overlooked local natural and human resources.

Or it can be done in a roughshod manner that can lead to fearsome environmental consequences with global implications, as well as devastating effects on indigenous ecosystems, human life, and health. Until very recently, trends have unfortunately been in the latter direction, but it now appears that modifications, and even reversals of these trends may be coming.

One reason for these changes is that many LDC development projects are partly funded by loans from the International Bank for Reconstruction and Development (The World Bank), and its affiliates, the International Development Association (IDA), and the International Finance Corp. Together, these organizations are sometimes called The World Bank Group, whose headquarters are in Washington, D.C.

In evaluating these projects, The World Bank Group very systematically takes environmental factors into account, and since 1974 has been directly funding environmental improvement projects. This is also increasingly true of most other organizations that provide LDC's with financial or technical help. Moreover, many of these nations have themselves become conscious of existing or potential environmental problems associated with development. Even some of the poorer ones have started their own programs, especially with respect to renewable energy supplies.

Some of the more fortunate LDC's that export oil or other valuable commodities enjoy large capital surpluses. These surpluses can fund rapid food supply expansion and industrialization, as well as the environmental safeguards that those nations, hopefully, would consider equally important. Two notable examples of wealthier nations that consider these environmental factors of industrialization very important are Kuwait and Nigeria. And Venezuela reportedly plans to move vigorously in this direction, as well.

But most LDC's, especially in Africa and southern Asia, are sorely lacking in capital; technical personnel, especially at skilled technician and foreman levels; and sources of energy. Because many of these countries are located in warm climate regions, various endemic diseases, including many parasitic ones, are a real barrier to development. Moreover, the specter of famine always lurks in the background.

Indeed, the desperate quest for food, fiber, and fuel in such countries has frequently brought about much ravishing of the environment. To help those very poor nations develop reliable supplies, and later, a technological base, while mitigating, and even reversing trends toward environmental damage, World Bank Group components and other organizations are providing portions of the necessary financial and technical assistance. They are also actively encouraging the establishment and evolution of workable local technologies.

Availability of funds

For a long time, World Bank Group personnel assigned to evaluation and oversight of LDC projects have taken environmental concerns into account as a matter of policy, but often in a unsystematic and perfunctory manner. However, in late 1970, this policy took better shape with the formation of the predecessor of the present Office of Environmental and Health Affairs, headed by environmental advisor James Lee. He is still in that post. Lee and his deputy, Ragnar Overby, reminded *ES&T* that this activity was set up almost two years before the United Nations Conference on the Human Environment (Stockholm, Sweden, 1972).

Environmental advisor Lee
wants development without pollution

Last fiscal year (July 1975–July 1976), the Bank loaned out at least $5 billion for all purposes. Of this sum, as far as the environment is concerned, the Bank advanced $246.5 million for water supply and sewage. Also, at least $38 million went for air pollution control projects. Most World Bank loans carry interest in the range 8.5–8.85%/y on loan money actually disbursed, plus a 0.75% fee on funds committed, but not yet disbursed. Moreover, included in industrial project loans is an estimated $75 million for various environmental purposes.

The Bank-affiliated IDA advanced more than $1.65 billion last year, of which $88.1 million were earmarked for water and sewer projects. The IDA generally furnishes "credits" at no interest; there is, however, a 0.75%/y service charge to cover administrative costs. Repayment can be over 40 years, following a grace period of 10 years. To qualify for an IDA credit, which comes out of World Bank surplus, a country must show a Gross National Product of less than $375 equivalent per capita. There are many such countries in Africa, Latin America, and southern Asia.

The World Bank has 127 member countries, and the IDA 116. For public health and environment, the Bank has 108 countries "under its wing," deputy environmental advisor Overby told *ES&T*.

World Bank: changing emphasis

In the past, as now, the World Bank's and its affiliates' emphasis has been on economic and technological development of various LDC's. However, the Bank kept a weather eye on the environmental implications of this developmental activity, although without a systematic procedure for identifying and examining these implications. Even more significantly, methods to prevent, or at least mitigate adverse environmental consequences of development were not devised, at first, advisor Lee told a Center for International Environment Information briefing held in New York last October.

Thus, the Bank saw a necessity to establish an environmental advisor's post, and did so in 1970 (*ES&T*, January 1973, p 16). The advisor and his staff were given a strong mandate to review and evaluate potential environmental effects of every investment project. Indeed, not only are ecological effects to be considered with a view to prevention or mitigation, but also health and socio-cultural effects.

For a clear idea of this policy, one should read, "Environmental, Health, and Human Ecologic Considerations in Economic Development Projects", published by The World Bank in May 1974. However, one should check its tables setting forth pollution standards of the various countries listed, to see if, and to what extent they have been changed since that time.

Also, previously, environmental matters were considered to the extent that they applied to other developments. Recently, however, there has evolved new emphasis on pollution abatement and environmental improvement in their own right, and actual money investment in such projects.

The first such investment was made early this decade when the Bank financed a wastewater treatment (wwt) system for the municipality of São Paulo, Brazil (*ES&T*, January 1973, p 17). Later, partly because of public clamor for abatement of pollution in its lakes and watercourses, Finland requested and received a 15-year loan of $20 million (*ES&T*, August 1975, p 710). It should be pointed out that Finland is not normally considered an LDC.

Since 1975, more such direct loans were made by the Bank or IDA. For instance, last year, Malaysia got a Bank loan of $21.5 million toward extending sewage facilities, so that by 1981, up to 400 000 people will be served in the Federal Territory of Kuala Lumpur (population, about

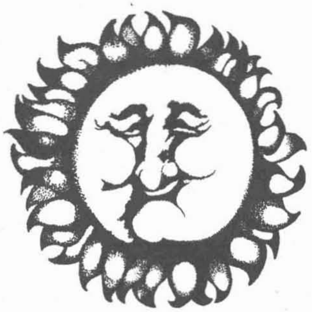
Nigeria's Ojikutu

The Federal Republic of Nigeria is the first African country to go full-speed ahead on environmental programs, and Raimi Ojikutu (*ES&T*, November 1974, p 972) is the man in charge. As director of environmental planning and protection for the Ministry of Housing, Urban Development, and Environment, Ojikutu is to oversee Nigeria's development of an environmental effort analogous to that of countries such as the U.S., Britain, Canada, and Japan. Funding comes under Nigeria's 1975–1980 Five-Year Plan for development.

A very high priority is being given to combating pollution from oil spills and oil refinery wastes. Another high priority is the fight against Nigeria's northern region's desertification. However, similar emphasis will be on industrial water pollution problems; development of domestic and industrial sewage treatment systems; solid waste disposal; and assessment and control of agricultural pesticides. Ojikutu told *ES&T* that concrete efforts in these directions have already started with planning for a centralized sewer system at Victoria Island in Lagos, Nigeria's present capital.

Ojikutu explained that Nigeria is encountering industrial pollution problems similar to those of the Developed Countries, because its capital gains from oil exports are bringing about rapid industrialization. But he noted that his country has problems parallel to those of poorer Third World states, and that among them are population pressures, inadequate food production with resulting malnutrition, and water-related and pest-vectored diseases. He is confident, however, that these difficulties can be surmounted in due course.

"When we in Nigeria have gained experience from our environmental programs, we hope to share it for the benefit of other African nations, as they begin to industrialize," Ojikutu said.



Africa: Some self-help programs

"Africa must stop believing that it has no aptitude for research and that it should be left to others." So said A. Moumouni, director of the Niger Solar Energy Office (ONERSOL, Niamey, Niger). The same should be said of all LDC's, for although a country may be short of financial, mineral, and other material resources, it does have people of ability and intelligence. They are a most valuable resource that will be increasingly applied to environmental improvement and developing renewable energy supplies, as well as regular industrial and agricultural projects.

Thus, at ONERSOL, founded in 1966, such local people have developed solar energy-using devices that are working now. For example, the Office built a 600-L water heater which is on line at the Grand Hotel in Niger's capital, Niamey. ONERSOL is also marketing a 200-L water heater which costs about CFA 180 000 ($620), has a 15–20-y life, and which Moumouni estimates can be amortized in 14–18 months. Other products are solar heating, cooling, distilling, and pumping systems, and solar batteries that help to transmit Niger's educational television programs. ONERSOL's factor was funded exclusively by Niger.

Neighboring Mali has had a Solar Energy Laboratory since 1964; its present director is Cheickné Traoré. He told *ES&T* that of the West African Economic Community (CEAO) countries, consisting of Ivory Coast, Mali, Mauritania, Niger, Senegal, and Upper Volta, Mali is the most advanced in on-stream solar energy utilization. The Laboratory has turned out solar water heaters and stills, cookstoves, dryers, and thermodynamic pumps, and is working on cooling. One such pump (50 kW) installed at Diré, Mali, this year, will provide irrigation for about 250 acres of land; electricity for a touristic village associated with the project; and running water for the whole city of Diré.

"Last year, the Laboratory was granted FM 30 million [$6.41 million], exclusive of equipment funds, Traoré said. He also noted that in the past, the Laboratory had its troubles obtaining money and technician help; however, it has made slow, but sure progress. "Its immediate goal," Traoré said, "is to provide water heating for all of Mali." But Mali's Ambassador to the U.S., Ibrahima Maciré Sima, told *ES&T* that a bigger goal is to come up with ways of cutting solar energy costs, and especially reducing the need for out-of-country source funding.

Other countries pursuing solar energy programs are Ghana, Nigeria, Senegal, Sudan, and Upper Volta. Similar programs are under way in the Middle East.

Last September, the CEAO held a meeting at Bamako, Mali's capital, specifically to discuss solar energy. Another aim was to formulate a plan to pool CEAO resources for regional solar energy development.

Trying to stop desertification is another on-going project in Niger. It is called "Operation Green Sahel," and consists of a carefully planned, scientific tree-planting and cultivation program.

---

750 000). The project's total cost is $60.5 million.

For part of the needs of a $74.9 million effort to clean air in Yugoslavia, the Bank loaned $38 million. That money will go to converting lignite-fueled (4–6% S) central heating plants to natural gas, and to connecting households into this gas at Sarajevo, which is presently one of the most SO_2-polluted small cities (population 300 000) in the world. Also, a natural gas transmission line will be built to the capital, Belgrade, and a distribution ring and service connections will be constructed. The Sarajevo project is part of a $145 million program in which the Bank's share will be about $85 million. The project will include water/sewer, as well as air programs.

Last year, water supply improvement, as well as sewage projects got Bank loans. These are in Kenya ($35 million), Mexico ($40 million), Panama ($12 million), Syria ($35 million), and Yugoslavia ($20 million). Not only is supplying water to more people an objective; an important consideration, in many cases, is the elimination of health hazards.

The IDA, also, was not idle last year, in this respect. It granted credits of $40 million to India toward upgrading water supply to benefit about 5 million city dwellers and 1.2 million villagers in the northern state of Uttar Pradesh. There was also a $26.6 million credit to Pakistan to improve water/sewage in Lahore; and a $21.5 million credit to Zaire to give more people access to water, and to reduce the incidence of waterborne diseases.

Health hindrances to development

Indeed, the present main thrust of World Bank and affiliate programs directly in the environmental field seems to concern improvements in water supply and wwt. However, not only water/sewer *per se*, but public health plays an important role. Here, public health might be defined in terms of diseases, rather than effects of industrial pollution. Since most LDC's, especially the poorer ones, are in tropical and sub-tropical areas, the disease factor takes on special significance.

That is not to say that industrial or municipal pollution is ignored. On the contrary, World Bank policy mandates consideration of man-made pollution during all planning, evaluation, and execution stages of each project.

For now, most tropical LDC water projects deal with supply, sewage, irrigation, and hydropower. For these purposes, it is difficult and costly enough to deal with environmental and health effects in the Temperate and Frigid Zones. In tropical regions, these problems are compounded, among other things, by the greater variety of diseases found there, some of which are almost pandemic.

One can list at least 36 water-related illnesses, not all of which are tropical. However, Temperate Zone afflictions such as cholera, typhoid, hepatitis, and the like, can be found in the tropics and subtropics, in addition to tropical pestilences, many of which are insect- or mollusc-vectored.

The latter include malaria, schistosomiasis (snail fever), onchocerciasis (river blindness), dengue, guinea worm, and others. They have been a formidable hazard of hydropower, agricultural, and even urban development, and call for special water and wastewater treatment approaches, and construction engineering.

Snail fever is a "good" example of a tropical disease stemming from poor water management and use. It is found in almost all warm-climate areas, and is caused by eggs of the parasitic worm, *Schistosoma,* of which there are three species of concern. Waste from infected humans release the worm's eggs to receiving waters, to lodge in the bodies of *Biomphalaria* snails. These snails find their way into irrigation water; lakes, especially man-made ones; certain wells; and other bodies of slow-moving or still water.

The worm larvae hatch in the snails' bodies, and are released to the water. They need not be ingested to infect a human, for *Schistosomae* can bore through intact skin. Schistosomiasis symptoms can range from lassitude to excretory bleeding to liver fibrosis or kidney destruction, and its varieties are not easy to treat. Moreover, treatment is not always successful, even at early stages of the disease.

Probably, the common denominator is that proper waste treatment, while important everywhere, is even more so in the warm climates in which most LDC's are located. There, the water-related disease factor has been a material barrier to agricultural, hydroelectric, and even urban development. To be sure, new techniques in water/wastewater project engineering, construction, operation, and maintenance are being devised to help to remove these hazards. However, that task will be monumental, but its necessity can partially explain why water matters often take precedence over air considerations where LDC environmental affairs are concerned.

No "Mr. Fixit"

Nevertheless, with industrialization and urbanization in the offing for LDC's, water (and other) pollution from these sources, and what to do about it, takes on increasing importance. In comparison to the disease factor, "that kind of thing can be easily handled," an official of the U.S. State Department's Agency for International Development (AID) told *ES&T*. Hopefully, his confidence in this respect will prove to be justified. For there are considerable technical, cultural, and economic hurdles in the way of procurement, installation, and operation of both process and anti-pollution systems/equipment in many LDC's.

A principal problem is that often, there is often no local "Mr. Fixit" one can hire or call upon when something goes wrong. "Mr. Fixit" is defined as the skilled, practical "hands-on" artisan at technician, craftsman, or foreman level. Perhaps, the wealthier LDC's—especially those that export oil—have the financial resources to bring in such people from abroad to work and train local people, in return for fabulous compensation packages. But most LDC's, many of them desperately poor, cannot afford these people or programs.

Jean Tixhon of The World Bank's Office of Environmental and Health Affairs gave a concrete example of how an air pollution control (apc) project in which he was involved suffered for lack of this type of personnel. It appears that apc equipment, to consist of electrostatic precipitators and baghouses, was considered to be the optimum approach to solving a potentially severe arsenic, cadmium, and lead poisoning problem.

That problem was associated with a lead smelter/refinery in an LDC. The apc systems would not only abate pollution, but possibly recover materials, as well. The contract to supply and install the systems went to a Western European company.

Like many LDC's, this one does not have a cadre of trained personnel to maintain the apc equipment and keep it running properly. So whenever a leak or other malfunction occurred, and even when routine upkeep was needed, representatives had to be flown in from Western Europe to do the necessary work.

Now, the firm has served notice that it can no longer send a man every time a minor problem develops, and said that LDC local technicians should be able to handle routine maintenance/repair jobs. But what technicians? At the time the apc equipment was installed, there were no local personnel of the necessary background and training to qualify as technicians. For all practical purposes, there still are few or none.

The foregoing is a brief summary of Tixhon's personal experience from one project for helping an LDC to embark on environmental control efforts. He told *ES&T* that this widespread lack of skilled, practical technician and foreman personnel in many LDC's is a most severe hindrance to both industrialization and pollution control activities in all fields.

On-site engineers and managers, whether they are local or from industrial countries, are stymied by the acute shortage of the skilled help they need to keep a plant running efficiently, and at capacity. Also, because of the lack of this support, as well as better economic opportunities elsewhere, many LDC nationals who earn degrees in scientific or technical disciplines often seek employment in industrialized countries, or wealthy, oil-exporting LDC'S.

Food, fiber, and fuel

Like the disease factor, the extreme shortage of capable technical trade help is only one serious problem facing LDC development and any environmental protection efforts that might be exerted. There are many others. As previously mentioned, with the main exception of the OPEC oil-exporting nations, LDC's are usually desperately short of capital, and of energy supplies. These shortages not only retard industrial development, but also development and expansion of food and fiber supplies, and whatever environmental controls that would apply to such development.

Indeed, many LDC's consider food/fiber/fuel (3F) supply development as being of higher priority than industrial development. This is quite understandable when one considers that some are on the verge of, or are actually suffering famine. This 3F supply development was a main subject of discussion between *ES&T*, the AID environmental affairs coordinator, and other members of AID's Office of Science and Technology.

One 3F-related topic was the agency's pest management program. This program appears to be very necessary, since more than 40% of the world's food and natural fiber supply is lost to insects, fungi, and rodents.

To combat these pests, as well as to suppress disease vectors, AID is involved in this program in numerous LDC's. In 1975, that agency was sued by the Natural Resources Defense Council (NRDC)

which charged that AID was using, and perhaps misusing, pesticides abroad that were deregistered or forbidden for U.S. use. The agency was enjoined from continuing such practices, and ordered to prepare an environmental impact statement (EIS) on its pest management program. That very comprehensive 2-volume EIS was completed on May 13. It can be seen at AID, Department of State, Washington, D.C. 20523. Contact Albert Printz, Environmental Affairs Coordinator.

Slash and burn

But careful, rational use of pesticides under a well-planned and executed program is only one of the many environmental problem areas of increasing 3F (food/fiber/fuel) yields. Another is the clearing and use of land, including very marginal land, for crop or animal raising. The indiscriminate way in which this land is cleared and used is a matter of great concern to AID.

It has often been thought that because riotous forest or jungle growth occurs in an area, that area is ideal for growing crops. This is one reason why many tropical wooded areas are being slashed and burned as quickly as the job can be done, so that farms, settlements, roadways, and other appurtenances of human habitation can be established.

Food and fiber are two of the 3F's. The third is fuel, and much of the tropical deforestation is aimed at producing firewood and charcoal—staple fuels in poor countries that cannot afford imported oil. Indeed, about one-half of the world's wood is used for burning in some form, AID geologist E. Walter Parham told *ES&T*.

Unfortunately for 3F development goals, these areas of luxuriant forest growth will commonly support crops for 2–3 years, Parham pointed out. The main reason is that the forest growth is fed by humus, overlying the actual soil, generated by decaying flora and fauna.

The soil itself is lateritic, and contributes little more than physical support. Such soil is rich in iron and aluminum, and poor in just about everything else. When its forest cover is removed, in certain cases, it eventually may take on bricklike characteristics.

When the forest cover is removed to convert such land for crop raising, the residual forest humus will sustain the crops with decreasing efficiency until its nutrient value is depleted. That process normally takes 2–3 years. Chemical fertilizers may extend this time, but once the soil hardens, nothing does much good.

If only a few acres have been cleared, the forest may slowly return over a number of years. However, land cleared in square-mile quantities may never reforest naturally, even if it is left alone for 1000 years, Parham said. He also told *ES&T* that many non-desert tropical areas worldwide are composed of such lateritic soils. In some parts of the humid tropics, where much deforestation is occurring, these weathered soils and subsoils can run as deep as 400 ft.

Other non-desert tropical areas are composed of volcanic or deltaic soils. These are more amenable to agricultural development, but must be carefully husbanded, or they, too, will rapidly become impoverished.

A man-made environmental disaster

A common sight in the streets of Port-au-Prince, capital of Haiti, and other towns there, is the charcoal vendors' carts. Why charcoal? Most Haitians could not afford any other fuel even before the traumatic 1974 oil price increase; now, of course, their situation is even worse. The accelerated demand for charcoal, as well as the search for arable land, has caused the near-total destruction of Haiti's once-lush tropical forests. Indeed, while 20 years ago, about 80% of Haiti was forested, at present, about 9% has forest. Of that 9%, approximately one-half is second-growth scrub.

Removal of the forests sharply increases the amount of sunlight striking the ground. In turn, the land mass is heated more, and made less water retentive. The loss of forest means less mass evapotranspiration (ET) to form rain clouds; ET is one major source of moisture in tropical land areas, such as Haiti. Then, the land mass gets less rain. Much more of what rain does fall runs off to the ocean.

For four consecutive years, Haiti has been in a severe drought situation, which USAID officials believe was materially exacerbated by the forests' destruction. Last year, for example, Haiti received only 68% of its normal rainfall.

Because it rains less, water tables go lower. Surface soil becomes dryer, and is washed away by the rains that do happen to fall; thus, the quest for more arable land—one reason for destroying the forests—fails. Because of human actions, what was once a rich tropical forest has become a semi-desert.

The economy has also been adversely affected. Since soil suitable for farming has been washed away, beans, for example, a staple food in Haiti, cost 45¢/lb. Five gal of drinking water is priced at 90¢ in a country where a poor person lucky enough to find some work earns less than $1.50/day. There is no longer sufficient water for Haiti's hydroelectric power.

Haiti is not the only country where such a man-made environmental disaster has occurred. Nigeria's Raimi Ojikutu told *ES&T* that parallel environmental and resulting economic effects are being felt on the island of Madagascar because of the wholesale destruction of its forests.

Agricultural and highway development and settlement are not the only reasons for wholesale destruction of tropical forests. It must be remembered that many LDC's are desperately poor, and had enough trouble affording petroleum products even before the 1973–1974 oil price increase. Now, with oil so expensive, these countries turn to wood and charcoal, even more than they have in the past. Also, some East African nations earn "petrodollars" through large exports of forest-derived charcoal to Persian Gulf countries where it is much in demand.

These are among the many environmental problems with which AID is concerned, particularly in the poorest-of-poor LDC's, in which the agency works by mandate of Congress. To attempt to save what forest is left, and broaden the economic base at the same time, the agency is trying to channel resources to encourage non-farming rural and village employment.

Appropriate technology

Destitute nations look to tropical forests as immediately accessible sources of fuel in the form of firewood and charcoal. Thus, the increasing cutting of trees without consideration of ecological effects, and the high cost of petroleum have heightened AID's interest in developing alternative, renewable, clean energy supplies for the countries in which it operates. Jerome Bosken, AID's energy specialist, told *ES&T* that about $15 million would be spent next year for that purpose.

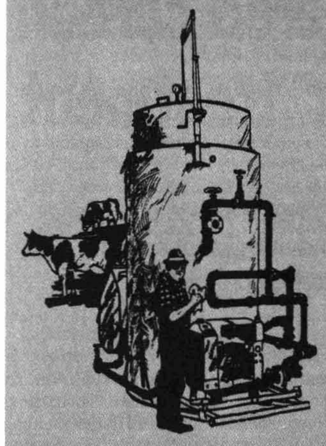
An often-discussed approach to helping poorer LDC's to develop these energy sources, and protect and improve the environment—the latter more in the water/wastewater field for now—is something called appropriate technology (AT). Appropriate technology seems to be a catch-all phrase defined as technology within the means of, and using resources locally available in these LDC's. AT might also entail use of traditional methods, in some cases. Presumably, this technology would evolve according to the needs and increasing sophistication of the local people.

Part of AID's efforts in rural areas aim in this direction. Indeed, Molly Kux, State Department liaison officer to AID, told *ES&T* that the agency is to set up an Appropriate Technology Institute (ATI). She said that Congress had allocated $20 million to AID for development of village technology, especially in poorest-of-poor nations.

Incidentally, last year, AID worked with about 50 countries, and a budget of approximately $3.9 billion, for all types of projects.

One example of AT for water treatment might be the use of plants in Sudan as described by the University of Khartoum's Samia al-Azharia Jahn (*ES&T*, May 1975, p 408). She explained how the seeds of certain local plants helped to clarify raw water. Perhaps evolution of this technol-

Biogas: an alternative fuel?



One widely discussed appropriate technology application is anaerobic digestion of animal, human, and other organic wastes to produce biogas—mainly methane. Its heating value can be 600–700 Btu/ft^3. Essentially, the techniques for producing it are based on the anaerobic digester devised by Ram Bux Singh of India, specially for LDC use. India, the People's Republic of China (PRC), and the Philippines are among countries involved in biogas systems development.

A PRC estimate is that a 10 m^3 digester can produce fuel gas equivalent to 7 tons of coal. In Miyang County, Szechuan Province, for example, there were 100 000 digesters by 1974, providing fuel for more than 76% of the population.

In the Philippines, five biogas pilot plants, each of which can satisfy cooking and lighting needs for five households, were on stream as of last March. One aim in that country is complete replacement of liquefied petroleum gas (LPG). At present, LPG use is to be reduced by 50%. This project started in 1973 as a result of the oil embargo; the first biogas set up now produces up to 30 000 ft^3/d at a flour mill.

But there are problems with biogas. The systems are not easy to build. Also, desperately poor farmers—and there are many—can afford neither the system nor the amount of animals, for example, necessary to provide enough "feedstock" to run it. Also, ways to collect the very diffuse wastes and water to operate the system are needed; they exist in the PRC, but not in many other places. Moreover, cement, the best tank material, is not cheap and readily available everywhere. On balance, though, biogas could be a viable alternative for fuel production, and organic fertilizer, as well, in numerous locations—even in the U.S.

Incidentally, in the PRC, a biogas approach furnishes cooking gas, and removes a disease vector at the same time. Human wastes, some containing *Schistosoma* (snail fever) eggs, is channeled into a water-seal, odorless latrine with a three-chamber sedimentation tank. Having no way of reaching snails, the eggs from the human waste die in a month. Other human waste-borne parasites die, as well. The wastes ferment anaerobically, producing methane, and safe fertilizer.

ogy will lead to isolation, and, eventually, synthesis of the actual chemical substances that clarify the water, so that a larger-scale, more effective job can be done.

Another possibility may be the use of cleaned or partially renovated water for aquaculture. Indeed, experiments at the Woods Hole Oceanographic Institution (Mass.) indicated that various edible marine organisms may be raised in certain types of polluted waters.

These organisms help to remove the pollution, and apparently metabolize the pollutants to innocuous substances, for indications are that they can be safely consumed. Similar experiments were tried in fresh water in Oklahoma and Texas (*ES&T,* May 1975, p 409). If this technique is successful, some water and food problems might be solved simultaneously in certain areas.

Another AT option could involve beneficiation of cellulosic wastes. Such wastes, for example, lend themselves to being easily-prepared substrates for the culture of single-cell protein for animal feed. They can also be fermented into glucose solution which, in turn, can be made into alcohol fuels (*ES&T,* September 1974, p 784, and November 1975, p 1011). In certain LDC's, carob pods, peanut waste, rice hulls, and bagasse (sugar cane waste) are likely substrates.

Thus, AT can offer options for LDC development coupled with food and energy production, and environmental control and improvement. However, certain problems must be solved; the sooner, the better. Those include evolution and actual physical transfer of this technology, putting it in place, and ensuring that it does not remain stagnant.

A main key to accomplishing these tasks would be careful, systematic training of local, "hands-on" technician personnel which, at present, are usually sorely lacking even in rich, as well as poor LDC's. One of AID's goals is to promote this kind of training, in keeping with the aim of developing rural or village non-farm employment, as well as better ways to improve food supplies.

Bound and determined

The problems and prospects for agrarian and technological development of both the richer and poorer LDC's, most of which exist in the world's warmer climates, are very numerous and differ greatly from nation to nation.

But one factor is common to all of them. Rich or poor, they are resolutely bound and determined to achieve a standard of living comparable to that of the Developed World; failure could bring about severe and widespread social and geopolitical manifestations, particularly in the poorer LDC's.

Naturally, few wish to deny these countries their aspirations. However, there is this growing worldwide realization: While it might bring apparent near-term benefits, indiscriminate development can have environmental and social consequences that could actually leave the nations involved worse off than they would be if there were no development at all.

Instead, there can be very careful planning specially tailored to the physical, geological, ecological, and climatic nature of the various LDC areas. Local technician cadres can be trained, and AT that blends traditional and newer methods with the use of locally available materials can be devised.

Moreover, the natural and human environment could be regarded and treated as a valuable resource, rather than an impediment to development. The acceptance of that view would constitute a major step in bringing to the LDC's the improved quality of life to which they certainly are entitled.

Additional reading

Aquaculture for the Developing Countries. Frederick W. Bell and E. Ray Canterbery. 288 pages. Ballinger Publishing Co., Cambridge, Mass. 02138. 1976. $20, hard cover.

Mazingira: The World Forum for Environment and Development. Periodical. Pergamon Press, Inc., Maxwell House, Fairview Park, Elmsford, N.Y. 10523. $10/year; $2.50/copy. A preferential rate of $6/year for subscribers in Africa, Asia, and Latin America is in effect.

Water, Wastes and Health in Hot Climates. Richard Feachem et al., Eds. xvi + 399 pages. John Wiley & Sons, Inc., 605 Third Ave., New York, N.Y. 10016. 1977. $22.95, hard cover.

Various publications from the EPA (Washington, D.C. 20460); United Nations Environment Program (Nairobi, Kenya); AID (Washington, D.C. 20523); and The World Bank (Washington, D.C. 20433).

Also, EPA is in the process of compiling an inventory of organizations and people concerned with international aspects of environmental affairs. This would include development. The inventory should be completed by late October or early November. Dolores Gregory of EPA's Office of International Activities is in charge of the project, and Peter Christich is coordinating it.

PAT REPORT
PRACTICAL, AVAILABLE TECHNOLOGY

Putting powdered carbon in wastewater treatment

Zimpro, Inc. improves the activated sludge process by adding carbon and regenerating spent carbon, using its wet air-oxidation process

A new wastewater treatment process makes powdered-activated carbon economical to use. It produces sparkling effluent from existing sewage treatment plants and copes with troublesome industrial wastes. This process combines adsorption on powdered-activated carbon with conventional biological treatment; the spent carbon is regenerated by wet air oxidation. Essentially a merger of secondary and tertiary treatment, in a biophysical scheme, this process has become a cost effective form of advanced wastewater treatment.

At Vernon, Conn., the carbon/wet oxidation system will replace trickling filters that are no longer effective on a domestic wastewater heavily laced with textile dye-house discharges. The system will meet strict BOD, COD, and suspended solids requirements, and clear up a serious color problem.

In Kimitsu, Japan, east of Tokyo, the process has been at work nearly two years on strong supernatant from the treatment of night soil (raw feces and urine). In a head-to-head comparison with activated sludge, carbon/wet oxidation reduced the COD content of diluted supernatant almost twice as effectively.

High strength industrial wastes have proved treatable by the process—particularly those from pharmaceutical, pesticide, and other chemical product manufacturing processes. In side-by-side studies, the carbon/wet oxidation system demonstrated superiority over activated sludge in removing BOD, COD, color, odor, and nitrogen, and, in comparison with the activated sludge system, provided better oxygen transfer characteristics.

The Liverpool Sewage Treatment Plant Medina County, Ohio, is being upgraded from conventional activated sludge to a 10 mgd advanced wastewater treatment facility with carbon/wet oxidation. Effluent quality, surpassing stream standards, are expected to be: BOD and SS of 5 mg/L or less, COD of 50 mg/L or less, and ammonia nitrogen of less than 1 mg/L.

Municipal projects

According to Richard Halishak of the consulting engineering firm of Richard T. Halishak & Associates, Inc. (Medina, Ohio), the carbon system was selected following studies that considered carbon/wet oxidation, high purity oxygen, and two-stage activated sludge.

"We evaluated for cost effectiveness and quality of treatment," he says. "We piloted the carbon system extensively and were impressed with the treatment effectiveness. At the same time, wet oxidation provided the answer for regeneration."

Halishak has designed the Liverpool facility as a regional plant that will serve three formerly separate sewer districts in the northwest quadrant of the county, including the city of Medina, the county seat. Influent will consist of domestic and rural discharges, as well as wastes from a number of manufacturing and light industrial operations.

"Standards are extremely high for Liverpool effluent," explains Halishak, "because the receiving stream—the West Branch of the Rocky River—has a low flow rate and may someday be used as a source of water for the city of Berea, 10 miles below the outfall. In addition, the Rocky is part of the Lake Erie watershed and flows through areas of metropolitan Cleveland being developed into a recreational greenspace."

Space is another reason the carbon/wet oxidation system was chosen. "The capacity of the plant will be expanded by more than a factor of six," says Halishak, "but the area of the treatment facility will only double."

Space and stream standards entered into the decision for carbon at Vernon, Conn., as well. A. R. Lombardi of Lombardi and Associates (Vernon, Conn.), co-engineer with the Anderson-Nichols consulting firm (Boston, Mass.), explains that the industrial content of Verno wastewater caused failures in existin sludge digesters and stripped tricklin filters of bacterial buildup. "We wante something that would give us bette treatment than activated sludge, an would handle industrial wastes," h says.

Though Vernon treatment will be improved, additional construction is bein kept to a minimum. In addition to th carbon regeneration building—not a bi space requirement—a new grit facilit and pumping station are being constructed.

New tankage has been added for carbon contact, but existing primary an secondary clarifiers, digesters, an trickling filter shells are all being saved o converted to other uses in the Lombard upgrading plan.

The new Vernon plant will handle 6.5 mgd, and effluent will be polished in a sand filter before release to the Hockinum River, a tributary of the Connecticu River.

Powdered carbon/wet oxidation applications

Site	Flow	Operation
Rothschild, Wis.	1 mgd	1972–73
Kimitsu, Japan	500 kL/day	1975
Oga, Japan	1200 kL/day	Under construction
Medina County, Ohio	10 mgd	Mid-1978
Vernon, Conn.	6.5 mgd	Late 1977–early 1978
Texas (Pharmaceutical mfgr.)	0.25 mgd	System designed
New Jersey (municipality)	5 mgd	Under design[a]
North Carolina (municipality)	12 mgd	Under design[a]
North Carolina (municipality)	9.5–13 mgd	Under design[a]
Michigan (municipality)	55 mgd	Under design[a]
New York (municipality)	7 mgd	Under design[a]

[a] Systems anticipated to begin construction within next 18 months

Industrial projects

The advantages of combining powdered carbon treatment with wet oxidation regeneration have been borne out on difficult-to-treat industrial wastewater, as well. Zimpro Inc. (Rothschild, Wis.) recently completed a treatability and design study for a major producer of pharmaceuticals and fine organic chemicals, testing the economy and effectiveness of the carbon/wet oxidation system.

Some of the wastewater was resistant to biological treatment, yet the high flow rates and dissolved solids contents eliminated incineration as a treatment alternative. Adding to the problem were wide variations in raw waste composition and load caused by production changes.

Objectives of the study were:

- to compare performance of the carbon/wet oxidation system against two-stage activated sludge
- to determine system nitrification, denitrification, oxygen transfer, and sludge characteristics.

Two pilot trains—a conventional two-stage activated sludge system, and a single-stage carbon/wet oxidation system—worked virtually continuously for four months on identical feed. The pilot plants treated a raw feed averaging 7470 mg/L BOD, 14 790 mg/L COD, 350 mg/L SS, and 690 mg/L TKN.

Waste sludge (powdered carbon + biomass) was withdrawn from the carbon system and was regenerated by wet air oxidation. Carbon was recycled through the system an estimated average of 4.8 times during the course of the study.

Virtually complete nitrification was achieved by the carbon/wet oxidation system. System vapors and oxidation off-gases were bubbled through the aeration tanks of both systems, with better removal of odors and hydrocarbons exhibited in the carbon system.

Effluent BOD was 11 mg/L for the carbon system, compared to 55 mg/L for two-stage activated sludge; effluent COD was 280 mg/L for carbon, 540 mg/L for activated sludge; TKN removal was 95.5% for the carbon system, and 13.8% with activated sludge.

In addition, adsorptive properties of carbon regenerated by wet oxidation compared well with virgin carbon across several parameters. Specific surface recovery was 54–66% in pores of less than 37 Å diameter, 110–130% in pores of 37–600 Å diameter, and 114–203% in pores greater than 600 Å—excellent area-pore size distributions for the application. Adsorption efficiencies of the regenerated carbon relative to virgin were 53–64% by iodine tests, 87–133% by methylene blue, 85–106% by erythrosin, and 100–150% by molasses color.

The pilot system also demonstrated unusual stability, and—with the continued operation of a $100 million chemical complex dependent upon reliable wastewater treatment—this way a key factor in the ultimate decision to build a full-scale carbon/wet oxidation facility. The 50 tons of activated carbon circulating in the aeration tanks, waiting to level out shock loads and accidental product spills, provided process security.

How it works

In the process, powdered-activated carbon is added directly to the aeration tanks of a conventional activated sludge system. The combination permits total treatment of the waste stream. Biodegradable organics are oxidized or assimilated biologically; non-biodegradables —including toxic and other harmful agents—are simultaneously adsorbed on the activated carbon. The adsorptive properties of the carbon can also be exploited for color and odor control.

System stability, aeration tank capacity, and high-mixed liquor suspended and volatile suspended-solids concentrations permit maintenance of a long sludge age which in turn is conducive to high levels of nitrification. Substantial denitrification is also possible because improved sludge density permits nitrogen to form without clarifier upset.

To make the system economical in the face of high costs for virgin carbon, however, effective regeneration is crucial. Wet air oxidation, developed by Zimpro Inc., is attractive because it operates at low temperatures and does not require a dewatering step. A portion of the spent carbon and associated biomass is wasted from clarifiers, gravity thickened, and then sent to a wet air oxidation unit (*ES&T*, April 1975, p 300). There it is pressurized, mixed with air, heated in heat exchangers, and passed through a reactor vessel where oxidation and regeneration take place. Oxidation is at temperatures of around 400–470 °F, the optimal temperatures for carbon recovery. Better than 90% of the original carbon can be recovered by wet oxidation.

A major factor adding to the cost effectiveness of the entire system is that associated biological solids are also destroyed in the wet oxidation carbon recovery step. This eliminates the need for secondary biological solids disposal.

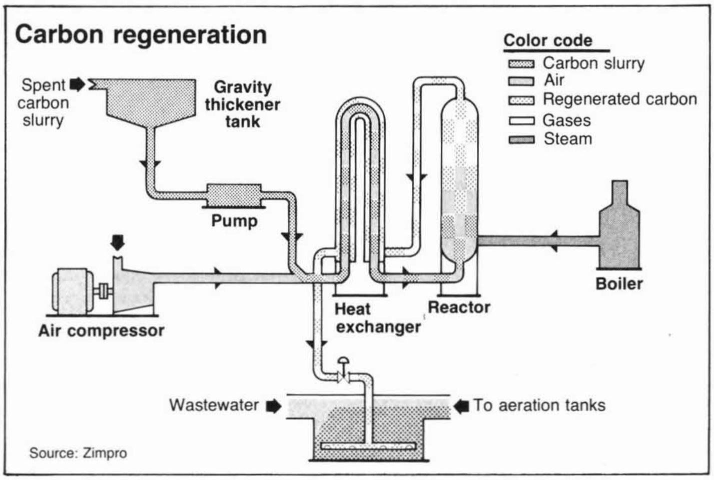
Cost effectiveness

The carbon/wet oxidation flow scheme has been compared with a number of other advanced forms of wastewater treatment in several different treatment situations.

In the Medina County, Ohio, 10 mgd project, the carbon/wet oxidation system was projected to be lower in both capital and operation/maintenance costs over 20 years than a pure oxygen system with ozone for disinfection.

In a recent study (Culp & Shuckrow, *Water and Wastes Engineering*, February 1977) the carbon/wet oxidation system also wins out favorably against activated sludge, and various powdered and activated carbon treatment schemes. Cost per million gallons treated was estimated at $433 for the carbon/wet oxidation process, compared to $410 for single-stage activated sludge with chemical coagulation and filtration, $582 for granular carbon with carbon regeneration by multiple hearth furnace, $774 and $867 for single- and multi-stage powdered-carbon systems, respectively, with carbon regeneration by fluidized bed incineration. The analyses were based on capital and operating costs for a 10-mgd plant over a 20-year period.

The ability of the system to nitrify and denitrify, the simultaneous oxidation of secondary solids in the carbon regeneration step, and the absence of a need to dewater carbon prior to or following regeneration, are major reasons for its cost advantages in municipal applications. In industrial treatment, the carbon/wet oxidation system appears quite cost effective against incineration because of the high costs for fuel and dewatering with the latter process.



Carbon regeneration

Source: Zimpro

OUTLOOK

Electric utilities seriously look at fabric filters

With increased use of low-sulfur western coal, baghouses may capture 35–50% of the particulate control market for this sector in 5–7 years

In 1970, fabric filter sales to electric utilities for fly ash control were nonexistent. Last year sales totaled about $14 million. This year sales will mount to $15–20 million. And by 1982 sales should hover near the $90–100 million mark. These figures were supplied to *ES&T* by Ken Aken, chairman of the Industrial Gas Cleaning Institute's (IGCI) fabric filter division, who cautions that IGCI tracks only bare hardward sales figures that exclude the cost of auxiliary equipment and erection.

To say the least, this penetration of the utility market has been very gratifying to the companies designing, engineering and constructing baghouses. And the future indeed looks promising. Today, 10% of utility air pollution control devices sold are fabric filter collectors. Should the economic climate for utilities remain good, fabric filter suppliers anticipate a surge in baghouse sales over the next two years. In 5–7 years these suppliers speculate that fabric filters will capture 35% (and possibly 50%) of the electric utility particulate control market.

Why the interest?

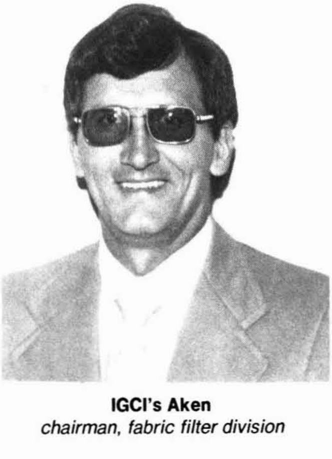
Fabric filters have been around for at least 80 years, and have found application in solving industrial control problems. The earliest use of fabric filters, in the late 1880's, was to control emissions from nonferrous metal smelters; today, these collectors are being widely used to clean the waste gas from steel-making furnaces and to collect dust in the cement industry. Utilities—free to burn oil and/or coal with no restriction on sulfur content—found electrostatic precipitators technically and economically viable systems for particulate matter control.

But 1970 saw enactment of the Clean Air Act with its tighter strictures on particulate and SO_2 emissions, and 1977 heard President Jimmy Carter's call for utilities to switch to coal to fire their boilers. Though widely spaced in time, both events force increased reliance on low-sulfur western coal. And therein lies the problem.

Because of the chemical characteristics of low-sulfur coal, the fly ash produced from the burning of this coal is a poor conductor of electricity. The fly ash is difficult to charge, which is a necessary precondition for the use of electrostatic precipitators, and once charged, the collected material on the plates of the precipitator is difficult to discharge. Engineers call this high resistivity.

Fabric filter baghouses, which act essentially like huge vacuum cleaners, require no preconditioning of the fly ash, and are able to efficiently filter the residue produced from the combustion of low-sulfur coal. In fact, baghouse collection efficiencies are usually rated at better than 99%.

Because precipitators are size and cost sensitive to the type of coal being burned, the size and cost of a precipitator designed to control emissions from low-sulfur coal could negate against these systems as the pollution control device of choice if high collection efficiencies are required. However, it is risky to generalize about economic and technical tradeoffs between fabric filters and precipitators because the pollution control device of choice is dependent on what engineers term "site specific factors."



IGCI's Aken
chairman, fabric filter division

Generally speaking, Sidney Orem, technical director of IGCI says that "Fabric filters will find application in new electric utility plants dedicated to the burning of western coal." But he cautions that utilities, traditionally conservative, are waiting to judge the ultimate bag life. If the bag life is only one year, then fabric filters become costly alternative systems; however, if bag life is five years, baghouses become very acceptable options.

Western Precipitation Division of Joy Manufacturing Co. supplied the first baghouses to four of six coal-fired utility boilers (175 MW total) at the Sunbury Station of Pennsylvania Power and Light, about 5 years ago. Bags from three baghouses were changed after two years' operation, but the fourth baghouse with the original bags has been operating well for about 4 years. However, this is considered a small unit, and utilities are waiting to see the performance of fabric filters on several larger units—Texas Utilities' two 575-MW Monticello Units 1 and 2 (about 80% of the flue gas will go through bag filters and the remaining 20% will pass through the existing electrostatic precipitator), and Southwestern Public Service's 350-MW Amarillo, Tex., unit—scheduled for start-up in 1978. At present, engineers calculate bag life at a minimum of two years.

New directions

Despite the fact that baghouses can efficiently collect the fly ash from coals of varying sulfur content, these units, as presently designed, can control only particulate matter. The problem of SO_2 control still remains unless the utility has flue-gas desulfurization units . . . or the bag can be treated to simultaneously collect particulate matter while absorbing SO_2 emissions.

The most promising treatment to date that uses baghouses is called dry sorption of SO_2 in which the bags are "seeded" with a naturally occurring dry sodium bicarbonate additive called nahcolite. Several companies have conducted laboratory-scale tests of this and other sodium carbonates, but only one company — Wheelabrator-Frye — has completed pilot testing of the process on a utility boiler. Wheelabrator conducted the test in conjunction with a consortium of 7–8 electric utilities (the Coyote Group), Bechtel and Superior Oil.

Wheelabrator coated its bags with nahcolite supplied by Superior Oil. The baghouse, operating on the Leland Olds Station of Basin Electric Cooperative at Stanton, N.D., was tested for six months.

Baghouse installations on utility boilers

Utility	Location	Equiv. MW	Startup Date
Board of Public Utilities	Kansas City, Kans.	44	1979
City of Colorado Springs	Colorado Springs, Colo.	200	1980
Colorado Ute Electric Assn.	Nucla, Colo.	13	1973
	Montrose, Colo.	12	1977
Crisp County Power Co.	Cordele, Ga.	10	1975
Minnesota Power & Light Co.	Cohasset, Minn.	75	1978
Nebraska Public Power	Bellevue, Nebr.	125	1976
New South Wales Electric Commission	Tallawarra Station	39	1976
	Wangi Station	180	1976
Pennsylvania Power & Light Co.	Holtwood, Pa.	44	1975
	Sunbury, Pa.	175	1973
Public Service of Colorado	Palisade, Colo., Unit 1	22	1977
	Palisade, Colo., Unit 2	70	1978
Sierra Pacific	North Valmey, Nev.	250	1981
Southwestern Public Service	Amarillo, Tex.	350	1979
Texas Utilities	Monticello, Tex.	880	1978

Source: Power Magazine, Jan. 1977

According to Dick Adams, vice president for systems and technology, the tests were successful. A report of the test results will be available from Wheelabrator later this month or next.

Adams feels that this nahcolite conditioning process is commercially feasible and that its introduction to the marketplace is dependent only on the availability of the carbonate. But that availability depends on commitments to mine the nahcolite. Three companies—Superior Oil, Industrial Resources and Rock School Corp.—are seeking mining rights. However, Larry Thaxton, vice president, fabric filter, Buell-Envirotech, points out that $10–14 million is involved in sinking a mine shaft and that the mining of this material is a serious drawback to the ultimate commercialization of the process.

Buell-Envirotech is supplying a baghouse to Colorado Springs Municipal Utility. But, in addition to the full-scale baghouse, Buell-Envirotech is also building a fully instrumented pilot-size baghouse on the 85 MW Martin Drake No. 6 boiler. A portion of the flue gas from the boiler will be diverted to the pilot baghouse for SO_2 removal. According to Thaxton, variously designed tests will be conducted; for example, the flue gas stream itself will be continuously seeded with different physical configurations of nahcolite (and other sodium salt compounds) and the bags will also be coated with nahcolite (and other sodium salt compounds) after a compartment of the baghouse has been cleaned. Test trials are scheduled to begin in May–June 1978.

Neither Wheelabrator-Frye nor Buell-Envirotech has received federal funds for their seeded fabric filter studies. EPA is now funding a feasibility study of the process and, depending on study results, may fund a demonstration project with a Southwestern utility in fiscal 1979.

Some problems

Because of the mining problems, Wheelabrator's reaction process with nahcolite will not be commercially available for at least another year, according to Adams. In the meantime, Atomics International Division of Rockwell International has developed a regenerative aqueous carbonate process that uses commercially available sodium carbonate as the SO_2 scrubbing agent.

In the Atomics International process, the sodium carbonate is dissolved and then spray-dried. The spray-drying unit, through which the boiler's gas stream passes, acts as a chemical contractor for SO_2 removal. The products formed are sodium sulfite, sodium sulfate and untreated sodium carbonate, which are entrained in the flue gas as fine particulate matter. The gas stream from which SO_2 is removed is then passed through a particulate matter control device—either a fabric filter or an electrostatic precipitator. The collected particulates are then treated to recover elemental sulfur and regenerate sodium carbonate, which can be reused in the spray-drier.

A demonstration of this process is planned at Niagara Mohawk's 100 MW Huntley Station; possible startup date, January 1980. The project is to be funded by a consortium of New York electric utilities—the Empire State Electric Energy Research Corp., of which Niagara Mohawk is a member, and the EPA.

Manufacturers of fabric filters

- American Air Filter Company, Inc.
- Buffalo Forge Co.
- Carborundum Co./Pollution Control Division
- C-E Air Preheater Co.
- Combustion Equipment Associates, Inc.
- DCE Vokes, Inc.
- Donaldson Company, Inc./Torit Division
- Dustex Division/American Precision Industries, Inc.
- Environmental Elements Corp./Subs. Koppers Company
- Envirotech Corp./Buell Emission Control Division
- Fisher-Klosterman, Inc.
- Fläkt, Inc.
- Fuller Company/Dracco Products
- Industrial Clean Air, Inc.
- Lear Siegler, Inc.
- MikroPul Corp.
- Peabody Air Resources Group
- Research-Cottrell, Inc.
- W.W. Sly Manufacturing Co.
- Standard Havens, Inc.
- Western Precipitation Division/Joy Manufacturing Co.
- Wheelabrator-Frye, Inc.
- Young Industries, Inc.
- Zurn Air Systems

Source: IGCI

Detractors of the SO_2 dry sorption process point to a solid materials-handling problem created by the formation of sodium sulfate, a soluble solid. If disposed of in the ground, this reaction product could easily leach into groundwater.

Adams counters by saying that the disposal problems are site specific and besides, any disposal problem may be offset by the fact that dry sorption of SO_2 is generally less costly than the purchase of a scrubber or low-sulfur western coals.

Another counter-argument can be found. In addition to Atomics International's regenerative aqueous sodium carbonate process, American Air Filter has a patented process for the regeneration of nahcolite.

Needless to say, the fabric filter people are excited by the potential to simultaneously control flue gases for particulate matter and SO_2 emissions.

Competition, fast and fierce

Fabric filters have successfully penetrated the electric utility market. Their share of the utility particulate control market, at the expense of electrostatic precipitators, may grow to 50%, although many company spokesmen felt this unlikely. More realistically, they estimated the share of the market at 35%.

There was general consensus, however, that over the next 5–7 years, fabric filters will establish a very firm place in the utility market, but they will not take over the primacy established by electrostatic precipitators.

The spokesman all agree that the market is there to be captured. But Bill Henke of Western Precipitation adds this note of caution: "Too many inexperienced companies are racing to get into the field and competition will be fierce." LRE

FEATURE

Is an electric vehicle in your future?

Perhaps. Short-trip household and industrial markets are ready to be tapped and, once penetrated, a solution to our energy and environmental problems may be at hand

Edwin C. Hackleman, Jr.
University of Connecticut
Storrs, Conn. 06286

For many years the automobile has played a major role in the development of the American economy and culture. It has provided the U.S. with an effective means of transporting goods and has provided the individual with unprecedented mobility. Although it was first developed as a simple means of transportation, the automobile now has such a variety of options available that many are no longer simply an efficient source of transportation but are also a pleasure to drive and a source of pride and social stature.

Unfortunately, today's transportation systems are producing some rather severe side effects that are giving rise to serious environmental problems for our large cities. Transportation, including private cars, airlines, trucks, and railways, lead all other sources of pollution, contributing approximately 42% of total emissions. EPA studies indicate that the automobile is the single largest polluter of our atmosphere.

The automobile is also feeling the pressure of its own internal inefficiencies. Environmental legislation to reduce emissions has further burdened the internal combustion engine with pollution control devices that have resulted in even lower efficiency. In addition, the number of cars on the roads has increased markedly. In 1974, just prior to the severe downturn in the economy and the resulting lull in new car sales, it was estimated that 12 000 additional cars join the pollution procession on the roads of America every day.

The transportation system consumes a majority of all the oil available for consumption in the U.S. In a 1974 quarterly report, Exxon Corporation stated that in 1970, transportation used 7.4 out of the 14 million barrels of oil consumed each day in this nation. The same report projects that by 1980, transportation will be consuming 11.5 out of the 21.5 million barrels of oil consumed each day. America's total energy needs by sources of supply are shown in Table 1. It is important to note how rapidly oil imports are increasing. By 1980 it is estimated that almost half of the oil consumed will be from foreign sources. Table 2 substantiates the figures reported by Exxon concerning the increasing amounts of energy consumed by transportation.

Because of the problems discussed, the future of today's automobile is being questioned. Technological studies are being conducted and changes are being implemented in attempts to increase the efficiency of the internal combustion engine while decreasing its polluting side effects. To date, the improvements have been minimally successful. A feasible and desirable alternative to today's automobile may be the electric vehicle (EV).

Alternative solutions

The search for a cleaner engine has produced several potential solutions to the pollution problem. The addition of exhaust controls, modifying automotive fuels, and readjusting the internal combustion engine are methods of minimizing automotive pollution that are least disruptive to established practices. However, these changes will bring relief only as long as the reduced emission per vehicle is not overtaken by the increasing number

of vehicles. Furthermore, two of these alternatives possess inherent weaknesses for providing any long-range solution.

First, the introduction of lead-free gas is not a complete solution, nor is its effect immediate. Lead-free gas will not be uniformly used until the cars designed to use leaded gas are off the road, perhaps many years hence. In addition, recent studies indicate that although the catalytic converter may be an effective way of limiting the amounts of carbon monoxide (CO) and carbon dioxide (CO_2) gases, one of the side effects of the process is the formation of sulfates.

Second, today's catalytically-equipped cars are not as mechanically sound as the older, leaded gas "burners." Current models often hesitate, and even stall, when the accelerator is depressed. When improperly tuned, these engines burn an excessive amount of gas. Even when tuned, they burn more gas because anti-pollution equipment has caused the new engines, size for size, to have less torque than previously, thereby requiring more rpm and gasoline to make up for it.

Modifications of the internal combustion engine such as the Wankel rotary engine, the turbine, and the steam engine have been considered, but their present state of technology does not offer any long-term solution either. The Wankel engine, first introduced to the U.S. in the Mazda, is lighter, cheaper, more powerful than the piston engine, and meets air quality standards. However, it is not efficient enough to provide any remedy to the fuel crisis.

The diesel engine has not gained popularity because it does not provide the flexibility, performance, and silence desired in a passenger car; and it produces smoke and odor. Although it has low hydrocarbon and carbon monoxide emissions, its high nitrogen emissions rule it out as a pollution-free engine.

Other alternatives—the stratified charge, sterling, hydrogen and steam engines—while technologically feasible, still have safety problems. For example, General Electric ruled their experimental SE-101 Steam car and Stirlec engine-electric hybrid unsuitable for passenger cars, but production of gas turbine-powered bus and truck engines is already being planned as internal combustion alternatives. Also, a hybrid vehicle has been developed that is powered by a 4-cylinder Otto-engine and an electric motor that can be used simultaneously or alternately. The basic idea is to make the vehicle independent of stationary battery charging.

Some experts feel that the strict safety regulations to improve the performance of the present engine in terms of the environment and safety may push auto prices so high that people will continue to use and repair their old, unsafe, polluting cars. They feel that, given more time by the EPA, the standards could be met by the auto industry at a lower cost to the consumers, and even the complete solution of some other form of engine might see rapid development if the producers were not forced to commit all their funds to improving the current engine.

These alternatives obviously do not provide a complete or permanent answer to the emissions or the energy problem. It is the contention of this author that the electric vehicle may be

TABLE 1

Sources of energy supply and demand (millions of barrels of oil/day equivalent)

Energy source	1960	1970	1980 (est.)
Hydroelectric	0.3 (1.4)[a]	0.4 (1.2)	0.6 (1.2)
Geothermal	—	0.003 (.1)	0.2 (.4)
Nuclear	—	0.1 (.3)	3.6 (7.5)
Natural gas			
(imported)	0.1 (.5)	0.4 (1.2)	1.9 (3.9)
(domestic)	5.8 (27.4)	10.3 (31.7)	10.0 (20.7)
Coal	5.3 (25.0)	7.4 (22.8)	10.5 (21.7)
Oil			
(imported)	1.9 (9.0)	3.5 (10.8)	10.0 (20.7)
(domestic)	7.8 (36.8)	10.4 (32.0)	11.5 (23.8)
Total	21.2	32.5	48.3

[a] % of total

Source: "Understanding the National Energy Dilemma," Center for Strategic and International Studies, Georgetown University, Washington, D.C., 1973.

TABLE 2

Uses of energy by various forms (millions of barrels of oil/day equivalent)

Form of use	1960	1970	1980 (est.)
Electricity generation	3.4 (15.5)[a]	7.1 (20.8)	13.2 (25.5)
Residential and commercial	5.0 (22.8)	7.5 (22.0)	9.9 (19.1)
Industrial	7.1 (32.4)	9.9 (29.0)	13.0 (25.1)
Nonenergy conversions	1.1 (5.0)	1.9 (5.6)	3.7 (7.1)
Transportation	5.3 (24.2)	7.7 (22.6)	12.0 (23.2)
Totals[b]	21.9	34.1	51.8

[a] % of total

[b] These sums do not equal those in Table 1 because the electricity generated is in turn used by the other forms listed.

Source: See Table 1

the answer for the future. Although it has only limited application as a source of transportation today, it is not far technologically from providing a long-range solution.

Product feasibility

Technologically, the electric car has not significantly improved in performance over the last 60–70 years. Basically, today's EV is a small, short-range, low-performance vehicle that has little chance of replacing the internal combustion automobile as a source of transportation. Currently, most EV's are capable of 30–50 mph, and have a range of 50–80 mi before recharging or battery replacement is needed.

There are several advantages of the EV. One is fuel economy. The average American automobile used over 700 gal/y of gasoline, and average fuel economy is less than 13.7 mpg. As a whole, internal combustion autos consume approximately 14% of all energy and 31% of all petroleum used in the U.S. Although it is possible to improve gas mileage by any number of methods, the internal combustion engine is at the peak of its inefficiency when it comes to the short-trip, stop-and-go routine of city driving.

When a gasoline-powered auto that gets 13 mpg is started (cold) and driven for four miles, it gets only about 8 mpg during the warming-up period. On the other hand, if it is left idling until warm, it uses even more gas since it is getting 0 mpg. In contrast, on short trips, the electric uses the same amount of energy, regardless of the temperature of the motor.

In addition, with a gas-powered auto, jackrabbit starts cost about 2 mpg. Electric cars, through the use of two to four resistors, accelerate more uniformly than do gas-powered cars, which use a transmission. Thus, the drain on the power supply on an electric car is almost constant, rather than fluctuating from heavy to light. A recent study stated that the average American car consumes approximately one cup of gas for every six minutes of idling. When not in motion, an EV uses no energy at all.

Another aspect of the fuel controversy is the recent concern over energy supply. Society must come to grips with the fact that petroleum resources will continue to be scarce and thus more expensive. Still it is rather idealistic to believe that many people will purchase an EV to promote the good of society as a whole. The real potential for EV sales is centered around the rising prices of gasoline. A recent study found that as gasoline prices increase, the buying intentions of an electric car also increase, and when gasoline prices rise to $1.00/gal, the total cost per mile of an electric car would be at most 9.1¢ as compared to 37¢ for a gas-driven luxury car, 19.3¢ for a gas-driven intermediate, and 16.5¢ for the gas-driven compact.

An area of transportation where the EV, at its current state of technology, has its greatest potential for immediate application is for short trips. There are millions of cars and commercial vehicles that travel less than 30 mi/day, and millions more that travel less than 30 mi to work and sit for 6–8 h when they could be recharging before making the return trip at night.

A study by the Department of Transportation clearly shows that a high percentage of automobile trips made by U.S. drivers are short in length (Table 3). The average length for all trips made in an automobile is 8.9 mi. Over 90% of all job-related trips, which comprise 67.2% of all trips made, are of less than 20 mi. In addition, the average automobile travels about 26 mi/day in large cities and moves on the average of 8.5–13 mi/h from 9:00 a.m. to 6:00 p.m.

While EV's do make poor highway cars, the above statistics seem to indicate that there is a very large number of transportation areas where the EV's are applicable at their current state of technology. An excellent example of one application of the EV is the typical postal route.

Low-operating costs, low pollution

The EV is much cheaper to operate than the gasoline-powered automobile. One reason is because the cost of electricity is normally less than half the cost of gasoline on a per mile basis. Studies indicate that the average cost of operating an electric car would be from 1–3¢/mi, as opposed to today's rather conservative figure of 10–12¢/mi for operating a gasoline-powered car, of which 2.5¢/mi is for gas.

An even greater advantage of the EV is that it requires only minimal maintenance. Since there are so few moving parts, the number of possibilities for breakdown is small. The EV would not incur the normal maintenance costs of tune-ups, oil changes, and muffler repair, nor the more serious problems of valve work and transmission repairs, all of which are linked to wear and tear on the internal combustion engine. In addition, the EV would be advantageous in colder climates because there is no problem starting it on cold days. Electric batteries and motors never freeze and rarely overheat.

Aside from good battery care, there is little else to do. Lubrication is as simple as greasing the garden tractor. In addition to low regular maintenance, commuters should find it advantageous to have their "gas pump" on the wall at home. A unique advantage of the electric vehicle is greater durability (particularly in stop-and-go situations) than an equivalent gasoline-powered vehicle.

TABLE 3

Automobile trips by trip length and purpose

	Trip length (miles)				% of automobile trips/ travel	Average trip length miles
Purpose	**5 or Less**	**6–10**	**11–20**	**20 or Over**		
Overall	62.4	16.8	12.5	8.3	100.0%[a]	8.9
Earning a living	51.8	20.1	17.3	10.8	36.2	10.2
Family business	74.2	14.3	7.8	3.7	31.0	5.6
Civic, educational & religious	78.8	12.0	6.2	3.0	9.3	4.7
Social & recreational	56.6	17.1	13.6	12.7	22.4	13.1
	Vehicle miles of travel					
Overall	15.7	15.4	21.5	47.4	100.0%[b]	—
Earning a living	12.6	16.1	25.9	45.4	41.6	—
Family business	27.6	20.4	21.3	30.7	19.3	—
Civic, educational & religious	35.0	20.3	19.0	25.7	4.9	—
Social & recreational	10.1	10.7	16.2	63.0	33.0	—

Source: U.S. Dept. of Transportation Report No. 10, May 1974.

[a] 1.1% unknown

[b] 1.2% unknown

Based on figures from golf-cart maintenance and life expectancies, the single, most common failure stems from abuse of the batteries, that is, letting them become completely discharged and letting them stand without recharging. This reduces battery life drastically. However, because there is so little to go wrong, the EV can be expected to last much longer.

The electric vehicle is nearly pollution free. As Americans become increasingly aware of the ill-effects of pollution on themselves and their environment, this benefit will become more desirable. Today, the areas where pollution has obviously made its greatest impact have been in the large cities. The internal combustion engine is simply not well suited for city driving, where emissions are higher than in open-road driving. These are the very areas of transportation where today's EV is best suited. Widespread adoption of the EV in the form of commuter cars, buses, delivery vans, and other short-range urban vehicles would greatly reduce the amounts of pollution in cities.

Disadvantages

The question has been raised as to whether the innovation of the EV will really reduce pollution in large cities. There have been many claims that the EV will not reduce pollution, even if it is adopted on a large scale. That is, the adoption of the EV will merely transfer the pollution problem from automobiles to the smoke stacks of the electric power plants. On the other hand, a spokesman from Commonwealth Edison Co. has claimed that "even without nuclear reactors, we could recharge 500 000 EV's at the low-load-night period without any change in smokestack emissions."

Although it is difficult to determine at this stage whether adoption of the EV would cause a significant increase in the output of emissions at power plants, there is another argument that should be considered. Widespread adoption of the electric car would simplify the control problem by reducing the need to regulate millions of privately-owned cars and trucks; only a small number of power plants would have to be regulated. In addition, increased adoption of nuclear generating plants, should this occur, will further simplify the problem, because of their minimal emissions.

The current state of technology has seriously limited the EV's in terms of speed, range, and size. The electric cars of today are absolutely not capable of replacing the average internal combustion automobile. But, nearly all of the limitations associated with the EV's performance and size are related to the energy provided by the lead-acid battery.

The major drawback of the lead-acid battery is that it wears out quickly because of repeated recharges. In addition, it is heavy, bulky, and does not produce much electrical density per pound. In order to increase both range and speed, additional batteries must be added, but the additional weight will in turn limit the performance levels that could be obtained.

Current developments

Therefore, the key to the long-run success of the EV depends upon the development of a new form of battery. The new battery must be compact, light weight, inexpensive, and have a high-power density. Here are some current developments in battery technology:

- The silver-zinc battery uses both silver and zinc electrodes to generate energy. This battery has an energy density of 40–60 Wh/lb, which is significantly greater than the lead-acid battery. However, the silver-zinc battery is an impractical substitute because of the scarcity and high cost of silver; it has a limited number or rechargings; and it is impossible to recover the silver once the battery is worn out.
- The sodium-sulfur battery has many advantages that are not found in other batteries: The elements of sodium and sulfur are plentiful and inexpensive, the battery is capable of being 60% recharged in two hours, and 100% recharged overnight, the battery has an energy density of 80 Wh/lb, and the sodium-sulfur battery will be mass-producible in several years. The only disadvantage of this battery is that it must operate at the high temperature of 570 °F. The problem lies not in providing the required insulation but in encasing the battery in a substance that will not crack in the event of accident.
- The lithium-sulfide battery, developed by the Argonne National Laboratory, operates at 700 °F and can be obtained for approximately $12 per kWh.
- The CGE-Marcoussis zinc-air battery, which uses a zinc-base slurry as a circulating electrode, offers a 40% weight reduction and can be fully recharged in one minute.
- The Energy Development Associates' 272-lb zinc chloride battery system offers 50 kWh of power, moderate cost, and twice the cycle life of lead-acid batteries.

It is important to remember that the long-run success of the EV as a viable transportation alternative to the internal combustion vehicle depends upon the development and commercial availability of an efficient battery. Until that time, the EV should concentrate on developing the desirable qualities it already possesses as an efficient method of short-range transportation.

The EV market

A major consideration in determining whether or not a new product will be successful is the attitude of the customers involved. Marketers must first determine who their prospective consumers are, and then identify their basic needs, desires, and evaluative criteria in new car selection. The proposed market must be large enough to warrant cost of production. In the case of electric vehicles, the costs are great if not mass-produced; therefore, a sizable market is necessary.

A major market segment for electric vehicles definitely exists in both public and commercial transportation. Delivery vans, buses, refuse trucks, and other vehicles that travel less than 100 mi/day at less than 30 mph are ideal candidates for electric-powered vehicles. Harbilt Electric Vehicles contends that every fleet operator has at least 15% of his vehicles tied up in runs that could be handled electrically.

Additional markets include resort vehicles, fork lifts, golf carts, and mine vehicles in which EV's have already proven themselves. Test delivery vans in operation in California have cost only 2.5¢/mi to operate, as compared to 5.4¢ for gas-powered vehicles. These vans can operate for two days without recharge at a top speed of 40 mph. The success of electric vehicles in these markets has influenced the serious manufacturer to set his sights on the attainable markets—the delivery routes. However, a large proportion of household travel is done in short trips in urban traffic. It is only logical that this market could be easily tapped as well.

It appears obvious that such a market does exist, but its size is questionable. The potential customers of electric automobiles are assumed to be families with two or more cars, incomes over $10 000, ecologically minded, and urban dwellers. On the basis of this assumption, conservative sales forecasts for 1980 range between 140 000–250 000 electric cars. After 1980, with the expected battery improvements, the pace of sales will undoubtedly increase. Estimates that from 20–40% of all cars will be electric by the year 2000 have also been predicted.

The EV is expected to be used as a second car, at least in the initial years; and with the second car market estimated at 25% of the total market, this represents a substantial number of buyers. But Americans are reluctant to accept drastic changes in car styles, and the design changes necessary to produce the most efficient electric car pose some problems in this area. The most significant change is size. In order to compensate for the heavy batteries, the weight of the car must be reduced, thereby resulting in a smaller car.

There is an increasingly large market for small cars; 35.9% of all cars sold in the U.S. in 1972 were compacts and subcompacts, up from 21.6% in 1969. Therefore, the small car has captured a substantial share of the market. However, the buyers also appear to want them equipped as big cars, as a majority of compacts sold are ordered with options such air conditioning, and power brakes and steering. Therefore, for an electric vehicle to be successful in this market, it would appear that it should be available with as many extras as possible. This poses more problems, as the batteries available barely have the power to operate the engine itself efficiently.

Part of the reason for the trend toward luxury is that automobiles are purchased as a status symbol, and the automobile is seen as a visible product by which people attribute certain characteristics to its owner. Until an efficient battery can be developed, this may be the single most difficult obstacle for EV marketers to overcome. If the electric vehicle can be made to be perceived as a status symbol, its chances of success would be substantially increased.

Another problem in design and technology is meeting consumer demands for fast, high-performance cars. With present technology, this is a problem with electric vehicles. But the capabilities for the EV appear to be consistent with "average" private car use. Therefore, especially in the second car capacity, this should not pose a great problem. Also, with the expected technological improvements in battery capacity, EV's will eventually be able to perform up to consumer standards.

Because the development of the electric auto has come about as a result of concern for the preservation of the environment, marketers must look at the effects the ecology movement has had on consumer behavior. Research studies have concluded that ecological concern permeates society; there are virtually no demographic segmentations. Buyers appear to respond affirmatively to ecologically relevant buying information, and buyers' perception of ecological products is dependent on their level of ecological concern. On this basis, it may be possible, through further research, to determine who are the ecologically concerned consumers, as they would be the most likely purchasers of an EV, and to expand the market by converting more to the ecologically concerned segment by convincing them of the seriousness of the environmental issue.

In conclusion, some implications

The areas of transportation where the electric vehicle may be used as an alternative to the internal combustion vehicle must be viewed in both short-run and long-run time frames. In the short run, the use of the EV is constrained by the lack of any significant technological development of the battery. However, there is no reason to wait for new developments before extensively marketing the EV. Currently, the EV is capable of providing an efficient means of transportation for a number of different areas—short-trip delivery vans, commuter cars, and second family cars. There is already a large market for vehicles in these areas.

In the long run, the EV is seriously limited in any widespread application under current technological constraints. However, sources indicate that technological breakthroughs have been made but are not yet commercially available. An example was the development of an EV called the Voltaire, which was capable of a recommended top speed of 90 mph, the ability to reach 107 mph at overload for brief bursts, and a range of 300–350 mi. Although the Voltaire was in the intermediate stages of development in 1971, over six years have passed and there is still no evidence of commercial availability. The Voltaire is only one of many examples of the inability of EV developers to make their products commercially available.

The final major hurdle that must be cleared by the EV is consumer acceptability. For many years the gas-powered automobile has been viewed as a status symbol and an extension of personality by a great number of U.S. drivers. The electric car promoters must emphasize the dollar efficiency of operating the EV and instill increased desire to get on the energy and environmental conservation bandwagon if it is to be a success.

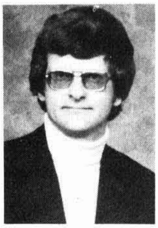
Additional reading

"A Cleaner, Safer Car: What Price Did You Have in Mind?", *First National City Bank Monthly Economic Letter,* April 1973, p 9.

Gottesman, C. A., "Electrics—How Far, How Fast?", *Automot. Ind.,* **150,** March 15, 1974, p 18.

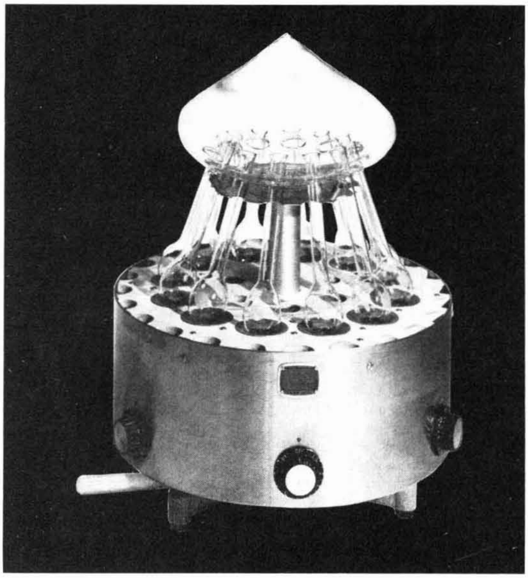
Norbye, J. P., "Clever Engineering Brings the Electric Car Closer to Your Driveway", *Pop. Sci.,* June 1974, p 40.

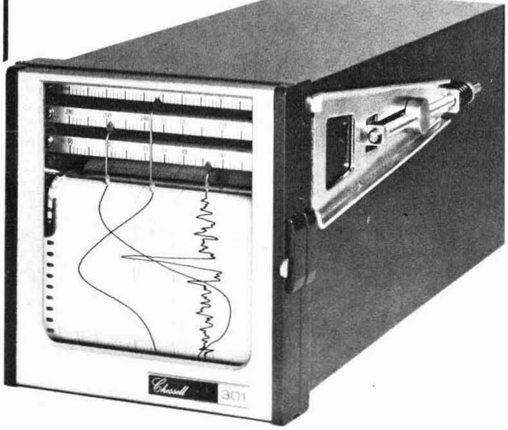
Overbeke, J. E., "Electric Vehicle Industry Sounds a Charge", *Ind. Week,* **181,** June 3, 1974, p 42.



Edwin C. Hackleman is assistant professor of marketing at the University of Connecticut. Dr. Hackleman is co-author with Louis E. Boone of **Marketing Stategy: A Marketing Decision Game** (Charles E. Merrill, 1975); he contributed to the book **Quantitative Methods for Management** (Houghton-Mifflin, 1976).

Coordinated by LRE




Chessell
301

Minimizing emissions from vinyl chloride plants

Available and future pollution control systems, though expensive, are required by law to protect the worker and his environment

Carl G. Bertram
Badger America, Inc.
Tampa, Fla. 33622

Vinyl chloride (chloroethene) is a synthetic organic chemical made from ethylene or acetylene and chlorine by using different processing schemes. The most common route is from ethylene; ethylene dichloride (EDC), an intermediate, is then thermally cracked to the monomer (VCM) and by-product hydrogen chloride (HCl). Hydrogen chloride is further reacted with ethylene (oxyhydrochlorination) to form more EDC.

In 1974, in the U.S., OSHA promulgated a stringent VCM standard. This standard requires that worker exposures be no more than 1 ppm on a time-weighted average and no more than 5 ppm for any 15-min period.

Table 1 shows the maximum worker exposure concentration permitted by various countries throughout the world. As can be seen from this table, the concern over angiosarcoma, a rare form of liver cancer, that has been linked to exposure to VCM, has become worldwide.

EDC, long considered a toxic substance, has also been classified as a suspected carcinogen that also causes kidney damage in animal tests. The U.S. government is presently considering a proposed EDC regulation that would set average exposure at 5 ppm and peak exposure at 15 ppm. It will not be long before other chlorinated hydrocarbons are similarly restricted.

Existing plants have had to make many modifications to reduce exposure to VCM, and are now taking steps to reduce exposure to EDC as well. New plants under construction face strict EDC/VCM exposure levels, restrictions and generally must meet stringent overall environmental pollution requirements. The greatest causes of air pollution from a VCM plant are continuous or intermittent process vent streams, which number about 10 per plant.

Abatement methods

Various methods have been proposed and actually used to treat process vent streams containing chlorinated hydrocarbons. From environmental and economic standpoints, one of the best solutions is the use of an incinerator-waste heat boiler followed by scrubbing of the flue gas, as shown in Figure 1. When the

TABLE 1

Worldwide maximum workplace VC concentrations [a]

Country	Year	VCM concentration
Belgium	1975	max. 200 ppm TWA [b]
Canada	1975	10 ppm TWA (8 h) to 25 ppm TWA (15 min)
Finland	1975	5 ppm TWA (8 h) to 10 ppm TWA (10 min)
France	1975	no limits
Germany	1975	technical standard value: max. 5 ppm [c]
Great Britain	1975	25 ppm TWA (8 h) to 50 ppm (15 min)
Italy	1975	50 ppm TWA (8 h) expected: 25 ppm (8 h) to 15 ppm TWA (15 min)
Japan		expected: 25 mg/m^3 (10 ppm)
The Netherlands	1975	10 ppm TWA (8 h)
Norway	1975	no value expected: 1 ppm TWA (8 h) to 5 ppm TWA (15 min)
Sweden	1975	5 ppm TWA (8 h) to 20 ppm TWA (15 min)
	1976	1 ppm TWA (8 h) to 5 ppm TWA (15 min)
Switzerland	1975	100 ppm max. expected: 10 ppm TWA (8 h)
U.S.A.	1976	1 ppm TWA (8 h) to 5 ppm TWA (15 min)
U.S.S.R.		30 mg/m^3 (12 ppm)

[a] Source: *Chem. Ing.-Tech.*, **47**, 1975.
[b] TWA = Time Weight Average
[c] Over the period of 1 hour the average concentration may not exceed three times the technical standard value.

steam generated can be taken as a credit, this solution minimizes the overall cost of pollution control.

Burning chlorinated hydrocarbons unfortunately results in HCl, along with CO_2 and water. The release of HCl to atmosphere, if permitted at all, is *not* desirable. Scrubbing the incinerator off-gas to form a dilute acid liquor or a salt solution is necessary; however, disposal of the scrubbing liquor can be a problem.

VCM plants located near the sea can dispose of a salt solution without major problems, but the cost of neutralizing significant amounts of HCl can become prohibitive. For this reason vent streams sent to the incinerator should contain a minimum of chlorinated hydrocarbons. Economic evaluation will determine the degree of treatment (clean up) that vent streams require prior to incineration.

Incorporating an incinerator-waste heat boiler scrubber (vent gas incinerator) into a VCM plant is not a simple matter because of the safety and corrosion aspects that need to be considered. Substantial instrumentation, including interlocks and automatic shutdowns, is required, plus a number of separate header systems to collect the process vent streams.

The process vent streams are not the only waste gas streams handled by the vent gas incinerator; a number of intermittent and miscellaneous vent streams can also be directed to the incinerator for disposal. The vent gas incinerator becomes the heart of the pollution-abatement system of the VCM plant.

Loading operations

The second largest source of emissions in a VCM plant is the loading operations; for example, loading of EDC or VCM into tank cars, tank trucks, barges or ships. The major problem areas associated with loading are shipping container venting and the cleaning of loading arms and lines after loading; several methods have been developed to minimize these emissions.

Loading EDC. Preferably, the atmosphere in the shipping container—in this example, a ship—should be inert before loading the EDC (Figure 2). When this has been established, the dual-pipe loading arm, containing a loading line and an equilibrium (balancing) line, can be connected. During loading the atmosphere in the ship is displaced to the EDC storage tank without net venting being required. After loading is completed the loading arm must be decontaminated so that it can be disconnected without venting EDC. The liquid loading arm is first drained into a jetty slop tank for eventual recycle back into the process. The loading arm is purged into the ship with nitrogen. The block valves on the ship's manifold are then closed and the equilibrium line purged with nitrogen back to the storage tank. The loading arm can then be safely disconnected and parked in a safe condition. Excess inert material in the EDC storage resulting from purging operations is disposed of in the vent gas incinerator.

Collecting systems

Category I
Vent streams containing oxygen; these must be carefully examined with regard to flammability and explosion hazards

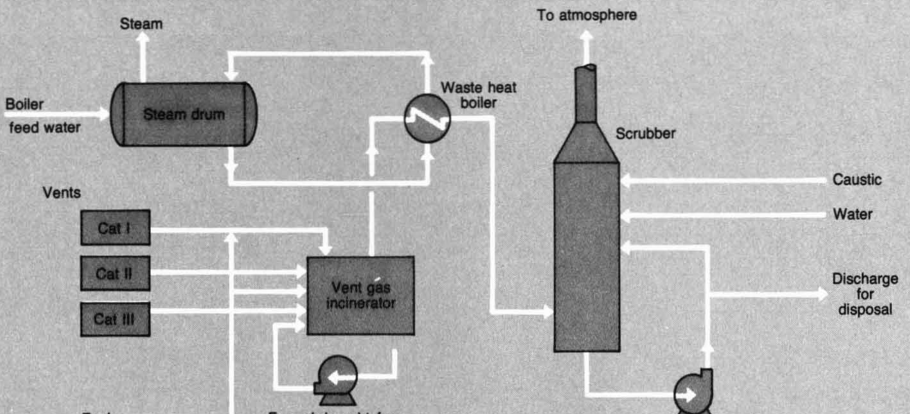
Category II
Wet vent streams (oxygen-free); these may contain water and must be kept free of HCl to avoid corrosion

Category III
Dry vent streams (oxygen-free); these contain traces of HCl and must be kept free of water to avoid corrosion

Loading VCM. Since VCM is a condensed gas, it is slightly more difficult to load than EDC (Figure 3). The ship to be loaded *must* contain VCM vapors or inert gases, with VCM vapors preferred. Theoretically, if no inert material and only VCM vapors are present, VCM can be loaded without venting. As in the case of EDC, the atmosphere in the transport container is displaced in the storage tank, with no venting of VCM realized. After loading, the loading arm must be purged with nitrogen prior to disconnecting.

FIGURE 1

Vent gas incinerator system, the scheme and costs



Typical operating costs for vent gas incineration/scrubbing for a balanced VCM plant

Utilities/chemicals	Consumption per metric ton of VCM	Unit price	Operating cost per metric ton VCM
Electric power	3 KW	$0.02	$0.06
Fuel	1.10 MM Btu	$1.2	$1.31
Steam (150–250 psig)	1.04 M lb.	$3.0	($3.12) credit
Boiler feed water	0.13 M gal	$2.50	$0.33
Process water	0.1 M gal	$0.50	$0.05
Caustic soda (100%)	10 lb	$0.13	$1.30
			($0.07) credit

Inert material will accumulate in the VCM storage sphere and cause excessive pressure in the sphere as it is refilled. A refrigerated vent condenser recovers the greater amount of VCM in the vent stream from the storage sphere. The chilled vent stream is then directed to the vent gas incinerator for final disposal thereby minimizing the emission of VCM.

Storage vents, pump seals, sample collections

Fairly large volumes of EDC, stored in cone-roof or dome-roof tanks, are required for smooth operation of a VCM plant. The atmospheric venting of these tanks can result in a substantial source of chlorinated hydrocarbon emissions. At storage temperatures of 30–40 °C, the vents from EDC tanks can contain 13–20% EDC by volume. Incineration of these out streams (Figure 2) is one way to eliminate this source of air pollution. As cone-roof or dome-roof tanks are limited to an internal pressure rating of 150–200 mm of water, an ejector system is normally used to feed the vent gases into the incinerator. For safety, the storage tanks are blanketed with nitrogen, with in-and-out breathing regulated by a split-range pressure controller.

Pump seals (single or double mechanical seals) are another source of emissions if EDC or VCM is the seal liquid. Where possible, the use of a compatible seal oil that contains *no* chlorinated hydrocarbons has solved this problem. In services where seal oil cannot be used, glandless pumps (canned or magnetic clutch type) are now being used with fairly good success.

Because of the crude sampling techniques of the past, workers collecting samples in a plant were exposed to fairly high levels of EDC and VCM. To avoid exposure, all samples containing EDC and/or VCM should be collected in bombs in a closed-loop system.

The basic concept is to trap a representative sample in the bomb and then purge the piping with nitrogen, which must be disconnected in order to remove the sample bomb safely. In the case of a VCM sample, the piping is purged to the flare, while in the case of an EDC sample (less volatile) the piping is drained and purged to a convenient low-pressure source within the process or to the closed-process sewer.

Equipment decommissioning

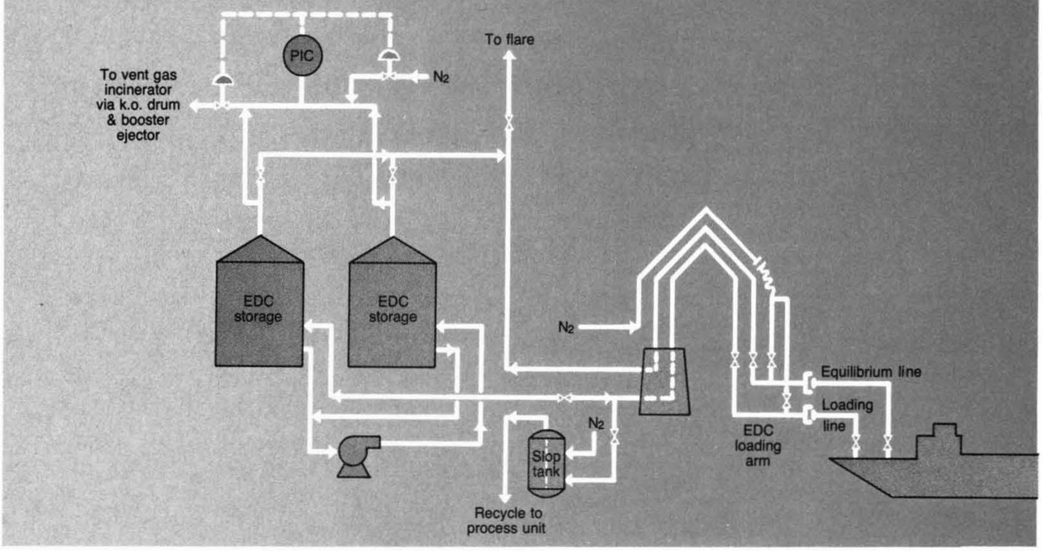
All equipment will sooner or later have to be prepared for inspection or maintenance. To decommission equipment without excessive EDC or VCM emissions, a number of support systems, representing a considerable investment, are required. To cover all equipment containing EDC and/or VCM, the following support systems are required:

- Process sewer—this is a completely closed system, located below grade, which drains into a sump tank; the vapors from this tank are directed via a knock-out drum and booster ejector to the vent gas incinerator.
- Contaminated water sewer—this system, located below grade, drains to an open sump; this system collects aqueous drains contaminated with EDC; water is separated from the organic layer in the sump and treated in the wastewater unit; the organic phase is sent to storage or recycled back to the process.
- Contaminated water header—this is a closed system to collect highly contaminated wastewater and direct water to a holding tank that is vented to the incinerator via a booster ejector; the wastewater is then treated in the wastewater unit.
- Steam-out collection system—this system collects all steam-out vapors containing chlorinated hydrocarbons; steam and condensable impurities are condensed and the noncondensable vapors are directed by an ejector to the vent gas incinerator.
- High-pressure nitrogen—this system is required for purging operations.
- Slop header system—this system collects substantial quantities of EDC (which may or may not contain small amounts of VCM) when equipment is decommissioned; it is a closed-piping system that empties into a slop tank with the vent gases directed to the incinerator or flare and the liquid sent to storage or recycled to the processes.
- HCl neutralization system—all dry HCl reliefs and vents are collected in this system and either scrubbed with water or neutralized with caustic soda to minimize release of gaseous HCl.

Utilizing these systems, a number of procedures can be followed to decommission equipment. For example, the decommissioning of pumps will occur at frequent intervals for maintenance, normally done during plant operation (Figure 4). For pumps in EDC service with suction and discharge valve closed, drain EDC from the pump and associated piping to the process sewer. Hook up nitrogen to the suction line and blow out the

FIGURE 2

EDC loading and storage venting



remaining EDC to the process sewer. With the pump drain closed, blow through the pumps discharge line to the process sewer. Repeat operation via the pump drain valve. The pressure gauge drain connection can also serve as a purge point.

Disconnect the nitrogen hose and hook up water to the suction line of the pump. Flush to the contaminated water sewer, first through the discharge line, then via the pump drain. Shut off the water flow, open the connection at the pressure gauge and drain the pump. The pump can then be safely dismantled.

For pumps in VCM service, with suction and discharge valve closed, drain VCM from the pump and piping to the blowdown pot. Liquid will collect in the drum with the vapor venting into the flare.

Purge the lines with nitrogen connected to the suction line of the pump, blowing VCM and nitrogen into the blowdown pot. To permit a controlled release of VCM vapor to the flare, electric heating panels that permit close temperature control are used on the blowdown pot. The use of steam as the heating medium is not recommended.

After purging with nitrogen, crack open small valve (on the pressure-gauge drain on pump discharge) and test VCM level with a photoionization-type analyzer. If the level is unacceptable, continue the nitrogen purge until a safe level of VCM is obtained. The operator doing this test should wear a fresh-air gas mask. When safe level is reached, stop nitrogen flow. The pump can then be vented to the atmosphere and dismantled.

Reboilers should be decommissioned by first isolating the reboiler from the column. For all reboilers containing essentially VCM, depressure tube side to the flare; for all reboilers containing essentially EDC, drain to the slop header. Using nitrogen hooked up to the reboiler, blow out EDC or VCM to the appropriate header.

Then crack open the steam to the shell side of the reboiler. Hook up steam and steam out the process side from bottom to top into the steam-out header. Stop steam-out and hook up service water to the reboiler, flushing downward to the contaminated water sewer.

The reboiler is now ready for removing the heads. Despite the precautions taken, there can still be a momentary release of residual fumes as the reboiler head is opened. Workers performing this operation should, therefore, wear fresh-air gas masks.

To decommission filters or strainers, "block-in" the filter and depressurize to the flare. Blow contents of filter to the process sewer or flare (depending on volatility of filter contents) by using nitrogen. Continue nitrogen purge until safe levels of chlorinated hydrocarbons have been achieved. When testing for safe levels the wearing of a fresh-air gas mask is recommended. The filter can then be dismantled for clean-out.

Complete tower system and other sources

Various detailed procedures can be followed to clear a tower system for maintenance work; however, the basic procedural concept will undoubtedly be in accord with that outlined below for a mixed EDC/VCM-containing system.

First, reduce inventory of VCM in the system to a minimum. Then vent the residual VCM that accumulated in the overhead system to the flare. Next add EDC to the tower system and "boil up", withdrawing condensed EDC from the overhead system while measuring VCM content in the EDC.

The EDC contents should then be delivered to "off-spec" storage, and residual hold-up in system should be discharged to the process sewer (for small volumes) or to the slop header system (for larger quantities).

Add water to the tower system and "boil up" this system at total reflux, while venting the reflux drum to the steam-out header. Drain contents of the tower to the contaminated water header and repeat water boil-up operation until EDC is reduced to a safe level.

The tower system can then be vented to the atmosphere and water added to lower the temperature of the column. Residual water is then drained to the contaminated water sewer and, after positive isolation and adequate ventilation, the tower system is ready for inspection.

There are a number of other sources which, if not properly controlled, can add to EDC and VCM emissions. The following are just a few of these sources, and solutions that may be adopted.

Blowdown of level gauges. Depending on volatility, materials are directed to the flare or to closed-process sewer.

Control valves. Control valves that require occasional maintenance are provided with vent and drain connections to purge the valve so that the valve can be removed without the risk of exposure.

Relief valves. Relief valves in critical service are provided with installed spares, as well as rupture disks on the inlet side of the

FIGURE 3

VCM loading and storage venting

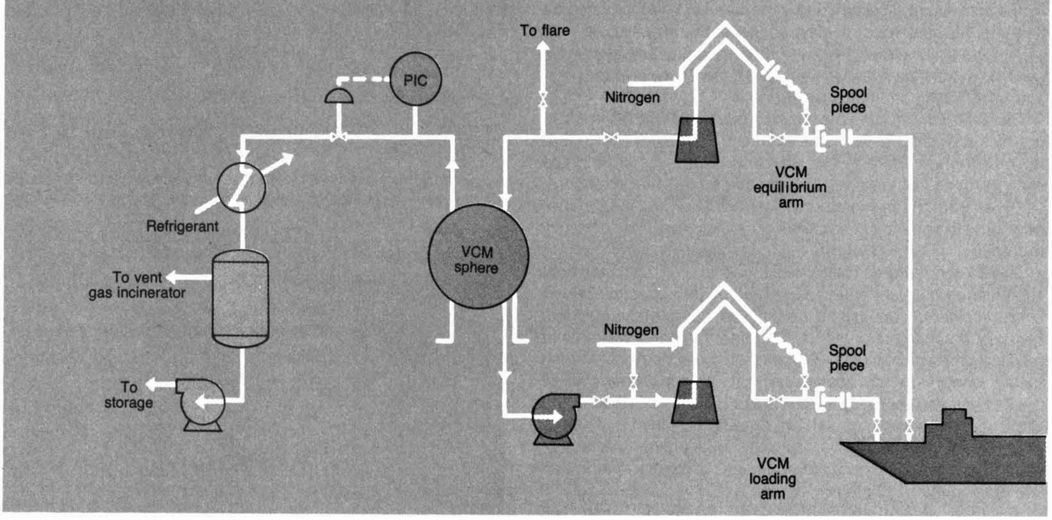
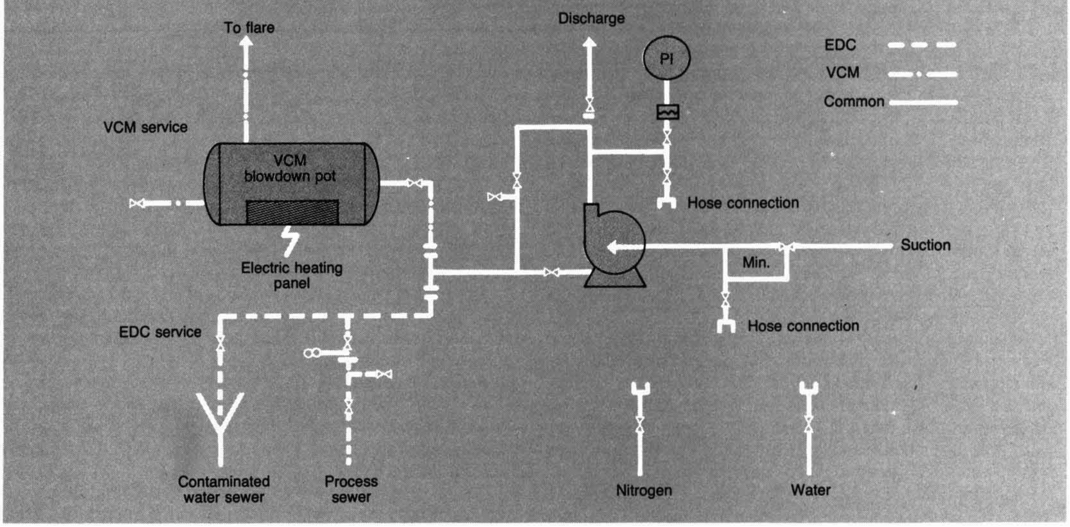


FIGURE 4
Decommissioning pumps



relief valves. This reduces corrosion and leaks through the valves.

Monitoring and back-up systems

To ensure a safe environment for workers and demonstrate compliance with government regulations, frequent and thorough monitoring is required. A safe working environment throughout the process facility can be achieved, with an adequate monitoring system, in essentially two ways:

- The system provides information on exposure of plant personnel and records of individual workers can be kept.
- The system helps ensure that emissions are kept to a minimum by providing an early warning of leaks and pinpointing the source of emission.

Three types of monitors are in common use today. A *continuous-monitoring system* is automatic and consists of a gas chromatograph to analyze air samples drawn in rotation from a number of locations in the plant. A computer is often used to calculate exposure levels, compile and print out results to provide a permanent record. Alarms and warning lights can also be tied into this system to alert personnel in the affect area.

A *portable analyzer* based on a flame ionization system is used to pinpoint the exact source of emission, usually after a high alarm from the continuous monitor.

Personnel monitoring measures the amount of EDC or VCM to which an individual worker is exposed. The key to this system is an instrument worn by the worker that absorbs chlorinated hydrocarbons from the air. On a regular basis, after exposure, samples from the personnel monitor are analyzed in the laboratory and the amount of each worker's exposure level carefully recorded.

The design features mentioned in this article plus analytical surveillance help to minimize EDC and VCM emissions. However, accidental emissions cannot be completely avoided. Failures, mechanical or otherwise, of equipment or systems at a critical time are inevitable. To safeguard personnel should such failure occur—or for operations that include some risk of over-exposure—back-up systems are usually provided in the plant, such as a fresh air system or self-contained air masks. Since most gas masks do not provide adequate protection against a high-VCM concentration, gas masks have limited usefulness in a VCM plant.

The fresh air system consists of an "air header" that runs throughout the plant with numerous, easily accessible stations for connecting air-fed respirators. Lightweight, reasonably comfortable air respirators can be used with this system, thus eliminating the need for bulky air cylinders.

Summation

Because of the health hazards associated with exposure to VCM and EDC, and the resulting government regulations, today's VCM plants must have extensive pollution-abatement systems. Minimizing emissions is expensive. To ensure that the plant operates safely, the workers are also required to follow arduous procedures. One thing is clear: there are no easy solutions to emission control.

Additional reading

Reich, P., "Air or Oxygen for VCM?", *Hydrocarbon Process.*, **55,** No. 3 (March 1976).

Bell, Z. G., Lafleur, J. C., Lynch, R. P., Work, G. A., "Control Methods for Vinyl Chloride", *Chem. Eng. Prog.*, **71,** No. 9 (Sept. 1975).

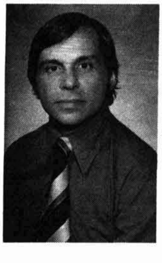
Wheeler, R. N., Sutherland, M. E., "Control of In-Transit VCM", *Chem. Eng. Prog.*, **71,** No. 9 (Sept. 1975).

Vervalin, C. H., "Curtail Vinyl Chloride Exposure", *Hydrocarbon Process.*, **55,** No. 2 (Feb. 1976).

Federal Register, **42,** 28154, June 2, 1977.

Huber, H., "Das Vinylchlorid-Problems," *Chem. Ing.-Tech.*, **47,** No. 19 (1975).

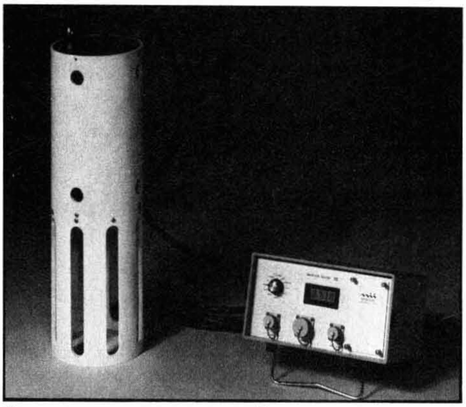
Acknowledgment should be given to Robert Vanheyst, a former Badger employee, who contributed significantly to the writing of this article.



Carl G. Bertram *is a senior process engineer with Badger America. He has extensive experience in chemical plant design.*

Coordinated by LRE

Martek measures up



instrumentation with water quality

The rugged low-cost Martek Mark VI Water Quality Monitoring System is the ideal portable system for recording of multiparameter data—temperature, conductivity, salinity or temperature-corrected conductivity, depth, dissolved oxygen, pH, and specific ions—in fresh or salt water to a depth of 300 meters. Accurate to within ± 1.0%, the system features digital readout, AC/DC operation, and integral recharging unit.

Add a Model EDP Environmental Data Printer and you can record up to 15 analog inputs as well as time of day and channel identification on both a digital magnetic tape cassette and digital paper printer. You can also record, accumulate, and subsequently process data through computers or other external data processors. Complementing the Mark VI are the Model DLS Data Logger and the Model PEW Portable Winch. The versatile Mark VI System can be utilized in profiling, onshore and shipboard installations, pumped sample systems, and industrial monitoring applications.

Martek-developed systems are designed to provide you, the user, with simple-to-use, reliable instrumentation. For the full story on our full line of water quality instrumentation, write to:

MARTEK INSTRUMENTS, INC.
17302 Daimler St., P.O. Box 16487, Irvine, CA 92713 (714) 540-4435
Manufacturers of Environmental Instrumentation

CIRCLE 29 ON READER SERVICE CARD

Effects of Petroleum on Arctic and Subarctic Marine Environments and Organisms

Edited by DONALD C. MALINS

VOLUME 1/**NATURE AND FATE OF PETROLEUM**

CONTENTS: *R. C. Clark, Jr. and D. W. Brown*, Petroleum: Properties and Analyses in Biotic and Abiotic Systems. *R. C. Clark, Jr. and W. D. MacLeod, Jr.* Inputs, Transport Mechanisms, and Observed Concentrations of Petroleum in the Marine Environment. *N. L. Karrick*, Alterations in Petroleum Resulting from Physico-Chemical and Microbiological Factors.

1977, 324 pp., $14.50/£10.30 ISBN: 0-12-466901-8

VOLUME 2/**BIOLOGICAL EFFECTS**

CONTENTS: *D. R. Craddock*, Acute Toxic Effects of Petroleum on Arctic and Subarctic Marine Organisms. *H. O. Hodgins et al.*, Marine Fish and Invertebrate Diseases, Host Disease Resistance, and Pathological Effects of Petroleum. *U. Varanasi and D. C. Malins*, Metabolism of Petroleum Hydrocarbons: Accumulation and Biotransformation in Marine Organisms. *F. G. Johnson*, Sublethal Biological Effects of Petroleum Hydrocarbon Exposures: Bacteria, Algae, and Invertebrates. *B. J. Patten*, Sublethal Biological Effects of Petroleum Hydrocarbon Exposures: Fish. *H. R. Sanborn*, Effects of Petroleum on Ecosystems. *W. N. Holmes and J. Cronshaw*, Biological Effects of Petroleum On Marine Birds. *J. R. Geraci and T. G. Smith*, Consequences of Oil Fouling on Marine Mammals. *R. C. Clark, Jr. and J. S. Finely*, Effects of Oil Spills in Arctic and Subarctic Environments.

1977, 512 pp., $14.50/£10.30. ISBN: 0-12-466902-6

A New Academic Press Journal
Ecotoxicology and Environmental Safety

Editors: FREDERICK COULSTON and FRIEDHELM KORTE
Managing Editor: IRA ROSENBLUM

Ecotoxicology and Environmental Safety publishes studies of the biologic and toxic effects caused by natural or synthetic chemical pollutants to ecosystems, whether animal, plant or microbial. The editors are particularly interested in reports about the entry and fate of chemicals in the biosphere and reports of qualitative and quantitative studies of the toxic effects of chemical pollutants and their impact on man. Articles using the techniques of analytical chemistry, histochemistry, pharmacology, pathology and immunology applied to chemicals arising from industrial effluents, fuels, industrial products, discharges into surface waters, effects of meteorological factors, radiation and catalytic actions on chemicals and metabolic transformation are welcomed. Short review articles of general interest to toxicologists are also included. Negative or confirmatory data are published when of sufficient interest.

Volume 1, 1977 (*Quarterly*)

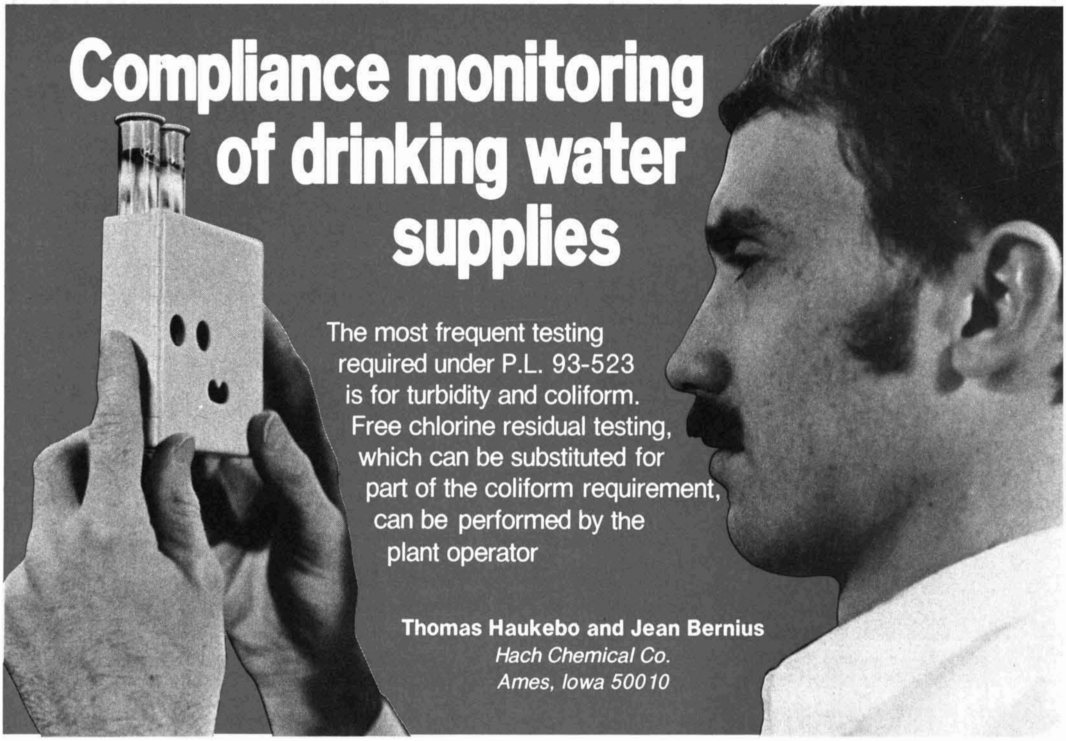
Institutional subscription rate, U.S.A.: $45.00; all other countries: $50.00 (Prices include postage.)

All journal subscriptions are payable in advance. Send payment with book order and save postage plus 50¢ handling charge. Orders under $15.00 must be accompanied by payment.

Prices are subject to change without notice.

ACADEMIC PRESS, INC.
A Subsidiary of Harcourt Brace Jovanovich, Publishers
111 FIFTH AVENUE, NEW YORK, N.Y. 10003
24-28 OVAL ROAD, LONDON NW1 7DX

CIRCLE 1 ON READER SERVICE CARD



Compliance monitoring of drinking water supplies

The most frequent testing required under P.L. 93-523 is for turbidity and coliform. Free chlorine residual testing, which can be substituted for part of the coliform requirement, can be performed by the plant operator

Thomas Haukebo and Jean Bernius
Hach Chemical Co.
Ames, Iowa 50010

"To assure a supply of drinking water which dependably complies with such maximum contaminant levels. . . ." With the signing of the Safe Drinking Water Act in 1974 (P.L. 93-523), it became the responsibility of the Environmental Protection Agency (EPA) and the states to ensure that safe water supplies are available to all users. As part of the program for meeting this goal, the EPA proposed a list of materials to be considered as possible health hazards when present in drinking water.

After much public discussion from environmental and other public interest groups, the National Drinking Water Advisory Council, state agencies, and others, the EPA's Interim Primary Regulations were issued on December 24, 1975. These regulations include:

- maximum allowable levels of ten inorganic chemicals and six organic pesticides
- maximum allowable levels of turbidity and coliform bacteria
- minimum monitoring frequencies for the contaminants
- how and when public notification must be given when any of the maximum allowable levels of contaminants cannot be met by the water system.

In addition to the Interim Primary Regulations, the EPA issued regulations on the maximum permissible levels of radionucleotides in July 1976, and secondary regulations on March 31, 1977. Secondary regulations deal with aesthetic water qualities that affect consumer acceptance, such as levels of sulfate, iron, and manganese. They are not legally enforceable.

Coliform and turbidity monitoring

Compliance monitoring under the Interim Primary Regulations for turbidity and coliform bacteria began June 24, 1977 in approximately 40 000 community public water systems across the country. Community systems include those serving a resident population of at least 25 people with at least 15 service connections. Noncommunity systems, defined primarily as serving the traveling public in campgrounds, resorts, and the like, will have to begin testing for those two parameters by June 1979.

For other contaminants, monitoring requirements are split by type of water supply. In community surface-water systems, monitoring for inorganic chemicals and pesticides must begin by June 1978. June 1979 is the deadline for community groundwater systems. Nitrate is the only chemical that noncommunity systems are required to monitor, with samples to be taken by June 1979.

Bulk of the work

The most frequent testing required under the Safe Drinking Water Act is for turbidity and coliform. Turbidity, one of the few tests that can be performed by the plant operator, must be tested on-site at least once daily with a nephelometer. Maximum permissible monthly average is 1 NTU.

Monitoring frequencies for coliform are dependent on community population. Water systems that serve up to 1000 persons must sample at least once a month. Systems with 12 000 users are to sample at least 13 times a month. The testing frequency increases with population, so a plant with over 25 000 users is required to take 30 samples/month; and those with over 5 million customers, 500 samples.

EPA regulations specify that only state-certified laboratories can perform coliform analyses by either the multiple-tube fermentation technique or the membrane-filter method. In addition to coliform, all other inorganic chemical and pesticides analyses must be performed by certified laboratories.

Recognizing the difficulties in collecting and transporting bacteria test samples, the EPA allows water plants to substitute free chlorine residual testing for up to 75% of their coliform monitoring requirement. (At press time, eight states—Ala., Ark., Conn., Ga., La., Miss., Neb., and Okla.—had accepted primary enforcement responsibility for Safe Drinking Water Act compliance. Several of these have taken the option not to allow free chlorine substitution. Individual state officials should be checked.)

Testing can be done by the plant operator. Samples must be taken at least once a day, at the rate of four times the bacterial testing requirement. A system required to send out 30 bacteria test samples a month to a certified laboratory could reduce that number to eight, then test the free chlorine residual 3 times a day, or at least 88 times in the month, to make up the balance.

DPD (N,N-diethyl-*p*-phenylenediamine) has been specified as the method of choice for the free chlorine analyses. It is a fairly recent method, having only gained acceptance in the water industry within the past six or seven years. Since it is a relatively new reagent, it seems appropriate to discuss some of DPD's characteristics and to offer a few suggestions for its best use in water testing.

Available chlorine reagents

Many methods have been reported for the analysis of chlorine. *Standard Methods,* 14th ed., lists at least eight different procedures for varying applications. When specifying a chlorine method, it is important to know what type of chlorine must be measured.

Free chlorine is formed by the simple dissociation of chlorine in water, and exists as hypochlorous acid (HOCl) and the hypochlorite ion (OCl^-). Free chlorine is considered the most effective disinfectant of the chlorine species.

Combined chlorine forms by the reaction of free chlorine with nitrogenous and organic compounds. Combined species include monochloramine (NH_2Cl), dichloramine ($NHCl_2$), and nitrogen trichloride (NCl_3). Most combined species require a longer contact time for disinfection and are not considered as efficient sanitizing agents.

For free chlorine measurements, syringaldrazine, DPD, stabilized-neutral orthotolidine, and leuco crystal violet methods are available. Some of these methods can also differentiate between free and combined species. DPD, leuco crystal violet, orthotolidine arsenite, and methyl orange colorimetric methods, and an amperometic titration using phenylarsine oxide (PAO) are some of the common differentiating procedures. To measure both combined and free chlorine (or total chlorine), the iodometric titration and the unmodified orthotolidine method can be used.

DPD for chlorine residual

First suggested for chlorine use by Dr. A. T. Palin in 1956 (British Patent 813,493), DPD works as an oxidation-reduction indicator. DPD reacts with a variety of oxidants, iodine, bromine, some oxidized forms of manganese, as well as chlorine, and can be used to quantitatively determine any of these, provided the others are known to be absent.

In its reaction with free chlorine, DPD is instantly and directly oxidized, losing one electron. The oxidized form is red. Combined chlorine species react more slowly than free chlorine, but can be catalyzed by adding small quantities of iodide to the indicator. The combined species react through a two-step mechanism where the chlorine species oxidize the iodide to iodine, which then reacts with the DPD.

If the analyst wishes to differentiate between monochloramine, dichloramine, and nitrogen trichloride, certain reaction conditions can be met. Generally, sequential iodide additions to the reaction mixture will allow analysis of the different species. Most water treatment plants, however, are interested only in the ratio of free to combined chlorine.

Though DPD is reported to follow Beer's Law up to 8 mg/L free chlorine, *Standard Methods,* 14th ed., recommends an upper limit for both the colorimetric and titrimetric procedures of 4 mg/L free chlorine or chloramine. Higher sample concentrations should be diluted with chlorine-free demineralized water.

Lower detection limit for the colorimetric test is about 0.02 mg/L (1-cm cell), depending on the instrument design. Visual methods are slightly less sensitive, with 0.05 mg/L the lowest concentration of visible color. The endpoint in tritrimetric analyses is detectable to about 0.05 mg/L free chlorine.

In a study published in *Standard Methods,* a synthetic unknown containing 800 μg/L free chlorine was analyzed in 19 laboratories by the DPD ferrous titrimetric method. Relative standard deviation was 39.8%, with a relative error of 19.8%. Twenty-six laboratories analyzed an unknown of 980 μg/L free chlorine with the DPD colorimetric method and obtained a relative standard deviation of 20.7% and a relative error of 15.6%. Analysis of the 800 μg/L unknown by the leuco crystal violet method by seventeen laboratories showed a relative standard deviation of 32.7%, with 7.1% relative error; while the methyl orange method in 26 laboratories yielded a 43.0% relative standard deviation and 22.0% relative error. It would appear the DPD method accuracy and precision is no worse than other available chlorine methods, and may be slightly better.

Test options okayed by EPA

For compliance monitoring, analysts can use titrimetric, visual, or spectrophotometric methods. Visual methods are not listed in APHA *Standard Methods.* In the titrimetric procedure, a 100-mL sample is buffered to about pH 6.5 with a phosphate buffer solution; 5 ml of indicator solution containing 0.1% DPD with sulfuric acid and EDTA is added; and the sample titrated with 0.0282N ferrous ammonium sulfate. Endpoint is red to colorless. The indicator is also available as a single powdered reagent that is already combined with buffer, EDTA, and the like.

Spectrophotometric analyses generally require a 10- to 25-mL sample buffered to about pH 6.5 with 0.5 mL of DPD indicator solution added. Absorbance is read at 515 nm. Calibration curves are prepared with either chlorine solutions or potassium permanganate. DPD has another absorbance maximum around 550 nm, but this is rarely used.

Test-kit methods offer the most convenience and simplicity. About 5 mL of sample is measured into a tube, reagent added, the sample mixed, and the color compared to a permanent standard, usually made of plastic or glass. Untreated water sample or demineralized water is used as a blank.

Testing considerations

Reagent stability: Great improvements have been made in DPD's stability since the method was introduced. The indicator solution, as suggested by Palin, has a rather short shelf life, which is further reduced by increased temperature. Nicolson found the indicator in solution deteriorated to a significant degree within one month. With the introduction of solid reagents, the stability has been increased considerably, so, under normal conditions, shelf lives of a year are not unusual. For longest shelf lives, the reagent should be protected from light and heat and stored in a refrigerator.

Interferences: When testing for free chlorine in the presence of high concentrations of combined chlorine, high free chlorine values may result from monochloramine breakthrough. This may show up in the spectrophotometric procedure as a continuous drift of the instrument readout to higher absorbance values. To avoid this problem, the free chlorine should be measured as soon as possible after reagent addition. When read at one minute, we have found 3.0 mg/L monochloramine will cause less than 0.1 mg/L interference in the free chlorine determination. Another advantage of this technique is it minimizes loss of chlorine caused by lengthy sample handling.

Since DPD does react with other oxidants such as bromine, iodine, and ozone, these must be absent for accurate chlorine test results. The indicator is generally free from other interferences from materials commonly found in drinking water supplies, though high levels of dissolved solids may cause turbidity with some reagent formulations. Incorporation of EDTA into the indicator also helps to prevent interference from copper and dissolved oxygen. Interference from oxidized manganese in the titrimetric procedure may be treated with potassium iodide and sodium arsenite.

pH control critical: If the buffer capacity is exceeded and the sample pH falls below about 6.2, interference from monochloramine breakthrough may occur. If sample pH is too high, dissolved oxygen may interfere. In these cases, sulfuric acid or sodium hydroxide should be added to bring the sample pH to about 6 or 7.

Glassware cleanup: If sample cells and/or titration vessels are not fully cleaned after use with DPD, the glass may become stained with oxidized reagent. This can cause a high reagent blank in colorimetric procedures. Should this occur, we have found several rinses with methanol will remove all traces of color.

Toxicity: Take normal care with DPD reagents, as with any chemical. Avoid ingestion and prolonged or repeated contact with the skin.

Product options

If titrimetric or spectrophotometric DPD methods are chosen, the analyst can purchase indicator powder from a number of manufacturers including Hach Chemical Co., Eastman Kodak Co., and Gallard-Schlesinger Chemical Manufacturing Co. Several distributors also handle the reagent. Indicator powder is produced as the free amine and as several water-soluble forms of DPD such as the oxalate and sulfate salts.

Indicator premixed with buffer and chelants is available in prepackaged unit doses from Hach Chemical Co., Hellige, Inc., LaMotte Chemical Co., and Taylor Chemical Co. Various distributors offer the combined reagent in compressed tablets.

If a test-kit method is chosen, several products are available. Test-kit methods are approved by the EPA for Safe Drinking Water Act Reporting and are recommended for on-site testing. Since low concentrations of free chlorine are very unstable in water, on-site testing is the best way to minimize error from chlorine loss during sample transport.

The concentration range for most kits is between 0.1–4.0 mg/L chlorine, which is in the limits for compliance monitoring. Compact kits can be purchased from Hach Chemical Co., LaMotte Chemical Co., Hellige, Inc., Taylor Chemical Co., and distributors such as Fisher Scientific Co.

A DPD chlorine analyzer for continuous monitoring is also available from Hach Chemical Co. This method is not accepted for reporting but can be used for control purposes, monitoring swimming pools, and the like.

Wastewater analysis

The DPD method of chlorine analysis is also accepted by the EPA for wastewater analysis, but only the spectrophotometric and titrimetric methods that are described in *Standard Methods,* 14th ed., are approved. The test-kit methods are not yet approved for NPDES (National Pollutant Discharge Elimination System) compliance monitoring.

Additional reading

Federal Register, **40,** No. 248, p 59580.

Bjorklund, J. G., Rand, M. C., *J. Am. Water Works Assoc.,* **60** (5), 608 (1968).

APHA *Standard Methods,* 14th ed., 1975, pp 311–333.

Nicolson, N. J., Water Research Association Technical Paper, T. P. 29 (1963), T. P. 47 (1965).

Thomas Haukebo *is a research chemist at Hach Chemical Co. and a member of the Standard Methods Joint Task Group on chlorine.*

Jean Bernius *is a technical writer at Hach Chemical Co.*

Effect of Environmental Variables on Collection of Atmospheric Sulfate

Robert W. Coutant
Battelle, Columbus Laboratories, Columbus, Ohio 43201

■ The performances of various filter media are determined relative to their use in collection of ambient sulfates. The effects of operational parameters and atmospheric variables on the collection of sulfates are investigated. Results show that sorption of ambient SO_2 by basic filter components can contribute to appreciable errors in apparent ambient sulfate levels. This interaction is affected by SO_2 concentration, relative humidity, and temperature. A chemical model relating the effects of these variables is presented.

The need for accurate determination of ambient sulfate levels has been intensified in recent years because of the identification of sulfates as significant health hazards. While progress has been made in reducing atmospheric levels of sulfur dioxide, corresponding reduction in ambient sulfate levels has not, in general, been well correlated with the reductions in sulfur dioxide (*1*). This fact, along with both direct and indirect criticisms of the standard Hi-Vol sampling techniques for ambient sulfate collection, has made obvious the need for a thorough investigation of sulfate sampling and analysis procedures.

Investigations such as those conducted by Lee and Wagman (*2*) and more recently by Radian personnel (*3*) and workers at Ford (*4*) have shown that filters commonly used for sulfate sampling can absorb SO_2 at ambient levels, and that this can lead to generation of extraneous sulfate during the sampling process. It can be inferred from other investigations (*5*) that the presence of potential SO_2 oxidation catalysts in ambient aerosols also may affect ambient sulfate measurements. Still other questions have been raised concerning the mechanical and dynamical factors involved in Hi-Vol sampling.

The present work includes consideration of the effects of filter type and composition, ambient SO_2 concentration, temperature, relative humidity, ambient gas composition, sampling time and velocity, sample storage time and conditions, and particulate composition (SO_2 oxidation catalysts) on the formation of extraneous sulfate, to provide a quantitative base for the assessment of sulfate sampling methodology.

Experimental

Apparatus. Ambient air was used as a base for all of the laboratory experiments. This was drawn into the laboratory at about 520 cfm through a stainless steel duct from a point some 20 ft above the building (ca. 50 ft above ground level). In the laboratory the air stream was divided through two parallel stainless ducts. At the top of each inside duct, injection ports and mixing orifices were added to enable spiking of the ambient air with various gases as needed for specific experiments. Sampling nozzles were fitted near the bottom of the parallel ducts, with provision for four identical sampling points in each duct. This arrangement permitted simultaneous isokinetic collection of as many as eight filter samples in any given run. Standard 142-mm Millipore filter holders were fitted with modified conical inlets to achieve uniform distribution of particles over the filter surface. Outlets from the filter holders were fitted with calibrated orifices, and pumping across the orifices was achieved via a vacuum manifold with a Stokes Microvac pump with a capacity of 80 cfm. Normal 24-h sample volumes were of the order of 1 m^3/cm^2.

Routine measurements were made of the SO_2 concentration (by flame photometry), NO_x (by chemiluminescence), the ozone concentration (by chemiluminescence), temperature, relative humidity, filter pressure drops, wind speed, and wind direction. Analyses for other gaseous components such as H_2S and NH_3 were made for specific experiments. Monitoring during the course of a run was automatic, with both stripchart readouts and paper tape accumulation for computer analysis.

Procedures. The above apparatus was used for basically two types of experiments: 24-h sampling runs and shorter term examination of SO_2 sorption by filter media and by filters preloaded with various potentially active SO_2 oxidation catalysts. In the 24-h runs, preweighed filters were mounted in the holders and were exposed to ambient air for a period of 24 h. The filters were then removed, weighed in a constant temperature/humidity room, cut in half, reweighed, and submitted for analysis. In most cases, one half of each filter was analyzed as quickly as possible, and the other half was stored for possible analysis at a later date. All reported sulfate values are corrected for blank sulfate contents obtained by analyses of filters from corresponding packages. Variations between samples collected on similar filters at the eight different sampling ports were random and were usually 1–3%, based on either the total masses or on the sulfate catches.

In shorter term SO_2 sorption runs, the air flow in one branch of the parallel duct system was spiked with SO_2 to some appropriate level between ambient and 300 ppb. This level was preset without a filter in place. The filter was then placed in the system, the SO_2 was turned on, and SO_2 concentrations before and after the filter were monitored as a function of time. Inasmuch as fluctuations in ambient temperature, relative humidity, and SO_2 concentration were prone to occur during these experiments, data displaying variations greater than 2% in any one variable were rejected.

In examination of potential catalyst effects, dispersions of the agents in alcohol were sprayed onto the filters. In most cases, reagent grade or pigment grade agents were used. However, the vanadium oxide employed was a presized sample (<17 μ) of fly ash from an oil-fired power plant, and one of the iron oxide samples was a fly ash sample from a basic oxygen furnace.

Table I. Filter Analyses (OES)

Element	Elemental content, wt %								
	MSA-1106BH	Gelman AE	Gelman AA	Spectro-grade	ADL	Mitex	Celotate	QAST	E 70/2075W
Al	3	3	2–4	3	0.1	1	0.0007	0.02	0.07
B	1	1	1	1	0.007	<0.001	0.0007	<0.002	1
Ba	0.01	0.2		0.1	<0.002	0.025	<0.0002		
Ca	8	8	1–2	8	8	0.03	0.003	0.02	0.5
Cd	<0.01	<0.01		<0.01	<0.01	<0.01	<0.0002		
Co	<0.001	<0.001		<0.001	<0.001	<0.001	<0.00007		
Cr	<0.002	<0.002	0.002	<0.002	<0.002	0.003	0.003	<0.002	0.002
Cu	<0.001	<0.001		<0.001	<0.001	<0.001	0.001		
Fe	0.04	0.04	0.1	0.04	0.02	0.05	0.0007	0.02	0.02
K	1	1	0.5	1	<0.02	0.8	0.01	0.01	0.4
Mg	2	2	1	2	0.01	0.02	0.002	0.01	0.2
Mo			<0.002					0.002	<0.002
Na	10	10	2–3	10	0.1	0.3	0.002	0.1	4–7
Ni	<0.001	<0.001	<0.001	<0.001	<0.001	0.002	<0.00007	0.001	<0.001
Pb			<0.002					<0.002	0.002
Sr	0.005	0.01	0.005	0.003	<0.002	0.002	<0.0002	<0.005	0.05
Ti	0.003	0.005	0.005	0.005	0.01	0.03	0.00007	0.003	0.003
V	<0.001	<0.001		<0.001	<0.001	0.002	<0.00007		
Zn	<0.01	0.1	<0.01	<0.01	<0.01	<0.01	0.001	<0.01	0.1
Zr	0.005	0.01		0.01	0.003	<0.001	0.00007		

Filter compositions were determined by standard optical emission spectroscopy (OES) techniques. Alkalinities and pH's for the filters were determined by ASTM D-202 procedures.

Results

Filter Composition. Listings of OES results for the various filter types studied are shown in Table I. Alkalinities and pH's for these same filter types are shown in Table II. It is notable in these results that the glass fiber filters display high concentrations of sodium, potassium, calcium, and other basic components and also show relatively high alkalinities and pH's. The high-purity silica filters display only slightly basic character, and the cellulose acetate (Millipore) and Pallflex E 70/2075 W filters are slightly acidic. Samples of the Gelman AE filters showed a slight variation in alkalinity with examples from different positions in the package; a filter from the top of the package displayed the lowest alkalinity. While a hot-leach procedure (ASTM-D-202) was used with most of the filters, one filter was leached at room temperature with the result of exhibiting only about half as much available alkalinity as the hot-leach samples.

Comparative Filter Responses. Two series of 24-h sampling runs were made to evaluate differences between the responses of different filter media. Results of these measurements are shown in Table III.

Storage Effects. Data given in Table IV are the results of an experiment designed to reveal the effects of storage environment on apparent sulfate collection. In this experiment, two filters of each of four different types were exposed to identical ambient sampling conditions for a 24-h period. Halves of the filters were then treated as follows: no storage—immediate analysis, storage for 4 weeks in dry air, storage for 4 weeks in wet air, and storage for 4 weeks in argon. Results of the sulfate analysis shown in Table IV indicate large differences between apparent sulfate collections by the various filter types. An analysis of variance of this data reveals no significant variation with respect to storage condition, but differences between the responses of different filter types are significant at the 95% confidence level.

Table II. Filter Alkalinities

Filter type	pH	Alkalinity, meq/g
MSA-1106BH	9.2	3.1×10^{-2}
ADL Quartz	8.1	1.0×10^{-4}
Mitex	7.0	0.0
Spectrograde	7.2	1.0×10^{-4}
Celotate	6.65	$(1.8 \times 10^{-3})^{a}$
Pallflex QAST	8.1	3.8×10^{-3}
Pallflex E 70/2075W	6.2	$(7.6 \times 10^{-3})^{a}$
Gelman AA	8.9	3.24×10^{-2}
Gelman AE[b]	9.4	4.0×10^{-2}
Gelman AE[c,d]	9.2	5.0×10^{-2}
Gelman AE[c,d]	9.3	4.89×10^{-2}
Gelman AE[c,d]	9.3	4.90×10^{-2}
Gelman AE[c,d]	9.2	4.34×10^{-2}
Gelman AE[c,e]	9.4	2.24×10^{-2}

[a] Acidic. [b] Batch A. [c] Batch B. [d] Different positions in same package. [e] Five-minute room temperature leach.

Catalyst Effects. A series of experiments was conducted to determine the possible significance of the presence of potentially active oxidation catalysts on the overall collection of ambient sulfate. These experiments included both short-term measurements of SO_2 absorption by filters that were preloaded with catalysts, and 24-h sampling runs. Potential catalysts included Fe_2O_3 (from three sources including a basic oxygen furnace fly ash), MnO_2, carbon (acetylene black), vanadium oxide (high vanadium fly ash), ferric sulfate, manganese sulfate, and a mixture of carbon, and the oxides of iron, vanadium, and manganese. None of these materials was found to increase the level of SO_2 absorption exhibited by the filter. In fact, the more acidic iron and manganese sulfate-loaded filters tended to display less SO_2 absorption than the blank filters. An analysis of variance for the 24-h sampling runs showed no significant effect (at the 90% confidence level) due to the presence of the oxides or carbon.

Table III. Filter Response Comparison

Run no.	Filter	SO_2, ppb	Apparent sulfate, μg/m^3
1A1	Mitex	180	25.8
1A2	Mitex	180	31.8
1A3	Spectrograde	180	(33.5)[a]
1A4	Spectrograde	180	(32.1)[a]
1A5	Gelman AE	180	46.8
1A6	Gelman AE	180	46.3
1A7	Celotate	180	26.6
1A8	Celotate	180	24.4
2A1	Mitex	225	11.9
2A2	Mitex	225	11.6
2A3	MSA 1106BH	225	25.2
2A4	MSA 1106BH	225	24.9
2A5	ADL-Quartz	225	12.9
2A6	ADL-Quartz	225	12.7
2A7	Spectrograde	225	16.8
2A8	Spectrograde	225	[b]

Average deviations (sulfate/flow values):
Between filter pairs, 2.9%
Between filter types, Run 1, 30.7%
Run 2, 36.4%

[a] Torn filter. [b] Sample lost.

Table IV. Effect of Storage on Apparent Sulfate

Filter type	Storage condition	Sulfate, μg/m^3
ADL	None	6.30
ADL	Argon	(6.00)[a]
ADL	Dry air	8.24
ADL	Wet air	6.85
Celotate	None	14.17[b]
Celotate	Argon	5.32
Celotate	Dry air	9.89[b]
Celotate	Wet air	8.16
Gelman AE	None	16.88
Gelman AE	Argon	16.69
Gelman AE	Dry air	17.19
Gelman AE	Wet air	17.66
MSA 1106BH	None	12.55
MSA 1106BH	Argon	15.49
MSA 1106BH	Dry air	11.88
MSA 1106BH	Wet air	14.32

[a] Sample lost, value estimated by Yates' method (Kirk, Roger E., "Experimental Design: Procedures for the Behavioral Sciences", pp 146–47, Brooks/Cole Publ., Belmont, Calif., 1968). [b] Questionable data.

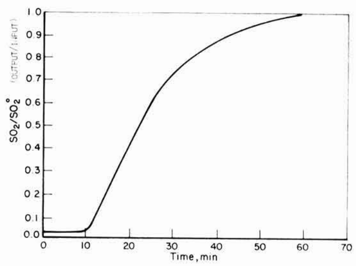


Figure 1. Typical SO_2 sorption response

SO_2 Absorption. Measurements of the absorption of SO_2 by various filter media were made under conditions similar to those encountered in ambient air sampling. Although spiking of the ambient air with SO_2 was employed in many of these runs, spiking levels were kept within the bounds of ambient levels.

A typical response curve obtained in these experiments is shown in Figure 1. Initially, the SO_2 concentration on the downstream side of the filter was close to zero. This low reading persisted for varying times depending on the nature of the filter, the SO_2 concentration, and the relative humidity. The independent effect of temperature was not readily obvious however. After some period of time, usually of the order of 5–15 min for the more basic filters, breakthrough of the SO_2 was observed, and the response curve followed an S-shaped approach to the input level of SO_2. The total amount of SO_2 absorbed was calculated from knowledge of the flow rates, concentrations, and numerical integration of the response curve. Blank runs, i.e., runs without a filter in the system, also were made, and data for the filter responses were corrected for the inherent system lag. Typical blank breakthrough times were of the order of 0.1 min, and blank corrections were of the order of 16 μg SO_2. Data for the total SO_2 sorption by various filter types are given in Table V for comparison of different filter behaviors. It is obvious from this table that the extent of SO_2 sorption by the more basic filters (MSA 1106-BH, Gelman AE, and Gelman AA) is significantly different from that of the other filters studied. Indeed, the responses of the acidic filters (Celotate and Pallflex E 70/2075 W) and the porous polymeric filters (Mitex, Fluoropore, and Polyimide) were indistinguishable from the blank. The more basic filters were therefore examined in more detail, with the results shown in Table VI.

Discussion

Chemistry of SO_2 Sorption by Filters. Many of the glass fiber filters commonly used for air pollution sampling are known to be hygroscopic and quite basic. For example, pH's, as measured by the ASTM D-202 procedure, are generally in the range of 8–10. It therefore seems appropriate to examine the utility of the concept of absorption of SO_2 on the moist-basic surface of these filters in terms of the well-characterized chemistry of absorption of SO_2 by basic solutions.

The sorption of SO_2 in basic solutions has been studied in some detail with regard to stack-gas cleanup systems. Much of the early work traces to a series of papers published by H.

Table V. SO_2 Sorption by Various Filters

Filter type	T, °C	RH, %	SO_2 Input, ppb	SO_2 Capacity, μg/cm^2
MSA 1106BH	25	51	230	6.04
Gelman AE	25	45	236	8.03
Gelman AA	18	49	181	4.65
Spectrograde	25	45	236	1.08
ADL Microquartz	25	44	236	0.36
Pallflex QAST	14	60	286	0.27
Duralon	25	69	236	0.45
Pallflex E 70/2075W	20	44	150	0.00[a]
Celotate	25	65	248	0.00[a]
Polyimide	25	50	150	0.00[a]
Mitex	26	50	260	0.00[a]
Fluoropore FA	26	50	260	0.00[a]
Fluoropore FH	26	50	260	0.00[a]

[a] Indistinguishable from blank.

Table VI. Sorption of SO_2 by Basic Filters

Filter type	T, °C	RH, %	SO_2 Input, ppb	SO_2 Capacity, $\mu g/cm^2$
MSA-1106BH[a]	25	40	150	5.63
	25	40	298	6.99
	23.8	65	154	6.13
	25	71	310	8.57
	25	51	230	6.04
	18	81	315	7.83
	18	81	150	6.44
	18	81	305	7.98
	18	78	150	5.70
	22	61	150	6.00
	22	61	298	6.47
Gelman AE[b] (Batch-A)	15	93.7	298	11.55
	22.8	41	150	6.06
	23.3	34.5	300	5.43
	25	45	326	8.03
	27.8	48	146	4.85
Gelman AE[c] (Batch-B)	26.5	44	207	6.58
	26.8	39	300	5.48
	27.3	38	405	6.48
Gelman AE[c] (Batch-B)	16	51	180	4.88
	11.5	87.2	199	5.04
	12.3	79.4	269	4.46
	11.3	92.7	199	4.79
Gelman AA[d]	17	49	181	4.69

[a] Alkalinity = 0.215 μ eq/cm^2, blank sulfate = 9.85 μg/cm^2. [b] Alkalinity = 0.303 μ eq/cm^2, blank sulfate = 1.1 μg/cm^2. [c] Alkalinity = 0.329 μ eq/cm^2, blank sulfate = 4.2 μg/cm^2. [d] Alkalinity = 0.254 μ eq/cm^2, blank sulfate = 0.39 μg/cm^2.

F. Johnstone and coworkers during the late 1930's and early 1940's (*6*). Because of the relatively unsophisticated procedures used by Johnstone, his work has been subjected to numerous reexaminations, including a program conducted by Coutant and Levy at BCL in 1968 (*7*). The result is that the sorption of SO_2 by various alkaline solutions has been reasonably well characterized over a fairly wide range of the variables.

For the purpose of the discussion, the chemistry of sorption of SO_2 in basic solution can be considered in terms of the following equilibria

$$SO_2 + OH^- \leftrightarrows HSO_3^-$$

$$HSO_3^- + OH^- \leftrightarrows SO_3^{2-}$$

with tacit recognition of the presence of other species such as M^+ (sodium, potassium, etc.) and SO_4^{2-} in the solution.

The equilibrium partial pressure of SO_2 in contact with such a solution is given by

$$P_{SO_2} \equiv P = K \frac{[HSO_3^-]^2}{[SO_3^{2-}]} \qquad (1)$$

where K is the overall equilibrium constant.

While Equation 1 accurately depicts the relationship between the equilibrium partial pressure of SO_2 and the concentrations of bisulfite and sulfite in solution, these latter parameters are not normally easily measured, especially with respect to the case of sorption on an alkaline filter. Therefore, following Johnstone's approach, we choose to make the following substitutions:

$$S \equiv [S^{+4}] = [HSO_3^-] + [SO_3^{2-}]$$

and by requiring electroneutrality,

$$C \equiv [M^+] = [OH^-] - [H^+] + 2[SO_3^{2-}] + [HSO_3^-] + 2[SO_4^{2-}]$$

Recognizing that, at equilibrium, $[OH^-]$ and $[H^+]$ will be relatively small compared to C and S, Equation 1 can be arranged to yield

$$P = KC \frac{(2\,S/C - 1 + 2[SO_4^{2-}]/C)^2}{(1 - S/C - 2[SO_4^{2-}]/C)} \qquad (2)$$

Equation 2 thus gives the partial pressure of SO_2 in terms of the concentration of metal ions and the ratio of absorbed sulfur to metal ion, S/C. The term involving the ratio of sulfate to metal ion is relatively insignificant for most filter media inasmuch as blank sulfates are usually quite low. However, this term is significant for at least one of the common filter media and is retained here for the sake of completeness.

Equation 2 was quite satisfactory for the type of results obtained by Johnstone and was used by him in correlation of data for a number of different kinds of alkaline solutions. However, the more precise work of Coutant and Levy showed that this type of equation fitted SO_2 equilibrium data over a wider range of variables if the C-term was replaced by $C^{2/3}$. Presumably, this form of the equation allows for variation in activity coefficients over a wider range of concentration.

Equation 2 can be rearranged and solved for S/C, the molar ratio of absorbed sulfur-to-metal ion in solution, with the result

$$S/C = \frac{(4 - q - 8\,z) + (q^2 + 8\,q - 16\,zq)^{1/2}}{8} \qquad (3)$$

where $q = P/KC^{2/3}$ and $z = [SO_4^{2-}]/C$. The concentration of the solution on the surface of the filter depends on the relative humidity; the filter will tend to absorb water until the equilibrium partial pressure of water of the resulting solution is equal to the partial pressure of water in the gas phase. For many salt solutions, the relationship between the water partial pressure and salt concentration is nearly linear, and the following expression is a useful approximation:

$$\lambda C = (1 - RH) \qquad (4)$$

where λ is a characteristic constant for a particular salt, and RH is expressed as a decimal fraction. Examination of handbook tabulations of λ and values of K given by either Johnstone, or Coutant and Levy indicates that at SO_2 partial pressures of the order of 10^2 ppb, $q \ll 1$. Therefore, Equation 3 can be simplified and combined with Equation 4 to yield

$$\frac{S}{C(1 - 2\,z)} = 0.5 + 0.354 \frac{P^{1/2}\lambda^{1/3}}{K^{1/2}(1 - RH)^{1/3}(1 - 2\,z)^{1/2}} \qquad (5)$$

Furthermore, it is recognized that the quantity $C(1 - 2\,z)$ is equivalent to the available alkalinity of the filter as measured by ASTM D-202, with the only significant difference being that the alkalinity is determined as the number of equivalents of base rather than as number of moles of base. Therefore, if S is expressed as the number of equivalents of SO_2 absorbed,

$$S/A = 1.0 + 0.708 \frac{P^{1/2}\lambda^{1/3}}{K^{1/2}(1 - RH)^{1/3}(1 - 2\,z)^{1/2}} \qquad (6)$$

Equation 6 thus indicates that the SO_2 sorption capacity of a filter should be directly proportional to the alkalinity of the filter and should vary directly with the square root of the SO_2 partial pressure and inversely with the cube root of $(1 - RH)$. Furthermore, the temperature dependence is implied by $K^{1/2}$, and a dependence on the blank sulfate content of the filter also is indicated. As suggested previously, this dependence on blank sulfate is insignificant for most filter media.

The nature of the base might be expected to influence the temperature coefficient of the equilibrium constant. However, Johnstone found that various bases including sodium, potassium, ammonia, and methylamine had similar temperature coefficients. His value for the potassium system was verified by the BCL work, with K being given as

$$K = \exp\,[6.111 - 4232/T\ ^\circ\mathrm{K}]\ (\mathrm{torr/mol/100\ mol\ H_2O}) \qquad (7)$$

Preliminary analysis of the data in Table VI consisted of a statistical examination with reference to the form of Equation 6. Because of the general consistency between temperature coefficients found by Johnstone and that found in the earlier BCL work, the function given in Equation 7 was used to normalize the experimental results to 25 °C. Regression techniques were then used to test the significance of the equation

$$S/A = a + bP^{1/2}/(1 - RH)^{1/3}(1 - 2\,z)^{1/2} \qquad (8)$$

Similarly, examination was made using the square root RH function that would result from Johnstone's original formulation of the chemistry. Correlation with the cube root function was slightly better, and an overall correlation coefficient of 0.87 was determined. The results of the analysis also indicated that the presence of the constant a was statistically significant, i.e., the filters tend to absorb some minimum amount of SO_2 regardless of the exposure conditions.

A more detailed analysis of the data was then conducted using the "least-squares-cubic" procedure developed by York (*8*). In applying this method, weighting factors were derived primarily from the results of the alkalinity and blank sulfate measurements which suggest uncertainties of ±7% in the left- and right-hand side variables in Equation 8. A plot of the data along with the resulting least-squares values of a and b is shown in Figure 2.

These experimentally determined values of a and b can be compared with corresponding values based on the Johnstone work and that of Coutant and Levy on vapor pressures of SO_2 over potassium sulfite solutions. If we use the handbook value of λ for sodium sulfate and maintain consistent units, the calculated value of b is 7×10^{-3}. This calculated value is only slightly more than 2 σ removed from the experimental value obtained in this work. The theoretical value of the intercept is obviously considerably different from the experimental value. However, alkalinities used in reducing these data were derived by the ASTM procedure involving hot leach of the filters. As noted in Table II, these "high-temperature" alkalinities are considerably greater than alkalinities derived from ambient temperature leaching of the filters. If it is assumed that the low-temperature value of the alkalinity more correctly represents the alkalinity available for SO_2 sorption during ambient sampling, the corrected value of the experimental intercept is 0.55 ± 0.13, and the theoretical value is only slightly more than 2 σ removed from the experimental value. In view of the very long extrapolation required between the previous work and the current results, this "approximate agreement" seems quite good, and it seems reasonable to apply the chemical model in discussing the sorption of SO_2 on the strongly basic filter media.

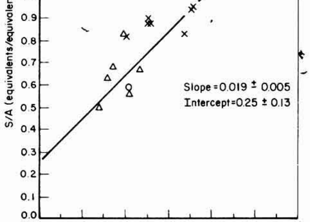


Figure 2. Effect of filter and atmospheric variables on SO_2 sorption

Some caution is due in interpretation and application of the model at very low SO_2 concentrations. Obviously, if no SO_2 is present, there can be no SO_2 absorption. The model, however, implies that some finite minimum capacity for SO_2 absorption exists, even at near-zero SO_2 levels, and it is assumed that the total SO_2 exposure is sufficient to satisfy that minimum capacity.

In reviewing SO_2 sorption data for other filter types, as shown in Table V, it is obvious that the chemical model presented above does not adequately represent the performances of the weakly basic filters. With these materials the absolute amount of SO_2 absorbed is much less than that absorbed by the strongly basic filters but still greatly exceeds that predicted from consideration of the alkalinities. In these cases, it may be that a small amount of water vapor is absorbed by capillary condensation and that this water serves as a sorbent for the SO_2. However, direct evidence for such a phenomenon is not seen in the current work.

Oxidation of Absorbed SO_2. The oxidation of sulfites has been considered in depth by a number of workers, e.g., Beilke et al. (*9*). The reaction is highly dependent on pH, with half-lives as short as 4–5 min being indicated by Schroeter (*10*) for solutions of sodium sulfite under conditions where the rate of oxygen supply is not a limiting factor. It is therefore expected that the rate of oxidation of SO_2 absorbed on basic filter media is quite high and that nearly all of the absorbed SO_2 would be oxidized within a normal 24-h ambient sampling period. Workers at Radian (*3*) found this to be true and reported conversion of about 90% of the absorbed SO_2 within a period of 2 h. Sulfite contents of selected 24-h filter samples collected in the present work were generally low relative to the total sulfur contents of the samples, confirming the notion of rapid conversion of sulfate.

Sulfate Sampling Error. It is obvious from the above discussion that, under any given set of atmospheric sampling conditions, the absolute sulfate error per unit filter area is fixed by the available alkalinity. However, ambient sulfate levels are usually reported as mass per unit volume of air. Thus, the relative error in the measured sulfate loading is inversely proportional to the flow per unit area. For practical purposes then Equations 7 and 8 can be combined and rewritten as

$$SO_4\ (\mu\mathrm{g/m^3}) = \frac{48\,A}{F}\left[0.25 + 1.57 \times 10^{-5}\,e^{2116/T}\left(\frac{P^{1/2}}{(1 - RH)^{1/3}(1 - 2\,z)^{1/2}}\right)\right] \qquad (9)$$

where F is the air volume per unit area ($\mathrm{m^3/cm^2}$) in a 24-h sample, and the units of A are $\mu\mathrm{eq/cm^2}$.

Table VII shows a comparison of some measured excess sulfate levels with corresponding values calculated from Equation 9. These are generally in good agreement and indicate that the model can be useful in estimating excess levels of sulfate due to SO_2 absorption.

Standard Hi-Vol procedures call for use of 24-h sampling volumes of 3–4.5 $\mathrm{m^3/cm^2}$. Figure 3 shows predicted levels of sulfate sampling errors, based on Equation 9, for these sampling rates and filter alkalinities of 0.1 and 0.3 $\mu\mathrm{eq/cm^2}$. Thus in the range of normal sampling conditions, the expected error due to SO_2 sorption on basic filters is between 0.3 and 3 $\mu\mathrm{g/m^3}$ depending on specific conditions and sampling variables. Excursions beyond this level of error are easily conceivable however, and it is obvious that the lower the sampling rate, the more sensitive the error is to changing environmental conditions.

Table VII. Experimental and Predicted Excess Sulfates

Run no.	Filter comparison	SO_2,[a] ppb	RH,[a] %	T,[a] K	Sulfate difference, $\mu g/m^3$	
					Exptl	Calcd[b]
3A	Gelman AE-ADL[c]	90	80	286	10.7 ± 0.8	11.3
3A	MSA-ADL[c]	90	80	286	7.2 ± 2	8.6
10B	Gelman AA-QAST (or ADL)[c]	125	98+	298	13.6	12.8
10B	Gelman AE-QAST (or ADL)	125	98+	298	16.3	17.9
11	MSA-QAST[d]	135	88	298	2.1	3.0

[a] Corresponding hourly averages selected to yield highest value for Equation 9. [b] Calculated by Equation 9. [c] Laboratory samples at $F = 1$ m^3/cm^2. [d] Standard Hi-Vol sample at $F = 3$ m^3/cm^2.

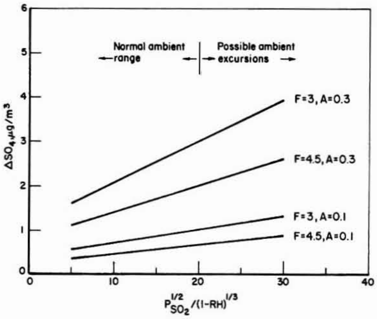


Figure 3. Relative sulfate sampling error

Conclusions

The principal error involved in sampling of ambient air for total sulfate particulate content is caused by the absorption and subsequent oxidation of ambient SO_2 in the presence of basic components of the filter medium. A model of this absorption process has been developed based on well-characterized chemistry of the sorption of SO_2 in alkaline solutions. This model relates the extent of SO_2 sorption to environmental conditions, including the relative humidity, temperature, and SO_2 concentration, and to filter characteristics such as alkalinity and blank sulfate content. An effect due to the rate of sampling per unit area of filter is implicit in the model. The results indicate that sulfate loading errors of the order of 0.3–3 $\mu g/m^3$ can be expected with the use of common glass fiber filters under normal Hi-Vol sampling conditions and that larger sulfate errors are possible under extreme sampling conditions.

Acknowledgment

The author expresses his appreciation to C. W. Spicer, J. Howes, G. W. Keigley, and D. Sgontz for their encouragement and assistance in performing the experimental work.

Literature Cited

(1) Frank, N. H., "Temporal and Spatial Relationships of Sulfates, Total Suspended Particles, and Sulfur Dioxide", paper presented at the 67th Annual Meeting of the Air Pollution Control Assoc., Denver, Colo., June 1974.

(2) Lee, R. E., Jr., Wagman, J., *Am. Ind. Hyg. J.*, **27,** 266 (1966).

(3) "Sulfur Dioxide Interferences in the Measurement of Ambient Particulate Sulfates", Final Report from Radian Corp. to Electric Power Research Institute, EPRI 262, January 1976.

(4) Pierson, W. R., Hammerle, R. H., Brachaczek, W. W., *Anal. Chem.*, **48,** 1808 (1976).

(5) Novakov, T., Chang, S. G., Harker, A. B., Science, **186** (4160), 259 (1974).

(6) Johnstone, H. F., *Ind. Eng. Chem.*, **27,** 587 (1935); *ibid.*, **30,** 101 (1938).

(7) Coutant, R. W., Levy, A., "Study of Phase Equilibrium in Selected SO_2 Sorbent Systems", unpublished report, data available on request.

(8) York, D., *Can. J. Phys.*, **44,** 1079 (1966).

(9) Beilke, S., Lamb, D., Muller, J., *Atmos. Environ.*, **9,** 1083 (1975).

(10) Schroeter, L. C., *J. Pharmaceut. Sci.*, **52,** 559 (1963).

Received for review December 9, 1976. Accepted March 21, 1977. Presented at the Division of Environmental Chemistry, 172nd Meeting, ACS, San Francisco, Calif., August 1976. Work supported by the U.S. Environmental Protection Agency under the technical direction of E. Wittgenstein.

Quantity and Relative Desorption Rates of Air-Strippable Organics in Industrial Wastewater

Louis J. Thibodeaux* and Jerry D. Millican

Department of Chemical Engineering, University of Arkansas, Fayetteville, Ark. 72701

■ The maximum quantity of organic material in wastewater that can be volatilized is determined. Volatile material desorbs readily during treatment operations employing air as a source of oxygen (i.e., stripping). Significant quantities desorb under natural environmental conditions as water flows in open channels and awaits or undergoes treatment in large open surface lagoons and basins. Odors and secondary air pollution sources are immediate consequences. An efficient desorption apparatus is developed to obtain experimental determination of the percent volatile organic content and the gross relative volatility. Sixty-four of 75 industrial samples contain detectable air-strippable fractions. The quantity of volatile material in industrial wastewater is significantly higher than expected.

It has long been suspected that some industrial wastewaters contain volatile organic materials that readily desorb into air by natural environmental processes or could be easily removed by air-stripping operations. Known volatile organics have been identified in a number of industrial wastewater samples by GC/MS techniques. The contact of wastewater with air is usually inevitable. A sizable chemical potential for desorption exists for many man-made organic chemicals. Interphase mass transfer can constitute a secondary air pollution source, and desorption of some chemicals from water provides an additional route for eventual global transport.

This work presents an experimental technique for determining the mass fraction of the organic carbon discharged via wastewater that can be readily desorbed to the air and the gross volatility with respect to water. The results of the experiment provide an additional test method to assess the environmental impact of a wastewater and provide another tool to study and characterize the nature of wastewater. Test results of 75 samples, the majority of which are industrial, are presented in an effort to assess the prevalence of significant volatile organic fractions in these sources.

The classical laboratory technique for studying the stripping of volatile chemicals from a wastewater is aeration (*1*). Air in the form of small bubbles is forced into the water via a subsurface diffuser. The rising bubbles agitate the liquid, extend the air–water interface, and collect and remove the volatiles from the water phase. A means of assessing the organic mass remaining in the aeration vessel is employed, and the raw experimental results consist of a set of concentration time data. As a laboratory technique this desorption method has some disadvantages. In general, the desorption rate is slow, and significant water evaporation occurs. As water is lost the effective interfacial area decreases, and the remaining volatiles are concentrated. Both of these occurrences complicate the interpretation of the transient experimental data. Submerged aeration, being gas phase dispersed, is also impractical for wastewater samples that have foaming tendencies.

Dilling et al. (*2*) modified the classical technique in an attempt to simulate the natural environmental desorption process in the laboratory. An artificial interface was not created; however, a mechanical stirrer was placed below the liquid surface to agitate the liquid and force packets of water to the surface replacing packets desorbed of volatiles. Dilling placed small quantities of selected low-molecular-weight halogenated organics in the vessel to study the natural desorption kinetics. Desorption studies of slightly volatile species will likely require considerable run time because the phases are not forced into an agitated state of contact. Desorption of wastewater samples was not performed.

Recirculating, Packed Column Desorption

Significant operating features of the desorption apparatus used in this study are shown in Figure 1. Liquid pumped from a flask irrigates a section of extended surface packing material and falls back into the flask. Air is forced into the apparatus entering below the packed section to effect countercurrent contact in the packing. Desorption is effected in the packed section as the gas and liquid, the dispersed phase, contact at multiple sites upon the stationary extended surface. A review of the analysis of the desorption process follows.

Single Component Desorption. An analytical model of the desorption of dilute aqueous solutions of gases and liquids in a packed column has been developed by Thibodeaux et al. (*3*). A differential balance on water and volatile species i yields the concentration time history of species i, $\chi_i(t)$, as a function of the mass of water remaining, $M(t)$, and the relative volatilization rate, K_i/a,

$$X_i(t) = X_{io}[M_0/M(t)]^{[(K_i/a)-1]} \qquad (1)$$

where X_{io} is the initial concentration (mg c/L), and M_0 is the initial mass of water in grams. K_i is the specific volatilization rate of species i in grams desorbed per gram fed, and a is the specific volatilization rate of water in grams evaporated per gram fed. The relative volatilization rate is so named because of its relation to the thermodynamic relative volatility of species i, α_i. The two related by

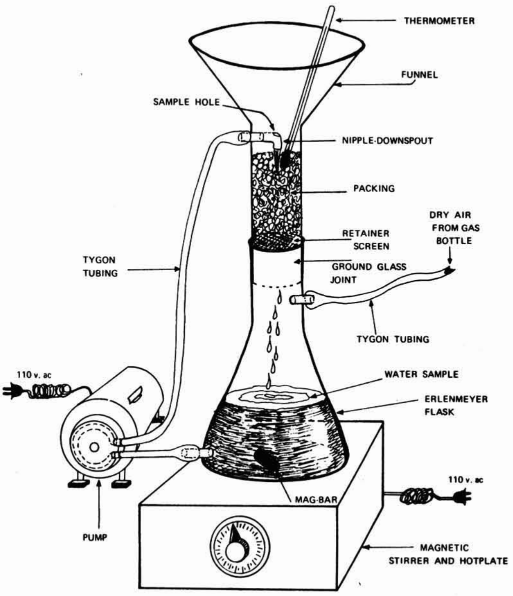


Figure 1. Intalox Saddle desorption apparatus

$$\alpha_i = \underset{Z \to \infty}{\text{limit}}\ (K_i/a) \qquad (2)$$

where Z is the height of the packed section (*4*). K_i/a is a dimensionless experimental observation which reflects the volatility of species i as it exists in the sample including any synergistic effects imparted by the multicomponent nature of the environment. A K_i/a greater than unity implies that species i is more volatile than water and concentration decreases as water evaporation increases. A K_i/a less than unity implies a lesser volatility than water and concentration increasing as water evaporation proceeds. Reinhardt (*5*) performed studies with selected pure components and simulated wastewater to verify Equation 1.

Multicomponent Desorption. Gross organic pollutant measures (i.e., BOD, COD, TOC) quantify the combined volatile and nonvolatile components concentration, $C°$; however, these measures can be expressed conceptually as the sum of the concentration of the volatile, C_v° and the nonvolatile, C_{nv}° portions:

$$C° = C_v^\circ + C_{nv}^\circ \qquad (3)$$

Concentrations in Equation 3 do not reflect the general multicomponent nature of most wastewater. A detailed theoretical development for desorption operations involving multicomponents is presented in ref. *3*. The following is a brief summary of the working relations needed for data analysis associated with the desorption apparatus.

The fractional organic mass time history of the sample, $F(t)$, is related to the n volatile and the m nonvolatile components by

$$F(t) = \sum_{i=1}^{n} F_i^\circ [M(t)/M_0]^{K_i/a} + \sum_{j=1}^{m} F_j^\circ \qquad (4)$$

where $F_i^\circ \equiv X_{io}/C°$ and $F_j^\circ \equiv X_{jo}/C°$. This equation shows that as run time proceeds and water is vaporized (*i.e.*, $M_t \rightarrow 0$) the nonvolatile fraction remains. Although a gross concentration measure cannot single out individual constituents, a slight change in the form of Equation 4 allows further study of the volatile fraction.

If the volatile fraction is assumed to be made of a single "pseudo volatile component", then Equation 4 can be reinterpreted as

$$F(t) = F_v^\circ [M(t)/M_0]^{K_s/a} + F_{nv}^\circ \qquad (5)$$

where $F_v^\circ \equiv C_v^\circ/C°$ and $F_{nv}^\circ \equiv C_{nv}^\circ/C° = \Sigma_{j=1}^{m} F_j^\circ$. All fractions are dimensionless. If only the volatile fraction is considered, Equation 5 may be transformed to yield

$$\log \phi(t) = (K_s/a) \log [M(t)/M_0] \qquad (6)$$

where $\phi(t) \equiv (F_t - F_{nv}^\circ)/F_v^\circ$. The experimental K_s/a is a fictitious lumped single component (i.e., pseudo volatile component) with a relative volatilization rate which is equivalent, in gross combined average behavior, to the n volatile components with individual K_i/a's. Reinhardt (*5*) has shown by experiment that K_s/a is not constant if the wastewater contains several components with differing relative volatilities. Equations 5 and 6 along with the results of a single desorption experiment can yield the volatile and nonvolatile concentrations and an estimate of the relative volatilization rate of the dissolved organics in a wastewater sample.

Desorption Apparatus and Experimental Procedure

A sketch of the desorption apparatus appears in Figure 1. The column consists of a male ground glass joint (~20 cm in height) topped with a glass funnel with a 10-cm opening. The internal diameter of the column was 3 cm and a stainless steel screen, supported on glass indentations, was placed near the bottom but above the ground glass joint. The column was packed to a height of 15 cm with ⅜-in. Intalox saddles. The top inlet nipple was fitted with a sample aperture. The catch basin consisted of an Erlenmeyer flask (500 mL) fitted with a ground glass female joint. An air inlet nipple and liquid outlet nipple complete the desorption apparatus. The relative positions of the nipples are shown in the sketch.

Auxiliary equipment consists of a peristaltic pump (tubing type with removable pump head), magnetic stirrers and hotplate combination, bottled dry air or nitrogen, and pressure regulator. Interconnecting tubing was Tygon. Apparatus arrangement is shown in the sketch.

A 300–350-mL aliquot, relatively free of suspended and settlable solids, is placed in the apparatus through the funnel and the entire system weighed. Water (rate preset at 130–160 L/min) recirculation is started, and the initial sample (1.00 mL) withdrawn. Air flow is adjusted at a rate so that flooding is incipient (~12 L/min STP). Operation at constant flow rates is continued for a period of 1–3 h withdrawing samples at time intervals of 5–10 min. Apparatus and remaining water are reweighed when finished. An accounting is made of all withdrawn water and evaporation losses. The liquid is maintained at 25 ± 1 °C by heating the contents in an Erlenmeyer flask.

Samples were analyzed for the organic content with an Oceanographic International Model 0524 (ampul type) Total Carbon System. Results are reported as mg total carbon/L. The raw experimental data consisted of water content, $M(t)$, and total carbon concentration, $C°(t)$, with desorption time, t.

The experimental volatile fraction obtained from a 60-min desorption experiment is calculated by

$$F_{v,e}^\circ = 1 - [C°(60)/C°][M(60)/M_0] \qquad (7)$$

Only for highly volatile material, which desorbs essentially to completion in an hour, is the ultimate volatile fraction, F_v°, equal to $F_{v,e}^\circ$. F_v° can be roughly estimated by preparing a graph of $F(t)$ vs. $M(t)$ and attempting to visually extrapolate the data to $M(t) = 0$. Once F_v° is obtained, Equation 6 is used to yield K_s/a. An analytical technique was devised and computerized to extract F_v° and K_s/a simultaneously from the raw data.

The analytical technique is based upon the heuristic notion that there are unique values of F_v° and K_s/a that will "best fit" Equation 6 to the transformed data (i.e., ϕ vs. $M(t)/M_0$) in a least-squares deviation sense. A computer algorithm was developed which performs a one-dimensional search (Golden Section) for F_{nv}° on the range [0.0, $F(60)$]. The algorithm produces unique values of F_{nv}° and K_s/a when the coefficient of variation is a minimum. Further details along with a program listing appear in ref. *4*.

Results and Discussion

A total of 75 wastewater samples representing 26 industry types were tested in the desorption apparatus. Industry representatives responding favorably to our request (by letter) for wastewater samples were instructed to procure and handle the sample in a specified fashion. A 500-mL sample obtained from the total wastewater effluent prior to any treatment operation (i.e., raw) during normal daytime hours was adjusted to a pH ≤ 3.0, placed in a small mouth plastic bottle sealed with rubber tape, and deposited in the U.S. mail. The tag attached to the bottle contained information on industry type, flow (MGD), and major products. The company name was not requested, and anonymous mailings could be performed.

All samples arrived "fresh", and no septic odor was detected. Odors emanating from the funnel were noted at various times. Tables I and II contain the experimental results. Table II shows data from an earlier study by Jones (*6*). Standard

Table I. Air Volatile Fractions in Industrial Wastewaters

SIC no., industry type, major products	Wastewater flow, 1000 gal/day	Raw concn, mg C/L	% Volatile fraction $F^{\circ}_{v,e}$	% Volatile fraction F°_{v}	Relative vol rate, K_S/a
0134, potatoes, Irish potatoes	174.	325.	26.1	31.2	17.3
0134, potatoes, Irish potatoes	321.	284.	8.1	11.3	7.8
0134, potatoes, sweet potatoes	477.	1340.	8.0	43.2	3.3
0172, grapes	317.	257.	19.8	21.2	16.3
0251, broiler, fryer, roaster chicken	?	133.	14.1	92.3	2.2
0251, broiler, fryer, roaster chicken	972.	121.	7.2	98.0	0.5
0251, broiler, fryer, roaster chicken	727.	471.	1.4	1.8	0.0
0251, broiler, fryer, roaster chicken[a]	422.	237.	30.8	83.7	4.4
0251, broiler, fryer, roaster chicken[a]	969.	132.	0.0	0.0	0.0
0252, chicken, eggs	90.1	640.	7.9	8.1	30.4
2033, canned fruits, vegetables, preserves, jams, and jellies	829.	85.	53.3	61.1	16.8
2033, canned fruits, vegetables, preserves, jams, and jellies	?	106.	29.7	31.0	27.8
2048, prepared feeds and feed ingredients for animal and fowl	?	808.	15.9	17.7	11.3
2099, food preparations, salt products	288.	42.	74.6	86.6	23.6
2291, felt goods, roofing felt mill	500.	112.	30.0	30.8	17.4
2297, nonwoven fabrics, material	?	54.	38.3	45.2	28.5
2421, wood products, walnut steaming	?	1640.	19.2	69.1	3.1
2491, wood preserving	?	204.	18.6	68.9	6.4
2499, wood products	?	8280.	0.0	0.0	0.0
2499, wood products, hardboard	200.	1300.	10.9	17.1	6.4
2621, paper mill, newsprint, and milk cartons	30000.	400.	25.5	28.1	19.3
2621, paper mill, pulp and paper	22500.	124.	9.4	12.9	0.0
2621, paper mill, paper products	?	3700.	4.4	63.5	1.2
2621, paper mill, paper products	?	3710.	8.5	78.4	0.8
2621, paper mill, paper products	?	2840.	52.5	59.1	1.8
2819, industrial inorganic chemicals	25.	17.0	36.5	70.9	25.8
2821, plastics materials, polyvinylchloride, polyethylene, polystyrene	30.	31.0	69.0	92.7	10.7
2824, synthetic organic fiber	11000.	716.0	26.3	29.8	17.0
2834, pharmaceutical preparations	?	102000.	58.5	71.4	10.0
2834, pharmaceutical preparations	140.	193.	74.6	75.3	48.5
2834, pharmaceutical preparations	90.	90.	54.1	67.5	11.4
2869, industrial organic chemicals, ethylene oxide and glycol, Cl_2, caustic, propylene oxide	4320.	46.	30.9	41.0	10.2
2869, industrial organic chemicals, bromine, and brominated organics	2880.	16.5	23.0	99.6	6.2
2911, petroleum refining	?	85.	24.1	98.4	4.7
2911, petroleum refining, fuel products	18000.	100.	38.4	41.9	30.9
2911, petroleum refining, gasolines, fuel oil[a]	2200.	18.	0.0	0.0	0.0
2911, petroleum refining	2500.	86.	35.4	52.5	14.9
2911, petroleum refining	31000.	138.	52.0	53.1	54.4
2911, petroleum refining, spent caustic	?	705.	22.4	25.1	17.0
2911, petroleum refining	2160.	45.	38.5	99.5	4.2
2911, petroleum refining, chlorinated hydrocarbons, tetra-ethyl lead, tetramethyl lead	14.4	61.	59.4	63.1	32.2
2911, petroleum refining, gasolines, and middle distillates	20600.	73.	49.0	97.2	10.0
2911, petroleum refining	8600.	73.	26.5	43.8	15.7
3499, fabricated metal products, nickel alloy, rod, sheet, wire	1500.	59.	77.3	82.7	30.6
3499, fabricated metal products[a]	14.5	161.	0.0	0.0	0.0
3499, fabricated metal products, plating, and grinding	375.	27.	33.1	98.9	2.3
3536, hoists, industrial cranes, and monorails[a]	1.84	5.0	0.0	0.0	0.0
3751, bicycles	246.	32.	0.0	0.0	0.0
3751, bicycles, boiler blowdown	5.0	5.0	0.0	0.0	0.0
4931, electric and other services, boiler blowdown	5.0	33.0	55.8	64.0	15.5
4952, sewerage systems, Fayetteville, AR[a]	6500.	97.	29.1	97.6	2.7
4952, sewerge systems, Springdale, AR	6000.	50.	13.2	79.	2.2
5172, petroleum and petroleum products tetra-ethyl chloride, tetra-methyl lead	10100.	98.	80.1	97.1	20.7
5172, petroleum and petroleum products, ethylene dibromide	14.4	2650.	28.5	36.5	9.3
5181, beer and ale	1800.	567.	18.5	97.2	3.4

[a] Initial concentration extrapolated based on concentration vs. runtime plot.

Table II. Air Volatile Fraction in Industrial Wastewaters [a]

SIC no., industry type, major products	Wastewater flow, 1000 gal/day	Raw concn, mg C/L	% Volatile fraction $F^{\circ}_{v,e}$	% Volatile fraction F°_{v}	Relative vol rate, K_s/a
0172, grapes	335.	202.	2.0	0.0	. . .
0251, broiler, fryer, roaster chickens	360.	78.	. . .	4.1	. . .
0251, broiler, fryer, roaster chickens	622.	122.	64.5	98.0	10.6
0251, broiler, fryer, roaster chickens	547.	206.	. . .	0.0	. . .
0251, broiler, fryer, roaster chickens	360.	80.	. . .	6.6	. . .
0252, chicken eggs	42.8	1550.	7.2	15.6	5.0
0253, turkey and turkey eggs	960.	2.1	. . .	0.0	. . .
1389, oil and gas field services, oil field blowpit	?	102.	15.4	19.4	9.3
2079, food, margarine, shortening	200.	236.	9.6	22.8	5.4
2621, paper mill, unbleached kraft	6000.	142.	14.6	26.3	4.4
2621, paper mill, tissue, plywood	42000.	136.	20.5	24.5	8.5
2621, paper mill	22000.	311.	55.6	93.5	5.8
2821, plastics and synthetic resins	12000.	452.	18.6	35.8	12.9
2834, pharmaceutical preparations	?	1850.	31.5	49.1	6.8
2834, pharmaceutical preparations	?	4100.	. . .	32.	2.9
2869, industrial organic chemicals, 1,3-butadiene	2000.	94.	43.1	50.6	41.6
2869, industrial organic chemicals, 1,2-di-chloroethane	432.	92.	56.5	57.5	25.1
2869, industrial organic chemicals, 1,2-di-chloroethane	?	60.6	57.8	58.7	31.0
3499, fabricated metal products, hand tools	76.2	51.	. . .	0.0	. . .
5172, petroleum and petroleum products	20000.	110.	45.0	58.0	10.7

[a] Experimental results of work performed by Jones (*6*).

industrial classifications are employed to systematically group the waste by industry type.

All samples contained carbon; the range was 2.1–102 000 mg C/L with a median of 122. Sixty-four samples (85%) contained detectable quantities of air-strippable organics. It is apparent from the tabulated data that industrial wastewaters contain a significant quantity of volatile organic material in solution of relatively high volatility.

Figure 2 is an example of the desorption kinetics observed. Two pharmaceutical samples are shown to contain approximately the same ultimate volatile fraction but display different relative volatilization rates. Once the F°_{nv} has been established, K_s/a can be obtained from analysis of the remaining volatile fraction by use of Equation 6. Graphical results of this operation are shown in Figure 3.

This work addresses the general question of the presence of volatile organics in wastewater. Sampling of a particular industry type was not exhaustive; therefore, results are only tentative. Table III contains a summary of F°_{v} and K_s/a results for 72 samples partitioned into five categories. Two municipal

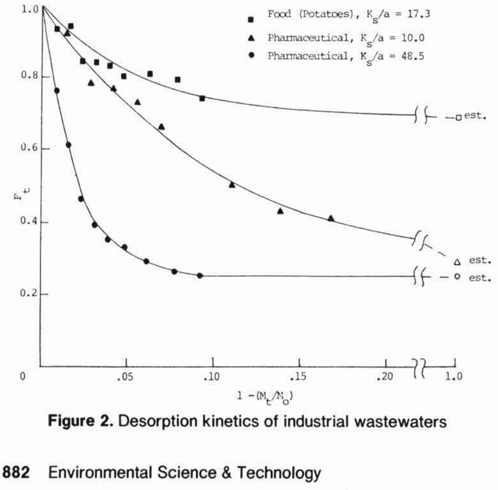


Figure 2. Desorption kinetics of industrial wastewaters

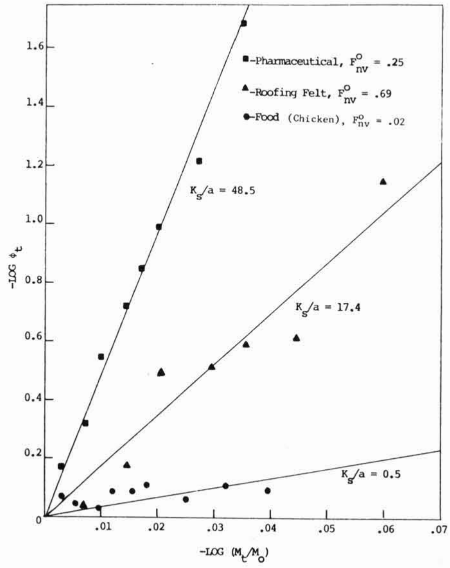


Figure 3. Relative volatilization rates of industrial wastewaters

Table III. Major Industry Summary

No. obs.	General ind. classification	Air-strippable fraction, F_v, % Min [a]	Med	Max	Relative volatilization rate, K_s/a Min	Med	Max
23	Food	0	21	98	0	6.6	30
14	Wood	0	38	94	0	5.1	28
13	Organic	30	58	99.6	2.9	11	49
14	Petroleum	0	53	99.5	0	13	54
8	Fabrication	0	0	99	0	0	31

[a] Min, minimum; med, median; max, maximum.

samples and one inorganic chemical industry sample were excluded.

The organic industry and the petroleum industry by nature should have considerable volatile material in the effluent waters. Raw material feedstock plus the in-plant operation suggest this. In general, chemical processes employing small organic molecules or subjecting large molecules to reactor environments that include high temperatures, pressures, and catalyst, which form smaller molecules, will discharge water containing these substances. The wood industry should also discharge some volatile material, although the raw material and the major products are not generally volatile. The pulping process is known to produce volatile by-products. The food industry is similar to wood in some respects. The main difference is that food preparation, including cooking and blanching, involves a milder chemical reaction environment. Food water F_v° is nearly half that of the wood water median, and K_s/a values are similar. The fabrication industry deals with solids both as raw material and product, while inplant operations usually exclude chemical processing with the exception of the use of organic solvents.

Conclusions

A desorption experiment has been developed to quantify the fraction, F_v°, and the relative volatilization rate, K_s/a, of the organic matter in wastewater that can be readily desorbed into the atmosphere. Test results of 75 samples indicate that a sizable quantity of the organic material discharged by the chemical processing industry readily desorbs into the air and/or is air strippable.

Literature Cited

(1) Eckenfelder, W. W., Jr., "Industrial Water Pollution Control", p 82, McGraw-Hill, New York, N.Y., 1966.
(2) Dilling, W. L., Tefertiller, N. B., Kallos, G. J., *Environ. Sci. Technol.*, **9** (9), 833 (1975).
(3) Thibodeaux, L. J., Estridge, R. B., Turner, B. G., *AIChE Symp. Ser., 124,* **68** (1972).
(4) Thibodeaux, L. J., Environmental Protection Technology Series, U.S. EPA-660/2-74-044, May 1974.
(5) Reinhardt, J. R., MS thesis, University of Arkansas, Fayetteville, Ark., 1972.
(6) Jones, J. R., MS thesis, University of Arkansas, Fayetteville, Ark., 1974.

Received for review October 8, 1976. Accepted April 5, 1977. Work supported by research grants from the U.S. Environmental Protection Agency, Grant No. R-801876, and the National Science Foundation, Grant No. ENG74-17316 401. Presented at the Division of Industrial and Engineering Chemistry, 172nd Meeting, ACS, San Francisco, Calif., Aug. 29–Sept. 3, 1976.

Effect of Chronic Exposure of Brook Trout to Sublethal Concentrations of Hydrogen Cyanide

Walter M. Koenst, Lloyd L. Smith, Jr.*, and Steven J. Broderius

Department of Entomology, Fisheries, and Wildlife, University of Minnesota, St. Paul, Minn. 55108

■ Brook trout, *Salvelinus fontinalis* (Mitchill), were exposed to various concentrations of hydrogen cyanide to determine the effects of continuous exposure on survival, growth, and reproduction. Continuous flow experiments were begun with adults 144 days prior to spawning and were continued through a 90-day growth period of the second generation. The maximum acceptable toxicant concentration (MATC) of hydrogen cyanide was between 5.7 and 11.2 μg/L based on the spawning data.

Cyanide is present in many industrial and municipal wastewaters. The most important source of cyanide pollution is from the effluents of metal finishing, metallurgy, steel processing, and petroleum industries. The most common forms of cyanide are free cyanide (HCN + CN^-), metallocyanide complexes, and organocyanides. Free cyanide in most natural waters is predominantly in the form of HCN, which has been determined to be the most toxic cyanide form (*1*).

Few published studies contain information on acute or chronic effects of cyanide on brook trout, *Salvelinus fontinalis* (Mitchill). Karsten (*2*) reported that all of eight brook trout died within 136 h at 0.05 mg/L free cyanide as CN, and all of six survived for 27 days at 0.02 mg/L. Neil (*3*) found 0.05 mg/L free cyanide as CN to be nonlethal to brook trout exposed for 40 days, while five of 10 died after 87 h at 0.08 mg/L CN. Neil tested fish at 9.5 °C, but Karsten did not report the test temperature. Neil also found that the swimming ability of brook trout was markedly impaired by sublethal levels of free cyanide as low as 0.01 mg/L CN.

The present study was undertaken to determine the effects of continuous cyanide exposure on brook trout survival, growth, first-generation spawning, and second-generation survival and growth. In addition, a relationship between acute and chronic toxicity was determined.

Materials and Methods

Experimental Apparatus. Adult brook trout were tested in 10 fiberglass tanks (210 × 54 × 54 cm) with a 30-cm standpipe 12 cm from the downstream end. The tanks contained a volume of 340 L. Each of two head tanks fed water to four cyanide treatments and a control. Dissolved oxygen and water temperature were regulated in each head tank. The test water was from a laboratory well and was transported through polyvinyl chloride pipe and polyethylene tubing to the experiment. A complete analysis of the well water was described by Smith et al. (*4*).

A diluter system similar to that described by Brungs and Mount (*5*), but utilizing a microswitch and two magnetic drive pumps, was used to control water flow. The toxicant dispensing system was similar to the one described by Mount and Warner (*6*). The dilution system dispensed 4 L of water every 2.5 min, providing a 99% replacement time of 17 h.

The adult fish in each tank were allowed to spawn in two boxes 50 × 38 × 15 cm deep described by Benoit (*7*). Eggs were removed on the day of spawning from each spawning box and placed in incubation cups made of acrylic plastic cylinders 6.5 cm o.d. with Nitex screen bottoms. Eggs were incubated in separate diluter systems employing 20-L glass aquaria. The egg cups were oscillated in the test water by means of a rocker-arm apparatus described by Mount (*8*). Brook trout juveniles were subsequently kept in the diluter system used for egg incubation. The diluter system was similar to that described for adults, but it utilized two solenoid valves instead of magnetic pumps. A water volume of 1.35 L was dispensed every 2.5 min, and a 99% replacement occurred in 3 h.

Test Water Conditions. Temperature, pH, and free cyanide concentrations in test waters were measured three times per week, and dissolved oxygen was measured twice per week. Free cyanide concentrations were determined by the Epstein colorimetric procedure (*9*), and from pH and temperature measurements the molecular hydrocyanic acid concentrations (HCN) were calculated using the ionization constants proposed by Izatt et al. (*10*). In all treatments the mean dissolved oxygen concentration ranged from 64 to 74% saturation, the pH from 7.94 to 8.01 and total alkalinity from 236 to 239 mg/L as $CaCO_3$. Nominal HCN concentrations for all tests were 5, 11, 22, 33, 44, 55, 66, and 77 μg/L. Temperatures of the adult brook trout experiments were varied on a seasonal basis. The temperatures were 14 °C, May; 15 °C, June–August; 12 °C, September; and 9 °C, October. All egg and juvenile tests were conducted at 9 °C. Eggs were incubated and hatched in the dark while fluorescent lights were used in all experiments at other stages. Photoperiod was adjusted bimonthly to simulate dawn-to-dusk times of Evansville, Ind. (*11*). The apparatus was enclosed in black plastic to shield fish from extraneous light and activity.

Experimental Design. Nineteen-month-old adult brook trout with mean weight of 103.9 g were obtained from the Wisconsin State Fish Hatchery in Osceola, Wis., on April 29, 1975. Ten fish were randomly placed in each experimental tank on the day of collection and were kept at 14 °C and treated 8 h per day for 3 days with 20 mg/L tetracycline. Water flow was stopped for 8 h during treatment, and the temperature rose 0.5 °C during this period. After treatment, fish were anesthetized with MS-222 for weighing and measuring. Fish were fed dry pellets at a mean rate of 1.3% of their wet body weight per day. Five days after fish were placed in the test tanks, the toxicant flow was started. The fish were weighed and measured at the start of each month until thinning.

On September 25 the adults were randomly thinned to two males and four females, except at 53.9 μg/L HCN where three females were present. On the same day a spawning box was placed in each tank at the downstream end, and a second box was placed in the middle of each tank on September 30. Spawning boxes were inspected daily for eggs. Total eggs, viable eggs, and number of spawnings were recorded for each test tank. All spawners were terminated 3 weeks after the last spawning or egg deposition. Gonads were inspected for development and to determine which fish spawned. From each spawning of 50 eggs or more, 50 randomly selected eggs were placed in incubation cups and the remainder, up to 250, were placed in other incubation cups for determination of viability. Viability was reported as the percentage of eggs which developed a neural keel within 12 days at 9 °C. Dead eggs were removed daily from the cups. At concentrations where no spawning occurred, control eggs were used to determine hatchability, juvenile survival, and growth.

When hatch was completed, 25 fry were randomly chosen for growth and survival tests. Weight at hatch was determined from discarded sac fry. The sac fry were kept in the incubation cups for 21 days and then released into the 20-L tanks. Since the hatching period was spread out over 3–6 days, the median hatch date was used to establish a growth period of 90 days. Temperature during incubation and growth of juveniles was maintained at 9 °C. The fish were measured at hatching and 30, 60, and 90 days after hatching, plus weighed at hatching and 90 days thereafter. Length was measured photographically (*12*) from snout to end of the caudal peduncle. The juveniles in the growth tests were fed Glencoe pellets two times per day and newly hatched brine shrimp once per day, ad libitum. The juveniles were reduced to 20 fish per tank at 60 days.

Growth data were transformed to logs and analyzed with one-way analysis of variance followed by Duncan's new multiple range test (*13*). One-way analysis of variance was used on the viability and hatch results with an arcsin square root transformation of the percentages.

Results

Growth and Survival of Adults. Adult brook trout grew to a mean weight of 229.2 g during 144 days of exposure to cyanide. No significant growth reduction was noted at any concentration ($p > 0.05$). One fish died in each treatment at 53.9, 64.9, and 75.3 μg/L HCN. The deaths occurred after the temperature was lowered to 9 °C.

Spawning. Spawning began on September 27, 1975, in one control tank and in the lowest HCN level, 5.7 μg/L (Table I). Spawning in other treatments started a few days later with peak spawning occurring the second week of October. Results from treatment at 21.8 μg/L HCN were omitted from the spawning analysis due to the high number of undeveloped females. Only one female developed eggs in this treatment, and the deposited eggs were infertile.

The number of eggs spawned per female decreased with an increase in HCN concentration above 5.7 μg/L (Table I). Regression analysis indicated that a significant downward trend occurred with a resulting regression described as $Y = 552.8 - 6.49\ X$, where Y = mean number of eggs spawned per female, and X = HCN (μg/L). The correlation coefficient between HCN concentration and egg spawned per female was −0.84.

Egg viability was determined for all spawnings, and no fertile eggs were found at 64.9 and 75.3 μg/L HCN. Statistical testing of the viability in the remaining treatments of all spawned eggs showed no significant effects due to cyanide ($p > 0.05$). A composite sperm sample from several untested fish was placed in each of the HCN concentrations used in the spawning tests with no apparent reduction in mobility ($p > 0.05$) at any level.

Table I. Egg Production of Adult Brook Trout Exposed to HCN (μg/L) for 144 Days Prior to Start of Spawning

HCN, μg/L	SD, μg/L	Sex ratio, M/F	Spawning	% Viability[a]	Mean eggs spawned per female	Mean weight of females, g
Control A	. . .	2/4	5	93.6	502	237.6
Control B	. . .	2/4	11	93.4	744	225.0
5.7	0.9	2/4	6	89.9	513	198.5
11.2	1.3	2/4	3	78.1	291	238.5
32.3	3.8	2/4	3	72.9	246	156.1
43.6	3.9	2/3	3	86.6	442	258.0
53.9	6.8	2/3	3	64.1	262	213.0
64.9	7.3	2/3	1	0	124	204.5
75.3	8.8	2/2	0	0	0	193.5

[a] Formation of neural keel.

Table II. Growth of Embryo and Juvenile Brook Trout Exposed to Various Levels of Cyanide

HCN, µg/L	SD, µg/L	$\bar{x}$ Wt at hatch, mg	Mean length, mm At hatch	30 days	60 days	90 days	$\bar{x}$ Wt at 90 days, mg
Control	...	40	13.6	19.6	29.9	41.5	1031
Control	...	42	13.7	20.3	29.3	39.8	910
Control	...	41	13.8	20.1	29.7	41.9	1150
Control	...	39	11.7				
Control	...	38	13.7				
5.6	0.84	43	14.4	20.6[a]	29.8[a]	40.1	937
5.6	0.62	41	12.9	20.4	31.8	43.6	1238
5.5	0.50	41	12.7				
5.7	0.50	38	12.6				
11.1	0.86	39	13.1	19.3	29.3	42.4[a]	1051[a]
11.5	2.60	42	13.6	20.6	29.2	44.1	1219
11.4	0.72	40					
21.6	1.69	40	12.7	19.7[a]	29.5	41.5	972
22.1	1.52	40	13.0	19.3	29.5	42.5	1067
33.2	2.60	...	12.0	18.7[a]	26.0[a]	37.1[a]	681[a]
33.4	2.13	38	12.3	18.6	25.7	37.4	762
32.5	2.15	36	12.8				
43.6	6.08	40	12.9	19.7[a]	26.4[a]	36.4[a]	668[a]
43.5	6.10	40	13.3	18.8	25.4	35.5	651
45.0	8.42	39	13.0				
55.9	4.98	41	12.1	18.0[a]	25.0[a]	32.8[a]	478[a]
54.7	7.43	40	12.5	19.0	24.8	32.3	460
55.9	7.68	42	12.2				
66.8	3.37	42	12.6	18.8[a]	23.4[a]	31.5[a]	387[a]
67.5	4.40	40	11.0	17.8	23.2	28.8	284
77.0	4.23	40	12.2	16.1[a]	21.8[a]	25.7[a]	196[a]
77.4	4.88	37	11.7	16.4	20.0	22.9	127
77.5	3.41	42	12.5				

[a] Mean significantly different from the control ($p \leq 0.05$).

Growth of Embryos and Juveniles. Length and weight of fry at hatch were not significantly different ($p > 0.05$) in any treatment or control, but growth of juveniles in HCN was reduced after hatch (Table II). After 30 days exposure no significant difference ($p > 0.05$) in length was found between 11 µg/L HCN and the control. All other treatments were significantly different from control growth ($p \leq 0.05$). Growth was greater than the control at 5.6 µg/L and less at all treatments greater than 11 µg/L HCN. Significant differences in growth ($p > 0.05$) were not found between 22 and 44 µg/L, 33 and 55 µg/L, and 55 and 66 µg/L. At 77 µg/L growth was less than controls and all other treatments. At 60 days the differences in linear growth between treatments were greatest ($F = 53.42$). No significant difference was found at this age between the control, 11 and 22 µg/L ($p > 0.05$). Length of fish at 5.6 µg/L was significantly greater than controls. Growth was less than the control ($p \leq 0.05$) at 33 µg/L HCN and greater concentrations. No significant difference ($p > 0.05$) in length was found between 33 and 44 µg/L and 55 and 66 µg/L, but at 77 µg/L HCN it was less than all other treatments.

At 90 days differences in length between treatments were marked. No significant difference ($p > 0.05$) was found between the control, 5.6 µg/L, and 22 µg/L. Growth at all other treatments was significantly different from one another ($p \leq 0.05$, $F = 41.38$), with growth at 11 µg/L being greater than the control and growth at 33 µg/L HCN and higher levels being progressively less with increasing concentration. Weight at 90 days was less diverse between treatments but had the same pattern of difference as lengths ($F = 37.01$). No difference ($p > 0.05$) was found between the control, 5.6 and 22 µg/L, between 5.6 and 11 µg/L, and between 33 and 44 µg/L. All treatments of 33 µg/L and greater showed a weight reduction ($p \leq 0.05$) when compared to the controls.

Embryo and Juvenile Survival. Embryo and juvenile survival was determined for each treatment (Table III). Control eggs were used in treatments when no successful spawning occurred (22, 66, and 77 µg/L HCN). No significant differences ($p > 0.05$) in hatchability of eggs exposed to cyanide were noted due to the high variability between replicates. Juvenile survival determined for a period of 90 days decreased with elevated cyanide concentrations. No significant differences were noted between the control and 5.5, 11, 22, 33, and 44 µg/L ($p > 0.05$). Survival at 55, 66, and 77 µg/L was different from the control survival ($p \leq 0.05$). No difference occurred between 55 and 66 µg/L, and survival at 77 µg/L was different from all other levels ($p \leq 0.05$).

Discussion

Growth was significantly reduced by cyanide at the early life stages, but no differences were noted in adults. During the early life stages from embryo to juvenile, growth effects were progressively more influenced by the cyanide concentration with an increase in age. This effect was also shown by Smith (unpublished data, Lloyd L. Smith, Jr., University of Minnesota) where a general increase in acute sensitivity to cyanide was shown in successive stages of brook trout eggs, sac fry, swim-up fry and juveniles. This age dependent effect, not shown for brook trout beyond the early juvenile stage, may be

Table III. Effect of HCN on Survival of Brook Trout Eggs to Hatching and from Hatching to 90-Day-Old Juveniles. Ranges in Parentheses

Nominal HCN, $\mu g/L$	Mean hatch, %	Mean survival from hatch to juvenile, %
Control	72.5 (6.3–100.0)	98.6 (96.0–100.0)
5.5	46.5 (22.4–98.0)	100.0
11	70.8 (16.5–100.0)	100.0
22[a]	72.0 (68.0–76.0)	94 (92–96)
33	70.0 (52.6–96.0)	100
44	72.9 (48.7–93.5)	100
55	81.3 (64.9–89.6)	84.0
66[a]	86.9 (81.3–92.4)	73.5 (64.0–83.0)
77[a]	76.7 (51.1–99.1)	30.0 (12.0–48.0)

[a] Data for treatments at 22, 66, and 77 $\mu g/L$ were from control eggs incubated and hatched at the indicated test treatment concentrations.

Table IV. Percentage Reduction in Mean Eggs Spawned per Female as Related to HCN Concentration

		Percentage reduction in spawned eggs per female	
HCN, $\mu g/L$	Mean eggs spawned per female	From Control A[a]	From lowest HCN concn, 5.7 $\mu g/L$
Control A[a]	502	. . .	. . .
5.7	513	. . .	. . .
11.2	291	42.0	43.3
32.3	246	51.0	52.0
43.6	442	12.0	13.8
53.9	262	47.8	48.9
64.9	124	75.3	75.8

[a] Control A used for comparison was the least productive control.

related to the physiological differences in the different life stages. The no-adverse-effect level of cyanide on brook trout growth after hatch is between 22.1 and 33.2 $\mu g/L$ HCN.

Based on a comparison of size of fish at each time period, growth of juveniles at 5.5, 11, and 22 $\mu g/L$ HCN was equal to or slightly better than the control fish, and growth was less at higher HCN concentrations. Comparison of the growth increment between each time period (0–30, 30–60, 60–90 days) shows that the percentage gain in length at concentrations of 33–66 $\mu g/L$ approached that of the control with an increase in time. This growth pattern was similar to what Leduc (*14*) found with coho salmon juveniles. The salmon exposed to free cyanide grew somewhat faster than the control fish during the second half of the experiment. This increase in growth after initial impairment was attributed to an increase in food conversion efficiency.

Adult mortality occurred in the highest three treatments (53.9, 64.9, and 75.3 $\mu g/L$) only when the temperature during the spawning tests was reduced from 12 to 9 °C. Smith (unpublished data) has shown that a decrease in temperature increases sensitivity of fish to HCN. Mortality of juveniles occurred after the swim-up stage. The level of no adverse effect on survival occurred between 44 and 55 $\mu g/L$.

The number of eggs spawned per female was considerably lower at HCN concentrations of 11.2 $\mu g/L$ and higher. A study reported by Jensen (*15*) showed that a 5% increase in mortality of zero-age-group brook trout results in a substantial decrease in yield. Jensen's theoretical analysis of the effect on yield by increased mortality rates shows that with 50% additional mortality at the zero-age group the brook trout population would become extinct. It is reasonable to assume that a decrease in spawning will also bring about a decrease in the zero-age group unless the spawning population deposits eggs in significantly greater numbers than are needed for normal maintenance. Therefore, on the basis of the demonstrated effect of cyanide on spawning, it can be anticipated that at 11.2 $\mu g/L$ HCN and higher a decrease in the abundance of the zero-age-class trout may be anticipated (Table IV). This projection is based on the percentage reduction compared to the control with the lowest egg production. When compared to the mean of the two controls, 5.7 $\mu g/L$ HCN would appear to show a substantial reduction in eggs spawned per female, but due to the high variability in spawning in the two controls, further study would be required to reach this conclusion.

The maximum acceptable toxicant concentrations (MATC) of hydrogen cyanide for the brook trout lie between 5.7 and 11.2 $\mu g/L$ on the basis of spawning data. The 96-h LC50 concentration of HCN for juvenile brook trout tested at 10 °C, pH 7.9, and 8.0 mg/L dissolved oxygen is approximately 94 $\mu g/L$ (Smith, unpublished data). Therefore, the application factor (MATC/96-h LC50) defined by Mount and Stephan (*16*) lies between 0.06 and 0.12 which is close to the application factor for fathead minnows estimated by Lind et al. (*17*). Lind's MATC (highest no-effect level) of hydrogen cyanide based on egg production was between 12.9 and 19.6 $\mu g/L$. The lethal threshold concentration of HCN for fathead minnow juveniles was reported to be approximately 120 $\mu g/L$. Therefore, his estimated application factor lies between 0.11 and 0.16. Lind's application factor was based on the highest no-effect level and LTC (lethal threshold concentration) ratio. The 96-h LC50 concentration of HCN for fathead minnows is the same as the LTC (Smith, unpublished data); therefore, the application factor for fathead minnows based on MATC/96-h LC50 would not be different from that reported by Lind et al.

Acknowledgment

Donavon M. Oseid helped design and construct the test apparatus. The Wisconsin Department of Natural Resources supplied the test fish.

Literature Cited

(1) Doudoroff, P., Leduc, G., Schneider, C. R., *Trans. Am. Fish. Soc.*, **95,** 6–22 (1966).

(2) Karsten, A., *Black Hills Eng.*, **22,** 145–74 (1934).

(3) Neil, J. H., "Some Effects of Potassium Cyanide on Speckled Trout (*Salvelinus fontinalis*)", paper presented at Fourth Ontario Industrial Waste Conference, Water and Pollution Advisory Committee, Ontario Water Resources Commission, Toronto, Canada, 1957.

(4) Smith, L. L., Jr., Oseid, D. M., Olson, L. E., *Environ. Sci. Technol.*, **10** (6), 565–68 (1976).

(5) Brungs, W. A., Mount, D. I., *Trans. Am. Fish. Soc.*, **99** (4), 799–802 (1970).

(6) Mount, D. I., Warner, R. E., "A Serial-Dilution Apparatus for Continuous Delivery of Various Concentrations of Materials in Water", U.S. Public Health Serv. Publ. 999-WP-23, 1965.

(7) Benoit, D. A., *Trans. Am. Fish. Soc.*, **103** (1), 144–45 (1974).

(8) Mount, D. I., *Water Res.*, **2,** 215–23 (1968).

(9) American Public Health Assoc., American Water Works Assoc., Water Pollution Control Fed., "Standard Methods for the Examination of Water and Wastewater", 13th ed., 1971.

(10) Izatt, R. M., Christenson, J. J., Pack, R. T., Bench, R., *Inorg. Chem.*, **1**, 828–31 (1962).
(11) American Public Health Assoc., American Water Works Assoc., Water Pollution Control Fed., "Standard Methods for the Examination of Water and Wastewater", 14th ed., 1975.
(12) McKim, J. M., Benoit, D. A., *J. Fish. Res. Board Can.*, **28**, 655–62 (1971).
(13) Steel, R.G.D., Torrie, J. H., "Principles and Procedures of Statistics", McGraw-Hill, New York, N.Y., 1960.
(14) Leduc, G., PhD thesis, Oregon State Univ., Corvallis, Ore., 1966.
(15) Jensen, A. L., *Trans. Am. Fish. Soc.*, **100** (3), 456–59 (1971).
(16) Mount, D. I., Stephan, C. E., *ibid.*, **96**, 185–93 (1967).
(17) Lind, D. T., Smith, L. L., Jr., Broderius, S. J., *J. Water Pollut. Control Fed.*, **49** (2), 262–68.

Received for review August 30, 1976. Accepted April 18, 1977. Sponsorship by the Minnesota Agricultural Experiment Station and the U.S. Environmental Protection Agency under Grant No. 802914.

Heavy Metals from Waste Disposal in Central Puget Sound

William R. Schell* and Ahmad Nevissi

Laboratory of Radiation Ecology, College of Fisheries, University of Washington, Seattle, Wash. 98195

■ One of the sources of the Puget Sound metals which are measured in this study—Pb, Cd, Zn, Hg, Cu, and Ni—is the liquid effluent from the Municipality of Metropolitan Seattle (METRO) sewage treatment facility which is discharged through diffusers at West Point, Seattle, Wash. The focus of this study (a part of the Puget Sound Interim Studies) is on the measurement of heavy metals in water, biota, and sediments collected near and far from the sewage treatment plant at West Point. Seasonal collections of water and biota samples show that there are few significant differences between the amounts and kinds of metals measured in samples collected near the outfall and at control stations. The concentrations of metals in Puget Sound water, except for Pb and Cd, are similar to the reported values for open ocean water. The intertidal and benthic biota show only small increases in concentrations at control stations. The sediment cores dated by ^{210}Pb techniques have given information on the history of metal accumulation in Puget Sound over the past 100 years. The concentrations of several metals in the surface sediments are 1–3.6 times greater than the concentrations in sediments deposited 50 years ago.

The key problems in the control of aquatic pollution are how to dispose of liquid wastes caused by man's activities and how to determine the amount of liquid waste that can be carried by the receiving waters without damage to the ecosystem. Information on the disposal of heavy metals into salt water from large municipal sewage disposal plants, such as the one at West Point in Seattle, is limited. An assessment of these disposal problems must include quantitative measurements of the levels of heavy metals in the ecosystem and the comparison between the natural levels and pollution levels in samples. This report presents data on concentrations of the heavy metals Cu, Cd, Pb, Hg, Ni, and Zn which have been measured in water, biota, and sediment samples collected near a domestic sewage outfall in Central Puget Sound and from control areas.

Puget Sound is a fjord-like estuary in Northwestern Washington State (USA), located some 200 km from the ocean and to the east of a coastal range of mountains. Marine water from the Eastern Pacific enters the Sound at depth through the Strait of Juan de Fuca; freshwater enters the estuary from several rivers, from local runoff, and from precipitation. Overall, the waters inside the Sound are a continuously changing mixture averaging about 10 parts ocean water and 1 part river water (*1*). Superimposed on the net surface outflow and deep inflow are large oscillating tidal currents. These tidal currents are the primary source of energy for vertical and horizontal mixing through the Sound. The volume of the basin is about 169 km^3 and encompasses an area of 2600 km^2; the mean volume of water in the tidal exchange is 8 km^3. With such a large volume of water constantly in motion, the mean residence time for much of the water is only 120–140 days. However, water in isolated inlets and in deep basins has a much longer mean residence time.

The sources of heavy metals entering Central Puget Sound, in addition to the natural input by rivers, are the liquid effluent from sewage, industrial waste, shipping, runoff water which carries eroded materials from land development areas, and atmospheric fallout. The largest sewage treatment plant located on the Sound is operated by the Municipality of Metropolitan Seattle (METRO) at West Point in Northwest Seattle. This single plant now processes most of the domestic and industrial sewage of Seattle and the surrounding region. The raw sewage receives primary treatment and sludge removal. The effluent is chlorinated prior to discharge through a 2.44-m diameter pipe extending 1113 m from shore. The diffuser section of the pipe has 203 ports of 11.4–14.6 cm diameter and is located at an average depth of 70 m (*2*). At the location of the discharge there are strong tidal currents which contribute to the mixing and dispersion of the effluent. The plant has an average dry-weather flow capacity of 470 million L a day and a peak hydraulic capacity of 1240 million L a day.

Experimental Methods

The locations of the West Point and three smaller outfalls (identified as water treatment plants, WTP) in Central Puget Sound are shown on the map in Figure 1. Water, sediment, and biological samples have been collected at stations located in the immediate vicinity of the West Point outfall and from several remote areas.

Two methods have been used in sampling the water column for heavy metals. The first is by closely spaced profile sampling through the pycnocline to the bottom, both within and away from the expected effluent plume, utilizing 30-L Niskin water bottles for the instantaneous collections (*3*). The second method is by continuously sampling over 1–2 h at two or three discrete depths with a polyethylene hose, a plastic pump, and Battelle large-volume water samples (BLVWS) made from polyethylene to minimize metal contamination (*4*). This sampling method concentrates certain heavy metals on filter/sorption beds in the field from large volumes of water. It also partitions the metals into the particulate fraction, >0.3 μm, using Millipore filters, and into the soluble fraction, using Chelex-100 resins. While the separation of the fraction of the total concentrations entering the marine waters into the

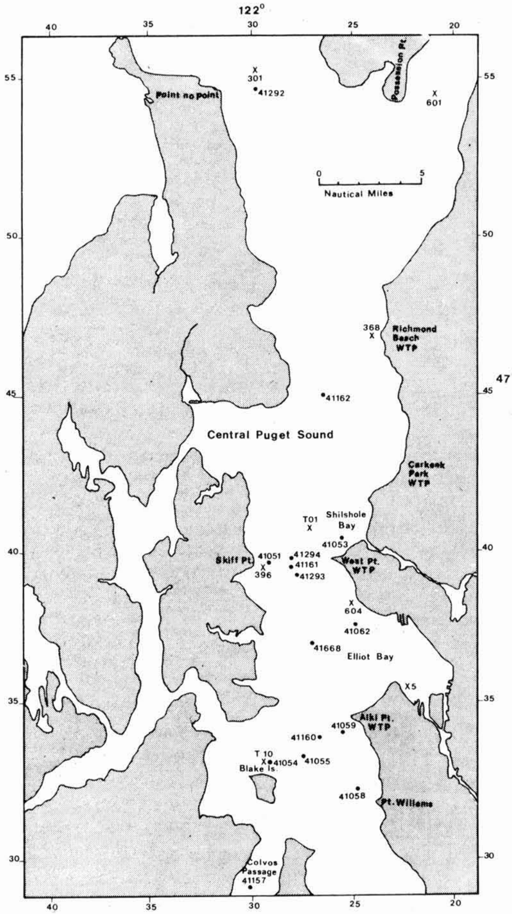


Figure 1. Location of water treatment plants (WTP) and sampling locations for cores, ●, and for water, X, in central Puget Sound

particulate, colloidal, soluble inorganic, soluble organic species would be desirable, no satisfactory method to accomplish this speciation has yet been devised. The BLVWS with sorption beds, however, do permit some field speciation to be made in addition to measuring the total concentrations. Detailed evaluation of the technique has been made recently by Huntamer (*5*).

The chemical and physicochemical speciation of heavy metals may be important to the mechanisms of uptake by biota. For example, the form of mercury in edible fish muscle is almost completely methylmercury (*6*) which is more toxic chronically than other forms of mercury. Other heavy metals have not been evaluated sufficiently to give toxicity guidelines for specific chemical states of metals in the marine environment.

The apparatus and the techniques for the integrated and discrete sampling methods have been calibrated internally against each other and externally with other institutions in a joint sampling cruise (*5*). The results showed that the total concentrations of heavy metals measured by the two methods were similar and that agreement was found for several heavy metal concentrations measured by the BLVWS technique compared to other techniques in the external intercalibrations as shown in Table I.

Sediment cores were taken with a 5-cm diameter gravity corer and a 3.5-cm damped piston corer, using plastic core liners. Benthic and pelagic samples of biota were collected with nets, using the College of Fisheries vessels, *R. V. Commando* and *Malka*; intertidal samples were collected by hand. All samples were placed in polyethylene bags and frozen immediately after collection.

Samples were processed under conditions which minimized possible contamination by heavy metals. The Millipore filters from the BLVWS were dissolved in distilled reagent grade HNO_3 and wet-ashed with $HClO_4$ (*7*). The resin beds from the BLVWS were placed in specially cleansed polyethylene columns and eluted with distilled reagent grade 2 M HNO_3 (*8*). The biological samples were dissected by using Teflon-coated tools and stainless steel knives, and then were dried and homogenized. The sediment core samples were sectioned into 1-cm slices and the outer 3-mm portions were removed; the sections were then dried, homogenized, weighed, and a portion was wet-ashed with distilled HNO_3 and $HClO_4$. **Note:** caution should be practiced when using $HClO_4$. After wet-ashing, the samples were diluted to volume with distilled 0.3 M HCl for atomic absorption spectrometry analysis (AAS) or for ^{210}Pb analysis (*9*). Small aliquots (0.5–1.0 g) of the dried biological and sediment samples were weighed accurately and placed in 2/5-dram polyethylene vials for neutron activation analysis (NAA). The Triga reactor at Washington State University, Pullman, Wash. (neutron flux of 10^{13} n cm^{-2} s^{-1}), or the teaching reactor at the University of Washington (neutron flux of 10^{12} n cm^{-2} s^{-1}) was used for the irradiations. After irradiation and a 1–2-week "cooling" period, the resulting radionuclides were measured by calibrated Ge(Li) detectors at the Laboratory of Radiation Ecology (LRE), and the

Table I. Inter- and Intra-Laboratory Comparisons of Batch and BLVWS Samples for Zn, Cu, Ni, Cd, Co, and Mn in Fresh (Lake Washington) and Salt (Juan de Fuca Strait) Water. Concentrations in $\mu g/kg$

	Zn	Cu	Ni	Cd	Co	Mn
			Juan de Fuca Strait			
Filtered						
OSU [a,c]	0.5	0.4	0.4	0.1	0.14	0.9
	0.6	0.8	1.3	0.1	0.15	1.1
LRE [b,d]	0.42	0.02	0.37	0.09	0.81	0.47
	0.47	0.02	0.50	0.20	1.02	1.27
Unfiltered						
OSU [c]	0.4	0.4	0.35	0.5	0.11	1.4
	0.5	0.4	0.36	0.6	0.15	1.2
LRE [c]	<0.02	0.87	. . .	0.03	0.18	. . .
	0.39	. . .	. . .	0.03	0.29	. . .
LRE [d]	0.50	0.05	0.43	0.10	0.91	1.67
	0.51	0.05	0.58	0.24	1.20	2.96
			Lake Washington			
Filtered						
OSU [c]	1.6	0.2	0.5	0.02	0.03	0.5
	1.3	1.3	0.7	0.02	0.06	0.7
LRE [d]	0.28	. . .	0.10	0.08	0.22	0.60
	0.17	. . .	0.42	0.16	0.40	1.28
Unfiltered						
OSU [c]	0.3	1.0	0.4	0.02	0.03	4.1
	0.3	1.0	0.7	0.01	0.3	4.1
LRE [c]	0.55	0.63	. . .	0.03	<0.02	. . .
	5.17	1.06	. . .	0.09	0.05	0.02
LRE [d]	0.72	. . .	0.10	0.33	0.18	4.53
	0.79	. . .	0.42	0.16	0.40	4.04

[a] OSU, Oregon State University, N. Cutshall. [b] LRE, Laboratory of Radiation Ecology. [c] Discrete water samples—solvent extraction. [d] Sequential BLVWS samples.

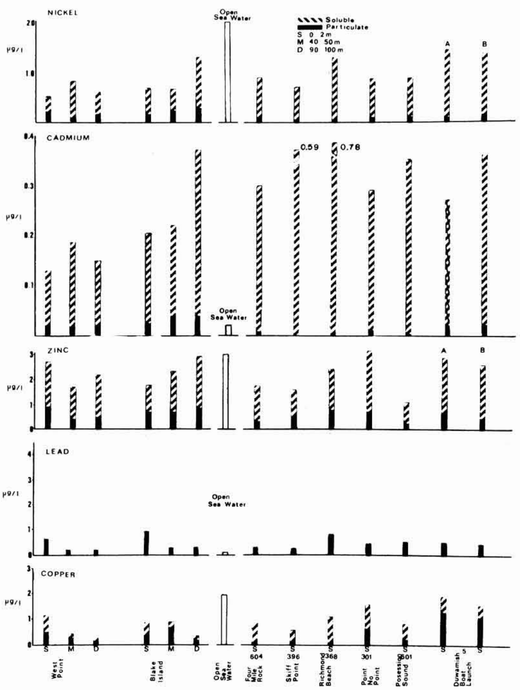


Figure 2. Concentrations of heavy metals in particulate and soluble fractions

Total concentrations of metals in water collected with BLVWS at eight locations in central Puget Sound are compared with open ocean water. Collections made at three depths: surface/S, 0.5–2 m; mid-depth/M, 40–50 m; and deep/D, 90–100 m. (Concentrations in µg/L ± 15% propagated analytical error)

spectral data were analyzed by computers. Blank, control, and standard (interlaboratory comparison) samples were measured together with each group of samples. The quality control of the measurements was monitored by an outside group who prepared "unknown" standard solutions of heavy metals for measurement with each group of samples.

Results and Discussion

The concentrations of the heavy metals Ni, Cd, Zn, Pb, and Cu in the water collected by using the BLVWS at the eight stations are shown in Figure 2. The histograms show the concentrations of heavy metals in the particulate (>0.3 µm) and soluble fractions of seawater from Central Puget Sound and the open ocean (*10*). The concentrations of Cd and particulate Pb in Central Puget Sound waters appear to be higher than those found in open seawaters. The concentrations of soluble Pb also were measured in samples (range, 2–7 µg/L), but were not included in Figure 2 because of the uncertainty of the measurements. This uncertainty resulted from the low collection efficiencies for soluble Pb (10–15%) found by using the BLVWS technique with sorption beds of Chelex-100. [See Nevissi and Schell (*11*) for the calculation method.] However, the particulate concentrations measured for all samples and the soluble concentrations measured for the metals, except for Pb, should be valid. Patterson and Settle (*12*) have illustrated the many contamination problems in measuring Pb from natural waters; the contamination problem cannot be completely ruled out in the measuring of our samples either. On the other hand, Riley and Taylor (*8*) found that Pb was retained on Chelex-100 with high efficiency from seawater samples; thus, the Pb would be expected to be collected as well as the other metals by the Chelex-100 used here. If the soluble Pb in Puget Sound is in a different chemical state than that measured by Riley and Taylor, then the low collection efficiencies found for the soluble Pb by the BLVWS technique could be understood. Additional effort needs to be made to resolve these discrepancies.

The results of the measurements can be illustrated best by comparing the concentrations of heavy metals in the water at two stations; for example, at West Point and Blake Island. The concentrations of metals found near Blake Island, which is far from any sewage treatment plant, are not markedly different from those found at the West Point Station which is downstream. The general circulation of surface water is from the south to the north, and the concentrations of most elements measured do not seem to be elevated nor much different at the two stations. The increase in metal concentrations which would be expected from the METRO outfall effluent has not been observed by measurements of samples collected in the water column. Zirino and Lieberman (*13*) report measurements of Pb and Cd in Puget Sound waters using an automated anodic stripping voltammetric instrument. They reported Cd values of 0.1 µg/L and Pb values ranging from 0.10 to 0.21 µg/L in the first leg of their cruise. However, during the second leg of their cruise, which followed four days later over essentially the same route, the values measured for Pb and Cd were a factor of three lower than those made on the first leg. These discrepancies were attributed to the rapid changes in water and/or instrument performances. No additional measurements were given to estimate their instrumental reliability at these low levels.

Certain biological samples may be indicators of metal buildup. Organisms show different uptake of metals, due to variations in feeding patterns and mechanisms, morphology, and environment. Within each organism the organs have varied capacities and storage times for trace metals which are related to their biological functions (*14*). The Bay mussel, *Mytilus edulis*, is prevalent in the intertidal zone and has been found to be an indicator organism for several metals (*15, 16*). The concentrations of Pb and Hg found in mussels are shown in Figure 3. Also shown in the figure are the metal concentrations measured in brown algae, *Fucus* sp., green algae, *Ulva* sp., and clams collected at the same times and locations as the mussels. The results of the analysis at each station are presented in the histogram from south to north, with the West Point outfall at the center. The concentrations of Pb appear to be slightly elevated at the West Point stations, with a range of values between 0.5 and 2 µg/g, wet weight. The Hg concentrations do not show a clear pattern for the different types of organisms at the sampling locations. The range of Hg values is 2–15 ng/g wet weight for all the biota measured; the guideline recommended by the Food and Drug Administration (FDA) for human consumption of shellfish is 500 ng/g wet weight (*17*).

Sediments are the sinks for the trace metals in the water column; thus, changes in the water concentration with time should be indicated in sediment core profiles. Dating sediment layers by the ^{210}Pb technique (*18*), together with the analysis of trace metals in the same core profile, has contributed to the understanding of local deposition of the metals in Central Puget Sound. The ^{210}Pb method measures the sedimentation rate, which can be used as a geochronological tool in evaluating the trace metal input over the past 10–100 years. We have dated 14 cores from different areas of Central Puget Sound by the ^{210}Pb radiometric technique (to be published elsewhere). The results show that there are wide variations in the sedimentation rates at different regions within Puget Sound (0.1–2 cm yr^{-1}).

The basic assumptions for the ^{210}Pb dating technique are: constant influx of ^{210}Pb from water column to the sediment,

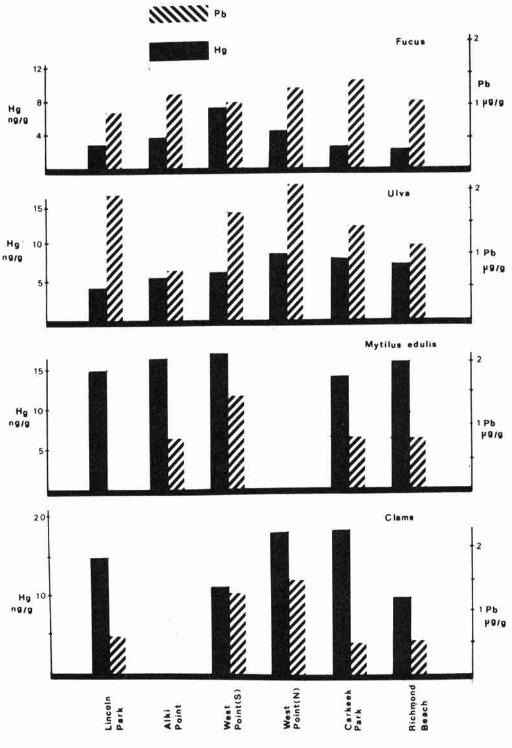


Figure 3. Concentrations of Pb and Hg in intertidal organisms (*Fucus*, *Ulva*, *Mytilus edulis*, and clams collected in central Puget Sound

Each value represents 5–30 individual organisms. (Pb concentrations in µg/g dry, ±15% analytical error; Hg concentrations in ng/g dry ± 15% analytical error)

constant sedimentation rate, and immobilization of ^{210}Pb within the sediment (*18*). These conditions may not be the same for all coring stations. The input of ^{210}Pb and trace metals to sediment at each location in Puget Sound depends on the currents, sediment morphology, biological activity in the sediment, and the proximity of stream and river input of sand and silt from the land. The organic carbon content of the sediments and the sedimentological parameters (percentage of gravel, sand, silt, and clay) have not been measured in the cores used for this study. However, a granulometric survey of the marine surface sediments from the Strait of Juan de Fuca and Puget Sound was reported by Roberts (*19*). By matching the core sampling stations from this study with the stations in the Roberts report, these sedimentological parameters as shown in Table II were estimated. Considering the above factors, an attempt was made to compare the past history of trace metals deposition at each core location with the present concentrations using the ^{210}Pb dating technique to establish the time history.

Examples of the typical core profiles for ^{210}Pb dating are shown in Figure 4. In core 41054, collected north of Blake Island, a gradual decrease in the ^{210}Pb concentration occurs with depth, and a sedimentation rate of 0.9 ± 0.1 cm/year was calculated. In core 41160 collected near Alki Point, an apparent constant ^{210}Pb concentration occurred to a depth of greater than 12 cm. At lower depths, the ^{210}Pb concentration decreased at a gradual rate, and a sedimentation rate of 0.37 ± 0.04 cm/yr was calculated. In core 41161, collected in a deep area near the West Point outfall, no change in the ^{210}Pb concentration was found from the surface to a depth of 46 cm. Because of this anomaly, an additional core from this area was collected at a different time, and similar results of the ^{210}Pb

Table II. Surface Sediment Enrichment of Trace Metals in Central Puget Sound. Average Concentrations in 1955–1975 Time Periods Are Divided by Those of 1900–1920 Period

Area	West Point				Elliott Bay		Alki Point					Control Stations		
Core #	41293	41294	41053	41051	41062	41668	41160	41059	41058	41055	41054	41162	41157	41292
Lat., N	47°39′43″	47°39′54″	47°40′30″	47°38′49″	47°37′40″	47°36′50″	47°33′5″	47°33′46″	47°32′31″	47°33′35″	47°33′35″	47°44′48″	47°29′5″	47°50′48″
Long., W	122°28′13″	122°27′49″	122°25′44″	122°29′14″	122°24′56″	122°26′52″	122°27′5″	122°25′23″	122°24′53″	122°28′5″	122°28′5″	122°25′42″	122°30′5″	122°30′44″
Water depth, m	246	240	100	190	175	196	250	157	187	183	196	283	102	160
Particle size, %[a]														
Sand	9.4	85.6	8.6	85.6	4.7	4.2	30.9	39.1	72.8	85.9	85.9	65.9	87.9	74.6
Silt	51.6	6.5	50.7	6.5	49.4	49.2	34.6	34.5	13.4	6.8	6.8	17.5	2.7	9.9
Clay	39.0	7.8	40.7	7.8	45.9	46.7	34.6	26.4	13.7	7.3	7.3	12.3	2.8	4.8
Zn	1.1	*b*	1.8	1.4	1.0	1.4	1.1	1.4	1.1	1.3	1.2	*b*	1.0	1.6
Ni	*b*	1.0	1.2	*b*	*b*	1.1	*b*	*b*	1.0	1.4	1.0	*b*	*b*	1.2
Cu	1.0	1.1	2.8	1.3	*b*	1.5	1.0	1.7	1.0	1.3	1.1	*b*	1.0	1.8
Pb	1.8	11.1	3.6	1.6	1.1	1.7	*b*	2.2	1.2	1.9	1.5	1.8	1.0	1.8
Cr	1.0	1.0	1.2	1.2	*b*	1.1	1.1	*b*	*b*	1.3	1.2	1.0	*c*	1.4
Mn	1.1	1.0	1.3	1.2	*b*	1.3	*c*	1.0	*b*	1.7	1.0	*c*	*c*	1.0
Co	1.0	1.0	1.2	1.2	1	1.1	1.0	1.0	1.0	1.2	1.3	1.0	*c*	1.0
Hg	2.4	1.3	1.8	1.3	*c*	*c*	1.4	1.7	1.3	1.6	1.6	*c*	*c*	6.1

[a] Reported by Roberts (*19*). [b] Metals depleted in top layers. [c] Not measured.

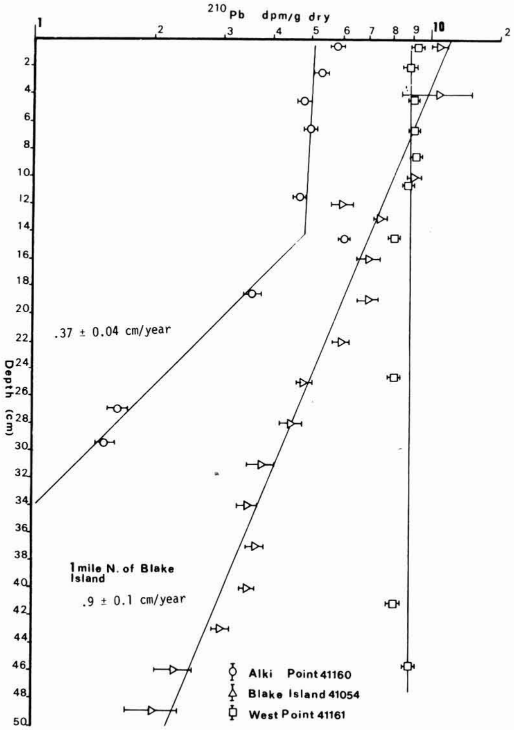


Figure 4. Examples of ^{210}Pb concentrations measured in three cores collected in central Puget Sound

Sedimentation rates determined by least-squares fit of data. (Concentrations in dpm/g, dry, ± SD single sample counting error)

concentrations were found. The ^{210}Pb concentrations did not follow the normal sedimentation profile at this location; at least 46 cm of sediment material with concentrations which were near the present atmospheric levels must have been deposited during a short time interval.

The observed deficiency of ^{210}Pb in the top section of core 41160 and the constant activity of ^{210}Pb in core 41161 could be attributed to: a higher sedimentation rate in recent years, mobilization of ^{210}Pb within the sediment column, bioturbation and mixing of ^{210}Pb to lower depths of sediment due to biological and bacterial activities, or a combination of the above factors. Since prior to January 1973 sludge was routinely discharged from the present outfalls into the Puget Sound, and since dredge spoil has also been dumped in this area periodically, the formation of man-produced sediment (*20*) near the outfalls appears to be the reason for these patterns in the sediment profiles. The discharge of dredge spoil into the Sound and the loss of metals from spoil deposition are discussed elsewhere (*21*).

Calculation of the approximate time of the deposition of the spoils has been attempted, but must be used with caution until further evaluations of the methods used are completed. These estimates of the time of deposition have been made by assuming that the sediment input of ^{210}Pb from the water column is the same for core 41054 as for the other two cores; this value is about 12 dpm/g. The upper 12 cm of core 41160 has a value of ca. 6 dpm/g. Thus, the time of the deposition of this material as sediment is calculated to be 24 years ago or 1952. The upper 4 cm of sediment appear to have returned to the pre-1952 rate (0.37 ± 0.04 cm/yr), although the data are limited to measurements of two sections of the core. The West Point core has a ^{210}Pb concentration of 9 dpm/g, dry weight. Thus, the time that this material was deposited is calculated to be about 10 years ago or 1966.

The heavy metals measured in these same core profiles are shown in Figure 5. Core 41054 has high concentrations of heavy metals in sediments even though it was taken at a region far from the outfall plume. The metal concentrations do not appear to have changed greatly at this station over the past 50 years (49 cm). The metal values measured in the surface section (Pb, 54 ppm; Cu, 52 ppm; Zn, 122 ppm; Cr, 47 ppm) are comparable to concentrations measured in sediment cores collected near the industrial areas and population centers of Puget Sound. The area where the core was taken must be a natural sink for sediment, which may be due partly to the eddies which are formed at the north end of Blake Island (*21*).

Core 41160 shows high and almost constant concentration of ^{210}Pb and heavy metals such as Hg in the upper 12 cm of sediment. Below 12 cm there is a gradual decrease of Hg concentration with depth to the level of 30 cm. This sediment layer (30 cm) is estimated by the ^{210}Pb measurements to have been deposited about the year 1900. The West Point core shows high and essentially constant heavy metal concentrations from the surface to 28 cm. These data, together with the ^{210}Pb values, which are essentially constant to a depth of 46 cm, point toward a single or short-time deposition of material at this location.

In an area which may be contaminated by man's waste material, the natural background of heavy metals cannot be obtained from any measurement of contemporary samples of the water, sediment, or biota. It must be determined from samples collected at a previous date, before man's impact. However, if measurements of samples are not available, an indication of the amount of heavy metals which were present at the previous date, at least in the sediments, may be obtained from the measurement of the heavy metal concentrations in accurately dated core profiles. It has been assumed that the migration of elements in the sediment profile is negligible, although this assumption may not be valid for certain elements, sediment types, and water conditions.

The use of the ^{210}Pb dating technique for 14 cores collected in central Puget Sound (to be published elsewhere) and the enrichment of the heavy metal concentrations in sediment layers between the time period of 1900–1920 and 1955–1975 are shown in Table II. Since the sedimentation rates differ at various core sampling locations, the ^{210}Pb dating technique has been used to reconstruct (normalize) the average concentrations of trace metals which were deposited as sediment during the above-mentioned time periods at each station. The most significant enrichment of several heavy metals is found at station 41053, which is located two miles north of the West Point outfall, and at station 41051 which is located two miles west of the West Point outfall. At these two stations the particle size measurements show that the silt and clay fractions are greater than at other nearby stations; this indicates that the pollutant heavy metals are associated with fine sediment particles. The maximum enrichment (station 41053) is for Cu (2.8) and Pb (3.6); all other metals measured have an enrichment of less than a factor of 2. The enrichment appears to be localized in the immediate vicinity of the outfall, although the data are too limited to give better regional distributions. Duplicate core samples gave results which were significantly higher (15–25%) than the analytical errors (3–5%). Part of the larger errors was attributed to the use of a single corer for sampling and identical locations could not be sampled easily due to drifting of the ship by the strong tides and winds.

Examples of the total input of the three metals Cu, Pb, and Zn in the Puget Sound are shown in Table III. Sources other than effluent from the METRO sewage treatment plant are shown to account for most of the metal concentrations mea-

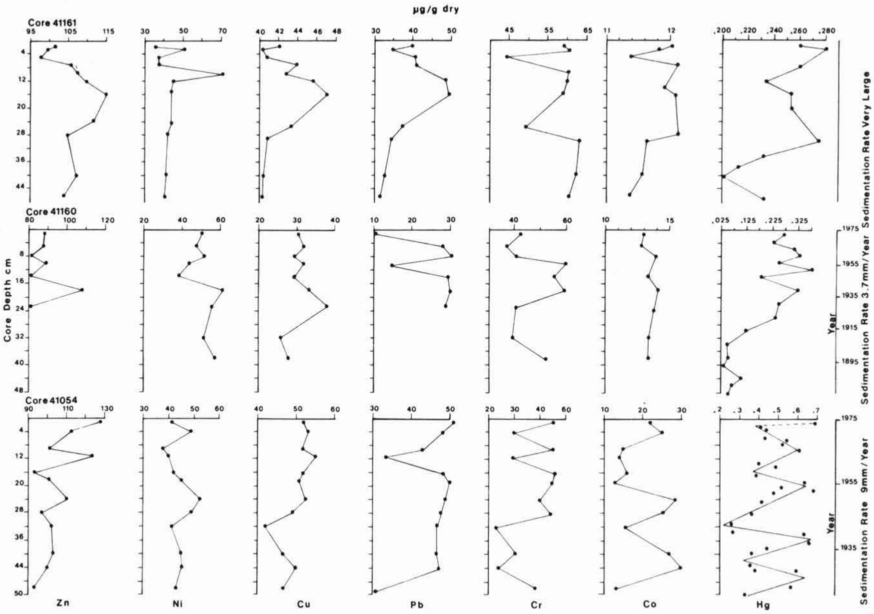


Figure 5. Concentration profiles of Zn, Ni, Cu, Pb, Cr, Co, and Hg in three cores collected in central Puget Sound (Concentrations in μg/g dry, ± 15% single sample analytical error)

sured in water, biota, and sediments (*22*). The input of Cu, Pb, and Zn from the West Point outfall is less than 1.5% of the total input from other sources (rivers, atmospheric input, vessels, advective input, urban runoff, and other municipal discharges). The effluent from West Point is diluted initially by a factor of ca. 100 at the diffusers (*23*) and then by a factor of ca. 5 during a single tidal cycle (*24*). Thus, the resulting net increase in water concentrations of trace metals near the outfall is not significantly greater than the concentrations measured at control stations.

Conclusions

The results of the measurement of heavy metals in Central Puget Sound waters show that effluent from the West Point sewage outfall does not greatly increase the existing concentrations of the heavy metals measured in the water column and in the biota. The concentrations of Pb and Cd in Central Puget Sound are higher than the average open seawater values; the concentrations of Cu, Zn, and Ni are at or below the open seawater values. The Pb and Hg concentrations measured in the intertidal organisms, *Ulva.* sp. (green alga), *Fucus* sp. (brown alga), mussels, and clams show a trend toward higher values near West Point, but the concentrations are within a factor of two at all stations and are probably similar to the within-sample variability. The amount of Hg found in the shellfish is lower by a factor of 10 than the FDA guideline on human consumption of shellfish.

The sediment measurements show that at certain locations rapid deposition of material with heavy metal concentrations has occurred. This probably has resulted from dumping dredge spoils or sludge from sewage treatment plants. The time of this dumping has been estimated by the ^{210}Pb dating technique of cores. The enrichment of heavy metals in sediment layers has been determined from the values obtained at the surface when compared with those values obtained from layers which were over 50 years old. The background heavy metal concentrations have been estimated from the deeper (older) layers of the cores, deposited prior to 1900. The total input of the Cu, Pb, and Zn from all sources into Puget Sound is much greater than the input from the West Point sewage treatment plant; less than 1.5% of the total concentration of each element is estimated to be coming from the plant. These data are similar to those of Crecelius et al. (*25*) for the As and Sb budget of Puget Sound, in that natural rather than man-made sources contribute most of the trace elements to Puget Sound. The study is continuing, and more measurements of heavy metals in samples are being made and tabulated for computer modeling studies. The results of the study should give a better evaluation of the existing concentrations, carrying capacity of the water, and sources and sinks of the heavy metals in Central Puget Sound.

Acknowledgment

We acknowledge the assistance given by D. Huntamer, S. Olsen, and R. Meixner for the chemical analyses; by C. Vick and R. King for the counting of samples and data processing; by G. Christian and E. Knudsen of the University of Wash-

Table III. Sources and Inputs of Copper, Lead, and Zinc in Puget Sound (Metric tons/yr) [a]

Source	Copper	Lead	Zinc	Estd SD, %
Rivers (Lake Washington Ship Canal included)	787	2032	1624	50
Metro's West Point Plant	29	9	56	10
Other municipalities in Puget Sound area	22	16	26	50
Atmospheric input	450	2730	820	50
Vessels' protective measures and fuel consumption	360–590	9–12	140–240	. . .
Urban runoff (Seattle)	15	350	50	. . .
Advective transport	306	1640	874	50

[a] From Zafiropoulos (*22*).

ington, Department of Chemistry, for the interlaboratory standard analyses and quality control; and to D. Zafiropoulos for collecting the budget information. The assistance of personnel at the Washington State University, Nuclear Radiation Center, Pullman, for neutron activation under the WSU-ERDA Reactor Sharing Program is appreciated.

Literature Cited

(1) Collias, E., McGary, N., Barnes, C. A., "Atlas of Physical and Chemical Properties of Puget Sound and Its Approaches", 235 pp, Univ. of Washington Press, Seattle, Wash., and London, England, 1974.

(2) Domenowske, R. S., Matsuda, T. I., *J. Water Pollut. Control Fed.*, **41**, 1613–24 (1969).

(3) Piper, D. Z., Murray, J., Hogarty, B., Svensson, C., "Progress Report to Municipality of Metropolitan seattle", W. R. Schell, Project Investigator, unpublished, June 1975.

(4) Silker, W. B., Perkins, R. W., Riecke, H. C., *Ocean Eng.*, **2**, 49–55 (1971).

(5) Huntamer, D., MS thesis, University of Washington, Seattle, Wash., 1976.

(6) "Methyl Mercury in Fish; A Toxicologic-Epidemiologic Evaluation of Risks. Report from an Expert Group", Nordisk Hygienisk Tidskrift, Suppl. 4, 1971.

(7) Smith, G. F., *Anal. Chim. Acta*, **8**, 397 (1953).

(8) Riley, I. P., Taylor, D., *ibid.*, **40**, 479–85 (1968).

(9) Beasley, T. M., PhD thesis, Oregon State University, Corvallis, Ore., 1968.

(10) GESAMP, "Joint Group of Experts on the Scientific Aspects of Marine Pollution (GESAMP) Review of Harmful Substances", IMCO/FAO/UNESCO/WMO/IAEA/UN, Provisional version, suppl. to sixth session, GESAMP Vi/10 suppl. 1, pp 18–19, IAEA, Vienna, Austria, 1974.

(11) Nevissi, A., Schell, W. R., in "Radioecology and Energy Resources", C. E. Cushing, Jr., Ed., 401 pp, Dowden, Hutchinson and Ross, Stroudsburg, Pa., 1976.

(12) Patterson, C. C., Settle, D. M., in "Accuracy in Trace Analysis", Proc. of the 7th Materials Research Symp., P. LaFleur, Ed., NBS Special Publ., in press.

(13) Zirino, A., Lieberman, S. H., "Analytical Methods in Oceanography", Advances in Chemistry Series, No. 147, pp 82–98, American Chemical Society, Washington, D.C., 1975.

(14) Hardisty, M. W., Huggins, R. J., Kartarand, S., Sainsbury, M., *Mar. Pollut. Bull.*, **5**, 12–15 (1974).

(15) Schell, W. R., Barnes, R., in "Aqueous-Environmental Chemistry of Metals", A. Rubin, Ed., 390 pp, Ann Arbor Science Publ., Ann Arbor, Mich., 1974.

(16) Segar, D. A., Collins, J. D., Riley, J. R., *Mar. Biol. Assoc., UK*, **51**, 131–6 (1971).

(17) FDA, "Action Level for Mercury in Fish and Shell Life, Notice of Proposed Rule Making", Dept. of Health, Education and Welfare, FDA, *Fed. Regist.*, **39**, No. 236 (Dec. 6, 1974).

(18) Koide, M., Soutar, A., Goldberg, E. D., *Earth Planet. Sci. Lett.*, **14**, 442–47 (1971).

(19) Roberts, R. W., "Marine Sedimentological Data of the Inland Waters of Washington State, Strait of Juan De Fuca and Puget Sound", Special Report No. 56, Dept. of Oceanography, University of Washington, Seattle, Wash., 1974.

(20) Bascom, W., *Sci. Am.*, **231**, (2), 16–25 (1974).

(21) Schell, W. R., Collias, E. E., Nevissi, A., Ebbesmeyer, C. C., "Trace Contaminants from Duwamish River Dredge Spoils Deposited off Fourmile Rock in Elliott Bay", final report for Municipality of Metropolitan Seattle by Laboratory of Radiation Ecology, University of Washington, Seattle, Wash., Dec. 1976.

(22) Zafiropoulos, D., University of Washington, Seattle, Wash., private communication, 1976.

(23) Bendiner, W. P., "Dispersion of Effluent from the West Point Outfall", final report for Municipality of Metropolitan Seattle by Applied Physics Laboratory, University of Washington, Seattle, Wash., Jan. 1976.

(24) Ebbesmeyer, C. C., Okubo, A., "A Study of Current Properties and Mixing Using Drogue Movements Observed Near West Point in Puget Sound, Washington", Municipality of Metropolitan Seattle, Seattle, Wash., 1974.

(25) Crecelius, E. A. Bothner, M. H., Carpenter, R., *Environ. Sci. Technol.*, **9**, 325–33 (1975).

Received for review May 13, 1976. Accepted April 20, 1977. Work supported by the Municipality of Metropolitan Seattle (METRO) under Contract No. Cr-2164.

Photochemical Production of Chlorinated Organics in Aqueous Solutions Containing Chlorine

Barry G. Oliver* and John H. Carey

Water Chemistry Section, Process Research Division, Canada Centre for Inland Waters, Burlington, Ont., Canada

■ The photochlorination of ethanol, *n*-butanol, and benzoic acid (organics which react slowly or not at all with chlorine thermally) is studied. The main reaction products for ethanol are acetic acid and acetaldehyde. Only minor quantities of chlorinated products such as 2-chloroethanol and 2-chloroacetaldehyde are produced in the reaction because hydroxyl radicals and chlorine atoms preferentially attack the hydroxyl α carbon in ethanol. For *n*-butanol and benzoic acid, a large number and quantity of chlorinated organics are produced by the reaction. Chlorinated organics can be produced photochemically by sunlight in waters being disinfected with chlorine.

Since the New Orleans Draft Analytical Report (*1*), the presence of organic substances in water and wastewater, particularly chlorinated organics because of their toxicity and persistence (*2, 3*), has been a matter of increasing public concern. The concentration of many chlorine-containing organic constituents in chlorinated effluents has been measured (*4, 5*). Other investigators (*6, 7*) have shown that the thermal chlorination of several aromatic compounds takes place easily under conditions utilized for water renovation. Volatile halogenated organics such as chloroform have been shown to be ubiquitously present in drinking water in North America and Europe (*8–12*).

While many organic compounds react with chlorine at neutral pH and ambient temperature, a large number of organic materials do not react or react very slowly under these conditions (*13*). There is a possibility that some of these unreactive compounds might react with chlorine under the influence of the ultraviolet light present in sunlight. This would be quite important since many cities that use river water for drinking purposes pump the water into open settling basins where chlorine and coagulants are added. The water has a residence time of from 1–3 days in these basins; therefore, it is exposed to a large dose of sunlight. Also, in typical wastewater treatment plants the effluent is chlorinated in open channels and discharged into lakes and rivers; photochemical reactions may also occur in this case. Three compounds, ethanol, *n*-butanol, and benzoic acid, which react slowly or not at all with chlorine at pH 7 and ambient temperature, were chosen for the study.

Experimental

Solutions were prepared from a 5% sodium hypochlorite solution and reagent grade ethanol, *n*-butanol, or benzoic acid.

Five hundred milliliters of solution in Pyrex flasks were irradiated in a Rayonnet photochemical reactor equipped with 350-nm ultraviolet lights. Light intensities were measured by use of ferrioxalate actinometry (*14*). The amount of ultraviolet light (1.3×10^{-8} einsteins/s cm^2) supplied to the solution in 30 min is equivalent to the UV light in about 2 h of sunlight on a typical day or 30 min of sunlight on a bright day. After each irradiation some sodium metabisulfite was added to the solution to consume any remaining chlorine and thus stop any further reaction. In every case, a dark reaction at the same temperature (≈30 °C) was run.

The concentrations of ethanol and its main photoproduct acetic acid were measured by gas chromatography with a Tracor 550 gas chromatograph equipped with a dual-flame ionization detector. A glass column (1.8 m, 6 mm o.d., 4 mm i.d.) packed with Tenax was used at 90 °C for the ethanol analysis and at 180 °C for the acetic acid analysis. A ^{63}Ni electron capture detector on the same chromatograph was used for the detection of chlorinated organics. Acetaldehyde was determined in cold H_2SO_4 with *p*-hydroxydiphenyl by measuring the absorbance of 568 nm ($a = 4.7 \times 10^4$) (*15*).

The wt % organic chlorine in the *n*-butanol and benzoic acid irradiated samples was determined by first extracting the sample after pH adjustment with several aliquots of ether. The ether was then evaporated to leave either a solid or liquid residue, and the wt % chlorine in this residue was determined by combustion in an oxygen atmosphere (*16*). This procedure converted all the organic chlorine to chloride which was then determined colorimetrically. Blanks run on equimolar solutions of sodium hypochlorite and sodium metabisulfite and on sodium chloride solutions showed virtually no interferences from the inorganic constituents of the solutions. Control reactions carried out in the dark showed that only minimal thermal chlorination (of the order of ≃0.1 wt % organic chlorine) was occurring. The efficiency of the ether extraction technique was >90% for the pure starting compounds, and the reproducibility of duplicate chlorine determination was better than ±5%.

Results and Discussion

The reactions described in this paper were carried out with solutions of much higher concentrations than those encountered in the environmental samples to facilitate the analysis of the reactants and products. The ≈10/1 ratio of chlorine to organic carbon is typical of that found in normal water treatment systems. A solution of 0.1 M chlorine and 0.01 M ethanol at pH 4 was irradiated for various lengths of time with 350 nm light in a Rayonnet photoreactor. The concentrations of ethanol and the major photoproducts, acetic acid and acetaldehyde, are shown in Figure 1. The ethanol concentration decreases steadily over the course of the irradiation while the acetic acid concentration increases. The acetaldehyde concentration increases in the early portion of the reaction, reaches a plateau, and then decreases. To within experimental error (±5%), the sum of the ethanol, acetic acid, and acetaldehyde concentrations throughout the irradiation is equal to the starting ethanol concentration. This indicates that the only major products of the reaction are acetic acid and acetaldehyde. The experiment was repeated with degassed solutions, and no change was observed in the product yields. Thus, oxygen does not seem to play a significant role in the reaction.

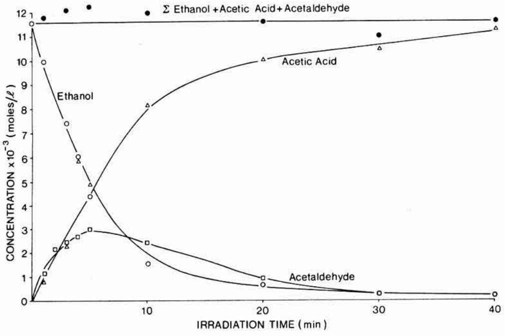


Figure 1. Concentration of ethanol, acetic acid, and acetaldehyde as a function of irradiation time at 350 nm (starting solution: 0.1 M chlorine, 0.0116 M ethanol, pH = 4)

At pH 4, essentially all the chlorine in the solution is in the form of hypochlorous acid (HOCl). Buxton and Subhani (*17*) have shown that the primary photochemical process of HOCl at 350 nm is:

$$\mathrm{HOCl} \xrightarrow{h\nu} \mathrm{HO\cdot} + \mathrm{Cl\cdot} \tag{1}$$

The initial quantum yields of acetic acid and acetaldehyde over the first 2 min of the irradiation are 2.6 and 3.7, respectively. To explain these high yields, the following chain process involving hydroxyl radicals and chlorine atoms is proposed:

$$\mathrm{CH_3CH_2OH + OH\cdot \rightarrow CH_3\dot{C}HOH + H_2O} \tag{2a}$$

$$\mathrm{CH_3CH_2OH + Cl\cdot \rightarrow CH_3\dot{C}HOH + HCl} \tag{2b}$$

$$\mathrm{CH_3\dot{C}HOH + HOCl \rightarrow CH_3CHO + H_2O + Cl\cdot} \tag{3a}$$

$$\mathrm{CH_3\dot{C}HOH + HOCl \rightarrow CH_3CHO + HCl + OH\cdot} \tag{3b}$$

$$\mathrm{CH_3CHO + OH\cdot \rightarrow CH_3\dot{C}O + H_2O} \tag{4a}$$

$$\mathrm{CH_3CHO + Cl\cdot \rightarrow CH_3\dot{C}O + HCl} \tag{4b}$$

$$\mathrm{CH_3\dot{C}O + HOCl \rightarrow CH_3COOH + Cl\cdot} \tag{5}$$

$$\mathrm{CH_3\dot{C}HOH\ (CH_3\dot{C}O,\ OH\cdot,\ Cl\cdot)} \\ \mathrm{+\ CH_3\dot{C}HOH\ (CH_3\dot{C}O,\ OH\cdot,\ Cl\cdot) \rightarrow} \begin{array}{c}\text{stable}\\ \text{products}\end{array} \tag{6}$$

The bulk (97%) of hydroxyl radical attack on ethanol occurs at the α carbon (*18*). Thus, it is not surprising that the only two major products of the irradiation are acetic acid and acetaldehyde. If attack occurred at the β carbon, diols and 2-chloro compounds would be produced by a similar reaction mechanism. In fact, small quantities of 2-chloroethanol and 2-chloroacetaldehyde (identified by comparison of gas chromatographic retention times with the pure compounds) have been observed in the irradiated samples.

Irradiation of *n*-butanol under the same conditions followed by qualitative analysis of the irradiated samples with a gas chromatograph equipped with an electron capture detector showed a vast increase in the number and quantity of chlorinated hydrocarbons in this system compared to ethanol. For *n*-butanol, only 34% of hydroxyl radical attack occurs at the α carbon (*18*). Therefore, the major OH· and probably Cl· reactions would involve carbon atoms further down the chain leading to chlorinated products by reactions such as:

$$\mathrm{CH_3CH_2CH_2CH_2OH + OH\cdot} \\ \mathrm{\rightarrow CH_3CH_2\dot{C}HCH_2OH + H_2O} \tag{7}$$

$$\mathrm{CH_3CH_2\dot{C}HCH_2OH + HOCl} \\ \mathrm{\rightarrow CH_3CH_2\overset{\overset{\large Cl}{|}}{C}HCH_2OH + OH\cdot} \tag{8}$$

The identification and quantification of the vast number of possible chlorinated and unchlorinated products in the *n*-butanol system were thought to be insufficiently fruitful and too tedious to warrant investigation. Instead, it was decided to determine the amount of photochlorination that was oc-

Table I. Wt % Organic Chlorine in Products of *n*-Butanol Solutions Containing 0.01 M Chlorine After 30 Min Irradiation at 350 nm

n-Butanol concn, mol/L	Wt % organic chlorine		
	pH 4	pH 7	pH 10
0.001	11.1	7.2	0.4
0.005	13.2	9.0	0.3
0.010	16.5	15.4	0.3

curring in the system by measuring the wt % organic chlorine in the irradiated samples at different chlorine to *n*-butanol ratios and at different pH's. The results are shown in Table I. The degree of chlorination increases with increasing *n*-butanol concentration, probably reflecting a more complete scavenging of the free radicals by the organic at higher concentrations. A high degree of chlorination occurs at pH 4 and 7, but very little occurs at pH 10. At pH 7, approximately 70% of the chlorine is present as HOCl. But at pH 10 all of the chlorine is present as OCl^-. At 350 nm the primary photoprocess for OCl^- is (*17*):

$$ClO^- \xrightarrow{h\nu} Cl^- + O$$

Chloride ions and oxygen atoms apparently do not react with *n*-butanol to produce chlorinated products; this is why very little chlorination occurs at high pH.

However, when ClO^- is irradiated at 254 nm, the primary photoprocess is (*17*):

$$\begin{aligned} ClO^- \xrightarrow{h\nu} Cl\cdot + O^- & \\ \searrow^{H_2O} & \\ OH\cdot + OH^- & \end{aligned}$$

At this wavelength, chlorine atoms and hydroxyl radicals should be produced. In fact, wt % organic chlorine values approaching those determined at lower pH and at 350 nm occurred when *n*-butanol/chlorine mixtures at pH 10 were irradiated with 254 nm light. Since this wavelength does not occur in sunlight reaching the earth, photochlorination processes are probably not significant at pH values greater than 9 or 10.

One further system studied was benzoic acid–chlorine–water at pH 7. A plot of wt % organic chlorine in the irradiated sample residues vs. irradiation time is shown in Figure 2. After 60 min irradiation the chlorine content reached 33%. This corresponds to about two chlorine atoms per benzoic acid molecule. In addition to photochlorination, in an aromatic system such as benzoic acid, phenols produced by hydroxyl radical attack may be thermally chlorinated. Salicylic acid was the only major photoproduct that could be identified at short irradiation times. Thermal chlorination of this and other phenols is the probable explanation for the large increase in chlorinated organic production, after the initial 15-min period of irradiation (Figure 2).

To demonstrate that photochlorination can occur in environmental samples, several gallons of Burlington raw water (from Lake Ontario) were collected and extracted using the carbon absorption minisampler (CAM) method (*19*). The dried chloroform extracts were redissolved in water and chlorinated at a 10/1 chlorine-to-organic carbon ratio. One-half of the sample was then irradiated for 30 min at 350 nm in the photoreactor, while the other half was allowed to react thermally with the chlorine for the same period of time. The wt % organic chlorine in the original dried extract was 0.09%. The chlorine content increased to 0.18% on thermal reaction with chlorine and increased still further to 0.28% in the presence of ultraviolet light.

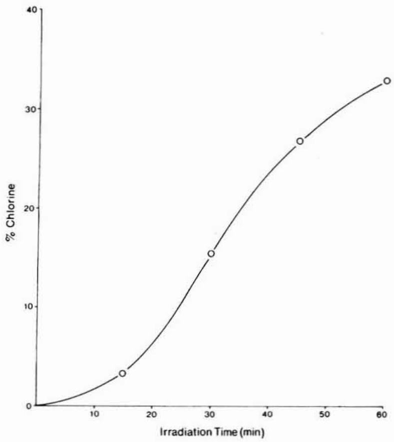


Figure 2. Wt % organic chlorine in reaction products as a function of irradiation time at 350 nm (starting solution: 0.01 M chlorine, 0.001 M benzoic acid, pH = 7)

Some organic materials which do not react thermally with chlorine under normal conditions of water renovation can react with chlorine under the influence of the ultraviolet light available in sunlight. An increase in the concentration of chlorinated organics in water prechlorinated and stored in settling basins open to sunlight is expected through the process of photochlorination.

Acknowledgment

The authors thank Karen Bothen for her technical assistance.

Literature Cited

(1) Environmental Protection Agency, Draft Analytical Report: New Orleans area water supply study, Lower Mississippi River Facility, Surveillance and Analysis Div., Region VI, 1974.
(2) Gehrs, C. W., Eyman, L. D., Jolley, R. J., Thompson, J. E., *Nature*, **249,** 675 (1974).
(3) Katz, B. M., Cohen, G. M., *Bull. Environ. Contam. Toxicol.*, **15,** 644 (1976).
(4) Jolley, R. L., *J. Water Pollut. Control Fed.*, **47,** 601 (1975).
(5) Glaze, W. H., Henderson, J. E., *ibid.*, p 2511.
(6) Carlson, R. M., Carlson, R. E., Kopperman, H. L., Caple, R., *Environ. Sci. Technol.*, **9,** 674 (1975).
(7) Reinhard, M., Drevenkar, V., Giger, W., *J. Chromatogr.*, **116,** 43 (1976).
(8) Bellar, T. A., Lichtenberg, J. J., Kroner, R. C., *J. Am. Water Works Assoc.*, **66,** 703 (1974).
(9) Bunn, W. W., Haas, B. B., Deane, E. R., Kleopfer, R. D., *Environ. Lett.*, **10,** 205 (1975).
(10) Symons, J. M., Bellar, T. A., Carswell, J. K., DeMarco, J., Kropp, K. L., Robeck, G. G., Seeger, D. R., Slocum, C. J., Smith, B. L., Stevens, A. A., *J. Am. Water Works Assoc.*, **67,** 634 (1975).
(11) Foley, P. D., Missingham, G. A., *ibid.*, **68,** 105 (1976).
(12) Rook, J. J., *ibid.*, p 168.
(13) Kobayashi, T., Okuda, T., *Water Res.*, **6,** 197 (1972).
(14) Hatchard, C. G., Parker, A. C., *Proc. R. Soc.*, **A235,** 518 (1956).
(15) Snell, F. D., Snell, C. T., "Colorimetric Metlhods of Analysis", Vol III, p 263, Van Nostrand, New York, N.Y., 1953.
(16) Welcher, F. J., Ed., "Standard Methods of Chemical Analysis", 6th ed., Vol II, p 389, Van Nostrand-Reinhold, New York, N.Y., 1963.
(17) Buxton, G. V., Subhani, M. S., *Trans. Faraday Soc. I*, **68,** 958 (1972).
(18) Adams, G. E., Willson, R. L., *ibid.*, **65,** 2981 (1969).
(19) Buelow, R. W., Carswell, J. C., Symons, J. M., *J. Am. Water Works Assoc.*, **65,** 57 (1973).

Received for review December 7, 1976. Accepted April 22, 1977.

Photochemical Ozone in Smoke from Prescribed Burning of Forests

Leslie F. Evans*, Ian A. Weeks, Anthony J. Eccleston, and David R. Packham[1]
Division of Applied Organic Chemistry, CSIRO, Melbourne, Australia

■ Systematic airborne measurements of ozone in the smoke plumes from the prescribed burning of forests demonstrate the extent to which ozone is generated by photochemical reactions. The ozone concentration in the upper layer of the smoke plume may exceed the Air Quality Standard of 80 ppb, but a simple diffusion model shows that the ozone concentration at ground level is only marginally affected except under special meteorological conditions. Measurements of the olefins and nitrogen oxides in smoke show conclusively that the olefin content of smoke is not sufficient to account for the ozone produced. The identity of the photoreactive hydrocarbon in the smoke is as yet unknown.

In recent years it has become the practice in many parts of Australia to reduce the density of flammable undergrowth in the drier forests by burning the undergrowth every five to seven years. Ignition by incendiaries dropped from aircraft has enabled areas up to 20 000 ha to be burnt per day, and in Western Australia particularly, the enormous smoke plumes so generated have raised questions concerning their environmental impact.

The initial airborne investigation of the plumes carried out by Vines et al. (*1*) was mainly concerned with the nature, properties, and dispersion of the *particulates* in the smoke.

In the course of a further series of flights in 1972, elevated concentrations of ozone were detected at the top of some of the smoke plumes (*2*); therefore, in the subsequent flights of 1973, 1974, and 1975 measurements have been sought of parameters relating to the photochemical generation of ozone. The interim results up to 1973 have been published elsewhere (*3*), while the present paper updates all the photochemical studies to 1975.

Most fires were prescribed fuel-reduction burns conducted in the spring in the southwestern coastal area of Western Australia (Table I) where the fuel type varied little and the burning conditions were closely controlled. The reproducibility of these plumes, coupled with the particularly clear air into which they were injected, provided a unique opportunity for a scientific study of the photochemistry of smoke. Other fires were attended to look for differences due to fuel type (Table II).

The analytical methods and other techniques which were developed to meet the needs of the program are described, and it will be seen how the difficulties associated with airborne instrumentation forced us to depend more on ground-based analyses of samples collected by the aircraft. In the light of the more accurate results so obtained, some of the conclusions of earlier publications have been modifiedslightly.

Experimental and Results

General Equipment. The aircraft (Cessna 337) was fitted with instruments for the continuous recording of the concentration of CO_2 and ozone, the light scattering coefficient, the temperature, and the altitude. The carbon dioxide and ozone concentrations were automatically compensated for changes in atmospheric pressure due to altitude.

In-flight samples of smoke were drawn through probes mounted on the wing of the aircraft. For ozone monitoring, the probes and tubing were fabricated of stainless steel and Teflon. Grab samples for analysis, or for subsequent irradiation experiments, were taken in bags made from Melinex (ICI Polyester) or FEP Teflon (Du Pont fluorinated ethylene-propylene). Both these materials transmitted about 85% of the sun's radiation between 300 and 400 nm.

To reduce the reactivity of the bags toward ozone, the bags were given a prolonged exposure to 40 ppm ozone. Thereafter, the decay of ozone at the 50-ppb level was about 10% per hour. (Note: 1 ppm = 10^{-6} vol ratio; 1 ppb = 10^{-9} vol ratio). Unless otherwise stated, all smoke samples were taken over the downwind edge of the fire area and deep within the plume where no appreciable ultraviolet radiation had penetrated. The altitude was between 700 and 2000 m. It was not always possible to sample the smoke during the peak of the fire; therefore, the carbon dioxide concentration of these samples is not necessarily the maximum concentration in the plume.

Carbon Dioxide Measurements. Because CO_2 was conserved during the time for which the plumes were studied, the concentration of carbon dioxide above the ambient level (ΔCO_2) was used as the absolute measure of the degree of dilution of the smoke.

The measurements of 1970, made by using Dräger tubes carried in the aircraft, indicated that ΔCO_2 in the smoke from Western Australia prescribed burns was between 45 and 180 ppm (*1*). Subsequently, a nondispersive infrared CO_2 meter (Unor 2, Maihak AG) was installed in the aircraft. Although this instrument was capable of an accuracy of 1 ppm when free of vibration and temperature changes, there were serious intermittent noise problems due to vibration when it was used in the aircraft. Therefore, for the 1975 flights the infrared measurements of ΔCO_2 were made on the ground, on smoke collected in flight in FEP Teflon bags. These measurements were accurate to ±2 ppm and showed that as Vines et al. (*1*) had suspected, the CO_2 measurements of 1970 were grossly overestimated.

Light Scattering Coefficient Measurements. Light scattering measurements have been made throughout by means of a nephelometer based on the design of Ahlquist and Charlson (*4*). The derived light scattering coefficient, b_s (m^{-1}), was shown by Evans et al. (*3*) to be numerically equal to four times the particulate concentration (g m^{-3}) in the smokes from Western Australian fuel-reduction burns. Subsequent flights established (see Table I) that for these same smokes, the value of ΔCO_2 (ppm) was numerically equal to 10^4 b_s (standard deviation = 10%). Measurements of b_s therefore served as a check on the measurements of CO_2 in smoke from fuel-reduction burns. As a result, it became apparent that the ΔCO_2 level of 45 ppm quoted by Evans et al. (*3*) for Fire 1 was probably an overestimate by the airborne UNOR meter, the true value being around 16 ppm (see Tables I and V). No such simple relation between b_s and ΔCO_2 exists for the other types of fire listed in Table II.

NO_2 Measurements. The 1974 measurements were made by the Saltzman method (*5*), with the smoke samples drawn through the bubblers while the aircraft circled in the plume. The 1975 measurements were made by a Thermo Electron Series 14D chemiluminescent NO_2 monitor, with the smoke samples collected in flight and analyzed on the ground. The clear air never contained more than 1 ppb NO_2.

The results given in Table I show that for the fuel-reduction burns of Western Australia, the ratio $NO_2/\Delta CO_2$ was between

---

[1] Division of Mineral Chemistry.

Table I. Analytical Results for Smokes from Western Australian Fuel-Reduction Burns. Samples Taken Deep Within Plume over Downwind Edge of Fire

Fire no.	Date	ΔCO_2, ppm	NO_2, ppb	b_s, m^{-1}	C_2H_4, ppb	C_3H_6, ppb
1	Dec. 6, 1972	16[a]	[b]	16×10^{-4}	[b]	[b]
2	Nov. 19, 1973	8	[b]	11×10^{-4}	[b]	[b]
3	Nov. 21, 1973	9	[b]	8×10^{-4}	[b]	[b]
4	Nov. 22, 1973	21	[b]	23×10^{-4}	[b]	[b]
5	Nov. 28, 1974	21	[b]	[b]	7	[b]
6	Dec. 6, 1974	21	14	[b]	10	$\simeq 5$
7	Dec. 2, 1974	22	14	19×10^{-4}	[b]	[b]
8	Dec. 3, 1974	12	8	[b]	10	$\simeq 2$
9	Dec. 6, 1974	12	9	[b]	5	$\simeq 2$
		52	50	[b]	43	10
10	Nov. 25, 1975	52	50	[b]	50	18
11	Nov. 26, 1975	36	20	[b]	24	5
12	Dec. 2, 1975	10	[b]	12×10^{-4}	5	2
13	Dec. 4, 1975[c]	16[c]	11[c]	13×10^{-4}[c]	8[c]	2[c]

[a] Derived from light scattering measurement. [b] No measurement made. [c] Sampled in the irradiated layer of the plume.

Table II. Analytical Results for Smokes from Variety of Burning Operations Other Than Western Australian Fuel-Reduction Burns. Samples Taken Deep Within Plume over Downwind Edge of Fire

Fire no.	Date	Location	Fuel type	ΔCO_2, ppm	NO_2, ppb	b_s, m^{-1}	C_2H_4, ppb	C_3H_6, ppb
14	March 16, 1973	Victoria	Clearing burn, dried windrows	85	[a]	10×10^{-4}	[a]	[a]
15	June 12, 1974	Darwin	Prescribed burn, 2-m grass	38	51	13×10^{-4}	[a]	[a]
16	June 18, 1974	Darwin	Wild fire, 2-m dry grass	67	106	17×10^{-4}	[a]	[a]
				33	51	8×10^{-4}	[a]	[a]
				37	40	16×10^{-4}	[a]	[a]
17	June 24, 1974	Darwin	Prescribed burn, swamp flats	49	56	26×10^{-4}	[a]	[a]
18	June 25, 1974	Darwin	Prescribed burn, swamp flats	51	67	[a]	[a]	[a]
				41	41	[a]	[a]	[a]
19	Dec. 3, 1975	Western Australia	Clearing burn, felled forest	132	52	157×10^{-4}	100	47
				61	20	122×10^{-4}	33	10
				122	48	[a]	[a]	[a]

[a] No measurement made.

0.6×10^{-3} and 1.0×10^{-3}. The ratio varied more widely for the burns described by Table II, and no systematic explanation can be given. On the whole, the ratio $NO_2/\Delta CO_2$ is comparable to the value of 2×10^{-3} which was obtained by Darley et al. *(6)* in the smoke obtained by burning fruit prunings in the Riverside burning tower.

It is noteworthy that we have never detected any nitric oxide in smoke.

Hydrocarbon Measurements. Although we recognized that the hydrocarbon content of smoke was undoubtedly complex, it seemed from the figures of Boubel et al. *(7)* on the olefin content of smoke, and from the 1970 measurements of carbon dioxide in smoke by Vines et al. *(1)* that the olefin content might well account for the majority of the ozone accumulation in sunlight. We therefore sought initially to measure only the C_2 to C_4 hydrocarbons.

The method was gas chromatography, by use of a 2-m column packed with Durapak/phenyl isocyanate Porasil C (Waters Associates, Framingham, Mass.). For such dilute smokes it was necessary to preconcentrate the olefins by adsorption at −140 °C onto Porapak Q (Waters Associates) followed by desorption at 120 °C onto the gas chromatograph. Because of the unexpectedly low density of smoke in 1974, the chosen preconcentration factor of 40 was unable to detect butenes but was sufficient to show that the ethylene/ΔCO_2 ratio was about 0.5×10^{-3}.

For 1975 the preconcentration factor was raised to 1000, raising the sensitivity of the method to 0.02 ppb for ethylene and 0.1 ppb for the butenes. Calibration with synthetic mixtures of hydrocarbons at the 15-ppb level established that the procedure was quantitative (to within a standard deviation of ±10%) for all C_2 to C_4 hydrocarbons with the exception of acetylene which, if left on Porapak Q for a few days is not recovered, probably because it polymerizes. Some tests in which the hydrocarbons were desorbed within minutes of adsorption showed that the concentration of acetylene in smoke was comparable to the concentration of ethylene.

The results, given in Table I, which are the average values of duplicate or triplicate preconcentrations from each smoke, established that for Western Australian fuel-reduction burns, the ethylene/ΔCO_2 ratio spanned the range 0.3×10^{-3} to 0.9×10^{-3}, and the ratio of propylene to ethylene was between 0.2 and 0.4. Butenes were always less than 10% of the ethylene and were deemed insignificant.

Samples of clear air taken in the vicinity of smoke plumes invariably contained less than 1 ppb of ethylene and less than 0.2 ppb of propylene.

Boubel et al. *(7)* found the ratio olefin/ΔCO_2 to be between 1×10^{-3} and 3×10^{-3}, depending on whether their fuel (grass) was dry or wet, respectively. In view of our very different fuels and different conditions of burning, their results are in remarkable agreement with ours.

Ultraviolet Radiation Measurements. Measurements of ultraviolet radiation were required for two purposes. First, measurements of ultraviolet flux within the smoke plume were required to test the hypothesis that the thickness of the ozone layer was limited by the failure of the ultraviolet to penetrate the plume. Secondly, when bags of smoke were irradiated on the ground, it was necessary to ensure that smoke haze, invisible to the eye, was not significantly reducing the sun's ultraviolet radiation.

Measurements were made in the wavelength band between 380 and 400 nm, by use of a suitably filtered photoconducting sensor (Clairex Electronics, Model 7 UV 20) modified to accept radiation from a solid angle of 0.5 steradians. The total ultraviolet flux was determined by adding the "direct flux" (obtained by pointing the sensor at the sun) to the "indirect flux" (obtained by pointing the sensor about 20° above the horizon and multiplying the measured signal by 4 π).

A particularly uniform plume was required to make meaningful measurements of ultraviolet intensity at a particular altitude in the plume. Fire 3 of 1973 provided such a plume, and the measurements, reported in Table III, were made at a level 600 m below plume top where b_s had the steady value of 26×10^{-4} m^{-1}, a value typical of fuel reduction burns during the peak of the fire. It is apparent that the total ultraviolet flux was reduced to about 5% of the value in clear sky.

Assuming Beer's law, the ultraviolet flux 300 m below plume top would be about 20% of the value in full sunlight. Such a reduction in ultraviolet radiation has been shown by Altshuller and Cohen (*8*) to dramatically reduce the rate of ozone generation; therefore, there is little doubt that the ozone is confined to the top few hundred meters of the plume because of the opacity of the plume to ultraviolet light.

Ozone Measurements. For ozone measurements in smoke plumes to be meaningful, the surrounding clear air must have a steady and reproducible concentration of ozone—a situation which is difficult to find in most countries because of the nearby sources of photochemical ozone. However, the clear skies of Australia are exceptional in this regard, particularly over the coastal area of Western Australia where the prevailing onshore wind has a fetch of some 6000 km over the Indian Ocean resulting in a steady background level, at the working altitude, of 28 ± 3 ppb, the level found by Galbally (*9*) in clear air elsewhere in Australia.

Prior to 1975, all ozone measurements were made with a Mast ozone sensor, Model 730-6, provided by Galbally (*9*) and calibrated by the Ehmert method. Since this instrument was prone to change sensitivity as the silver electrode aged, it was checked in clear air at 1700 m altitude. If it failed to read between 25 and 30 ppb ozone, the electrode was replaced.

In smoke there was a possibility of interference by SO_2. However, a number of spot checks showed that the passage of smoke through a CrO_3 oxidizer did not perceptibly alter the Mast reading; therefore, it was not thought necessary to use the CrO_3 oxidizer routinely. Not until 1975, when a Bendix ozone monitor (Model 8002) became available, did it become evident that while both instruments read correctly the concentration of ozone from a calibrated source, in smoke from Western Australian fuel-reduction burns the Mast sensor consistently read lower than the Bendix monitor by an amount roughly proportional to the concentration of the smoke, the error being minus 35 ppb ozone per 100 ppm ΔCO_2.

This error could be due to SO_2, since in the dilute smokes normally encountered, the error is small and could well have been overlooked by the spot checks with the CrO_3 oxidizer. There has been no opportunity to repeat these checks.

In concentrated smoke the error could be serious. For example, we reported earlier (*2*) that immediately above the fire the ozone concentration was less than the clear air value and was generally zero. It seems now that this apparently low reading was probably due to the interference of smoke with the Mast sensor. There is an obvious requirement to repeat this particular measurement with an airborne chemiluminescent ozone monitor.

On various flights, ozone concentrations higher than the ambient level of 28 ppb were detected at the top of the smoke plume, the concentration rising to a maximum some distance downwind, as described earlier (*2*).

The plumes from wild fires and clearing burns contained 50–150 ppm ΔCO_2 and generated the highest ozone concentrations. In the Darwin wild fire (No. 16, Table II) the Mast sensor recorded 85 ppb ozone. In the Victorian clearing burn (No. 14, Table II) it recorded 100 ppb ozone after 45 min irradiation and 200 ppb after a further 40 min irradiation in a bag (*2*). Similarly, a bag sample from Fire 19 (Table II) developed 104 ppb ozone when irradiated for 40 min (Table IV).

In the plumes from Western Australian fuel-reduction burns, the Mast sensor commonly recorded an ozone maximum of 60–75 ppb at a distance downwind of the fire corresponding to about 1 h irradiation in sunlight. The ΔCO_2 concentration of these plumes was around 20 ppm; therefore, the true ozone concentration, after correcting for smoke interference, may have reached 80 ppb. The results of three well-documented fires are given in Table V.

If the olefins in the smoke had been responsible for the observed ozone generation, there would have been a loss of olefin after irradiation. An estimate of this loss was made by sampling the smoke from Fire 13 at the point where the smoke had been irradiated for about an hour and the ozone had reached its peak value of 60 ppb (Table V). Neither the ethylene/ΔCO_2 ratio of 0.5×10^{-3} nor the propylene/ΔCO_2 ratio of 0.13×10^{-3} was significantly lower than the average values of these ratios in *unirradiated* smoke.

Although the maximum concentration of ozone was observed at the point downwind of the fire where the smoke had been sunlit for about an hour, one could not be certain whether this maximum was due to the completion of the photochemical reaction or to dilution of the smoke by entrainment of clear air.

To study the photochemical reaction unhindered by dilution, we took grab samples of unirradiated smoke, analyzed them for NO_2 and CO_2, and then exposed the bags to sunlight on the ground while monitoring the ozone concentration. To some bags additional NO_2 was added to simulate the behavior of smoke which entrained emissions of NO_2. The sunlight intensity during these experiments did not vary by more than 10% with respect to clear sunlight at 2 p.m.

The results given in Table IV show how the ozone levels rose with time, with no appreciable increase in the ozone concentration after 70 min irradiation. The maximum ozone levels were somewhat lower in the bags than in the free plume. For example, by interpolation of the data of Table IV, one would expect a bag sample containing 16 ppm ΔCO_2 to exhibit an ozone maximum between 30 and 45 ppb, whereas in a free plume of the same ΔCO_2 concentration, we found 60 ppb ozone (Fire 13, Table V).

Many factors may have contributed to this difference. In bag experiments the ultraviolet is attenuated 15% by the walls; also the walls absorb about 5% of the ozone formed during an experiment. But most important of all, there appears to be a loss of ozone during the transport of bags of smoke from the plume to the ground (about an hour). In the free plume there

Table III. Attenuation of Sun's Ultraviolet by 600 m of Smoke

	Ultraviolet flux, arbitrary units		
	Direct	Indirect	Total
Sunlight in clear air	66	34	100
Sunlight in smoke	1	4.5	5.5

Table IV. Results of "Bag" Irradiations of Smoke Sampled from Four Western Australian Fuel-Reduction Burns and One Clearing Burn

			Ozone, ppb		
Fire no.	ΔCO_2, ppm	NO_2, ppb	Before Irradiation	After 40 min irradiation	After 70 min irradiation
9	12	[a]	4	30	33
10	10	10	5	35	45
		50 (Spiked)	5	47	[a]
11	41	20	[a]	50	58
		60 (Spiked)	[a]	82	102
12	10	10	[a]	21	[a]
		50 (Spiked)	[a]	40	[a]
		90 (Spiked)	[a]	35	[a]
19	92	30	[a]	104	[a]

[a] No measurement made.

Table V. Ozone Concentration and Other Parameters of Plume at Point of Highest Ozone Concentration in Three West Australian Fuel-Reduction Burns

Fire no.	Date	Peak ozone, ppb	ΔCO_2, ppm	Wind speed, m s^{-1}	Distance downwind of fire, km
1	Dec. 6, 1972	65	16[a]	5	29
7	Dec. 2, 1974	75	22	4	15
13	Dec. 4, 1975	60	16	8	27

[a] Derived from light-scattering measurement.

is generally about 20 ppb ozone present even before irradiation, whereas by the time the bag samples have reached the ground the ozone concentration has fallen to 4 or 5 ppb (Table IV). If we allow for this difference in *initial* ozone concentration, the ozone actually generated during irradiation is much the same irrespective of whether irradiation is carried out in the plume or in bags. This suggests that bag irradiations are a reasonable simulation of the irradiation of the free plume.

Two conclusions follow from Table IV. First, the ozone maximum is reached in about 1 h, confirming that the photochemical reaction is complete within this period. Secondly, the ozone maximum can be increased 50% if the smoke is spiked with 50 ppb NO_2, although the evidence of Fire 12 (Table IV) suggests that greater amounts of NO_2 induce no further increase.

General Discussion

Fundamental Aspects. There is little doubt that the ozone which we have detected in smoke plumes originates from photochemical reactions. Unirradiated smoke generates no ozone, and measurements of ultraviolet flux in plumes show a good correlation between the depth of the elevated ozone layer and the effective depth of penetration of the ultraviolet radiation.

In light of our more accurate CO_2 measurements, it is now apparent that the initial plume from a fuel-reduction burn has only about 20 ppm ΔCO_2 and the corresponding olefin concentration averages only 16 ppb.

When this smoke is irradiated, the *increase* in ozone concentration is two to three times the concentration of olefins, whereas it is generally agreed (*10*) that the ozone generated is less than the initial olefin content, at least down to the 250-ppb level of olefin. Furthermore, the *rate* at which ozone accumulates in smoke is higher than one expects from the photooxidation of the dominant olefin, ethylene (*11*). Finally, irradiation of smoke for 1 h causes little, if any, depletion of the olefin content.

Thus, all the evidence suggests that unless the olefins are unexpectedly active at the low concentrations found in smoke, other photoreactive hydrocarbons must be present.

We are aware that terpenes may participate in the photochemical process—their rate of ozonolysis being 10–1000 times faster than the rate of ozonolysis of ethylene (*12*). Terpenes, if present in sufficient concentration in smoke, could therefore account for both the excessive ozone accumulation and the unusually high *rate* of accumulation. Preliminary calculations suggest that the terpene content of our fuels might be marginally sufficient to explain the discrepancy. The unsaturated aldehydes are also likely contenders, and we intend to study this aspect further.

Environmental Aspects. As for most pollutants, the environmental impact is largely dictated by the meteorological parameters which govern the rate of dispersion.

High-intensity burns for clearing purposes create formidable smoke plumes in which the ozone concentration can exceed 100 ppb, but these plumes, because of their strong convective activity, reach high altitudes where they are safely dispersed.

On the other hand, fuel-reduction burns are by no means as convective and are normally trapped beneath an inversion. Furthermore, the demands of the burning program are such that it is not always possible to choose days when the wind will blow the smoke away from smoke-sensitive areas. In the upper layer of such plumes the ozone level may exceed the USA Air Quality Standard of 80 ppb, but the important environmental question is whether fuel-reduction burning can give rise to objectionable concentrations of ozone *at ground level.*

Clearly, we are unable at this stage to predict the pollution potential of all plumes from fuel-reduction burns, but we can comment usefully on the behavior of a plume which we believe to be representative of the majority of fuel-reduction burns, i.e., a plume which has an initial ΔCO_2 concentration of about 20 ppm and drifts downwind at 4–8 m/s beneath an inversion at 2000 m above ground.

The dispersion of such a plume has been well documented by Vines et al. (*1*) in their study of the Busselton fire of December 16, 1970. Their data show that the plume reached the ground about 50 km downwind of the fire, at which point the core of the plume (some 7 km wide) was half the density of the plume at the downwind edge of the fire.

To estimate the ozone content of the plume at the point where the plume reaches the ground requires data regarding vertical mixing and ultraviolet intensity throughout the plume. These data are not available; nevertheless, an upper limit to the ozone at ground level may be set by assuming that the whole plume receives the full intensity of ultraviolet radiation, thus generating, at most, 80 ppb ozone throughout the full depth of the plume. This ozone-laden plume is subsequently diluted by an equal volume of clear air containing possibly 30 ppb ozone, yielding a resultant ozone concentration at the ground of, at most, 55 ppb—a figure safely below the Air Quality Standard.

It would therefore seem that under normal dispersion conditions, typified by the Busselton fire of 1970, the generation of ozone is not sufficient to warrant restrictions on fuel-reduction burning. Indeed it should be emphasized how misleading it is to judge the degree of pollution by the optical density of the haze. City hazes for which b_s is 4×10^{-4} m^{-1} may be 10 times as abundant in photoreactive gases as forest smoke of the same optical density.

During meterological episodes in which low-level inversions and light winds persist for several days, even the smoke from fuel-reduction burns can make an appreciable contribution to the pollution of an already overburdened urban atmosphere, particularly if the smoke entrains emissions of nitrogen oxides from other sources.

In this context, perhaps the most significant conclusion is that the photochemical reactions in smoke are essentially complete within an hour. Smokes which have drifted in sunlight for more than an hour present no pollution problem other than that due to the ozone and other irritants which have already developed and which can be readily measured at the point where the smoke enters the smoke-sensitive area.

Acknowledgment

We thank the West Australian Forests Department, the Victorian Forestry Commission, and the Forestry Branch of the Northern Territory Administration for the generous use of their facilities and their cooperation in the planning of this program.

Literature Cited

(1) Vines, R. G., Gibson, L., Hatch, A. B., King, N. K., MacArthur, D. A., Packham, D. R., Taylor, R. J., "On the Nature, Properties and Behaviour of Bush-fire Smoke", CSIRO Aust., Div. Appl. Chem., Tech. Paper No. 1, 1971.
(2) Evans, L. F., King, N. K., Packham, D. R., Stephens, E. T., *Environ. Sci. Technol.*, **8,** 75 (1974).
(3) Evans, L. F., King, N. K., MacArthur, D. A., Packham, D. R., Stephens, E. T., "Further Studies of the Nature of Bush-fire Smoke", CSIRO Aust., Div. Appl. Organic Chem., Tech. Paper No. 2, 1976.
(4) Ahlquist, N. C., Charlson, R. J., *J. Air Pollut. Control Assoc.*, **17,** 467 (1967).
(5) Saltzman, B. E., *Anal. Chem.*, **26,** 1949 (1954).
(6) Darley, E. F., Burleson, F. R., Mateer, E. J., Middleton, J. T., Osterli, V. P., *J. Air Pollut. Control Assoc.*, **11,** 685 (1966).
(7) Boubel, R. W., Darley, E. F., Schuck, E. A., *ibid.*, **19,** 497 (1969).
(8) Altshuller, A. P., Cohen, I. R., *Environ. Sci. Technol.*, **17,** 467 (1967).
(9) Galbally, I., "Ozone and Oxidants in the Surface Air near Melbourne, Victoria", Proc. Int. Clear Air Conf. Melbourne, 1972.
(10) Altshuller, A. P., Kopczynski, S. L., Lonneman, W. A., Becker, T. L., Slater, R., *Environ. Sci. Technol.*, **1,** 899 (1967).
(11) Altshuller, A. P., Bufalini, J. J., *ibid.*, **5,** 39 (1971).
(12) Grimsrud, E. P., Westberg, H. H., Rasmussen, R. A., *Int. J. Chem. Kinet., Symp. No. 1,* 183 (1975).

Received for review August 23, 1976. Accepted April 25, 1977.

Thermal Decomposition of Peroxyacetylnitrate in the Presence of Nitric Oxide

Richard A. Cox* and Michael J. Roffey

Environmental and Medical Sciences Division, Atomic Energy Research Establishment, Harwell, Oxfordshire, UK

■ The thermal reactions occurring in mixtures containing peroxyacetylnitrate and nitric oxide at part-per-million concentrations in synthetic air are investigated. In the presence of NO, peroxyacetylnitrate decomposes at a measurable rate at room temperature, with accompanying oxidation of NO to NO_2. The results can be explained by a mechanism involving the following reactions: $CH_3COO_2NO_2 = CH_3COO_2 + NO_2$ (1), $CH_3COO_2 + NO_2 = CH_2COO_2NO_2$ (2), and $CH_3COO_2 + NO = CH_3CO_2 + NO_2$ (3). The effect of variation of the NO/NO_2 ratio and the temperature on the rate of oxidation of NO to NO_2 allows evaluation of the rate constant ratio $k_2/k_3 = 0.54 \pm 0.17$ and the Arrhenius expression $k_1 = 10^{14.90 \pm 0.60} \exp(-104.0 \pm 3.2 \text{ kJ/RT}) \text{ s}^{-1}$. Thermochemical kinetic considerations give an approximate value for the heat of formation of peroxyacetyl nitrate, $\Delta H_f°$ ($CH_3COO_2NO_2$ = -241 ± 40 kJ mol^{-1} and for the absolute value of the rate constant $k_2 = 1.4 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at 300 K. The implications of these results for the behavior of peroxyacetylnitrate in the laboratory and in the atmosphere are discussed.

Early chemical studies of photochemical smog revealed that a previously unknown compound, peroxyacetylnitrate (PAN) was produced when part-per-million concentrations of certain hydrocarbons were irradiated with UV light in the presence of air containing traces of nitrogen oxides (*1*). Subsequent studies (*2, 3*) showed that PAN is formed from the reaction of peroxyacetyl radicals with NO_2,

$$CH_3COO_2 + NO_2 = CH_3COO_2NO_2 \qquad (2)$$

the main precursor for these radicals in the atmosphere being acetaldehyde. The sink processes by which PAN is removed from the atmosphere are not well known, although dry deposition at the ground or on vegetation (*4, 5*) and also reaction with nitric oxide (*6*) have been suggested as being important. Clearly, any new information regarding the chemical behavior of PAN in the atmospheric environment is of interest.

We recently reported a kinetic study of PAN formation in the flow system photolysis of gaseous nitrous acid–acetaldehyde–air mixtures (*3*). Hydroxyl radicals were produced by photolysis of HONO, and these led to the production of acetyl peroxy radicals from acetaldehyde:

$$OH + CH_3CHO = H_2O + CH_3CO \xrightarrow{O_2} CH_3COO_2 \qquad (4)$$

Competition between Reaction 2 leading to PAN formation and the reaction of CH_3COO_2 radicals with NO was observed with $k_3/k_2 \simeq 1.7$:

$$CH_3COO_2 + NO = CH_3CO_2 + NO_2 \qquad (3)$$

During the course of this study when HONO–CH_3CHO–air mixtures were irradiated for long periods in a static system, so that a relatively large amount of PAN was present in the system, thermal oxidation of NO to NO_2 occurred when photolysis was stopped. Although there was no measurable decay of PAN, the presence of this product was responsible for the NO oxidation in the dark. The initial rate of the dark oxidation of NO in the photolyzed mixtures was best described by a process zero-order in NO and first order in PAN concentration. Schuck et al. (*6*) reported similar observations in mixtures containing PAN and NO diluted in N_2, and they also observed decay of PAN during the oxidation of NO. At least 2 mol of NO were oxidized per mole of PAN decomposed. Although Schuck et al. (*6*) did not invoke a radical mechanism, the most plausible explanation would seem to be thermal decomposition of PAN to form radical species which are capable of oxidizing NO to NO_2. Stephens et al. (*7*) observed thermal decomposition of gaseous PAN held at approximately 323 K for several hours, but at room temperature it was apparently stable for days.

The absence of any significant decay of PAN in our experiments could be explained if the radicals reacted to form ultimately OH radicals, which could react with the acetaldehyde present, thereby leading to the production of more PAN. Clearly, this hypothesis needed to be tested, and the nature and rate of the thermal decomposition reaction of PAN established. In the present study a detailed investigation was made of the thermal reactions occurring in PAN–nitric oxide–air mixtures at temperatures between 286 and 323 K. The results allowed evaluation of the Arrhenius parameters for the thermal decomposition of PAN, elucidation of the decomposition mechanism, and an unambiguous determination of the relative rate constants for the reactions of CH_3COO_2 radicals with NO and NO_2. Since the completion of this study, Pate et al. (*8*) reported a room temperature study of the thermal decomposition of PAN in the presence of NO and other gases. Their results and conclusions are in excellent agreement with our own.

Experimental

Mixtures containing PAN diluted in synthetic air (20% O_2, 80% N_2) were prepared and stored in a 200-L bag constructed of Tedlar (Du Pont) film which could be irradiated by two banks of 10 × 20 W fluorescent UV lights (Philips L20/05) to effect the photochemical synthesis of PAN in situ. Synthesis was via the Cl_2 photosensitized reaction between acetaldehyde and nitrogen dioxide, diluted in synthetic air.

$$\tfrac{1}{2}Cl_2 + CH_3CHO + NO_2 + O_2 \rightarrow CH_3COO_2NO_2 + HCl$$

Gay et al. (*9*) reported a 95% yield of PAN from the photolysis of part-per-million concentrations of CH_3CHO, NO_2, and Cl_2 in the ratio 2:2:1, with only traces of side products such as CO, HCO_2H, HNO_3, and CH_2O. We obtained slightly lower yields (approximately 80% based on the amount of aldehyde taken), but after 60 min of irradiation, at least 90% of the NO_x (i.e., total gas-phase nitrogen compounds) present in the 200-L bag was PAN, the remainder being NO_2, traces of methyl nitrate, and probably $HONO_2$. Ozone was also formed during the photolysis and was subsequently removed by adding an equivalent amount of NO or by allowing the mixture to stand overnight, when most of the ozone was removed by surface destruction. Mixtures containing 1–5 ppm PAN, prepared in this way, were apparently quite stable, decaying at a rate of only a few percent per day.

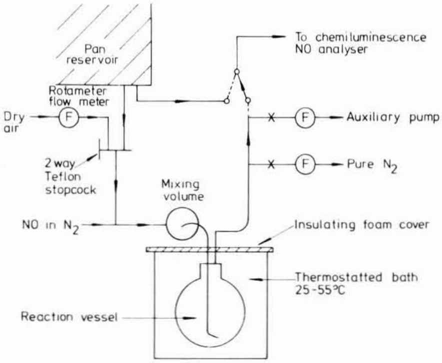


Figure 1. Schematic diagram of flow apparatus for measurement of thermal oxidation of nitric oxide in presence of PAN

The decomposition of PAN in the presence of nitric oxide was studied both in a static system and in a flow system. In the static system the required concentration of nitric oxide was simply metered into the bag containing a dilute PAN mixture while the bag was kneaded vigorously to assist mixing. The total time for NO addition and mixing was 2–4 min, and the changes in the concentrations of NO, NO_2, and PAN could then be followed for an hour or more. The static experiments were conducted at room temperature (295–298 K).

The temperature dependence of the oxidation of nitric oxide in the presence of PAN was investigated in a flow system illustrated in Figure 1. The reaction vessel was a spherical borosilicate glass flask, effective volume 140 mL, immersed in a thermostated water bath. Gas mixtures were withdrawn from the PAN reservoir through a mixing vessel (50 mL) and then through the thermostated reaction vessel by using the pumping system in the NO_x chemiluminescence analyzer. Nitric oxide was added upstream from the mixing vessel which was at room temperature. The flow rate through the reaction vessel was measured at room temperature and pressure, upstream from the vessel, and could be adjusted up or down by using an auxiliary pump or by metering pure N_2 into the gas stream at the reaction vessel outlet. The flow system was similar in principle to that used previously for photolysis experiments (*10*). Reaction times were calculated from the effective volumetric flow rate at the appropriate temperature. The vessel contents were assumed to be well mixed and at the same temperature as the bath so that reaction rates could be calculated from the stirred-flow reactor formula:

$$-\frac{dC}{dt} = \frac{F}{V} \times \Delta C$$

where $\Delta C = C_{\text{inlet}} - C_{\text{outlet}}$. The amount of reaction occurring in the mixing vessel at room temperature was negligible. In these experiments low conversions (a few percent or less) were used, and only the removal rates of nitric oxide could be determined with sufficient accuracy. To determine ΔC for NO, a constant flow of dry air with the required flow of NO was set up through the reaction vessel to the chemiluminescence analyzer. The dry air flow was then replaced by gas from the PAN reservoir, and the observed change in NO concentration, ΔC, recorded. All sampling and flow lines were of ⅛-in. o.d. PTFE to minimize adsorption of PAN and nitrogen oxides.

The techniques for the analysis of nitrogen oxides, etc., including PAN, by use of a commercial NO–ozone chemiluminescence analyzer (TECO Model 12A) were previously described in detail (*3, 10, 11*). PAN was selectively removed from gas streams with near 100% efficiency, by use of 0.05 M aqueous NaOH, allowing it to be measured in the presence of NO and NO_2. A small correction was made for the apparent loss of NO_2 in the NaOH (*11*). The analyzer was calibrated daily with a standard mixture of NO (113 ± 5 ppm) in N_2. PAN and methyl nitrate were also analyzed by gas chromatography with electron capture detection, as described previously (*3*). The peak height response to PAN was determined with mixtures containing a constant concentration of PAN as determined by chemiluminescence. Methyl nitrate was not measured quantitatively in this work; it was always a very minor fraction of the total NO_x present.

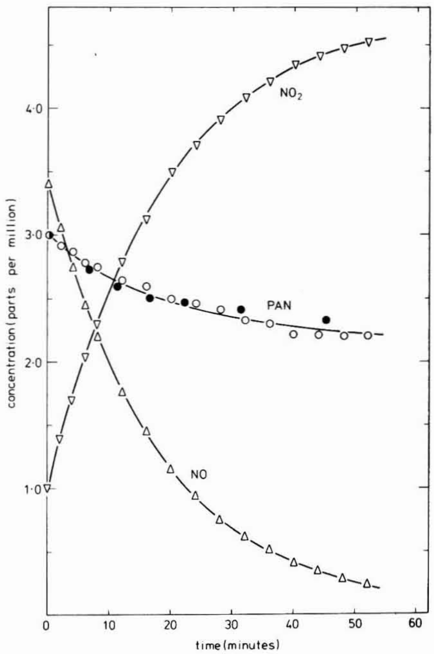


Figure 2. Concentration–time curves following addition of 3.5 ppm NO (Δ) to mixture containing 3.0 ppm PAN (O) and 1.0 ppm NO_2 (∇) in 1 atm $N_2 + O_2$ at 23 °C

Filled points show PAN concentration as determined by gas chromatographic analysis; open points by chemiluminescence

Acetaldehyde and chlorine were commercial products (B.D.H. Ltd., CP grade). Nitrogen dioxide was prepared as required by the addition of excess O_2 to a measured quantity of pure nitric oxide in a glass cell. Nitrogen (high purity) and oxygen (breathing grade) were taken directly from cylinders (B.O.C. Ltd.)

Results

Static System. Figure 2 shows concentration vs. time curves for PAN, NO, and NO_2 following the addition of NO (3.5 ppm) to a mixture containing PAN (3.0 ppm) in $N_2 + O_2$ at 296 K. The NO was quite rapidly oxidized to NO_2, the reaction continuing until nearly all the NO had been removed after about 60 min. The PAN concentration also declined at a rate approximately proportional to the rate of NO oxidation, with a mean value of Δ_{NO}/Δ_{PAN} for successive 5-min reaction steps of 4.9 ± 1.7, based on the chemiluminescence measurements of PAN. This compares well with the overall value of $\Delta_{NO}/\Delta_{PAN} = 4.35$, determined by the gas chromatographic measurements for PAN. Prior and subsequent to the addition of NO, the PAN concentration in this mixture remained constant for several hours, to within the reproducibility of the gas chromatographic analysis (i.e., ±3%).

The PAN–NO reaction was also examined in the presence of acetaldehyde in an attempt to simulate the reaction conditions in the photolysis of nitrous acid–acetaldehyde mixtures, when thermal oxidation of NO occurred without apparent loss of PAN. Figure 3 shows the effect of 10 ppm CH_3CHO on the decay of PAN and NO following two successive additions of NO. Both experiments exhibited only a very slight decline in PAN concentration in contrast to the behavior with no added CH_3CHO (Figure 2).

Flow System. Rate measurements in the flow system were made at temperatures in the range 286–328 K, constant to 0.1 K. At each temperature the change in NO concentration, ΔC, was measured for different reactor residence times at a constant initial NO concentration and also at constant residence time with varying amounts of added NO.

The effect of residence time, t, on ΔC in selected experiments with different PAN concentrations and temperatures is illustrated in Figure 4. These data were obtained with fixed NO concentrations of approximately 1 or 2 ppm. ΔC increased linearly with t up to at least 12 s but showed a positive intercept at $t = 0$. This intercept was independent of NO concentration, showed no systematic variation with temperature, but varied somewhat for different PAN mixtures. Some mixtures contained a small amount of ozone (as measured by chemiluminescence with ethylene), and this would be expected to lead to rapid removal of NO on the short time scale involved. In practice, $\Delta C_{t=0}$ was determined experimentally for each temperature and each PAN mixture, and was subtracted from the observed ΔC values to determine the nitric oxide reaction rate. At each temperature the nitric oxide removal rate was determined at constant residence time with different initial NO concentrations, so that the effect of varying the ratio $[NO]/[NO_2]$ over a wide range could be established. As the ratio $[NO]/[NO_2]$ increased, the rate of nitric oxide oxidation also increased but approached a constant value at values of the ratio above about 5.

At 286 K no measurable reaction of NO was observed. At temperatures below 303 K, the observed ΔC values were of the same magnitude as the $\Delta C_{t=0}$ values over the accessible time scale in the flow reactor, which precluded accurate measurements of the rate of NO oxidation as a function of [NO]. The results for the NO dependence at the higher temperatures are summarized in Table I together with data for a single NO concentration at the lower temperatures. At each temperature the rate measurements were quite reproducible and showed no erratic behavior which might be expected if heterogeneous reactions were occurring. As will be shown later in the kinetic analysis (Table II), the NO oxidation rate in the static system

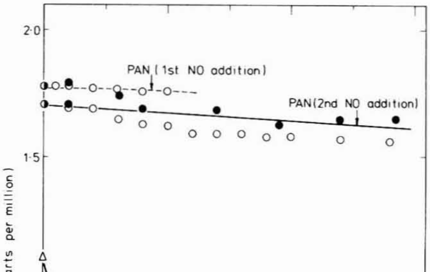


Figure 3. Concentration–time curves following two successive additions of NO to mixture containing PAN in presence of 10 ppm CH_3CHO in 1 atm $N_2 + O_2$

Filled points show PAN concentration as determined by gas chromatography; open points by chemiluminescence; $T = 25$ °C

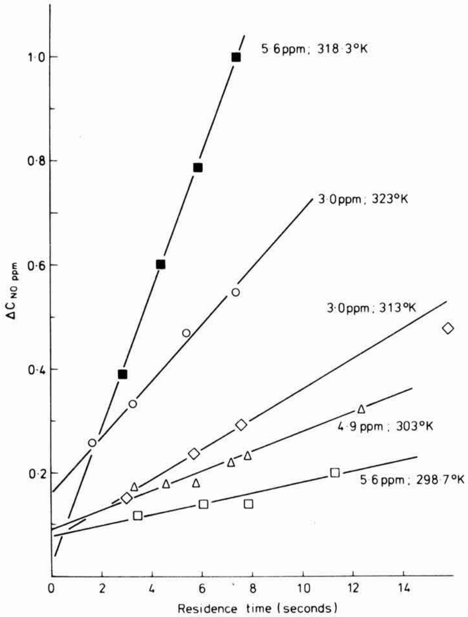


Figure 4. Effect of reactor residence time on change in NO concentration in thermal reaction of PAN + NO mixtures

Initial PAN concentrations (in ppm) and temperature (in K) given on graph. Initial NO concentrations: □, ■, △ = 2.2 ppm. ○, ◇ = 1.1 ppm

was consistent with that in the flow system within the experimental error, despite the markedly different nature of the reactor surfaces.

Kinetic Analysis of Results

The oxidation of NO to NO_2 in the presence of PAN and its dependence on the ratio $[NO]/[NO_2]$ can be best explained if PAN exists in reversible equilibrium with its precursor species, i.e., the acetylperoxy radical and nitrogen dioxide:

$$CH_3COO_2NO_2 \underset{k_2}{\overset{k_1}{\rightleftarrows}} CH_3COO_2 + NO_2 \qquad (1, 2)$$

In the presence of NO, Reaction 3 can compete with Reaction 2, as

$$CH_3COO_2 + NO \rightarrow NO_2 + CH_3CO_2 \qquad (3)$$

was shown in our previous study of the photolysis of nitrous acid in the presence of acetaldehyde (*3*). From this study it was also concluded that degradation of the acetoxy radical produced in Reaction 3 occurred by the following reactions:

$$CH_3CO_2 \rightarrow CH_3 + CO_2 \qquad (5)$$

$$CH_3 + O_2 (+ M) \rightarrow CH_3O_2 \qquad (6)$$

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2 \qquad (7)$$

$$CH_3O + O_2 \rightarrow CH_2O + HO_2 \qquad (8)$$

$$HO_2 + NO \rightarrow OH + NO_2 \qquad (9)$$

The hydroxyl radical produced ultimately from this sequence can react either with NO, NO_2, or with acetaldehyde, if present:

$$OH + NO (+M) \rightarrow HONO \qquad (10)$$

$$OH + NO_2 (+M) \rightarrow HONO_2 \qquad (11)$$

$$OH + CH_3CHO \rightarrow H_2O + CH_3CO \xrightarrow{O_2} CH_3COO_2 \qquad (4)$$

Table I. Rate Data for Thermal Oxidation of NO in Presence of PAN

Temp, K	$[NO]/[NO_2]$ [a]	$-dNO/dt$, ppm $s^{-1} \times 10^2$
328.0	0.085	6.9
PAN = 5.61 ppm	0.183	15.1
NO_2 = 1.06 ppm	0.253	19.1
t = 2.75 s [b]	0.505	29.4
$\Delta C_{t=0}$ = 0.15 ppm [c]	0.813	32.2
	1.59	34.9
323.0	0.22	5.14
PAN = 3.05	0.35	6.97
NO_2 = 1.02	0.60	9.30
t = 7.3 s	1.31	11.97
$\Delta C_{t=0}$ = 0.17	2.08	12.57
318.3	0.171	6.21
PAN = 5.61	0.303	9.03
NO_2 = 1.07	0.571	12.30
t = 5.8 s	1.49	14.0
$\Delta C_{t=0}$ = 0.07	3.45	15.4
313.0	0.64	3.33
PAN = 3.40	1.16	4.27
NO_2 = 0.85	1.68	4.86
t = 5.6 s	3.33	5.35
$\Delta C_{t=0}$ = 0.04		
308.3	0.351	1.99
PAN = 5.61	0.584	3.43
NO_2 = 1.09	1.076	3.94
t = 6.0 s	2.11	3.99
$\Delta C_{t=0}$ = 0.11	3.50	3.38
303.0	0.373	0.77
PAN = 4.95	0.653	1.35
NO_2 = 0.87	1.03	1.97
t = 6.5 s	2.10	1.98
$\Delta C_{t=0}$ = 0.092	4.63	1.56
298.7	2.72	1.13
PAN = 5.61		
NO_2 = 1.09		
t = 6 s		
$\Delta C_{t=0}$ = 0.10		
294.0	2.09	0.83
PAN = 7.31		
NO_2 = 0.94		
t = 17 s		
$\Delta C_{t=0}$ = 0.10		

[a] Mean ratio $[NO]/[NO_2]$ in the stirred flow reactor. [b] t = reactor residence time. [c] $\Delta C_{t=0}$ = change in NO concentration by extrapolation to t = 0; see Figure 4.

Note that Reaction 4 produces acetylperoxy radicals again, which can reform PAN in Reaction 2. Thus, in the presence of acetaldehyde, oxidation of NO to NO_2 by Reaction 3 and subsequent reactions can occur without any apparent loss of PAN, as observed experimentally. In the absence of acetaldehyde, OH radicals will be removed by Reactions 10 and 11 which terminate the radical chain; therefore, PAN will decompose at a rate equal to the rate of Reaction 3. The maximum number of NO molecules reacted for each occurrence of Reaction 3 is 4, i.e., $\Delta_{NO} = 4\ \Delta_{PAN}$ according to this scheme.

The experimental value for this stoichiometric relationship (between 4 and 5) is slightly higher than expected; this may be due to the presence of some residual acetaldehyde from the PAN synthesis, which would lead to low values for Δ_{PAN}.

For quantitative analysis we apply the steady-state approximation to the CH_3COO_2 radical, which we assume to be produced only by Reaction 1 in the absence of acetaldehyde (Equation i).

$$[CH_3COO_2] = \frac{k_1 [PAN]}{k_2[NO_2] + k_3[NO]} \qquad \text{(i)}$$

The rate of oxidation of NO is given by:

$$-\frac{d[NO]}{dt} = \alpha k_3[NO][CH_3COO_2] \qquad \text{(ii)}$$

where α is the total number of NO molecules oxidized following Reaction 3. Substitution of Equation i in ii and rearrangement gives:

$$\frac{[PAN]}{\dfrac{d[NO]}{dt}} = \frac{1}{\alpha k_1}\left\{1 + \frac{k_2}{k_3}\frac{[NO_2]}{[NO]}\right\} \qquad \text{(iii)}$$

Thus, if α is constant, a plot of $[PAN]/(d[NO]/dt)$ vs. $[NO_2]/[NO]$ should be linear. The quantity αk_1 can be determined from the intercept, and the rate constant ratio k_2/k_3 from the slope to intercept ratio. Figure 5 shows the data from Table I, plotted according to Equation iii. The data showed a linear relationship at all temperatures. A linear relationship over a wide range of $[NO_2]/[NO]$ ratios was also obtained for the data from the static experiment without added acetaldehyde, which are also plotted in Figure 5. In the presence of acetaldehyde, Reaction 1 is not the only source of CH_3COO_2 radicals; therefore, Equation iii does not apply. A summary of the values of k_1 and k_2/k_3, determined by least-squares regression analysis for the slopes and intercepts, is given in Table II.

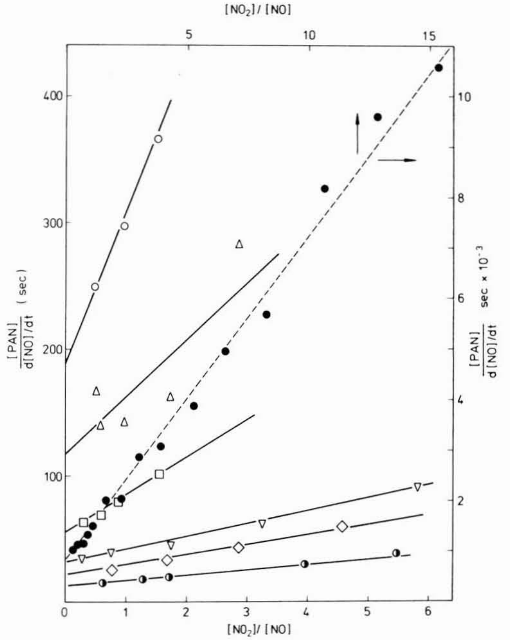


Figure 5. Plot of quantity $[PAN]/(d[NO]/dt)$ vs. $[NO_2]/[NO]$ at different temperatures

◑ = 328 K, ◇ = 323 K, ▽ = 318.3 K, □ = 313 K, △ = 308.3 K, ○ = 303 K, ● = 296 K (from static experiment)

Table II. Slopes and Intercepts from Plots of PAN/(d[NO]/dt) vs. [NO$_2$]/[NO]

Temp, K	Slope, s	Intercept I, s	αk_1 s^{-1} ($\times 10^2$)	k_2/k_3 (= slope/I)
328.0	5.96 ± 0.38	8.88 ± 2.1	11.3 ± 2.7	0.671
323.0	9.0 ± 0.17	18.2 ± 0.5	5.49 ± 0.15	0.494
318.3	10.0 ± 0.8	30.6 ± 4.0	3.26 ± 0.42	0.328
313.0	31.0 ± 1.5	53.1 ± 1.4	1.88 ± 0.05	0.583
308.3	48.4 ± 16.7	118.6 ± 26	0.84 ± 0.18	0.408
303.0	149 ± 44	191 ± 64	0.52 ± 0.17	0.780
298.7[a]	. . .	. . .	0.24 ± 0.12	. . .
296.0[b]	654 ± 17	763 ± 112	0.13 ± 0.02	0.857
294.0[a]	. . .	. . .	0.14 ± 0.10	. . .

[a] $[NO_2]/[NO]$ dependence insufficiently well defined for analysis by Equation iii; k_1 calculated from observed rates at NO/NO_2 ratio given in Table I, and assuming $k_2/k_3 = 0.6$. [b] Static experiment.

The quantity αk_1, as determined from the intercepts, increased rapidly with temperature. An Arrhenius plot of this data is shown in Figure 6, from which the slope and intercept were determined by least-squares regression. Assuming $\alpha = 4.9 \pm 1.7$, we obtain the following Arrhenius expression for the effective first order rate constant for decomposition of PAN in air at 1 atm pressure:

$$k_1 = 10^{14.90 \pm 0.60} \exp\,(-104\;000 \pm 3\;200\; J/RT)\; s^{-1}$$

(error limits are σ the standard deviation). The ratio k_2/k_3 determined from the slope/intercept ratio showed considerable scatter but did not exhibit any significant trend with temperature. The mean value of $k_2/k_3 \simeq 0.54 \pm 0.17$ compares very favorably with the value for this ratio obtained from the photolysis of nitrous acid in the presence of acetaldehyde (*3*), $k_2/k_3 = 0.59$.

Discussion

Thermochemistry and Kinetics of PAN Decomposition. The measured Arrhenius parameters for Reaction 1 are entirely reasonable for the homogeneous gas-phase decomposition of a large molecule into two smaller free radical fragments. If we take into account the uncertainty in the stoichiometry factor α, the preexponential factor A_1 is clearly close to $10^{15}\ s^{-1}$, which compares well with the following values reported for the similar decomposition reactions of nitrogen pentoxide (*12*) and methyl nitrite (*13*):

$$N_2O_5 \rightarrow NO_3 + NO_2 \quad A = 10^{14.76}\ s^{-1};\ E = 88.1\ kJ\ mol^{-1}$$

$$CH_3ONO \rightarrow CH_3O + NO \quad A = 10^{15.8}\ s^{-1};\ E = 172.2\ kJ\ mol^{-1}$$

At pressures near 1 atm, the rate constants for decomposition of both N_2O_5 (*14*) and CH_3ONO (*13*) are approaching their high-pressure limiting values. Since PAN is a more complex molecule than these, its "fall-off" behavior, i.e., the transition from 1 to 2 order decomposition kinetics is likely to occur at lower pressures than for N_2O_5 or CH_3ONO. It seems reasonable to assume, therefore, that the measured values of A_1 and E_1 from the present study refer to the unimolecular decomposition of PAN near the high-pressure limit, when the rate constant is independent of pressure.

The A factors for all three decompositions considered here are somewhat higher than normal for unimolecular reactions, i.e., 10^{13} to $10^{14}\ s^{-1}$. This is often found, however, for decompositions in which a single bond breaks to form two polyatomic radical fragments; it is believed to reflect the increase in en-

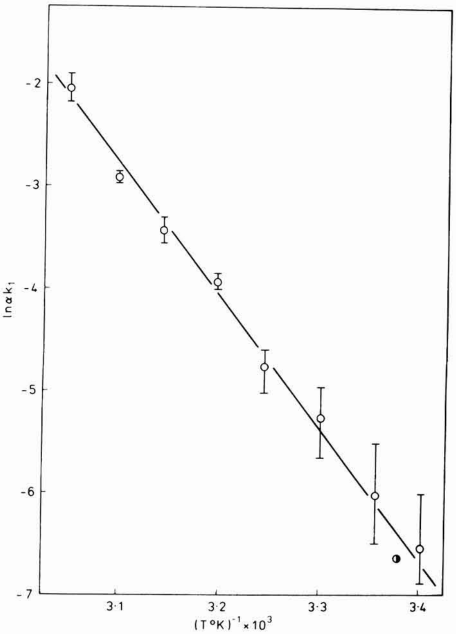


Figure 6. Plot of ln α k_1 (from Table II) vs. $1/T$ (K)
Open circles = flow system results; filled circle = static system result

tropy associated with the formation of an activated complex in which free rotation about the breaking bond can occur (*15*).

The activation energy for decomposition of PAN lies between that for N_2O_5 and CH_3ONO, and the low value reflects the weakness of the $O—NO_2$ bond in this peroxy compound. By analogy with other radical–radical combination reactions, we expect little or no activation energy for the reverse reaction (Reaction 2). The value of E_1 may therefore be equated with the enthalpy change for Reaction 1 at temperatures near 300 K and to within the experimental error, this is equal to the standard enthalpy change $\Delta H°_1 = 104.0 \pm 3.2$ kJ mol^{-1}. Experimental values for the standard heats of formation are not available, either for PAN or the acetylperoxy radical. However, $\Delta H°_f$ (CH_3COO_2) may be estimated with an uncertainty of between ±20 and ±40 kJ mol^{-1}, if it assumed that the dissociation enthalpy for peracetic acid, D ($CH_3CO_3 - H$) $\simeq D$ ($H - O_2H$) = 376 kJ mol^{-1}, and using group additivity rules (*16*) to calculate the heat of formation of peracetic acid, $\Delta H°_f$ (CH_3CO_3H) = −329 kJ mol^{-1}. Thus $\Delta H°_f$ (CH_3COO_2) = D ($CH_3CO_3 - H$) + $\Delta H°_f$ (CH_3CO_3H) − $\Delta H°_f$(H) = −171.1 kJ mol^{-1}. The experimental value of $\Delta H°_1$ can now be used to calculate the heat of formation of PAN:

$$\Delta H°_f\,(CH_3COO_2NO_2) = \Delta H°_f\,(CH_3COO_2) + \Delta H°_f\,(NO_2) - \Delta H°_1 = -241.2 \text{ kJ mol}^{-1}$$

The uncertainty in this quantity ($\leq \pm 40$ kJ mol^{-1}) comes mainly from the uncertainty in the estimation of $\Delta H°_f$ (CH_3COO_2), since the activation E_2 is unlikely to be more than a few kJ mol^{-1}. Our experimental value is in good agreement with the value of $\Delta H°_f$ ($CH_3COO_2NO_2$) = 238.3 kJ mol^{-1} calculated by Domalski (*17*) using bond additivity rules.

The preexponential factor A_2 may be estimated from the experimental value of A_1, if the standard entropy change for Reaction 1 can be evaluated:

$$\log \frac{A_1}{A_2} = \frac{\Delta S°_c}{2.303\,R}$$

$\Delta S°_c$ refers to a standard state of 1 mol L^{-1} and is related to the normal thermodynamic value (standard state = 1 atm, 298 K) by

$$\Delta S°_c = \Delta S° - \Delta nR\,[\ln (0.0821\,T)]$$

The standard entropies of PAN and CH_3COO_2 at 298 K have not been determined experimentally but can be estimated using the group additivity constants given by Benson (*15*). We obtain $S°$ ($CH_3COO_2NO_2$) = 431 J mol^{-1} K^{-1} and $S°$ (CH_3COO_2) = 332.3 J mol^{-1} K^{-1} (using peracetic acid as a model) which, together with the standard entropy of NO_2 (239.5 J mol^{-1} K) gives $\Delta S°_c = 114.1$ J mol^{-1} K^{-1}. The estimated uncertainty in $\Delta S°_c$ is not more than ± 20 J mol^{-1} K^{-1}, giving $\log_{10} A_2 = -11.8 \pm 1.2$ cm^3 molecule^{-1} s^{-1}. If E_2 is zero, this may be equated with k_2, i.e., $k_2 = 1.4 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, with an uncertainty of + or − a factor of 10. Although of rather limited accuracy, this provides the first experimentally based estimate of the absolute rate constant for this important peroxy radical reaction. Using the experimental value of the ratio k_2/k_3, we also obtain $k_3 = 2.7 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. These values are consistent with the emerging picture of rather rapid reactions of peroxy radicals with atoms, radicals, and radical-like species, in contrast to the addition and H- abstraction reactions of HO_2 and RO_2, which tend to be rather slow at ambient temperatures.

Removal of PAN in Lower Atmosphere

Due to the rapid rates of Reactions 2 and 3, clearly in the atmosphere as well as in the laboratory, the fate of acetylperoxy radicals will depend only on the relative concentrations of the nitrogen oxides NO and NO_2. At 25 °C the rate constant for decomposition of PAN to CH_3COO_2 radicals is 4.5×10^{-4} s^{-1}; if all these radicals were removed, for example, by reaction with NO, PAN would decompose with a half-life of 26 min at this temperature. However, since NO_2 is normally the dominant oxide of nitrogen present in the atmosphere, decomposition of PAN will be slower than this. The actual rate at which PAN is destroyed is given as a function of the temperature (inasmuch as it affects k_1), and the ratio [NO]/[NO_2] by the following expression:

$$-\frac{d}{dt} \ln\,[\text{PAN}] = k_1 \left\{1 - \frac{1}{1 + (k_3[\text{NO}]/k_2[\text{NO}_2])}\right\} \quad \text{(iv)}$$

Table III shows the half-life of PAN for four typical atmospheric regimes, i.e., rural and urban air during daytime and nighttime, calculated according to Equation iv.

Firstly, during nighttime in unpolluted rural air, when nitric oxide is completely removed by reaction with excess ozone, thermal decomposition does not provide a net sink for PAN. In urban areas during nighttime, particularly in stagnant air, the emission of nitric oxide from combustion sources may exceed the supply of ozone needed to oxidize all of the NO to NO_2. Under these conditions the ratio [NO]/[NO_2] can exceed unity, and the removal of PAN by thermal decomposition will

Table III. Lifetimes of PAN with Respect to Thermal Decomposition for Various Atmospheric Regimes

	Day, 25 °C	Night, 15 °C
Urban	2.7[a]	2.8
	(0.1)	(1.0)
Rural	0.7	∞
	(0.32)	(0)

[a] Lifetime in hours as calculated from Equation iv. Figures in parentheses show corresponding [NO]/[NO_2] ratios.

be limited primarily by the air temperature. At 15 °C a minimum half-life of approximately 2.5 h is predicted.

In daylight, NO is always present in atmospheres containing NO_2, due to photodissociation of NO_2:

$$NO_2 + h\nu(\lambda < 400\ \text{nm}) = NO + O(^3P)$$

The concentrations of NO, NO_2, and ozone which coexist are given by the photostationary state equation (Reaction 1):

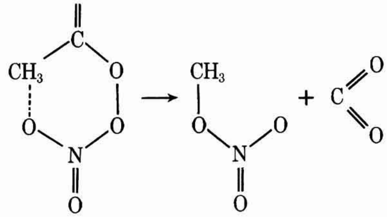
$$\frac{[NO][O_3]}{[NO_2]} = 16\ \text{ppb (at 298 K and solar zenith angle of 45°)}$$

The daytime $[NO]/[NO_2]$ concentration ratios given in Table III were calculated for urban and rural situations using ozone concentrations of 160 and 50 ppb, respectively. The corresponding half-lives at 25 °C for PAN show that thermal decomposition provides a significant sink during daylight hours in both rural and urban situations at this temperature. At 15 °C the PAN removal rate is a factor of four slower than at 25 °C.

It is of interest to compare the magnitude of this thermal sink with estimates of the ground destruction rate of PAN based on the deposition velocity measurements of Garland and Penkett (*5*). For grass and soil surfaces they found a deposition velocity of 0.25 cm s^{-1}. With an effective mixing height of the polluted layer of 1000 m, which would be a typical average daytime value, this gives an effective half-life for removal of PAN of 77 h, much slower than the gas-phase removal. At nighttime, however, there is normally no effective gas-phase sink; furthermore, atmospheric mixing may be limited to a few tens or hundreds of meters, giving rise to a larger effective sink at the ground. The presence of a daytime source (and sink) for PAN in the surface atmosphere and a nighttime sink at the ground provides a satisfactory explanation of the diurnal variations observed for PAN in rural air (*5*). When pollution emissions of nitric oxide exceed the ozone available for conversion to NO_2 (in large cities), the thermal gas-phase sink may dominate even during the nighttime. However, both the gas-phase and the surface sinks for PAN are much weaker than for ozone, which accounts for the comparatively frequent overnight persistence of PAN in urban air (*18*).

Decomposition of PAN on Storage

Samples of PAN for calibration of air pollution instrumentation are normally stored as dilute gaseous mixtures in compressed nitrogen. Stored at approximately 285 K these mixtures are quite stable, with slow decomposition occurring only over a period of months (*6, 7*). Under these conditions the major decomposition products are equimolar amounts of methyl nitrate and CO_2 with a small, variable amount of nitromethane (*7*). It has been suggested (*7*) that they are formed by decomposition through a six-center transition state:



but this is inconsistent with the homolytic dissociation process suggested on the basis of the present results. We propose that the observed products of the slow decomposition of PAN in N_2 can be explained by the following reactions:

$$CH_3COO_2NO_2 \underset{2}{\overset{1}{\rightleftarrows}} CH_3COO_2 + NO_2$$

$$2\,CH_3COO_2 \xrightarrow{12} 2CH_3CO_2 + O_2$$

$$CH_3CO_2 \xrightarrow{13} CH_3 + \boxed{CO_2}$$

$$CH_3 + CH_3COO_2 \xrightarrow{14} CH_3O + CH_3CO_2$$

$$CH_3O + NO_2 \xrightarrow{15} \boxed{CH_3ONO_2}\ \text{(methyl nitrate)}$$

$$CH_3 + NO_2 \xrightarrow{16} \boxed{CH_3NO_2}\ \text{(nitromethane)}$$

Note that Reactions 13 and 14 comprise a chain reaction involving CH_3 radicals. A strong dependence of the decomposition rate with temperature is expected since $[CH_3COO_2]\ \alpha\ k_1{}^{1/2}$ and the rate of initiation of the chain reaction by Reaction 12 is proportional to $[CH_3COO_2]^2$. This thermally initiated chain decomposition also explains the tendency of pure PAN to explode (*7*).

The ready decomposition of PAN to radical species may well contribute to the irreproducibility in the elution characteristics of PAN in gas chromatographic analysis, which has been noted by a number of workers, and also to its known phytotoxic effects (*7*).

Acknowledgment

We thank J. Alistair Kerr, University of Birmingham; Dick Derwent, AERE; and Heiko Nieboer and Joop Van Ham, TNO, Delft, for helpful discussions.

Literature Cited

(1) Leighton, P. A., "The Photochemistry of Air Pollution", Academic Press, New York, N.Y., 1961.
(2) Louw, R., Van Ham, J., Nieboer, H., *J. Air Pollut. Control Assoc.*, **23**, 716 (1973).
(3) Cox, R A., Derwent, R. G., Holt, P. M., Kerr, J. A., *J. Chem. Soc. Faraday Trans. I*, **72**, 2061 (1976).
(4) Hill, A. C., *J. Air Pollut. Control Assoc.*, **21**, 341 (1971).
(5) Garland, J. A., Penkett, S. A., *Atmos. Environ.*, **10**, 1127–31 (1976).
(6) Schuck, E. A., Stephens, E. R., Price, M. A., Darnall, K. R., 163rd American Chemical Society Meeting, Boston, Mass., 1972.
(7) Stephens, E. R., Darley, E. F., Taylor, O. C., Scott, W. E., *Int. J. Air Water Pollut.*, **4**, 79 (1961).
(8) Pate, C. T., Atkinson, R., Pitts, J. N., Jr., *J. Environ. Sci. Health, Environ. Sci. Eng.*, **A11** (1), 19 (1976).
(9) Gay, B. W., Jr., Noon, R. C., Bufalini, J. J., Hanst, P. L., *Environ. Sci. Technol.*, **10**, 82 (1976).
(10) Cox, R. A., *J. Photochem.*, **3**, 175 (1974).
(11) Atkins, D.H.F., Cox, R. A., "The 365 nm Photolysis of Nitrous Acid Vapour in Air", AERE Rep. R-7615, HMSO, London, England, 1973.
(12) NBS Tech. Note 866, "Chemical Kinetic and Photochemical Data for Modelling Atmospheric Chemistry", D. Garvin and R. F. Hampson, Eds., p 41, NBS, Washington, D.C., 1975.
(13) Batt, L., McCulloch, R. D., Milne, R. T., *Int. J. Chem. Kinet. Symp.*, 1, 441 (1975).
(14) Mills, R. L., Johnston, H. S., *J. Am. Chem. Soc.*, **73**, 938 (1951).
(15) Benson, S. W., "Thermochemical Kinetics", Wiley, New York, N.Y., 1968.
(16) Benson, S. W., Buss, J. H., *J. Chem. Phys.*, **29**, 546 (1958).
(17) Domalski, E., *Environ. Sci. Technol.*, **5**, 443 (1971).
(18) Lonneman, W. A., Bufalini, J. J., Seila, R. L., *Environ. Sci. Technol.*, **10**, 374 (1976).

Received for review November 18, 1976. Accepted April 25, 1977. Work sponsored by the UK Department of the Environment.

Isotopic Organic and Inorganic Mercury Exchange in River Water

Akira Kudo*, Hirokatsu Akagi, D. C. Mortimer, and Donald R. Miller
Division of Biological Sciences, National Research Council of Canada, Ottawa, Ont., Canada K1A 0R6

■ Isotopic exchanges between organic and inorganic mercury were observed for Ottawa River water as well as for polar and nonpolar organic solvents. The concentration of mercury investigated ranges from 0.1 to 100 ppm, and the exchanges were observed for 24 h under vigorous mechanical mixing at a temperature of 21 °C. No or very little (less than 0.52%) isotopic exchange was observed in the Ottawa River water. There was no difference between the two exchange directions, i.e., $^{203}HgCl_2 \rightarrow CH_3HgCl$ and $CH_3{}^{203}HgCl \rightarrow HgCl_2$. The additional conditions of adding salts, acid, or alkali, changing temperature to 40 °C, and prolonging the mixing period did not change the results.

Isotopic mercury exchanges between organic and inorganic forms have been observed for nearly 25 years (*1–5*). Two schools (Ingold et al. vs. Abraham et al.) are debating the detailed mechanisms of the exchange of mercuric and alkyl mercuric compounds for high mercury concentration ranges (over 10 000 ppm) in polar organic solvents (*6–10*). However, no direct observation of isotopic mercury exchange has been reported for aquatic environmental conditions for the low concentration range of mercury (under 100 ppb) in which the most environmental mercury concentrations in water fall (*11, 12*). This reports a recent observation that there is no or very little isotopic mercury exchange in low concentration for the Ottawa River water as well as for polar and nonpolar organic solvents.

Materials and Methods

A combined technique of radioactive tracers and thin-layer chromatography (TLC) was applied to determine, quantitatively, organic and inorganic forms of mercury (*13*). Mercuric chloride and methylmercuric chloride, both labeled with radioactive mercury-203, were used to observe isotopic mercury exchange from both sides, i.e., $^{203}HgCl_2 \rightarrow CH_3HgCl$ and $CH_3{}^{203}HgCl \rightarrow HgCl_2$.

A dithizone–benzene extraction method was applied for this experiment. The recovery of mercury for the determination was up to 91%. Dithizone–benzene extract was then applied to the TLC (Polygram, cel 400) with a methylcellosolve–water solvent system. R_f values for mercuric and methylmercuric forms, respectively, were 0.36 and 0.66. All experiments were conducted at 21 °C and for triplicate samples. Radioactive methylmercuric chloride (New England Nuclear) had a radiological impurity as mercuric chloride (2.18 ± 0.10%). This was caused by degradation of radioactive methylmercury. With an increase in time, the proportion of the impurity increased. For example, after 6 months in the dark, the radioactive methylmercuric chloride solution contained 20% of radioactive impurity as mercuric chloride. However, at this time, radioactivity of the solution decreased to 7.033% of the original value (half-life 47 days). Therefore, this amount of the impurity was subtracted from experimental results.

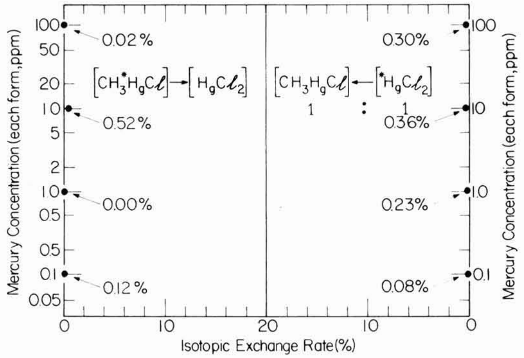


Figure 1. Isotopic mercury exchanges for various concentrations in Ottawa River water (after 24 h, concentration ratio was 1 to 1 for both directions)

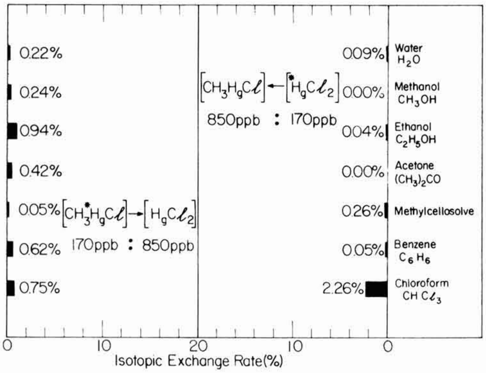


Figure 2. Isotopic exchange rates between methylmercuric and mercuric chloride in various solutions (after 24 h)

Two sets of experiments were carried out to observe isotopic mercury (mercuric and methylmercuric) exchange: changing mercury concentration in the Ottawa River water (0.1, 1, 10, and 100 ppm for each form), and changing solvents (water, methanol, ethanol, acetone, methylcellosolve, benzene, and chloroform) and fixing mercury concentration at a 1 (0.170 ppm, radioactive) to 5 (0.850 ppm, stable) ratio. To promote the isotopic exchange, vigorous mechanical mixing was applied to the samples for 24 h.

Results and Discussion

No or very little (less than 0.52%) isotopic exchange was observed in the Ottawa River water (Figure 1). There was no difference between the two exchange directions, i.e., $^{203}HgCl_2 \rightarrow CH_3HgCl$ and $CH_3{}^{203}HgCl \rightarrow HgCl_2$. Furthermore, there was no difference in exchange rates for various mercury concentrations ranging from 0.1 to 100 ppm. Additional experiments were also carried out under different conditions: mercury concentrations 1–10, 1–0.1 ratio (radioactive); adding salt (2 N NaCl), acid (2 N HCl), or alkali (2 N NaOH); changing temperature to 40 °C; and prolonging the mixing period up to 4 days. Similar results (no or very little isotopic exchange) were obtained.

Organic solvents did not change the low isotopic exchange rates after 24 h of mixing (Figure 2). This was true for both exchange directions, $^{203}HgCl_2 \rightarrow CH_3HgCl$ and $CH_3{}^{203}HgCl \rightarrow HgCl_2$. To increase isotopic exchange rates, mercury concentration of the stable form was five times (0.850 ppm) higher than that of the radioactive form (0.170 ppm). Slightly higher exchange rates were observed in chloroform for both directions. In general, the exchange rates are higher for $CH_3{}^{203}HgCl \rightarrow HgCl_2$. However, the higher exchange rate observed in this direction might suggest decomposition of methylmercuric chloride to mercuric chloride (not isotopic exchange) during experimental processes.

Clarkson (*14*) also observed no or a negligible isotopic exchange rate between metallic mercury and organomercurials covalently bonded to a carbon atom. Elemental mercury vapor and organomercury in tissue were placed in a sealed box during 45 h. In this case, the mercury concentration in tissue was 10 000 ppm. For a mercury concentration of 20 000 ppm, Hughes et al. (*6*) observed the exchange rate of 67.6% during 8 h. However, only one direction ($HgBr_2 \rightarrow CH_3HgBr$) was observed, and the exchange reaction was conducted in ethanol at 100.2 °C, which is far from natural aquatic conditions. Of course, radioactive methylmercuric chloride ($CH_3{}^{203}HgCl$) has been commercially produced through application of the isotopic exchange phenomena. For example, the exchange technique [$^{203}Hg(NO_3)_2 \rightarrow CH_3HgCl$] is used under very limited specific conditions by the New England Nuclear Corp.

Isotopic exchange reactions between methylmercuric and mercuric chloride only were observed in this study. No other forms of mercury compounds were investigated. Furthermore, this study was conducted in very limited environmental conditions. Therefore, at this stage the results must be treated considering these limiting factors.

If this result (no or very little isotopic exchange) is applicable for low mercury concentrations (at most 100 ppm) and various aquatic environmental conditions, it is possible that the mercury transport and transfer mechanism in natural environments can be investigated using radioactive mercury tracers for each individual mercury compound. For example, the methylation rate from inorganic mercury or demethylation rate in aquatic systems can be determined quantitatively.

Acknowledgment

We thank E. Javorsky and M. Y. Pinard for their assistance.

Literature Cited

(1) Cross, J. M., Pinajian, J. J., *J. Am. Pharm. Assoc.*, **XL** (2), 96 (1951).
(2) Nefedov, V. D., Sinotova, E. N., "Collected Works on Radiochemistry", p 113, Leningrad Univ. Press, 1955.
(3) Nefedov, V. D., Sinotova, E. N., *Z. Fiz. Khim.*, **30,** 2356 (1956).
(4) Reutov, O. A., *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 684 (1958).
(5) Reutov, O. A., *Angew. Chem.*, **72,** 198 (1960).
(6) Hughes, E. D., Ingold, C. K., Thorpe, F. G., Volger, H. C., *J. Chem. Soc.*, **1961,** p 1133.
(7) Charman, H. B., Hughes, E. D., Ingold, C. K., Volger, H. C., *ibid.*, p 1142.
(8) Hughes, E. D., Volger, H. C., *ibid.*, p 2359.
(9) Abraham, M. H., Dodd, D., Johnson, M. D., Lewis, E. S., O'Ferrall More, R. A., *J. Chem. Soc. (B)*, **1971,** p 762.
(10) Abraham, M. H., Grellier, P. L., Hogarth, M. J., *J. Chem. Soc. Perkin Trans. 2*, **1974,** p 1613.
(11) Kudo, A., Townsend, D. R., Miller, D. R., *Prog. Water Technol.*, **9,** 923 (1977).
(12) Miller, D. R., Ed., Ottawa River Project (#3), National Research Council of Canada, Ottawa, Ont., Canada, 1976.
(13) Takeshita, R., Akagi, H., Fujita, M., Sakagami, Y., *J. Chromatogr.*, **51,** 283 (1970).
(14) Clarkson, T. W., "Chemical Fallout, Current Research on Persistent Pecticides", M. W. Miller and G. G. Berg, Eds., p 274, Charles C. Thomas, Publ., Illinois.

Received for review December 21, 1976. Accepted April 26, 1977. Research carried out as part of the Ottawa River Project, a joint study of the National Research Council Laboratories (NRCL) and the University of Ottawa.

Physical Model of Marine Phytoplankton Chlorination at Coastal Power Plants

Joel C. Goldman* and John A. Davidson
Woods Hole Oceanographic Institution, Woods Hole, Mass. 02543

■ A physical model of the impact of coastal power plant chlorination on marine phytoplankton was developed. Several steady state biomass levels of the test alga *Phaeodactylum tricornutum* were established in continuous cultures by varying the concentration of phosphorus in the growth medium. The algae were then exposed to combinations of chlorine and temperature stress for 1 h, and deviations from the prestress steady state were observed over long periods of time. Three types of response occurred that were a function of the applied chlorine/biomass ratio: no effect, effect followed by recovery, and complete washout. It is suggested from the results that, given the typical organic loads present in coastal waters, excessive levels of chlorine may be in current use, and that the effects on entrained phytoplankton probably have little bearing on the ultimate effect on the standing crop in the receiving water. The most important considerations were the hydrologic, biological, and chemical qualities of the receiving waters themselves.

Based on recent reports there is a general consensus of opinion that chlorination practice at coastal power plants for fouling control leads to serious impairment of phytoplankton productivity in entrained waters (*1*). This conclusion, for the most part, has been based on two types of studies: comparative field estimates of photosynthetic activity (measured by the classical ^{14}C incubation technique) at the intake and discharge stations of power plants (*2–5*), and by laboratory studies using similar techniques for observing immediate and short-term responses of natural and artificially cultured phytoplankton populations after chlorine exposure (*1, 5*).

There are a number of reasons why the above techniques at best only provide a partial picture of the impact of chlorine on phytoplankton populations in receiving waters: entrained phytoplankton represent only a fraction of the actual population residing in the receiving water; phytoplankton generation times are rapid enough so that even though there may be serious inhibition of photosynthesis and actual destruction of a large percentage of entrained phytoplankton, those surviving organisms are capable of recovery and subsequent restocking of the standing crop when returned to the receiving water; in many plants chlorination is practiced during only a small fraction of the day; any persistent effects of the toxicant in marine receiving waters are minimal—both free chlorine and chloramine compounds, or their bromine counterparts which are formed in seawater (*6*), are quickly degraded through the combined oxidation of organic matter and the inorganic decomposition of the halites to highly oxidized forms, not recoverable by the standard amperometric technique (*5, 7, 8*); and the formation and presence of persistent organochlorine compounds in trace quantities, although not necessarily acutely toxic to phytoplankton (the actual effects are unknown) can possibly be biomagnified during transport through the marine food chain (*9*), with the result that the effects will be manifested only over a very long time period.

To examine the question of the "recoverability potential" of marine phytoplankton after entrainment, a physical model of a power plant was developed consisting of a series of continuous phytoplankton cultures. Long-term phytoplankton responses were measured after short-term exposure to combinations of chlorine and temperature increase so as to simulate typical power plant conditions.

Physical Model

Under typical power plant conditions, phytoplankton cells are exposed to a sudden and combined temperature rise and chlorine dosage in the condenser system. The actual residence period of a cell after being stressed can vary from 10 to 20 min to several hours before discharge back to the receiving water, depending on plant design (*10*). During this time and in the subsequently short time after discharge where dilution is usually significant, water temperatures are reduced to ambient levels and chlorine is dissipated so that the cell is once again back in its natural environment.

The continuous culture can conveniently be used to simulate the above conditions. By virtue of the inherent characteristics of this culture technique, a steady state cell population can be established as a function of fixed environmental conditions, i.e., light intensity, temperature, dilution rate (media flow rate/culture volume), and concentration of limiting nutrient in the medium (*11*). This leads to two basic relationships (*12*):

$$\mu = D \qquad (1)$$

and

$$X = Y(S_0 - S_1) \qquad (2)$$

in which μ is the specific growth rate $[T^{-1}]$, X is the steady state phytoplankton biomass $[\mathrm{ML}^{-3}]$, S_0 and S_1 are, respectively, the influent and residual concentrations of the limiting nutrient $[\mathrm{ML}^{-3}]$, and Y is the yield coefficient (biomass/amount of limiting nutrient assimilated). Because S_1 is usually very small at low growth rates ($S_0 \gg S_1$) and Y is a constant for a fixed D, $X = YS_0$ is a good approximation of biomass at low μ values (*12*).

Hence, the physical model consists of first establishing steady state levels of X as a function of S_0 at a set D and temperature T_1. Then simultaneously T_1 in the culture is rapidly increased to T_2, and chlorine is continuously applied. After a fixed time, T_2 is quickly lowered back to T_1, chlorine dosage is stopped, and residual chlorine remaining is removed by addition of a strong reducing agent, sodium thiosulfate. Any hydromechanical damage to phytoplankton cells during entrainment cannot be simulated by the physical model, but does not appear to be important with microbes (*4*).

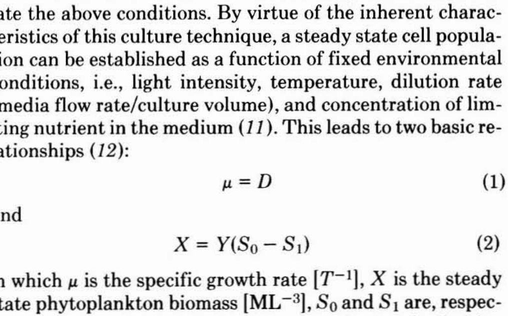


Figure 1. Schematic diagram of continuous culture system

1) Ice-filled styrofoam chest, 2) media supply bottle, 3) media feed line, 4) peristaltic pump, 5) cut-off pipet, 6) overflow port, 7) overflow bottle, 8) intake for temperature-control water, 9) glass water jacket, 10) discharge, 11) magnetic stirrer, 12) stirring bar, 13) air line, 14) air valve, 15) cotton wool filter, 16) activated carbon filter, 17) chlorine feed line, 18) peristaltic pump, 19) chlorine supply bottle

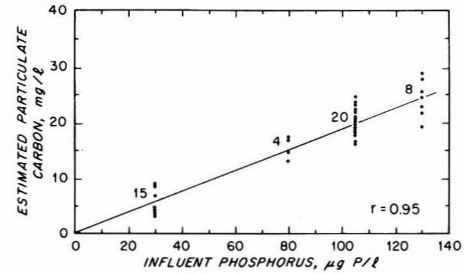


Figure 2. Relationship between influent phosphorus to continuous culture and steady state particulate carbon for *Phaeodactylum tricornutum*

Numbers indicate number of data points

Depending on the level of stress (combined ΔT and chlorine addition), three types of time-dependent responses can result: no effect on the cells, and steady state is unperturbed; a portion of the cells is killed or shocked, leading to initial cell washout ($\mu < D$), but ultimate recovery and repopulation ($\mu > D$), forcing the population back to the original steady state level ($\mu = D$); and complete cell death ($\mu = 0$), with total washout occurring.

This physical model can be used to measure, not only the "recoverability potential" of the population after being stressed, but also the effect of biomass concentration on the required chlorine dosage to produce one of the above responses.

Experimental

A bank of 12 1-L continuous cultures was divided into three sets of four units. Each set had an individual temperature control system. The basic culture design is described in detail elsewhere (*13*), but the pertinent features include continuous lighting at about 0.03 langleys/min (visible spectrum), temperature control by circulating water through glass jackets on the outside of each culture, mixing with stirring bars and aeration (the latter was turned off during periods of chlorine dosage), and media and chlorine addition by peristaltic pumping from separate supply bottles. The temperature control system was plumbed so that when a rapid increase in culture temperature was desired, an additional circulating water bath at the higher temperature was valved into the system and the bath at the lower temperature was valved out. The process was reversed to return the temperature to the preset level when desired. A schematic of the entire apparatus is shown in Figure 1.

A monoculture of a test alga *Phaeodactylum tricornutum* (clone TX-1) from the Woods Hole Oceanographic Institution culture collection was used in all experiments. Media were artificial seawater: 400 mM NaCl, 20 mM $MgSO_4$, 20 mM $MgCl_2$, 10 mM $CaCl_2$, 10 mM KCl, 2 mM $NaHCO_3$, 1.7 mM KBr, 0.2 mM H_3BO_4, 0.4 mM $NaNO_3$, 0.1 mM $Na_2S_1O_3$, and trace metals and vitamins in a twofold dilution of f-medium (*14*). Phosphorus as NaH_2PO_4 was added as the limiting nutrient at four different levels—P_0 = 30, 80, 105, and 130 μg P/L—to establish a wide range of biomass concentrations (Figure 2). All media were prepared in distilled, deionized, and activated carbon-treated water to ensure that no dissolved organics were present that might place a demand on the chlorine added. All media were kept at 8–10 °C by placing the supply bottles in styrofoam ice-filled chests. One medium supply bottle fed four units simultaneously.

For all experiments a D of about 0.3 day^{-1} was maintained. At the prestress temperatures used (15–25 °C), this value represents about 15–40% of the maximum growth rate of a wide spectrum of marine algae (*15*). A typical experimental run consisted of establishing a population of *P. tricornutum* at a desired temperature (usually 20 °C, although some experiments were carried out at 15 and 25 °C) and then exposing the cells to different combinations of ΔT and free chlorine for 1 h. In some experiments chloramine was substituted for free chlorine. Toxicant was administered from two separate substocks of freshly prepared chlorine made from NaOCl (or chloramine made from equimolar concentrations of NaOCl and NH_4OH), one for the initial addition and one that was pumped in and mixed with the flowing media to sustain the initial concentration. During the period of toxicant dosage the aeration was turned off to minimize volatilization of chlorine or chloramine to the atmosphere. Medium pH was ~8.0 and increased slightly to 8.05–8.35 in the cultures, depending on the level of biomass present. After 1 h, toxicant dosage was stopped, aeration resumed, sodium thiosulfate added, and the temperature quickly lowered. Temperature changes up to ΔT = 15 °C were achieved in less than 15 min. Medium flow was maintained for up to 2–3 weeks, and periodic observations of culture biomass were made: during the 12 h after toxicant treatment, observations were made every 3–4 h and daily thereafter. In some cultures sodium thiosulfate was added during the steady state period prior to the chlorination and heat treatments to test for possible effects on phytoplankton growth; no such effects were observed.

Biomass was routinely measured as culture absorbance on a Bausch and Lomb Spectronic 88 spectrophotometer at 600 nm on 2-mL samples and converted to an equivalent cell count (CC) and particulate carbon (PC) concentration. This was done to avoid disturbing the continuous flow that would have occurred if routine measurements had to be made on larger samples (25–50 mL) for PC. Cell counts were made periodically and random measurements of PC with a Perkin-Elmer 240 elemental analyzer were made about 2 days before and after the toxicant application. Both parameters were well correlated with culture absorbance (Figure 3), although much better correlation was observed with PC (r = 0.99, $P < 0.001$, df = 56) than with CC (r = 0.83, $P < 0.001$, df = 83).

All chlorine measurements were made by amperometric titration (*16*) on a Fischer and Porter titrator (No. 17T1010) with a chart recorder attached for more sensitive end-point determination. Phenylarsine oxide was the titrant, and the samples were buffered at pH = 4. Chlorine measurements

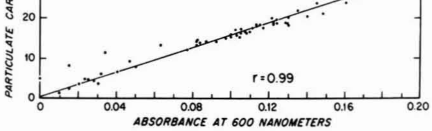


Figure 3. Relationships between absorbance and A) cell counts, and B) particulate carbon for *Phaeodactylum tricornutum*

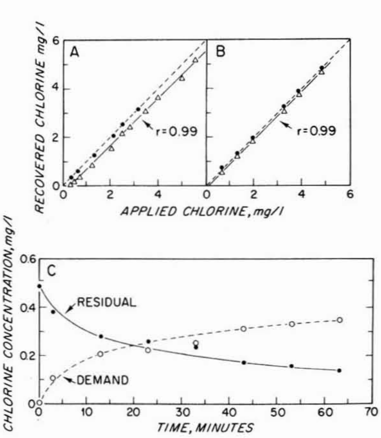


Figure 4. One-hour chlorine demand of artificial seawater media
A) Free chlorine; B) chloramine, circles: distilled water, triangles: halogen; C) time decay of free chlorine in seawater: initial concentration = 0.49 mg/L

Table I. Summary of *Phaeodactylum* Response to 1-h Exposure to Either Free Chlorine or Temperature Stress at Ambient Temperatures of 15 and 25 °C

Temp, °C	ΔT, °C	Influent P, µg/L	Cl_2 dose, mg/L	Cl_2/PC ratio	Result
15	5	105	0	0	None
	10	105	0	0	None
	15	105	0	0	None
	0	105	0.02–0.44	0.001–0.024	None
25	5	105	0	0	None

Table II. Summary of *Phaeodactylum* Response to 1-h Exposure to Combinations of Free Chlorine and Temperature Stress at Ambient Temperature of 20 °C

ΔT, °C	Influent P, µg/L	Cl_2 dose, mg/L	Cl_2/PC ratio	Result
5	105	0	0	None
10	105	0	0	None
0	105	0.12–0.24	0.007–0.012	None
0	30	0.11–0.92	0.027–0.108	Recovery
0	80	0.19–0.32	0.017–0.019	None
0	80	0.50–1.86	0.029–0.126	Recovery
0	130	0.18–0.32	0.014–0.015	None
0	130	0.72–2.52	0.038–0.099	Recovery
5	105	0.02–0.76	0.001–0.040	None
5	105	1.28–2.70	0.056–0.122	Recovery
10	30	0.59–1.64	0.123–0.653	Washout
10	80	0.44	0.04	None
10	80	1.29	0.107	Recovery
10	80	1.11	0.138	Washout
10	130	0.88	0.034	None
10	130	0.59–1.57	0.042–0.091	Recovery
10	130	1.42	0.140	Washout

Table III. Summary of *Phaeodactylum* Response to 1-h Exposure to Combined Chlorine (Chloramine) at Ambient Temperature of 20 °C

ΔT, °C	Influent P, µg/L	Cl_2 dose, mg/L	$ClNH_2$/PC ratio	Result
0	30	0.02–0.03	0.008–0.034	None
0	30	0.05–0.10	0.029–0.057	Recovery
0	130	0.15–1.40	0.007–0.029	None
0	130	0.60–3.72	0.037–0.080	Recovery

were not made on the cultures because 200 mL of sample is required, which would have destroyed the continuity of continuous flow. However, estimates of the 1-h chlorine and chloramine demands of the media alone were made by comparing toxicant losses in a static culture unit filled with either distilled water or medium under the same conditions as in the flowing cultures.

To examine the possibility of permanent effects on the growth rate of *P. tricornutum*, regrowth studies were carried out on cells that recovered after toxicant exposure. Small inocula of cells from the above cultures, plus from a nonstressed control culture, were added to media (with 130 μg P/L) and kept on batch growth at 20 °C. Cell counts were initially ~1.3 $\times 10^3$/mL and were taken daily thereafter. At the end of exponential growth, cells from the toxicant-treated cultures were again used as inocula for fresh media, and the experiment was repeated.

Results

Chlorine Demand of Media. There was a small but persistent chlorine demand of the artificial seawater media during the 1-h static incubation studies: complete recovery occurred when distilled water was chlorinated with either free or combined chlorine, but with artificial seawater the recovery was consistently about 0.36 mg/L less than the applied level for free (Figure 4A) and 0.10 mg/L for combined chlorine (Figure 4B). Based on one decay study (free chlorine dosage of 0.49 mg/L), the rate of chlorine demand was initially rapid (>50% loss in 10 min), and even though declining at 1 h, did not seem to be completely satisfied (Figure 4C).

Phytoplankton Chlorination Studies. A total of 104 experimental runs were carried out: 28 with temperatures stress only, 39 with chlorine dosage only, 30 with combined heat and chlorine stress, and 17 with exposure to chloramines only. All free and combined chlorine dosages are reported as the weight ratio of chlorine applied to estimated particulate carbon present in the culture at the time of dosage (Cl_2 or $ClNH_2$/PC). The results, summarized in Tables I–III and Figures 5–8, were divided into the three aforementioned types of responses: no effect, effect and recovery, and complete washout.

A fairly consistent pattern of responses occurred. Temperature shock alone for 1 h to T_2 = 30 °C from T_1 values of 15, 20, and 25 °C had no affect on steady state populations (Figure 5). Similarly, free chlorine dosage at all biomass levels did not disturb the steady state when the Cl_2/PC ratio was less than ~0.02–0.03 (Figure 6B). In the Cl_2/PC range of ~0.03–0.13, the cells were affected and initial washout occurred, but recovery took place over time, leading to a return to the prestress biomass levels (Figure 7). Finally, above a Cl_2/PC ratio of ~0.13, complete washout occurred (Figure 6A). The responses to chlorine dosage per unit biomass were quite consistent regardless of the biomass present (Figure 7).

Although the studies with chloramines were not carried out with heat increase, the general response to chloramine dosage ($ClNH_2$/PC) was very similar to that with free chlorine (Table III).

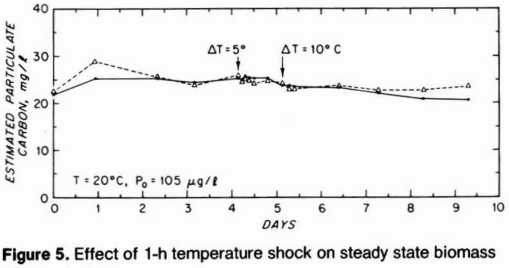


Figure 5. Effect of 1-h temperature shock on steady state biomass

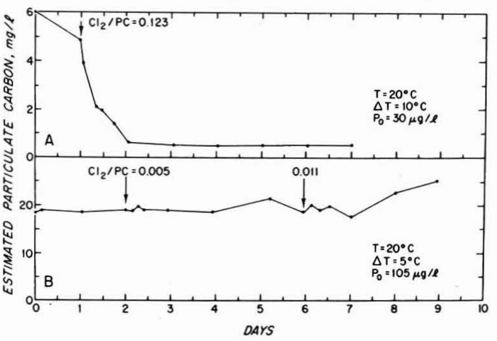


Figure 6. Effect of 1-h chlorine dosage on steady state biomass

A) Cl_2/PC = 0.123, complete washout (0.50 mg/L PC = 0 absorbance units); B) Cl_2/PC = 0.005–0.011, no effect

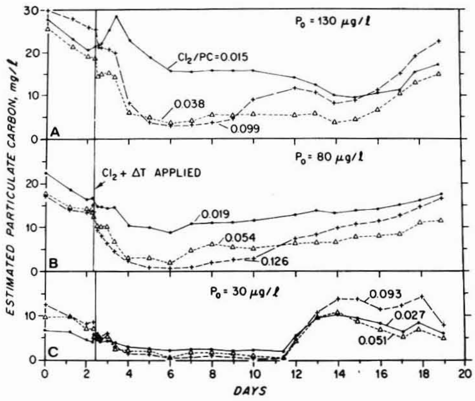


Figure 7. Effect of 1-h chlorine dosages at varying influent *P* and resulting biomass levels on steady state; $\Delta T = 0$

Regrowth Studies. Growth rates of all cultures (control, free chlorine, and chloramine treated) were virtually identical during the regrowth studies (Figure 8). The growth lags displayed by the treated cells in the second regrowth study (Figure 8B) undoubtedly occurred because both inocula were taken at the end of exponential growth in the first batch experiment (Figure 8A), where phosphorus depletion occurred, placing the cells in a physiologically stressed state. However, once the lag phase was overcome, exponential growth was equal again to the control.

Discussion

There are several restrictions in trying to extrapolate the results of the study to natural water situations. First, the dilution (or growth) rate of 0.3 day^{-1} was chosen somewhat arbitrarily, although it is of the same magnitude as natural phytoplankton growth rates in coastal waters (*17*). The ranges of Cl_2/PC ratios that led to one of the three responses thus are valid only for the fixed *D*. Washout of *P. tricornutum* cells when dosed with chlorine occurred simply because $\mu < D$. If *D* was less than 0.3 day^{-1}, the Cl_2/PC ratio that led to complete washout might have been higher than ~0.13, as determined in this study. A second restriction is that the response of *P. tricornutum* to chlorine cannot be readily extrapolated to natural populations, as others have found differential effects of chlorine on a variety of marine species (*1, 18*). And third, the biomass levels used in this study (*PC* = 6–25 mg/L)

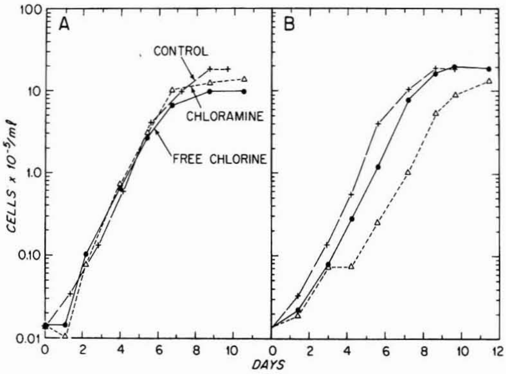


Figure 8. Growth of *Phaeodactylum tricornutum* in batch culture after recovery from chlorine and chloramine dosage in continuous culture
A) Inocula from continuous cultures; B) inocula from end of first batch study

are over an order of magnitude greater than those found in natural waters. In fact, in most coastal waters, phytoplankton biomass represents only a fraction of the total particulate carbon (*19*). The results are thus conservative, but still serve to demonstrate the kinds of phytoplankton responses that are possible.

Three important conclusions can, however, be drawn from the results presented: the degree of chlorine toxicity to marine phytoplankton is clearly a function of the biomass present; phytoplankton not killed by chlorination are capable of renewed growth once recovered, with no apparent permanent effects on growth rates; and the degradation of chlorine is controlled, not only by the dilution capacity of the receiving water, but also by entrainment residence periods and water quality.

These conclusions, although not entirely new, do reinforce the concept that results based only on short-term responses to chlorine exposure in the entrained waters, for the expressed purpose of determining the impact on the receiving waters, are inconclusive.

The most important factors influencing the impact of chlorine on receiving waters are the dynamic hydrologic, biological, and chemical qualities of the receiving waters themselves. For example, the most serious consequence of coastal power plant chlorination is the potential for persistent chlorinated compounds to enter the marine environment. Free chlorine, as shown in Figure 4A and C for artificial seawater, is readily dissipated through the auto or catalytic decompositions of the halites. For natural seawater the dissipation is more pronounced due to the presence of particulate and dissolved organics that are readily oxidized by chlorine (*5, 8*).

Chloramines are more persistent than free chlorine (Figure 4B), and exotic organochlorine compounds that may be formed are highly refractory (*9*). Because chloramines appear to be equally toxic as free chlorine to phytoplankton (Table III) and considerably more toxic to some invertebrate larvae (*20*), the long-term threat to the receiving water will depend on the ammonia level in the entrained (or receiving) water, the chlorine dosage and demand at the point of application, and the subsequent dissipation in the entrainment system prior to discharge. The fate and toxicity of organochlorine compounds, on the other hand, are virtually unknown and hence represent the most serious potential effect of chlorination.

The demonstration that phytoplankton biomass level determines the types of response to a given chlorine dosage is not surprising, since the chlorine concentration required for establishing a desired residual for water and wastewater disinfection is entirely dependent on the amount of organics present (*21*). The actual mechanisms of chlorine inhibition of phytoplankton growth are completely unknown. It may well be that cell surface area rather than weight is the main factor controlling the response, but for mixed phytoplankton populations it is more useful to consider an easily measured parameter such as PC or chlorophyll as an indication of this effect.

Typical chlorine dosages at coastal power plants vary from ~0.3 to 5.0 mg/L applied chlorine, usually administered for 10–20-min periods up to several times daily (*22*). Consider then a hypothetical situation in which a chlorine dosage of 0.3 mg/L is administered for a total of 1 h per day to entrained water containing 2 mg/L PC. The Cl_2/PC ratio is then 0.15, and if the Cl_2/PC results of this study are typical, then very high phytoplankton mortality in the chlorinated entrained water would be expected. Indeed, others have shown very high reductions in photosynthesis immediately after chlorination at power plants (*2–4, 23*), suggesting that Cl_2/PC ratios under field conditions are very high. In fact, it is conceivable that the levels of chlorine commonly used could be reduced and still effectively control fouling. Carpenter et al. (*4*), for example, found that chlorine dosages from 0.1 to 1.2 mg/L at the Millstone Point nuclear plant on northeastern Long Island Sound all resulted in >79% reduction in photosynthetic activity immediately after chlorination.

For the above hypothetical example, the percentage of entrained water subjected to chlorination is 5% daily. If we consider the worse case of complete destruction of phytoplankton during periods of chlorination, the net effect on productivity in receiving waters is small considering the continuous import of new water and cells to the vicinity of the power plant, and the potential for increased growth of the population not chlorinated due to an easing on the competition for nutrients by the death of the chlorinated cells.

The noneffect of short-term exposure to elevated temperature alone, as shown in this study, is similar to results from field studies (*1, 2, 4, 23, 24*); in several instances, depending on ambient and elevated temperatures, enhanced productivity has actually been observed (*4, 23*), which most likely would contribute to offsetting losses due to short-term chlorination.

Indeed, there is strong evidence supporting the argument that current chlorination practice at power plants has had little, if any, impact on primary productivity in coastal receiving waters: at several locations diminished productivity has yet to be demonstrated (*2, 4, 5*); the recoverability potential of cells not killed, as shown in the current work, is more than likely a contributing factor to these findings. In fact, there have been similar observations at power plants of recovery in photosynthetic rate between the point of chlorination and final discharge (*3, 23*), and after chlorine exposure in laboratory batch studies (*18*). The full recovery of *P. tricornutum* growth rates after recovery to either free or combined chlorine (Figure 8) is encouraging, but certainly not conclusive evidence, that natural populations may respond similarly.

In conclusion, assessing the impact of chlorination on phytoplankton productivity in receiving waters is a far more complicated task than simply measuring changes within the power plant itself. There is little question though that the most serious impact of chlorine is on entrained larval zooplankton which spawn intermittently, particularly those of commercial importance (e.g., lobsters, oysters, clams, and many fish). For example, Capuzzo et al. (*25*) have shown that lobster larvae are more sensitive to chloramines than free chlorine at concentrations below the level of detectability (<0.01 mg/L). As suggested by Eppley et al. (*5*) and reiterated here, the gross impact of chlorine on phytoplankton is minimal compared to effects on organisms higher up the food chain.

Acknowledgment

Thanks are gratefully given to J. P. Clarner and Helen Quinby for their technical assistance.

Literature Cited

(1) Gentile, J. H., Cardin, J., Johnson, M., Sosnowski, S., "Power Plants, Chlorine and Estuaries", Environmental Protection Agency Ecological Research Monograph EPA-600/3-76-055.
(2) Hamilton, D. H., Flemer, D. A., Keefe, C. W., Mihursky, J. A., *Science,* **169,** 197–98 (1970).
(3) Brook, A. J., Baker, A. L., *ibid.,* **176,** 1414–15 (1972).
(4) Carpenter, E. J., Peck, B. B., Anderson, S. J., *Mar. Biol.,* **16,** 37–40 (1972).
(5) Eppley, R. W., Renger, E. H., Williams, P. M., *Estuarine Coastal Mar. Sci.,* **4,** 147–61 (1976).
(6) Lewis, B. G., "Chlorination and Mussel Control. I: The Chemistry of Chlorinated Sea Water: A Review of the Literature", Central Electricity Research Laboratories Note RD/L/N 106/66, Leatherhead, Great Britain, 1966.
(7) Carpenter, J. H., Macalady, D. L., "Chemistry of Halogens in Seawater", R. L. Jolley, Ed., pp 177–93, Proc. Conf. on the Environmental Impact of Water Chlorination, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1976.
(8) Wong, G.T.F., Davidson, J. A., *Water Res.,* in press.
(9) Jolley, R. L., *J. Water Pollut. Control Fed.,* **47,** 601–18 (1975).
(10) Davies, R. M., Jensen, L. D., *ibid.,* pp 2130–42.
(11) Herbert, D., Elsworth, R., Telling, R. C., *J. Gen. Microbiol.,* **14,** 601–22 (1965).
(12) Goldman, J. C., *Water Res.,* **10,** 97–104 (1976).
(13) Brewer, P. G., Goldman, J. C., *Limnol. Oceanogr.,* **21,** 108–17 (1976).
(14) Guillard, R.R.L., Ryther, J. H., *Can. J. Microbiol.,* **8,** 229–39 (1962).
(15) Goldman, J. C., Carpenter, E. J., *Limnol. Oceanogr.,* **19,** 756–66 (1974).
(16) Standard Methods, 14th ed., Am. Pub. Health Assoc., Am. Water Works Assoc., 1976.
(17) Eppley, R. W., *Fish. Bull.,* **70,** 1063–85 (1972).
(18) Hirayama, K., Hirano, R., *Mar. Biol.,* **7,** 205–13 (1970).
(19) Riley, G. A., *Adv. Mar. Biol.,* **8,** 1–118 (1970).
(20) Capuzzo, J. M., Lawrence, S. A., Davidson, J. A., *Water Res.,* **10,** 1093–99 (1976).
(21) Fair, G. M., Geyer, J. C., Okun, D. A., "Water and Wastewater Engineering, Vol, 2", Wiley, New York, N.Y., 1968.
(22) White, G. C., "Current Chlorination and Dechlorination Practices in the Treatment of Potable Water, Wastewater and Cooling Water", R. L. Jolley, Ed., pp 7–22, Proc. Conf. on the Environmental Impact of Water Chlorination, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1976.
(23) Fox, T. L., Moyer, M. S., *Chesapeake Sci.,* **16,** 66–8 (1975).
(24) Briand, F.J.P., *Mar. Biol.,* **33,** 135–46 (1975).
(25) Capuzzo, J. M., Goldman, J. C., Davidson, J. A., Lawrence, S. A., *Mar. Pollut. Bull.,* in press.

Received for review November 4, 1976. Accepted April 29, 1977. Project supported by Contract No. E(11-1)-2532 from the U.S. Energy Research and Development Administration to the Woods Hole Oceanographic Institution.

NOTES

Algae Removal by High Gradient Magnetic Filtration

Ruth Yadidia, Aharon Abeliovich, and Georges Belfort*
Environmental Health Laboratory, Graduate School of Applied Science and Technology, Hebrew University, Jerusalem, Israel

■ A parametric method was used to study the removal efficiency of both laboratory and high-rate oxidation pond-grown *Scenedesmus obliquus* from dilute solutions by use of high gradient magnetic filtration. The removal was accomplished by coadsorbing the algae and magnetite in the presence of ferric chloride and by placing the mixture for a given residence time in a magnetic filter. Both for the laboratory and pond-grown algae, excellent chlorophyll removals (>90%) were observed for small residence times, low magnetic fields, and reasonable flocculant dosages.

The need to remove algae from various waters for water renovation, protein concentration, or power utilization (*1*) has necessitated a search for reliable economical separation methods. Methods that have been studied include filtration, flotation, centrifugation, coagulation and settling, and ion exchange (*2, 3*). Centrifugation is considered the most reliable method, but it is relatively expensive. Thus, the coagulation–flotation method which appears to be economically more attractive than the centrifugation method has received much attention (*4–11*). For harvesting algae for use as a food, effective, cheap, nontoxic flocculants must be sought. This has proved to be an unusually difficult problem (*9, 10*).

This study was initiated to evaluate the feasibility and to determine the optimum operating conditions of removing laboratory and high-rate oxidation pond-grown *Scenedesmus obliquus* from dilute solutions by use of coagulation–high gradient magnetic filtration (C–HGMF). The principles, devices, and applications of the process are well documented (*12, 13*). Important advantages of this process are very high permeation fluxes, an order of magnitude higher than high-rate sand filtration, high removal efficiencies, and small land area utilization.

Two groups have recently reported research results obtained by use of C–HGMF for environmental purposes. The first group devoted its attention to the removal of suspended particles such as viruses (*14*) and phosphates on alum-coagulated clay (*15, 16*). They suspended in the solution magnetic particles (usually Fe_3O_4, magnetite) which were coagulated with the suspended particles to be removed. The solution was then passed through a magnetic field focused on a porous screen which retained the magnetic flocs. The product water was then collected essentially particle free. Mitchell et al. (*17*) conducted preliminary experiments for the removal of algae by C–HGMF and found that algae were removed as efficiently as bacteria. Bitton et al. (*18*) reported algal removal efficiencies of between 55 and 94% (by counts) from five Florida Lakes by use of alum as a flocculant and a commercial magnetic filter.

The second group involved in HGMF research and development concentrated on the removal of heavy metals from industrial wastewaters (*19, 20*). Their approach was based on heavy metal complexation in which a magnetic stable precipitate of ferrite ($M_xFe_{3-x}O_4$) is removed by HGMF. They also suggested the possibility of separating phosphates, algae, bacteria, and viruses from wastewaters.

As mentioned above, both variants of the C–HGMF process offer the possibility of algae removal. However, because of the encouraging preliminary results of Mitchell et al. (*17*) and Bitton et al. (*18*) for algae removal, it was decided to study their approach in detail. Here, we present the results of a study to remove algae from both "clean" and "dirty" dilute solutions by coagulation and high gradient magnetic filtration (C–HGMF).

Materials and Methods

Because the naturally dominating algae in the high-rate algae pond (HROP) is *Scenedesmus obliquus,* axenic cultures of the algae were grown in the laboratory on Zehnder and Gorham medium no. 11 for 8–12 days at 30 °C in artificial light (cool white fluorescent lamps, $2 \cdot 10^3$ erg·s^{-1}·cm^{-2} at the surface of the flasks) (*21*). The "dirty" culture was obtained from a high rate oxidation pond, HROP (*9, 10, 22*), which is 40 cm deep and has a capacity of about 100 m^3.

The magnetite was obtained from Fisher Scientific Co., Fair Lawn, N.J., USA, and the technical grade ferric chloride FeCl was supplied by a local source (Chemorad, Israel). $FeCl_3$ was used instead of $Al_2SO_416H_2O$ since it produced stronger more resilient flocs and because of its relatively low toxicity. The harvested algae could possibly be considered as a protein supplement after removal from the HGMF and separation from the magnetite.

Apparatus and Procedure. Magnetite and ferric chloride were successively added in batch experiments to 750-mL samples of algal suspensions (0.1–1 g/L dry weight) obtained either from the laboratory or the pond. After lowering the pH to 4, the mixtures were agitated at room temperature with an impellar at approximately 80 rpm^{-1} for 1 min and 20 rpm^{-1} for 9 min. This procedure was based on the standard method for coagulation as suggested by the Water Research Association (*23*). To compensate for the low strength and poor design of the available magnet [evidently, a "Bitter magnet", which consists of a solenoid directing its magnetic field upward or antiparallel to the flow, establishes a higher field gradient and induces a stronger field than the "Davis tube" used here (*12, 13*)], semistatic experiments were conducted as follows: a 10-mL pipet with its head cut containing steel wool (80% void volume) was used to draw up the well-mixed sample of algae, magnetite, and ferric chloride. It was then placed between the magnet poles for the required residence time, t_r. Thereafter, the solution was allowed to flow out of the pipet at about 1 mL/s or 26 gal/(ft^2/min).

This procedure is different from the procedure reported by Bitton and Mitchell (*14*) for virus (bacteriophage T_7) removal by C–HGMF. They used a continuous flow method. The method presented here should probably result in higher removals under similar conditions than the continuous method, since the shear force due to flow is much reduced here, resulting in a force balance favoring adsorption and thus filtration removal. The continuous method is probably more practical, although the method used here is entirely adequate in determining the effect of various parameters on algae removal. Chlorophyll was used as a measure of algae mass and was determined according to the method of Talling and Driver (*24*).

Results and Discussion

As a result of some preliminary experiments to remove algae from the Ein Karem HROP effluent by use of the Bitton and Mitchell (*14*) continuous flow method, it was discovered that algae removal efficiency was directly affected by the size of the magnetite particles. By use of magnetite from a local Israeli source (average particle size ~31 μm) and from Fisher Scientific Co. (average particle size ~12 μm), the algae removal efficiencies were 25 and 90%, respectively. Also, flocs of algae and magnetite were more stable during the magnetic filtration step if $FeCl_3$ was used in place of alum [$Al_2(SO_4)_316H_2O$] as a flocculant. As would be expected from the theory (*12*), a change in the strand diameter of the stainless steel wool should effect the algae removal efficiency. To check this, two grades of stainless steel screens varying in strand diameter from 150 to 300 μm (obtained from Yates Products, 711 W. Ivy Street, Glendale, Calif. 91204) were used.

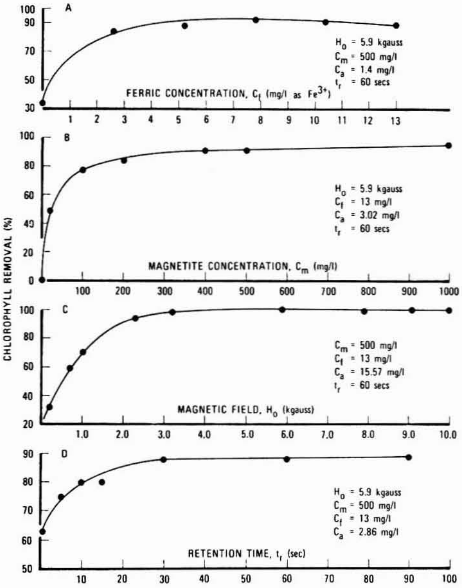


Figure 1. Chlorophyll removal efficiency as a function of several process parameters for laboratory-grown *Scenedesmus obliquus* algae

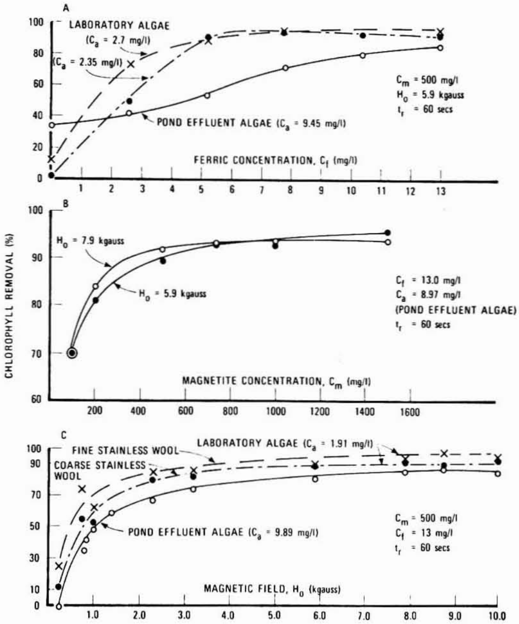


Figure 2. Chlorophyll removal efficiency as a function of several process parameters for laboratory- and pond-grown *Scenedesmus obliquus* algae

The effect of each of several independent variables—ferric chloride concentration, magnetite concentration, applied magnetic field and retention time—on the removal efficiency of the C–HGMF process is discussed below. The results are summarized in Figures 1 and 2.

Laboratory-Prepared Algae. *Ferric Chloride Concentration, C_f.* Varying the ferric ion concentration, C_f, for a given set of experimental conditions increased the percentage chlorophyll removed by C–HGMF from 32% at $C_f = 0$ to about 90% at $C_f = 5$ mg/L. This is shown in Figure 1, A. Thus, without a flocculant the algae and magnetite appeared to coadsorb, whereas at very high C_f concentrations the percentage chlorophyll removed appeared to decrease slightly. The experiments described below used $C_f = 13$ mg/l; however, it is possible that under conditions different from those tested (i.e., at very high applied magnetic fields, H_o, or smaller diameter magnetite particles), little or no bridging ions would be needed to obtain high chlorophyll removals.

Magnetite Concentration, C_m. From Figure 1, B, for as low as $C_m = 20$ mg/L, the chlorophyll removal was 48%. Under the given set of conditions, the chlorophyll removal continuously increased with C_m, albeit slowly above $C_m = 300$ mg/L.

Applied Magnetic Field, H_o. Maximum chlorophyll removal occurred at above about $H_o = 3.2$ kG for the conditions listed in Figure 1, C. As mentioned earlier, the magnetic filter design or the Davis tube used in these experiments is less efficient in producing a high field-gradient than the solenoid design, or Bitter magnet, which produces a magnetic field counter to the flow direction. Thus, it is possible that with the latter design, lower applied magnetic fields, H_o could remove more algae (or chlorophyll).

Retention time, t_r. After about 30 s of retention time, t_r, the chlorophyll removal reached a maximum for the conditions listed in Figure 1, D. Also note that 63% chlorophyll removal was obtained for very short retention times, i.e., $0 < t_r < 1$ s.

Effluent from High-Rate Algae Pond (HROP). Because of the variability of the Ein Karem municipal sewage feed to the HROP, the pond effluent containing algae exhibited large ranges of water quality parameters. For example, see Table I. Flocculant consumption by factors other than algae-magnetite coagulation must also be considered in evaluating the optimum flocculant dosage for the pond effluent.

In addition to suspended solids such as algae, bacteria, humic acids, and any other colloids commonly found in raw sewage, factors such as phosphate concentration, alkalinity, and biological and chemical oxygen demand are known to consume the flocculant (*9*). Experimental correlations similar to those of Ramani (*25*) for the consumption of alum by alkalinity and phosphate are very specific and not transferable to different effluents. Particle size and number also effect the efficiency of coagulation.

A study was conducted to determine the size and number of particles (including algae, bacteria, and other suspended solids) in the high-rate pond effluent. A bimodal distribution was obtained using a Model A Coulter counter with a 50-μm aperture with which particles only above 2 to 3 μm could be sized. When number count was plotted against particle diameter, maxima at about 4.6 and 7.4 μm appeared for the diameter of the bacteria and algae, respectively. Below about 3 μm, the beginning of a new peak appeared. This indicated the possible existence of smaller particles than bacteria suspended in the media. These particles, together with the bacteria and other flocculant consumers, could easily cloud the flocculant requirements for optimum dosage to remove algae. It is for this reason that chlorophyll, not particle count, was used as a measure of algae removal efficiency.

Coagulation–Magnetic Filtration of HROP Effluent. *Ferric Chloride Concentration, C_f.* The pond effluent usually contained a chlorophyll content (C_a) of about three times that of the laboratory-prepared algae. Except for the case $C_f = 0$, the chlorophyll removal efficiency in Figure 2, A was always lower for the pond effluent than for the laboratory algae. This can be explained by the fact that both more algae and other flocculant consumers were present in the pond effluent. Why the chlorophyll removal efficiency was higher at $C_f = 0$ for the pond effluent may have been due to the presence of natural flocculants and/or the high suspended solids enhancing depth filtration—adsorption of the organics in the pond effluent onto the porous stainless steel wool would have assisted in algae attachment and removal. Only at high C_f (~13 mg/L) did the removal efficiencies for the pond effluent approach that of the laboratory-prepared algae.

Table I. Range of Water Quality Parameters for Effluent of High-Rate Algae Pond[a]

Parameters	Min-max, mg/L	Mean, mg/L
Chemical oxygen demand (COD)	205–770	561
Biological oxygen demand (BOD)	50–185	103
Suspended solids	60–650	310
Phosphate	2.7–18.5	8.56
Alkalinity ($CaCO_3$)	250–500	350

[a] Results collected by H. Shechter and Rivka Kalbo over a period of four months (January–April) and are averages for 18 days.

Magnetite Concentration, C_m. An increase in C_m, as shown in Figure 2, B, resulted in the maximum chlorophyll removal of about 95% at about $C_m \approx 1200$ mg/L for the pond effluent algae. The removals were usually better at the higher applied fields, and more magnetite was needed to reach maximum removals for the pond effluent ($C_m \approx 1200$ mg/L in Figure 2, B) than for the laboratory-prepared algae ($C_m \approx 500$ mg/L in Figure 1, B).

Applied Magnetic Field, H_o. The trend for the chlorophyll removal efficiency vs. H_o was similar for both waters as shown in Figure 2, C. Again removal efficiencies were higher for the laboratory-prepared algae. Also, the removals increased with a decrease in strand diameter. This may have been due to the strand diameter per se, or it may just have been the result of an increased surface area since both screens used were of the same weight.

Economics

Since C–HGMF has only reached the developmental stage of laboratory experiments and pilot plant tests for wastewater treatment applications, reliable cost estimates for commercial plants are not available at present, while those that are available should be viewed with skepticism. Below, some recent estimates from the literature are presented and compared with the costs of dissolved air flotation for algal removal.

For a 2-mgd facility embodying coarse screening, coagulation, magnetite recycle, and HGMF, Mitchell et al. (*26*) estimate a capital cost of U.S. $545 000 and maintenance and overhead of $0.26/kgal of treated capacity. They also estimate operating costs for a 15-mgd treatment plant of $0.05/kgal for removal of suspended solids from blast furnace scrubber water from steel mills. This appears to be rather optimistic in spite of the larger capacity plant and the fact that the magnetite was unnecessary. Harland et al. (*27*) suggest operating costs at $0.05–0.10/kgal for treatment of 40-mgd municipal effluent. Several methods have been suggested for recovery of the magnetite. These include using the magnetic properties, density differences, or chemical properties of the magnetite-algae floc (*27*).

In comparing the costs to treat about 1 mgd of algal effluent by C–HGMF and dissolved air flotation, besides makeup to the recycled magnetite, the process flow sheets are essentially the same. The following estimated operating cost was obtained from Iannicelli (*28*) for an 84-in. HGMF for 30 s retention time on a 30 wt % slurry:

	Cost/h
Amortization of installed separator ($1 600 000) over 10 yr (80 000 h)	$20.00
Magnetic power (400 kW @ 2¢ kWh) (switching magnet off for flushing easily offsets rectification losses)	8.00
Pumping and flushing power (200 kW @ 2¢ kWh)	4.00
Labor (incl. benefits)	5.50
Maintenance	4.00
	Total U.S. $41.50

For a typical commercial 84-in. diam and 20-in.-high HGMF separator (free volume ~ 1726 L ~ 455.9 U.S. gal for a porosity of steel screen of $\epsilon = 0.95$), the flow velocity is about 40 in./min (101.6 cm min^{-1}). At this rate the HGMF will process about 912 gpm or 1.3 mgd (4971 m^3 day^{-1}). On a filtration basis, this is equivalent to 24 gal/ft^2/min (0.978 cm s^{-1}) which is 10 times the rate of the conventional sand filter. For a solids content of 0.105 (w/w)% (500 ppm algal plus bacteria et al. + 500 ppm magnetite + 50 ppm FeCl$_3$) and a 80% duty cycle, the dry solids treated per hour are about 0.191 short tons per hour (tph) or 174 kg/hour. Thus, the estimated operating cost (on a wet basis) to treat 912 gpm of algal effluent is $0.76/kgal. Based on recent studies for algae removal by dissolved air flotation, Bare et al. (*11*) estimate treatment costs of about $0.107/kgal for a 1.0-mgd plant.

The earlier cost estimates of Oswald and Golueke (*29*) for coagulating and flotating or sedimentating algae were $20–25/ton of algae (dry weight) as compared to $217/ton (≡ $41.50/0.191/ton) for HGMF estimated from Iannicelli (*28*). Note that with both of the above cost comparisons, the HGMF costs are based on a slurry of 30 wt % as opposed to the less than 1 wt % algal solution for the dissolved air flotation process. Obviously, for the HGMF to treat such a dilute solution, the treatment costs would be drastically lowered as is evidenced by the cost estimates of Mitchell et al. (*26*) and Harland et al. (*27*) above.

Conclusions

In spite of the poor design of the laboratory HGMF, algal removals above 90% were obtained with 5–13 ppm FeCl (as Fe^{3+}) as a primary flocculant and 500–1200 ppm magnetite (Fe$_3$O$_4$) as a magnetic seed for laboratory-prepared and pond-grown algal suspensions.

By use of the parametric method, optimum conditions for the removal of algae have been established. For laboratory-prepared feed at $C_a \approx 2.5$ mg/L, maximum removals occur if $t_r \approx 30$ s, $H_o \approx 3.5$ kG, $C_m \approx 500$ mg/L, $C_f \approx 5.0$ mg/L. For the pond effluent at $C_a \approx 8.75$ mg/L, maximum removals occur if $t_r \approx 60$ s, $H_o \approx 9$ kG, $C_m \approx 1200$ mg/L, $C_f \approx 13.0$ mg/L.

As commercial plants and reliable cost estimates become available, the advantages of high treatment rate, high removal efficiency, and small land utilization may justify extensive use of C–HGMF in the treatment of industrial and municipal effluents. Although the available cost estimates appear encouraging, they were not based on actual commercial operating experience and should therefore be viewed with skepticism.

Acknowledgment

The authors thank David Mahlab, Eric Mendoza, Ralph Mitchell, and Hillel Shuval for their valuable suggestions and assistance; David Shaltiel for his encouragement; and Z. Low for loaning us the magnet.

Literature Cited

(1) Brown, J. G., "Algae Power", presented at the 3rd Nat. Conf. on Complete Water Reuse, Paper 10e, Cincinnati, Ohio, June 27–30, 1976.

(2) Golueke, C. G., Oswald, W. J., *J. Water Pollut. Control Fed.*, **37**, 471 (1965).

(3) Middlebrooks, E. J., Porcella, D. B., Gearheart, R. A., Marshall, G. R., Reynolds, J. H., Grenney, W. J., *ibid.*, **46** (12), 2676–95 (1974).

(4) Van Vuuren, L.R.J., van Duuren, F. A., *ibid.*, **37** (9), 1256–62 (1965).

(5) Cillie, G. C., van Vuuren, L.R.J., Stander, G. T., Kalbe, F. F., "Advances in Water Pollution Research", Vol 2, Proceedings of the 3rd Int. Conf. in Munich, Water Pollution Control Fed., Washington, D.C., 1966.

(6) Dryden, F. D., Stern, G., *Environ. Sci. Technol.*, **2** (4), 268–78 (1968).

(7) McGarry, M. G., Tongkasawa, C., *J. Water Pollut. Control Fed.*, **43** (5), 824–35 (1971).

(8) Ort, J. E., *Water Waste Eng.* (Sept. 1972).

(9) Shuval, H. I., Belfort, G., Dor, I., "Development of Combined Systems for Algae Production and Wastewater Reclamation", submitted to National Council for Research and Development, Prime Minister's Office, Jerusalem, Israel, see Section II (principal investigator, G. Belfort), 1974.

(10) Shuval, H. I., Belfort, G., Dor, I., Abeliovich, A., *ibid.*, see Section III, p 151, 1975.

(11) Bare, W.F.R., Jones, N. B., Middlebrooks, E. J., *J. Water Pollut. Control Fed.*, **47** (1), 153–69 (1975).

(12) Oberteuffer, J. A., *IEEE Trans. Magnetics,* **9** (3), 303–06 (1973).

(13) Oberteuffer, J. A., *ibid.*, **10** (2), 223–28 (1974).

(14) Bitton, G., Mitchell, R., *Water Res.*, **8**, 549–51 (1974).

(15) de Latour, C., *IEEE Trans. Magnetics*, **9** (3), 314–16 (1973).

(16) Bitton, G., Mitchell, R., de Latour, C., Maxwell, E., *Water Res.*, **8**, 107–09 (1974).

(17) Mitchell, R., Bitton, G., de Latour, C., Maxwell, E., "Magnetic Separation: A New Approach to Water and Wastewater Treatment", presented at 7th Conf. of IAWPR in Paris, Paper 12C (i), Sept. 9–13, 1974.

(18) Bitton, G., Fox, J. L., Strickland, H. G., *Appl. Microbiol.*, **30** (6), 905–08 (1975).

(19) Okamoto, S., *IEEE Trans. Magnetics*, **10** (3), 923–26 (1974).

(20) Okudo, T., Sugano, I., Tsuji, T., "Removal of Heavy Metals by Ferrite Coprecipitation Technique", presented at the IEEE Int. Conf. on Magnetics, London, England, April 1975.

(21) Zehnder, A., Gorham, P. R., *Can. J. Microbiol.*, **6**, 645–60 (1960).

(22) Shelef, G., Schwarz, M., Schechter, H., "Prediction of Photosynthetic Biomass Production in Accelerated Algal-Bacterial Wastewater Treatment Systems", in "Advances in Water Pollution Research", S. H. Jenkins, Ed., Pergamon Press, London, England, 1973.

(23) WRA (Water Research Assoc.), Technical Inquiry Report TIR No. 248(A), October, "Technique for Laboratory Coagulation Tests", Stevenage, England, UK.

(24) Talling, J. F., Driver, D., "Some Problems in the Estimation of Chlorophyll in a Phytoplankton", Proc. Conf. Prim. Prod. Measur., Marine and Freshwater, Hawaii, U.S. Atomic Energy Center, TID-7633, pp 142–46, 1963.

(25) Ramani, A. R., PhD thesis, University of California, Berkeley, Calif., 1974.

(26) Mitchell, R., Bitton, G., Oberteuffer, J. A., *Sep. Purif. Methods*, **4** (2), 267–303 (1975).

(27) Harland, J. R., Oberteuffer, J. A., Goldstein, D. J., "High Gradient Magnetic Filtration Pilot Plant", presented at 80th Nat. Meeting, AIChE, Paper 32b, Boston, Mass., September 7–10, 1975.

(28) Iannicelli, J., "Assessment of High Extraction Magnetic Filtration", prepared with support of NSF (RANN) ISRU, Washington, D.C., 1974; for copies write to Aquafine Corp., 157 Darien Highway, Brunswick, Ga. 31520.

(29) Oswald, W. J., Golueke, C. G., Chap. in "Single Cell Protein", D. I. Mateles and S. Tannebaum, Eds., MIT Press, Cambridge, Mass., 1969.

Received for review September 28, 1976. Accepted May 2, 1977. Research supported by a grant from the National Council for Research and Development, Israel, and the GSF München, Germany.

Heavy-Metal Pollution from Automotive Emissions and Its Effect on Roadside Soils and Pasture Species in New Zealand

Neil I. Ward, Robert R. Brooks*, and Edward Roberts[1]

Department of Chemistry, Biochemistry and Biophysics, Massey University, Palmerston North, New Zealand

Colin R. Boswell

Computing Service Centre, Victoria University, Wellington, New Zealand

■ Concentrations of cadmium, chromium, copper, lead, nickel, and zinc were determined by atomic absorption spectrophotometry in soils and pasture species along a major motorway in New Zealand. Enhanced levels of all elements were found and correlated well with traffic densities. Concentrations in soil profiles decreased with depth and showed that the source of pollution was aerial deposition from motor vehicles. About a third of the aerial burden of each element was removable by washing of vegetation species. Highest accumulations of heavy metals were usually found on white clover, and the lowest on *Paspalum* grass. Elemental concentrations in pasture species were usually well correlated with traffic densities, particularly in the case of the grass, Yorkshire fog. Plant/soil correlations for individual heavy metals were in general poorer than for relationships involving traffic densities and concentrations in plants and soils.

Lead particulate pollution from automotive emissions and other industrial sources has been extensively investigated in recent years (*1–7*). Apart from lead, very little attention has been paid to the possibility of pollution from other heavy metals derived from automobiles. However, Lagerwerff and Specht (*8*) reported the presence of cadmium, nickel, and zinc (as well as lead) in soils and grasses at roadsides. These elements were presumably derived from motor vehicle exhausts and, for a site with 48 000 vehicles per day, had the following range of concentrations (μg/g dry weight) for surface soils in the interval 8–32 m from the road: cadmium, 0.94–0.24; lead, 540–140; nickel, 7.40–2.40; and zinc, 162–114. Corresponding values for grasses were: cadmium, 0.75–0.48; lead, 51.3–18.5; nickel, 3.8–1.3; and zinc, 40–30.3.

The toxicity of all the above elements toward humans has been well documented (*9*), and because of the paucity of data on pollution by these elements (except in the case of lead) from motor vehicle exhausts, there is clearly a need for further studies on these and other heavy metals. This need is further reinforced by the fact that neither of the previous studies had included chromium or copper (both of which are components of motor vehicles), and neither had attempted to correlate elemental concentrations with traffic densities.

In the work presented in this paper, we have studied concentrations of cadmium, chromium, copper, lead, nickel, and zinc in soils and pasture species along a busy motorway in Auckland City, New Zealand, and have correlated concentrations with traffic densities at each collection locality.

Experimental

The Auckland Motorway is situated to the south of New Zealand's largest city, Auckland (population approximately 700 000). The sampling sites were selected at 17 interchanges on a 1-m-wide, grassed median strip located in the center of the motorway.

Surface soils (0–1 cm) were collected at all 17 sites, and soil profiles were sampled at nine sites by means of a 0.5-cm-diam core extractor. The cores were subsequently divided into twenty 0.5-cm sections. Background soil samples were taken from the same soil type at distances well away from the effect of motor vehicle emissions. Soils were then dried for three days at 60 °C and sieved to −60 mesh. Digestion of 0.1-g samples of soils was carried out with 10 cm^3 of a 1:1 mixture of concentrated nitric and hydrofluoric acids contained in 50 cm^3 polypropylene squat beakers. The solutions were taken to dryness over a water bath, and the residues were redissolved in 2 M hydrochloric acid.

The pasture species sampled from the median strip of the Auckland Motorway were: *Lolium perenne* L. (perennial ryegrass), *Trifolium repens* L. (white clover), *Poa annua* L., *Dactylis glomerata* L. (cocksfoot), *Holcus lanatus* L. (Yorkshire fog), *Bellis perennis* L. (daisy), *Paspalum dilatatum* L., and "flatweeds" of the genera: *Plantago, Bellis,* and *Crepis.*

Pasture samples were divided into unwashed and washed portions for analysis, the washing being carried out by agitation in about 20 L of slowly running water. Samples weighing about 5–10 g were oven-dried at 150 °C, ashed at 450 °C, and dissolved in 2 M hydrochloric acid in the ratio of 5 cm^3 of acid to 0.050 g of ash. Further dilutions were carried out when required.

All solutions were analyzed by flame atomic absorption by use of a Varian Techtron AA-5 instrument fitted with a BC6 background corrector to correct for nonatomic absorption. Wavelengths (nm) of the absorption lines used were: Cd 228.8, Cr 357.9, Cu 324.8, Ni 232.2, Pb 217.0, and Zn 213.9. Concentrations were in most cases sufficiently high to obviate the need for separation or preconcentration procedures.

Results and Discussion

The mean concentrations of cadmium, chromium, copper, lead, nickel, and zinc in surface soils sampled from the various interchanges (grouped according to traffic density) are presented in Table I. All six elements show significantly higher levels along the motorway compared with background areas.

Although elemental levels are considerably higher than background for all elements, there was a possibility that in some cases, the soil had been transported from elsewhere in the city during the construction of the motorway and that the high levels were due to naturally high concentrations of some elements in the basaltic soils of the Auckland area. This could apply to chromium and nickel, though not to the other elements which are not usually enriched in basaltic substrates. To confirm the true origin of heavy metals in the soils, a number of soil profiles were analyzed. Decrease of elemental concentrations with depth would indicate surface contamination from motor vehicles, whereas unchanging concentrations would show that anomalous heavy-metal levels were a function of the substrate itself.

Figures 1 and 2 show concentrations of six elements in soil profiles from nine interchanges divided into three groups according to traffic densities. It is clear from these figures that elemental concentrations invariably decrease with depth at

---

[1] Agronomy Department, Massey University.

Table I. Mean Concentrations (μg/g Dry Weight) of Heavy Metals in Surface Soils and Vegetation (Unwashed) from 17 Interchanges (Grouped According to Traffic Density) of Auckland Motorway, New Zealand

Material	Mean traffic density, vehicles/24 h	No. of interchanges	Concentrations of pollutant Cd	Cr	Cu	Ni	Pb	Zn
Soils[a]	>50 000	5	2.2	80	200	105	2200	480
	40 000–50 000	5	0.7	66	57	87	1650	250
	20 000–39 000	4	0.4	56	27	65	1250	180
	10 000–19 000	3	0.3	50	22	60	780	130
	Background	...	<0.2	9	12	8	14	64
Vegetation[b]	>50 000	5		4.0	30	3.7	350	
	40 000–50 000	5		3.1	23	4.3	320	
	20 000–39 000	4		2.6	17	3.0	270	
	10 000–19 000	3		2.4	13	2.6	140	
	Background	...		0.6	10	0.9	5	

[a] Soil values represent means of five replicates of one sample at each site. [b] Vegetation values represent five replicates of one composite of 10 species from each site.

all sampling sites and that this decrease is most apparent at the interchanges with the heaviest traffic densities. At the busiest sites, elemental concentrations decrease by an order of magnitude in a depth of only 10 cm. Concentration patterns of elements in all soil profiles indicate that these elevated levels in surface soils are due to extraneous sources (presumably motor vehicle emissions) and are not a function of soil type.

Elemental concentrations in pasture plants (without regard to species) are also shown in Table I. The data do not include figures for cadmium because concentrations were at or below the limit of detection (0.2 μg/g) and were scarcely distinguishable from background. Zinc values have also been excluded because the natural concentration of zinc in vegetation is relatively high (50 μg/g dry weight) and it was not possible to differentiate values from background. Although, for the sake of brevity, values for washed samples are not shown in Table I, it was noted that washing removes about one-third of the heavy-metal burden of the vegetation and indicates its superficial deposition upon the pasture species. For unwashed material, concentrations on the busiest intersections are about eight times higher for chromium, three times as high for copper, six times higher for nickel, and 100 times as high for lead. As may be expected, lead is quantitatively the greatest pollutant among the four elements studied.

Our values for heavy metals in soils and vegetation when compared with those obtained by Lagerwerff and Specht (*8*) for a site with similar traffic density (40 000 vehicles per 24

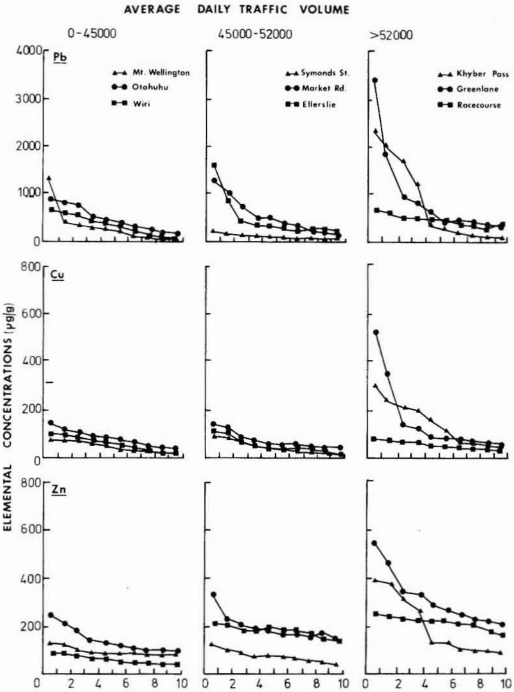


Figure 1. Concentrations (μg/g dry weight) of lead, copper, and zinc in soil profiles from nine interchanges of Auckland Motorway, New Zealand

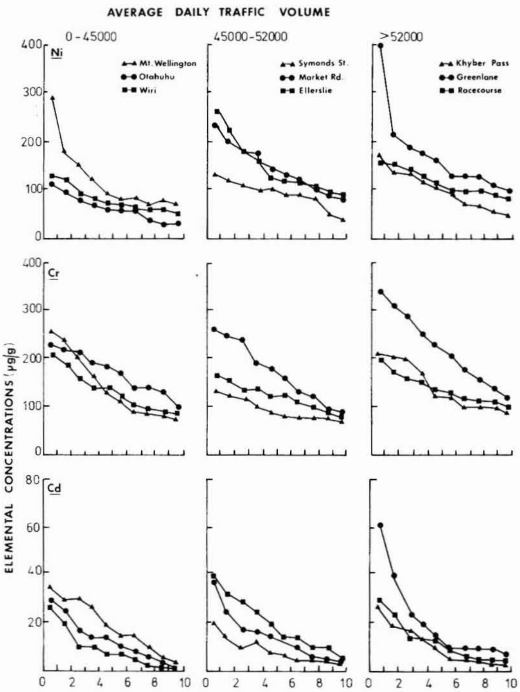


Figure 2. Concentrations (μg/g dry weight) of nickel, chromium, and cadmium in soil profiles from nine interchanges of Auckland Motorway, New Zealand

Table II. Mean Concentrations ($\mu g/g$ Dry Weight) of Heavy Metals in Unwashed Pasture Species (Roots, Leaves, and White Clover Stolons) Sampled at Greenlane Interchange of Auckland Motorway, New Zealand

Vegetation	Cr	Cu	Ni	Pb
	Concn (mean of 5 replicates of 1 composite sample)			
White clover (WC)				
Roots	3.9	60.6	5.2	645
Leaves	3.8	50.4	4.7	638
Stolons	3.4	43.9	3.3	707
P. ryegrass (PR)				
Roots	5.8	28.8	4.0	480
Leaves	2.3	20.8	2.6	345
Poa annua (PA)				
Roots	1.1	22.0	2.5	460
Leaves	3.9	31.2	3.3	546
Yorkshire fog (YF)				
Roots	2.9	25.6	2.8	408
Leaves	2.3	27.3	3.3	553
Flatweeds (FW)				
Roots	2.2	27.0	1.8	225
Leaves	1.7	22.6	3.1	1044
Daisy (D)				
Roots	0.9	9.2	0.7	165
Leaves	1.6	18.3	1.5	313
Paspalum (P)				
Roots	1.7	18.0	0.7	213
Leaves	1.0	18.3	1.3	305
Cocksfoot (C)				
Roots	2.2	28.8	2.0	376
Leaves	1.9	15.6	0.7	332

h) are higher for lead and nickel in soils and higher for lead in vegetation. This difference can be explained by the greater proximity of our sites to the line of traffic.

Although elemental concentrations were obtained for all vegetation species at each sampling site, for the sake of brevity, values for only one site (Greenlane) are shown (Table II). The data in Table II show obvious interspecific differences in the heavy-metal burden of pollutants. All parts of white clover (roots, leaves, and stolons) usually show considerably greater concentrations of chromium, copper, lead, and nickel. The enhanced levels do not appear to be a function of the shape of the leaf, because other broad-leafed species such as daisy and "flatweeds" have considerably lower accumulations of most elements. Washing usually removed about one-third of the aerial burden from leaves of all species (data for washed samples are excluded for the sake of brevity). *Paspalum* grass tends to have the lowest aerial burden of any of the pollutants studied. The experiments indicate expected elemental levels in pasture species adjacent to major highways, and if grazing close to such sources of pollution must be undertaken, then clover should be avoided and grasses such as *Paspalum* encouraged.

To assess the relationship between traffic densities and the two further variables of pollutant concentrations in soils and vegetation, Spearman rank correlation coefficients were computed for all possible pairs of variables involving each of the six heavy metals studied. These relationships are shown in Table III. In all cases there is at least a significant ($P < 0.05$) relationship between traffic density and elemental concentration in surface soils. These relationships are very highly significant for the elements chromium, copper, lead, and zinc. The less definite correlation for cadmium is probably because there were relatively few sites at which this element could be measured accurately.

The relationships between traffic density and concentration in vegetation show that the grass, Yorkshire fog, is usually the best overall indicator of traffic density from its content of four heavy metals. By contrast, only the copper content of cocksfoot reflects traffic density.

As may be expected, the vegetation/soil relationships which do not involve a direct correlation with traffic density are, in general, weaker and fewer in number. Most species show a mutual relationship for copper, lead, and nickel, but only white clover and paspalum give a plant/soil relationship for chromium.

From the data presented in Table II, there can be no doubt that motor vehicle traffic is responsible for the buildup of all six heavy metals in soils and vegetation along the motorway. The source of the lead is obviously leaded gasoline, as has been so well established in the literature. Lagerwerff and Specht (*8*) have suggested that cadmium and zinc are found together in lubricating oils as part of many additives such as zinc-di-

Table III. Significance [a] of Relationships Between Three Variables of Traffic Densities, Concentration of Pollutants in Vegetation (Unwashed Leaves), and in Surface Soils from Auckland Motorway, New Zealand

Pollutant	First variable	Concn in vegetation[b] (second variable)							
		WC	PR	PA	YF	FW	D	P	C
Cr	Concn	S	. . .	S	. . .	. . .	. . .	. . .	. . .
Cu	in	S	S	S	S	S*	S*	S**	S
Ni	surface	S**	S	S	S*	. . .	. . .	. . .	. . .
Pb	soils	S**	S*	S**	S**	S	S**	S	. . .
Cr	Traffic	S	. . .	S*	S*	S*	. . .	. . .	. . .
Cu	densities	S*	S	S*	S**	. . .	S*	S**	S
Ni	at	S	. . .	S	S*	S	. . .	. . .	. . .
Pb	interchanges	S	S*	S**	S*	S	S*	. . .	. . .
		Concentrations in soils (second variable)							
Cd	Traffic				S				
Cr	densities				S**				
Cu	at				S**				
Ni	interchanges				S				
Pb					S**				
Zn					S**				

[a] Significance calculated from Spearman rank correlation coefficients: S**, very highly significant, $P \leqslant 0.001$; S*, highly significant, $0.001 \leqslant P \leqslant 0.01$; S, significant, $0.01 \leqslant P \leqslant 0.05$. [b] See Table II for meaning of symbols.

thiophosphates where cadmium may be an impurity in the original zinc used to prepare the additive. The same authors reported 20–90 μg/g cadmium in car tires as a probable result of use of zinc-diethylcarbonate (and associated cadmium contamination) in the process of vulcanization.

Nickel and chromium are frequently used in chrome plating, and copper is a common constituent of piping and other components of engines and chassis. The presence of these elements in soils and vegetation along motorways is probably due to mechanical wear and tear which deposits these metals in the fine dust of the roadway and therefrom to soils and vegetation.

The extent to which the above heavy metals (apart from lead) constitute a hazard to public health is a question somewhat outside the scope of the present work, but because of their known toxicity to humans, this question should be studied further.

Acknowledgment

The authors express their appreciation to J. E. Cox and J. Brown of the Soil Bureau Substation DSIR, Mount Albert, Auckland, for their kindness in obtaining soil cores for the present survey and to H. H. McCoach for providing soils from a background area.

Literature Cited

(1) Cannon, H. L., Bowles, J. M., *Science*, **137**, 765 (1962).
(2) Page, A. L., Ganje, T. J., *Environ. Sci. Technol.*, **4**, 140 (1970).
(3) Ward, N. I., Brooks, R. R., Reeves, R. D., *Environ. Pollut.*, **6**, 149 (1974).
(4) Olson, K. W., Skogerboe, R. K., *Environ. Sci. Technol.*, **9**, 227 (1975).
(5) Dedolph, R., Ter Haar, G., Holtzman, R., Lucas, H., *ibid.*, **4**, 217 (1970).
(6) Rabinowitz, M. B., Wetherill, G. W., *ibid.*, **6**, 705 (1972).
(7) Ward, N. I., Reeves, R. D., Brooks, R. R., *N.Z. J. Sci.*, **18**, 261 (1975).
(8) Lagerwerff, J. V., Specht, A. W., *Environ. Sci. Technol.*, **4**, 583 (1970).
(9) World Health Organization, "Health Hazards of the Human Environment", WHO, Geneva, Switzerland, 1972.

Received for review December 22, 1976. Accepted May 2, 1977.

CORRESPONDENCE

SIR: Dr. Dimitriades (*1*) has made significant progress in the search for an oxidant control strategy based on emission reductions. Despite the questionable long-term reproducibility (common to all smog chambers) of his unpublished smog chamber data, he has included the effects of NO_x and HC on the oxidant maxima. Further progress along these lines has included computer modeling complete with the effects of realistic light intensity (*2, 3*). An ozone isopleth diagram generated by these studies is shown in Figure 1. The purpose of this letter is to point out that the apparent safe area increasing with increasing NO_x (the isopleth lines of positive slope) is an artifact of the static chamber and model assumptions used, that if two further parameters, mixing and dilution are accounted for, the safe area disappears in terms of protecting the public. Consideration of rural hydrocarbons leads to the conclusion that only NO_x control can reduce the area over which large-scale low-level ozone episodes occur.

Reference *3* states:

> *If the oxidation of NO by organics is delayed sufficiently so that the sun has passed its zenith before significant amounts of NO_2 are created, photodissociation of NO_2 will be reduced, and less ozone will be allowed to accumulate.*

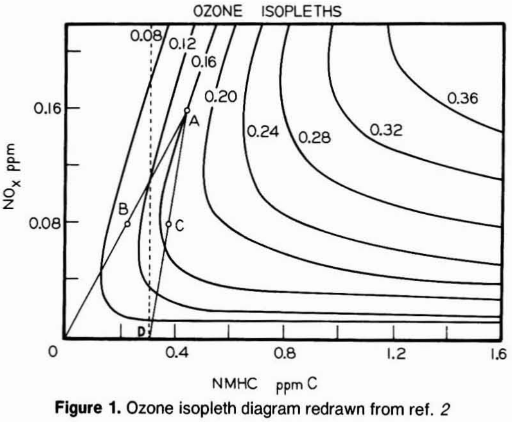


Figure 1. Ozone isopleth diagram redrawn from ref. *2*

This time for oxidation of NO to NO_2 is a significant factor in reducing the maximum ozone observed in chambers or in models. When NO_x is measured at a ground level station, vertical mixing up to an inversion layer brings down air bearing some ozone (and relatively little HC or NO_x). If we assume 40 ppb O_3 in this air from aloft, then all levels of NO less than enough to make 40 ppb in the mixed layer will be rapidly converted to NO_2. This initial conversion of NO to NO_2 by vertical mixing enables smog chemistry to start faster (*4*) even though O_3 is used up.

The effect of vertical mixing thus causes the atmosphere to start its smog chemistry at NO_2 whereas NO is used in the chamber studies. This effect is particularly important if one uses a surface NO reading as the initial input, whereas in the whole mixing layer it may rapidly become NO_2.

Diffusion also is important in eliminating the apparent "safe" area; thus, in ref. *2*:

> *A "worst case" approach was adopted to describe the dispersion of pollutants. A zero wind speed was assumed and the only dispersion of pollutants considered was that caused by the daily lifting of the inversion layer. The worst mixing occurs along the West Coast where there is only a 100-meter difference between the mean summer morning and afternoon mixing heights. Over a 9-hour period this corresponds to a 3 percent per hour dilution rate.*

Blumenthal et al. (*5*) have shown experimentally that diffusion and mixing can give a worse "worst case" than the static system modeled. This effect can be demonstrated using Figure 1. Thus, in terms of dose, if one considered the point A (O_x = 0.16 ppm) then lateral dilution below an inversion base with absolutely clean air can lead to B (O_x = 0.10 ppm). However, the air mass is now twice as large; thus, on the average twice as many people are affected, and the violation of the standard, although not so severe, lasts longer for any given wind speed. Worse yet, clean rural air contains 0.2–0.4 ppm NMHC (*3*). Dilution by a factor of two with this air leads to the point C (O_x = 0.17 ppm), a worse violation for twice the affected population for a longer time.

If natural sources of NMHC are taken as 0.3 ppm C for clean rural background, and if we assume total control of man-made HC emissions, then oxidant formation is constrained to the dashed line on Figure 1. On this line NO_x concentrations are the only factors which control oxidant formation. Since the rural NO_x background is close to zero (*3, 4, 6, 7*), any level of NO_x will be diluted toward the point D on the HC axis. For any NO_x input sufficient to exceed 0.06 ppm NO_x, maximum oxidant potential from Figure 1 is about 0.14 ppm O_3. Rural violations of the 0.08 ppm standard will occur wherever NO_x exceeds about 0.04 ppm. This rural NO_x concentration will only be encountered in areas near man-made sources (as shown in ref. *3*). Only NO_x reduction will control the area over which the violation occurs. Note, however, that urban HC control can limit rural excursions to $<\sim$0.14 ppm O_3 according to Figure 1, and could eliminate excessive suburban O_3 excursions.

Overall, I offer a warning that controls which are based implicitly on the concept "less NO_x worse O_x" should be viewed with suspicion in terms of protecting the general public. The fact that high NO_x emissions in a downtown area can prevent a downtown sensor from seeing high ozone levels is of little comfort to the suburban resident. Ideally, in a complete rational strategy the effects of dilution and dispersion must be considered along with NO_x. The experimental studies of Jeffries et al. (*8*) in which the importance of mixing is considered can help in this effort, together with the coupled diffusion and chemistry models currently under development (*9–12*). Hydrocarbon control alone will reduce the severity of local ozone episodes, but apparently only NO_x control can reduce the large areas over which lesser violations occur.

Literature Cited

(1) Dimitriades, B., *Environ. Sci. Technol.*, **11**, 80 (1977).
(2) Dodge, M. C., "Combined Use of Modeling Techniques and Smog Chamber Data to Devise Ozone Precursor Relationships", Proc. Int. Conf. Photochemical Oxidant Pollution and Its Control, Raleigh, N.C., Sept. 1976.
(3) U.S. Environmental Protection Agency, "Effectiveness of Organic Emission Control Programs as a Function of Geographic Location", Office of Air Quality Planning and Standards, Jan. 1977.
(4) Weinstock, B., in "Chemical Reactions in Urban Atmospheres", L. A. Tuesday, Ed., p 54, Elsevier, New York, N.Y., 1971.
(5) Blumenthal, D. L., Smith, T. B., White, W. H., "The Evolution of the 3-D Distribution of Air Pollutants During a Los Angeles Smog Episode July 24–26, 1973", MRI75 Pa-1370, 1975.
(6) Liu, S. C., Cicerone, R. J., Donahue, T. M., *Tellus*, in press (1977).
(7) Noxon, J. F., *Science*, **189**, 547 (1975).
(8) Jeffries, H. E., Fox, D., Kamens, R., EPA Oxidant Conferences, Raleigh, N.C., Sept. 1976.
(9) Eschenroeder, A. O., "An Assessment of Models for Predicting Air Quality", ERT Document, ERT W-75-03.
(10) Friedlander, S. K., Seinfeld, J. H., *Environ. Sci. Technol.*, **3**, 1175 (1969).
(11) Reynolds, S. D., Liu, M. K., Hecht, T. A., Seinfeld, J. H., *Atmos. Environ.*, **8**, 563 (1974).
(12) Rasmussen, R. A. Robinson, E., "The Role of Trace Atmospheric Constituents in a Surface Ozone Model", Proc. Southwest Conference on Rural Oxidants, Dallas, Tex., 1974.

Donald H. Stedman
Dept. of Atmospheric & Oceanic Science
University of Michigan
Ann Arbor, Mich. 48109

SIR: Basil Dimitriades began his article, "Oxidant Control Strategies. Part I. Urban Oxidant Control Strategy Derived from Existing Smog Chamber Data" [*ES&T*, **11** (1), 80 (1977)], by listing the main criticisms of EPA's Appendix-J oxidant control strategy. His final criticism states, "Recent findings suggest that the current strategy may be much less effective in alleviating the oxidant problems in downwind suburb areas and in rural areas." We feel this is somewhat misleading. It implies that the oxidant problem originates in the city and is compounded by transport from the city. In "Evidence of Atmospheric Transport of Ozone into Urban Areas" [*ES&T*, **9** (1), 59 (1975)], Coffey and Stasiuk pointed out that in New York state the oxidant standard will be exceeded in any city regardless of the extent of the control strategy in that city because of long-range ozone transport. Data from others show that this is the case throughout at least the Northern Midwest and the Northeast. Recently, we transmitted data taken in aircraft flights to EPA showing ozone levels exceeding 250 ppb upwind and into New York City with little or no observable effect of a nitric oxide shield in midafternoon. Obviously, even complete control of hydrocarbons in New York City is insufficient to permit attainment of the oxidant standard in that city.

We agree with Dr. Dimitriades that hydrocarbon controls will be the most effective way of controlling levels of photochemical oxidants. However, we would not wish to rely only on his smog chamber approach. There are severe limitations in determining ozone/precursor relationships at low (<0.15 ppm) ozone concentrations in smog chambers. Thus, this technique may not lend itself to a rationale analysis of the oxidant (ozone) problem in much of the United States. Solutions must be pursued on a regional basis. We hope EPA carefully reads Dr. Dimitriades' cautions in his discussion before it continues to base solutions for the national oxidant problem in terms of Los Angeles meteorology and smog chamber technology.

Harry H. Hovey, Jr.
Division of Air Resources
New York State Dept. of Environmental Conservation
50 Wolf Road
Albany, N.Y. 12233

SIR: Basil Dimitriades' paper on oxidant control strategies (*1*) represents a form of research needed to resolve current conflicts surrounding oxidant-precursor mechanisms.

On page 86, preparing for a rationale employing his Figure 8, the author states, "Thus, the 6–9 a.m. precursor concentration observed at a monitoring site clearly is not wholly and solely the cause of the oxidant observed later in the day, at the same or at any other site." He then employs the values: "... maximum 1-h oxidant observed in the region's ambient air, ... the maximum 6–9 a.m. value of NMHC-to-NO_x ratio, ... and annual NO_2 mean ...", in order to calculate how those parameters should be altered to achieve a 20% rollback.

I have these questions:

- Does the author accept the notion that the precursor pollutants may be log-normally distributed? [See, for example, Larsen (*2*)]. Would his approach be altered assuming log-normality? Note that Figure 2 of Larsen, loc. cit., indicates that in an urban situation (there, Washington, D.C.) the annual maximum 3-hourly concentration of NO_2 may exceed the annual average by more than 10 times.
- How would we identify, in time and space, precursor mixtures that are indeed responsible for observed oxidant concentrations?
- Unless such precursor mixtures can be identified, how can a reasonable rollback formulation be developed?

I appreciate having this opportunity to comment.

Literature Cited

(1) Dimitriades, B., *Environ. Sci. Technol.*, **11** (1), 80 (1977).
(2) Larsen, R. I., *J. Air Pollut. Control Assoc.*, **19** (1) (Jan. 1969).

James W. Ford
243 Cazenovia Street
East Aurora, N.Y. 14052

SIR: Dr. Stedman's comments are understood to be essentially as follows:

- The questionable long-term reproducibility of Dimitriades' "unpublished" data makes it inappropriate to determine effects of NO_x and HC on oxidant maxima.
- The upper part of the isopleth diagram (Dr. Stedman's Figure 1) depicting a beneficial effect from NO_x increase is an artifact of the static chamber and model assumptions used; mixing and dilution should be considered.
- Dilution/mixing with air containing O_3 or natural hydrocarbons could increase oxidant or population exposure or both.
- Only NO_x control can reduce the large areas over which lesser violations of oxidant air quality standard occur.

In response to the first comment, Dimitriades' data have been previously published both in a scientific journal (*1*) and in much more detail as a U.S. Bureau of Mines Report of Investigations (*2*). The data were obtained in an experimental test program completed within a period of approximately 6 months. The published reports include graphs from which the precision-related data scatter can be judged.

This author disagrees with Dr. Stedman's other comments. Those comments appear to reflect a misunderstanding of the intended applicability of the O_3 isopleths. These isopleth diagrams are intended for use upon the *urban O_3 problem only*—as was clearly explained in the Dimitriades articles (*3*, *4*)—and not upon the rural problem. Thus, increase of the NO_x emissions in *urban* areas with low HC-to-NO_x ratio will have a beneficial effect on the oxidant-related air quality. The effect of such NO_x increase upon the downwind rural areas will not necessarily be beneficial. Dr. Stedman's comments regarding the roles of natural hydrocarbons, of O_3 from aloft, and of the NO_x factor upon rural air quality have some merit but are in some respects incorrect and certainly far from delineating the effects of all factors that have a role in this extremely complex problem. A discussion of the rural oxidant problem, however, is not relevant to the subject here.

This author agrees with Mr. Hovey's comments. It is indeed true that the Dimitriades model (*3*, *4*) has only "local" validity, that is, is applicable only in situations in which oxidant/O_3 is produced from local emissions. Situations in which the problem is caused largely by oxidant/O_3 transported in the region call for different, as yet not quantified regional models. Alternatively, the Dimitriades model could be used but only after simplifying assumptions are made.

Mr. Ford's first comment apparently pertains to the NO_2-to-precursor relationship, a subject of peripheral interest only in the Dimitriades article (*3*). Whether the ambient precursor pollutant concentrations are or are not log-normally distributed is irrelevant to the subject, as it is the possibility that "the annual maximum 3-hourly concentration of NO_2 may exceed the annual average by more than 10 times". For the purpose of calculating oxidant-related control requirements by the Dimitriades model, it is necessary that the NO_2-dictated NO_x control requirements first be determined. To determine such requirements, one may assume a 1:1 relationship between NO_x and NO_2—as was assumed by Dimitriades (*3*) for illustrative purposes—or any other relationship.

In response to Mr. Ford's questions on the identification of the precursor sources responsible for the observed oxidant problem, there are aerometric techniques by which the oxidant contribution of the local emissions can be estimated. The sources responsible for the transported-in oxidant cannot be pinpointed, a problem for which the solution probably lies in development of area-wide control strategies. Questions of such nature are treated in forthcoming EPA documents including some new control guidelines (*5*) and the newly revised Air Quality Criteria for Photochemical Oxidants and Oxidant Precursors.

Literature Cited

(1) Dimitriades, B., *Environ. Sci. Technol.*, **6**, 253 (Mar. 1972).
(2) Dimitriades, B., "On the Function of Hydrocarbon and Nitrogen Oxides in Photochemical Smog Formation", U.S. Bureau of Mines, RI7433, Sept. 1970.
(3) Dimitriades, B., *Environ. Sci. Technol.*, **11**, 80 (Jan. 1977).
(4) Dimitriades, B., "An Alternative to the Appendix-J Method for Calculating Oxidant- and NO_2-Related Control Requirements", International Conference on Photochemical Oxidant Pollution and Its Control Proceedings, EPA-600/3-77-001b, U.S. Environmental Protection Agency, Research Triangle Park, N.C., Jan. 1977.
(5) *Fed. Regist.*, **42**, 9202 (Feb. 15, 1977).

Basil Dimitriades
Environmental Sciences Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, N.C. 27711

INDUSTRY TRENDS

The **Dow Chemical Co.** (Midland, Mich.) has asked the State of Michigan to rescind its suspension of the registration of purified pentachlorophenol antimicrobial, tradenamed Dowicide EC-7. Dow says that the purified grade is less hazardous than is the technical grade.

Eppinger Furniture, Inc. (Elmsford, N.Y.) is demonstrating how building lighting into furniture can save energy in buildings.

Niagara Mohawk (Syracuse, N.Y.) and eight other utilities are progressing with joint development of 56 commercially operational 26 000-kW fuel cells for use by the early 1980s.

AG Brown Boveri & Cie. (Baden, Switzerland) said that it has been proved that a water sterilizing unit equipped with only one of the company's ultraviolet lamps can sterilize drinking water flowing at 100 m^3/h, and containing 10^5 bacteria/cm^3.

The **Solar Energy Industries Association** (Washington, D.C.) has praised President Carter for recognizing solar energy as a "here and now technology, and not some distant futuristic product."

SF Air Control, Inc. (Old Greenwich, Conn.), a member of the Fläkt Group, has a contract for $11 million from Martin Marietta Aluminum, Inc., for two dry-dust removal and fluoride recovery plants.

Great Lakes Instruments, Inc., maker of pH, conductivity, dissolved oxygen, and turbidity instrumentation, is constructing a new manufacturing facility at Brown Deer, Wis., north of Milwaukee.

Dravo Van Houten, Inc. will make a study of safety practices related to the design/construction/operation of offshore pipelines for the U.S. Department of Transportation.

Radian Corp. (Austin, Tex.) has a 33-mo, $265 383 contract to identify and characterize nonvolatile organic chemicals in drinking water.

Balston Canada Ltd. has been formed at Mississauga, Ontario, to serve "growing demand" for Balston filter products throughout Canada, and expects these Canadian activities to accelerate rapidly.

Freeport Minerals Co. (New York, N.Y.) announced that a long-term contract for sale of the remaining 50% of its new uranium recovery project's output has been virtually completed.

Taylor Division of Sybron Corp. (Rochester, N.Y.) has received a $1.4 million contract for a computer system to control a wastewater treatment plant being built by the town of Amherst, N.Y.

Systems Control, Inc. (Palo Alto, Calif.) announced the successful year-long operation of the advanced digital control system at the Franklin, Ohio, wastewater treatment plant of the Miami Conservancy District.

Horiba Instruments, Inc. (Irvine, Calif.) has purchased the Vehicle Emission Computer Systems business of Interautomation (Ann Arbor, Mich.).

Lockheed Missiles & Space Co., Inc. (Sunnyvale, Calif.) has completed the design of a boat-mounted device capable of recovering spilled oil in seas as high as 5 ft. The device will be the largest of the "CLEAN SWEEP" patented disc skimmers.

Envirotech/Chemico Air Pollution Control will furnish a hooded quench car to U.S. Steel at the Clairton Works in Pennsylvania, to control coke-pushing emissions.

A **Hewlett-Packard** minicomputer is controlling the formation of 33 huge caverns in a large German underground salt deposit, which will hold about 30% of legally required West German oil reserves of about 90 million bbl.

Davy Powergas Inc. (Lakeland, Fla.) will proceed with a Phase I study and definitive cost estimate for a gas scrubbing facility for Getty Refining and Marketing Co. The facility would use the Wellman-Lord SO_2 Recovery Process.

Air Resources, Inc. (Palatine, Ill.) will install the first LO-CAT hydrogen sulfide (H_2S) oxidation process at the refinery of Plateau, Inc. (Farmington, N. Mex.). The process makes sulfur which will be used to improve soil.

Combustion Engineering's C-E Lummus subsidiary will start detailed work on a $600 million coal gasification plant in North Dakota for American Natural Resources Co. This work will involve engineering.

Two **Dorr-Oliver Inc.** "Clariflocculators", 225 ft in diameter, and able to treat 45 mgd of wastewater, have been installed by International Paper Co., at its Androscoggin mill.

Environmental Tectonics Corp. (Southampton, Pa.) has recently completed shipment of 14 large Mobile Water Purification Units (1500 gph each) to the government of Iran.

United International Research, Inc. (Hauppauge, N.Y.) says that Atane, an additive that the company produces, can improve octane performance of gasoline by 6%, and can be used instead of lead.

Electric Auto Corp. (Caparra, P.R.) has received a license from Electric Fuel Propulsion Corp. (Detroit, Mich.) to use FPC's technology in the design of a small electric car that will include aerodynamic features.

Solartron International, Inc., has been formed at Nashville, Tenn., to manufacture and distribute a broad line of solar heating/cooling products. The products will use air instead of water as a medium.

The Bureau of National Affairs (Washington, D.C.) said that a survey it did revealed that the Occupational Safety and Health Act of 1970 did little to improve safety records at 124 companies surveyed. What did increase was reporting/record-keeping costs.

Flack & Kurtz (New York, N.Y.) will show American Polymers Corp. (Paterson, N.J.) how to recover waste heat in a plant and use it again for air conditioning.

The American Petroleum Institute (Washington, D.C.) has endorsed proposed legislation that would encourage research on the effects of oil on ocean marine life, but said that goals should be clearly spelled out.

SF Air Control, Inc. (Old Greenwich, Conn., *ES&T,* July 1977, p 643), which specializes in air and gas treatment and cleaning, has changed its name to Flakt, Inc.

Dames & Moore (Los Angeles, Calif.) will perform an environmental assessment of possible routes for a proposed 132 000-V transmission line in southern suburban Cleveland (Ohio) for Cleveland Electric Illuminating Co.

Met-Pro Corp. (Harleysville, Pa.) signed a $360 000 contract to provide Fybroc fiberglass vertical pumps for wastewater treatment to the Puerto Rico Water Resources Authority (San Juan, P.R.).

Stanley Consultants, Inc. has been selected to conduct Phase II of the Ohio Statewide Solid Waste Management Plan. Included will be estimates of markets for end products of solid waste processing.

Weston Environmental Consultants-Designers has an ERDA contract for at least $450 000 to make full environmental assessments for coal liquefaction and off-shore oil exploration/drilling/technology.

The **Hamon Cooling Tower Division** of Research-Cottrell, Inc., has a letter of intent from Union Electric Co. (St. Louis, Mo.) for design/construction of two natural draft cooling towers. Approximate cost: $23 million.

The **Alaskan Arctic Gas Pipeline Co.** (Washington, D.C.) was "shocked and disappointed" by the Canadian National Energy Board's conditional approval of the rival Alcan Highway route for transporting natural gas from the Arctic.

Watervliet Paper Co., Inc. (Watervliet, Mich.) announced the successful start-up of its half-million dollar clarification system for removing solids from wastewater, and eliminating odor from spray irrigation.

Schuch Engineering Co., Inc. (St. Petersburg, Fla.) is supervising a construction project for a plant to produce insecticides and intermediate chemicals at Makhteshim Darom, Israel. The plant will have special safety devices and pollution controls.

The **Nichols Engineering & Research** subsidiary of Neptune International Corp. has an exclusive license to market a new powdered carbon regeneration system developed by CPC International.

The **Heil Co.** (Milwaukee, Wis.) is providing a Model 72A refuse shredder system as part of a $3.1 million solid waste disposal system for Lewiston, Maine. The shredder can handle up to 50 tph, and costs just under $644 000.

The **Graver Water Division** of Ecodyne Ltd. (Canada) will supply nearly $2 million worth of water treatment equipment, and install it at Ontario Hydro's generating station at Thunder Bay.

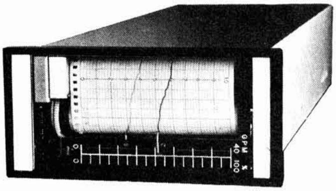
Standard Oil of Ohio has placed into operation a wastewater treatment unit as part of a system to meet clean water rules that took effect July 1. It can handle 7000 gpm.

National AirOil Burner Co., Inc. (Philadelphia, Pa.), manufacturing combustion and pollution control engineers, has established a new branch office at Bedford, England, to serve European customers.

NUS Corp. (Rockville, Md.) has a subcontract from Union Carbide to help to prepare environmental assessments for the National Waste Terminal Storage Program for radioactive wastes.

WAPORA, Inc. (Washington, D.C.) and the French National Institute of Applied Chemical Research will form a jointly-held organization in France. It will be called ENVIROPACT, and will work in Europe (except Scandinavia) and all of Africa.

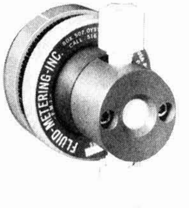
NEW PRODUCTS



Electronic chart recorder
Designed for use in water and wastewater facilities, the solid-state recorder accepts 4–20 mA dc, 0.25–1.25 V dc or converted time-pulse signals. A servo-positioner operates the pen indicator and optional high/low alarms. General Signal **101**

Pyrometer
Designed to cover temperatures from 1400–3900 °F (750–2150 °C), the pyrometer is available with digital or analog temperature readouts. Emissivity correction is automatic; temperature controller functions can be added to the control unit. Response time is adjustable 0.3–10 s. Capintect Instruments **116**

pH meter
Claimed to be the smallest pH meter, the transistorized unit weighs only 5 oz. Accuracy and readability is 0.1 pH and response time is reported to be 6 s. Devon Products **117**

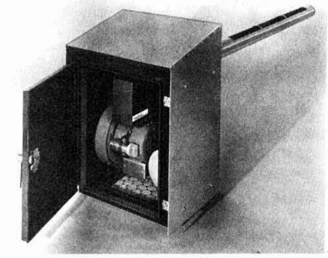


Metering pump
The panel-mounted pump is capable of handling viscous or corrosive liquids without check valves, flexing tubes or diaphragms. Variable displacement starts at 0.01 mL/revolution; flow range is 0–200 mL/min at up to 200 rpm; and flowspeed relationship is linear. The pump is self-priming. Fluid Metering **102**

Gas detector/analyzer
The system consists of the detector kit and pump inhalator. Detector tubes for over 140 toxic vapors are available. OSHA compliance logs and data-keeping record forms are supplied with each kit. Easton R/S Corp. **104**

Water-saving device
The device installed in a flush toilet tank limits the normal 6 gal flush to only 3–4 gal required. However, the normal full flush can be reinstated by holding down the flush handle for a full 10 s to deliver the entire contents of the water tank. Wiegand Enterprises **118**

Pressure transmitters
The line of transmitters features a common secondary element and a full line of primary elements that measure differential pressure, liquid level, gauge pressure, flow and absolute pressure. Adjustment span ratio is 10:1. Protection from radio frequency interference is designed into the transmitters. Sybron Corp. **119**

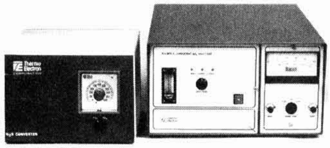


Opacity monitor
With its weather cover, this portable unit can monitor opacity and optical density on a semi-permanent basis of emission sources that include baghouses and electrostatic precipitators. The weather cover enclosure protects the transmissometer sensor probe. The air purge regenerative blower provides a source of clean filtered air. Dynatron **105**

Dissolved oxygen analyzer
Measures trace levels of dissolved oxygen over ranges of 0–20 ppb in boiler feedwater systems. Two voltage outputs of 0–1 V fixed and 0–1 V adjustable are standard. The analyzer case can be wall or panel mounted. Rexnord Instrument **120**

IR spectrometer
This Fourier transform IR spectrometer with an autosampling accessory permits molecular identification of samples continuously. Samples can be interchanged at random and spectra can be plotted or stored for future use. Scan times are 0.5 s at 8 cm^{-1} resolution. Block Engineering **121**

Cordless recorder
Powered by alkaline batteries, the recorder is capable of unattended operation for three months. Two models can monitor for temperature or for general purpose recording at remote sites. Nightingale and Associates **132**

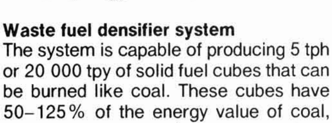


H_2S analyzer/monitor
The solid-state design permits long-term unattended operation because chemical reagents are not required. The unit is suitable for pollution control monitoring, and for use in the power, chemical and paper industries. ThermoElectron **106**

Boiler blowdown system
This automatic system maintains safe dissolved solids levels, minimizes blowdown and ensures minimum energy loss. The system is comprised of a sampling module and a control package. The sampling module includes the conductivity sensor and flow rate valves, while the control package includes the conductivity transmitter and air supply regulator. Johnson-March **122**

Ozone generator
The air-cooled system produces a maximum ozone concentration of about 3% from air and 6% from oxygen. The small unit produces 90 g/day of ozone at 1% by weight from air or 250 g/day at 2% by weight from oxygen. Union Carbide **123**

Pinch valve
Three-way diverter pinch valve is available with standard 125#–150# ANSI flange connections in sizes 1.5–10 in. This valve is suited for use in water and air pollution systems. RKL Controls **124**



Waste fuel densifier system
The system is capable of producing 5 tph or 20 000 tpy of solid fuel cubes that can be burned like coal. These cubes have 50–125% of the energy value of coal, depending on the type of waste combustibles used as raw material. The densifier system is part of what the manufacturer sells as an energy factory designed to collect and convert waste into sellable fuel. Papakube Corp **107**

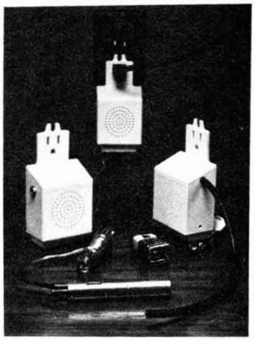
Depth filter
Newly designed water filter uses the entire filter media to remove particulate matter. The larger particles are captured at the top and the finer particles are removed in the lower layers. Particles down to 10 μ in diameter are removed. Culligan International **133**

Weather data transmitter/receiver
Parameters measured include precipitation, water level, snow level and temperature. This instrument keeps personnel at the central station apprised of conditions at remote sites. The transmitter can be left unattended for up to one year. Sierra Environmental Products **109**

Sonic oil burners
Plants are able to burn No. 6 fuel oil and other heavy residual fuel oils without smoke, a reduction in soot and, according to the manufacturer, a savings in fuel. The atomizing nozzle, with the aid of compressed air or steam, shatters oil into a fine, highly combustible mist. Sonic Combustion Systems **110**

Flow meter
The oval positive displacement flow meters measure low flows of 0.5–10.5 gph for gasoline or 0.3–10.5 gph for light oil with a sustained accuracy of ±1% or better. The meters can be used with a variety of liquid hydrocarbons in a temperature range of 14–140 °F. Emerson Electric **125**

Sampling pump
This smaller and lighter pump can be used for filter sampling and bag filling. It has both negative and positive pressure ports. The pump operates in a "pulsing" manner, at flow rates of 1–20 L/h (0.25–5.5 cc/min); a continuous flow setting allows high flow rates of 90 L/h (25 cc/min). It can be used for industrial hygiene and ambient air quality studies. Environmental Measurements **111**

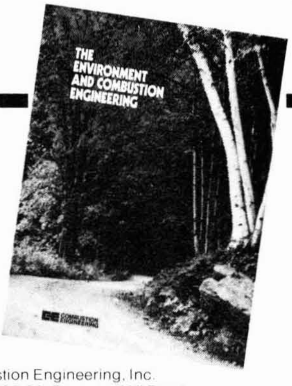


Alarm system
Designed to emit a loud, 85 dB continuous signal, pulsed two times/s when voltage or temperature drops. SGA Scientific **112**

Oil skimmer
In addition to oil spills, the skimmer will remove oily wastes and surface residue from wastewater treatment. The skimmers provide flow volumes from 20–175 gpm. The pump permits use of a semi-open, nonclogging impeller that can handle up to 20% air without locking. Skim, Inc. **126**

Dosimeter
The unit is an automatic personal noise exposure monitor. Exposure is displayed

---



no more messing around with burets

You don't need them with Hach's new Digital Titrator. It's a complete titration system that fits in your hand. There's no filling or washing fragile glassware. You don't spend valuable time preparing or standardizing titrant solutions. You don't waste titrant. And you don't need any special testing techniques.

Just twist on a cartridge and dip the delivery stem in your sample. Titrate by turning the knobs. Sample concentrations are read directly in mg/l from the Titrator's digital readout counter. Accuracy is ±1% on multiple turn titrations.

Hach's Titrator employs disposable titrating solution cartridges. Titrants are higher strength, more economical to use than regular titrating solutions.

Many different titrants are available: acids, bases, silver nitrate, thiosulfate, and phenylarsine oxide.

So quit messing around with burets. For more information about Hach's Digital Titrator call toll free 800-247-3986. Iowa residents, call collect 515/232-2533.

HACH CHEMICAL COMPANY
First in Water Analysis

P.O. Box 907 ■ Ames, Iowa 50010 U.S.A.
TWX: 910-520-1158
And: Hach Europe S.A./N.V.
B.P. 51, 5000 Namur 1, Belgium

CIRCLE 5 ON READER SERVICE CARD

on a 5-digit LED digital readout that extends from 000.01–999.99. A reading of 100.000 indicates 100% exposure and correlates with OSHA criterion number 1. Quest Electronics **127**

Liquid filters
The 24 sq in. filter press, equipped with a hydraulic closure, removes all solid contaminants of 0.1 μ or larger. Plate and frame filters are also available in 30 and 36 sq in. sizes. Star Tank & Filter Corp **114**

GC/MS with CI/EI
This latest gas chromatography/mass spectroscopy unit permits the analysis of a sample simultaneously by chemical ionization and electron impact ionization. Extranuclear Laboratories **113**

Injection pumps
Stroke adjustment, measured in increments of 1/10 000 in., can be made while the pump is in operation. The pump can deliver pressures up to 25 000 psi and volumes up to 2100 gpd. Aqua-Dyne Engineering **128**

Cascade impactor
This improved unit includes a high-capacity preseparator for particles larger than 10 μ. In addition, the top two stages have been modified to improve air flow and collection efficiency. Andersen 2000 **129**

Air velocity meter
Two measurement ranges are provided 0–30 m/s (0–6000 ft/min) and 0–3 m/s (0–600 ft/min). This portable anemometer operates over a wide range of temperatures. A 0–2.5 V recorder output is provided. Aikenwood **130**

Automatic liquid sampler
This permanently installed, nonclogging device can be used to sample raw sewage, sludge, slurry, pulp and paper waste and particle-free liquids. The system consists of an electronic controller, remote sampler, sample bottle and clear tubing. No pumps or vacuums are needed. Environmental Measurement Systems **131**

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.

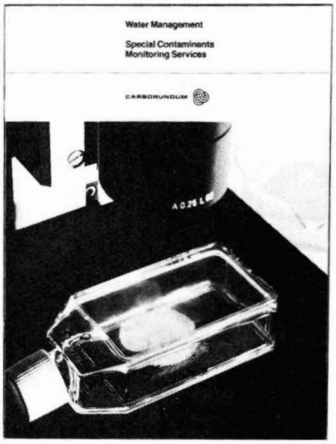
For specialized microcontaminants monitoring and analytical services, call on Carborundum.

The R&D/Water Management Division of The Carborundum Company can provide monitoring and analytical services for:

☐ Trace organics
☐ Viruses
☐ Asbestos
☐ Heavy metals
☐ All toxic and hazardous industrial wastes as defined by EPA
☐ Other microcontaminants

Monitoring services include equipment to concentrate viruses, trained field personnel to conduct sampling programs, specialized laboratories equipped with computerized GC/MS for organic compound analyses, a scanning electron microscope coupled to an energy dispersive x-ray spectrometer for asbestos analyses and isolated virus assay facilities.

Send for our free color brochure on microcontaminant monitoring.



Water Management
Special Contaminants
Monitoring Services
CARBORUNDUM

The Carborundum Company
R&D/Water Management Division
P.O. Box 1054
Niagara Falls, New York 14302
Telephone 716-278-6347

CARBORUNDUM

CIRCLE 4 ON READER SERVICE CARD

NEW LITERATURE

Metal bellows. Brochure outlines variety of standard and special metal bellows and how they solve problems of thermal expansion, vibration, and exhaust gases. Chromalloy American Corp. **151**

Fume coalescers. "Fume Coalescer Bulletin BFC-1" describes how to control submicron liquid and soluble solid fumes with collection efficiencies of 99.5% or more on particles smaller than 3 μ. Beltran Associates, Inc. **152**

Gasoline recovery. Form 8-GVR-2 describes a new device that enables service stations to recover gasoline vapors for reuse. Recovery can exceed 90%. Edwards Engineering Corp. **153**

Gas chromatography. Reprint of article, "Optimization of Gas Chromatography Resolution", by Eli Grushka, a foremost authority in the field, is available, and tells how resolution can be improved. Analabs, Inc. **154**

Dryers. Brochure describes TURBO-DRYER that uses little power, has minimal fire/explosion hazard, and can dry sludge, pastes, and other such substances, even when they are objectionable or corrosive. Wyssmont Co., Inc. **155**

Microanalysis. Brochure describes the Microscan 9 computer-controlled x-ray microprobe analyzer. Higher throughput of samples than in scanning electron microscope, according to company. Cambridge Instrument Co., Inc. **156**

Ultrafiltration. Publication No. 424C describes totally integrated ultrafiltration system for concentrating or desalting macromolecular solutions of 200–2000 mL or more. Amicon Corp. **157**

Dust collectors. Data sheet, "Peabody Jet-Ese pulse-jet dust collector", describes features and gives information on that type of dust collector. Peabody Air Resources Equipment Co. **158**

Improved wastewater treatment. Technical Data Sheet 1377A explains how mutant bacteria can treat wastewater by degrading refractory hydrocarbons, and other chemicals, and break down unwanted color as well. Polybac Corp. **159**

Refuse shredder. Data Sheet Picture Page P-781-A describes 60 by 84 in. shredder; a large shredder used at Recovery I (New Orleans, La.), and others. Gruendler Crusher & Pulverizer Co. **160**

Solvent recovery. New Publication, *Hoyt Pollution News,* answers questions on elimination or recovery of solvent fumes and odors. Case studies are given. Hoyt Manufacturing **161**

Vinyl chloride sampling. A total source sampling system for vinyl chloride is described in information now available. GII Enterprises, Inc. **162**

Microcontaminant monitoring. Brochure A-11 000 describes monitoring and analytical services for detecting trace organics, viruses, asbestos, and other toxic/hazardous materials in water. The Carborundum Co. **163**

Noise analysis. Short-form bulletin outlines unique services relating to vibration/noise analysis of rotating equipment and machinery. Failure prediction is also featured. Dyna Vibes Corp. **164**

Mercury decontamination. Information available describes mercury spill control kit that cleans up spilled mercury and absorbs residual vapors. J.T. Baker Chemical Co. **165**

Grease filters. Form GF-1898 tells how to design and install grease filters aimed at cleaning kitchen exhaust air, and includes safety procedures and codes. Research Products Corp. **166**

Wet scrubbers. New brochure covers the company's line of impingement plate wet scrubbers, which remove particulates and mist. Turn-key capabilities are offered. UOP Inc. **167**

Sludge disposal. Bulletin R-1 on React-O-Therm tells how these units are designed for thermal destruction of liquid wastes, slurries, and sludges, and how they operate without polluting the air. Maximum over 300 gph. Applications are given. Met-Pro Systems, Inc. **168**

Sewage treatment. Brochure describes company's construction products for sewage treatment plants. Armco Steel Corp. **169**

PVC pressure pipe. Information describes Super Bell-Tite C-900 Watermain, which is PVC pressure pipe for municipal water systems, that meets AWWA C-900 specifications. Clow Corp. **170**

Solvent recovery. Data Sheet 0705-24 provides information on solvent recovery monitoring, solvent vapor breakthrough, and gaseous detection of "hot spots". Mine Safety Appliances Co. **171**

Filtration media. Bulletin describes "Armalon" filtration media designed to remove particulate matter from a broad range of hot, corrosive gases. Media are inert to many oxidizing agents. Du Pont **172**

Energy Information. Brochure, "Energy Sources", lists publications concerning energy, much of them source material that dates back to the last century, and presents original work. Pergamon Press **180**

Pesticide respirators. Data Sheet 10-00-06 tells about respirators and masks to be worn when pesticides and certain fumigants are to be sprayed or otherwise handled, even when concentrations are not immediately dangerous to life and health. Mine Safety Appliances Co. **181**

Wastewater disinfection. Report, "Municipal Disinfection with Ozone and without Filtration", tells how coliform kills were complete, and BOD, turbidity, phosphates, and other pollutants were reduced by 98%. TII Corp. **182**

Scrubber supports. Bulletin 269-377-5 describes fiberglass scrubber support systems and applications, including one in which noxious fumes were removed, and only a water mist emerged. Fibergate Corp. **183**

Sewage sludge use. Bulletin No. 121 explains how sewage sludge can be disposed of either as auxiliary fuel, or as marketable fertilizer. C-E Process Equipment **184**

Solids removal. Bulletin 1400 lists 14 types of equipment for coarse solids collection and grit washing to reduce costs of waste treatment, and improve efficiency. FMC Corp. **185**

Environmental capabilities. Brochure, "Air/Water/Sound", describes company capabilities in solving air, water, and noise pollution problems, Environmental Elements Corp. **186**

Filter press. Bulletin FP-1 lists features and specifications for equipment that separates liquids and solids under high pressure through unique patented methods. Fred S. Carver, Inc. **187**

Waste gas use. Brochure tells how to fire waste heat sources, such as gas turbine exhaust, and how to incinerate combustibles in gas streams, thereby obtaining heat that would otherwise be lost. Ask for Bulletin DB-77. Coen Co. **188**

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.

Strainers/filters. Catalog SF-11 lists new line of convoluted line strainers and heavy-duty filters. Useful in hydraulic and low-pressure systems; filters are high capacity. The Lenz Co. **189**

Respirator. Data Sheet 10-00-07 describes Paint Spray Respirator for worker protection, approved by NIOSH and the Mining Enforcement and Safety Administration. Mine Safety Appliances Co. **190**

Gas chromatographs. Bulletin No. GC-10 lists line of gas chromatograph and ancillary equipment for biochemicals. Kontes Instrument Group **191**

Chart recorders. Brochure lists a family of rugged, inkless strip-chart recorders, 1–6 channels. Elnik Instruments, Inc. **196**

Apparatus. TEK-DATA 2 Catalog lists a whole line of laboratory apparatus, some of which is very useful as liquid sample concentrators for water pollution control studies. Tekmar Co. **197**

Dust collector. Brochure describes Unimaster fabric dust collector with filtration areas of 70–250 ft^2. Components can be put together in many different configurations. DCE Vokes, Inc. **198**

Pipette. Brochure describes MICRO-DOSER pipette that dispenses 25 liquid samples without refilling, and uses disposable assemblies. Applications in water analysis. Oxford Laboratories Inc. **199**

Magnetic separation. "Magnetic Separation: Recovery of Saleable Iron and Steel from Municipal Waste" (EPA/530/SW-559). Single copies. U.S. Environmental Protection Agency, Cincinnati, Ohio 45268 (write direct).

Wind energy. Report FEA/B-77/121 is entitled, "Wind Energy Conversion Systems Manufacturing and Sales Activity 1975 and 1976". Federal Energy Administration, Room 211, Old Post Office Bldg., Washington, D.C. 20461, Attn: Solar Energy (write direct).

Leachate handling. "Attenuation of Pollutants in Municipal Landfill Leachate by Clay Minerals: Part 2—Heavy-Metal Adsorption." Illinois State Geological Survey, Urbana, Ill. 61801 (write direct).

Halomethanes. "Trichlorofluoromethanes in Ground Water—A Possible Indicator of Ground-Water Age." Technical Report No. 90. Water Resources Research Center, Purdue University, West Lafayette, Ind. 47907 (write direct).

The St. Lawrence River. "Biological Characteristics of the St. Lawrence River" aids in evaluation studies. College of Environmental Science and Forestry, State University of New York, Syracuse, N.Y. 13210 (write direct).

"Can We Fish Again". New EPA film on the threat of toxic substances. Free loan, user pays return postage. FilmComm Inc., 208 S. La Salle St., Chicago, Ill. 60604 (write direct).

Gas from landfills. "Recovery of Landfill Gas at Mountain View" is an engineering site study done in California. Single copies. U.S. EPA, Cincinnati, Ohio 45268 (write direct).

Refinery effluents. Reports discuss many aspects of refinery effluents in water and air. Stichting CONCAWE, Van Hogenhoucklaan 60, The Hague, The Netherlands 2018 (write direct).

Energy from refuse. Brochure, "Refuse Energy Systems with Resource Recovery as Alternatives to Landfill", gives investment broker's view on the subject. William F. Fuller, White, Weld & Co., Inc., 91 Liberty St., New York, N.Y. 10006 (write direct).

BOOKS

Wind Engineering. E. Mowforth, Ed. Periodical. Multi-Science Publishing Co. Ltd., The Old Mill, Dorset Place, London E15 1DJ, England. $10, individuals whose organization subscribes; $40, multi-user organizations.

This periodical is devoted to engineering aspects of the use of wind energy. In the first volume, for example, surface wind behavior, wind noise, energy conversion on a large scale, and other matters concerning energy extraction are discussed.

How to Remove Pollutants and Toxic Materials from Air and Water; a Practical Guide. Marshall Sittig. xiii + 618 pages. Noyes Data Corp., Mill Rd. at Grand Ave., Park Ridge, N.J. 07656. 1977. $48, hard cover.

Pollutants do little or nothing to enhance the quality of water and air. Unfortunately, their number is nearly legion, and their removal is imperative. This book provides the latest information on what these pollutants are, from acetone cyanohydrin to zinc smelter effluents, or lists patents in areas concerning their control. In the great majority of cases, control methods are also set forth in detail.

Energy—A Crisis in Public Policy. Melvin R. Laird. 23 pages. American Enterprise Institute for Public Policy Research, 1150 17th St., N.W., Washington, D.C. 20036. 1977. $1.25, paper.

"Sadly and ironically, the greater the time, attention, and effort devoted to energy problems by the government, the more counterproductive have become our policies," says the author. He charges that government policies cause shortages, calls for a large degree of deregulation, and a new Department of Energy. Laird is a former congressman and Secretary of Defense.

Insect Control in the People's Republic of China (CSCPRC Report No. 2). 229 pages. National Academy of Sciences, 2101 Constitution Ave., N.W., Washington, D.C. 20418. 1977. $11.25

Many of the problems associated with insecticides in the Western world are now becoming apparent in China. Yet there is one countervailing factor, and that is the immense human labor force. For example, using light traps, workers removed insects and egg cases by hand. Also, biological control agents, such as birds and other predators, are in use. This book is a report on a visit to China by a delegation sponsored by the Academy.

Energy Technology IV: Confronting Reality. 496 pages. Government Institutes, Inc., 4733 Bethesda Ave., Bethesda, Md. 20014. 1977. $28.

This work comprises presentations by well-known experts on energy at the 4th Energy Technology Conference, held at Washington, D.C., in March. For instance, there is a forecast that coal use will triple, and nuclear fusion, wind, biomass, and the like, will provide only 10% of U.S. needs by the year 2000. Experts were from a cross-section of government, industry, academia, and other groups.

Wind Technology Journal. Periodical. Herman M. Drees, Ed. Wind Technology Journal, P.O. Box 7, Marstons Mills, Mass. 02648. 1977. $15/year for American Wind Energy Association members; $20/year for non-members.

This journal emphasizes technologies that are logical extensions of those within the domain of wind energy conversion. Among subjects presented are engineering of wind energy systems; blade design and fabrication; and other technological aspects of wind energy conversion and utilization.

Reprocessing of Spent Nuclear Fuels in OECD Countries. 47 pages. OECD Publications Center, Suite 1207, 1750 Pennsylvania Ave., N.W., Washington, D.C. 20006. 1977. $5.

Of late, nuclear fuel reprocessing has become very controversial, and this holds true in Organization for Economic Cooperation and Development (OECD), as well as other countries. The report emphasizes that reprocessing is done to conserve energy resources, but there may also be other economic and waste management advantages. The whole subject of reprocessing vs. "throwaway", weapons, the fast breeder, and other related topics come under discussion.

Potential Electric Power Shortages—Where and Why. Lawrence P. Hawkins and Gerald D. Gunning. 100 pages. Energy Consulting Services Division, The Chase Manhattan Bank, N.A., 1 Chase Manhattan Plaza, New York, N.Y. 10015. 1977. $400.

This incisive report presents a comprehensive analysis, by region, of the electric power industry, and its demand, supply, and costs. It forecasts fuel costs, capital costs, load growth, sales, prices, and other pertinent trends. The report takes a long, careful, and expert look at what will happen in the electric power industry over the next 10 years.

Ecological Sanity. George Claus and Karen Bolander. xv + 592 pages. David McKay, Inc., 750 Third Ave., New York, N.Y. 10017. 1977. $16.95, hard cover.

The so-called "Ecology Lobby", such as it may be, is a very well-intentioned group. But on numerous occasions, their Doomsday pronouncements and predictions will not stand up in the light of cold scientific examination. This book aims at looking at environmentalism in terms of objective science, and discusses what catastrophes could occur if extremists of the environmental movement get their way in some instances.

Toxicology Annual, Volume 2. Charles L. Winek, Sydney P. Shanor, Eds. xii + 272 pages. Marcel Dekker, Inc., 270 Madison Ave., New York, N.Y. 10016. 1977. $29.50, hard cover.

"Name your poison," the old saying goes. Some poison ends up in the environment. This volume covers poisonings in domestic animals; beryllium in the environment; carcinogenesis/mutagenesis, and other toxicological topics of interest.

Insecticide and Fungicide Handbook for Crop Protection, 5th ed. Hubert Martin, Charles R. Worthing, Eds. xvi + 427 pages J.B. Lippincott Co., East Washington Square, Philadelphia, Pa. 19105. 1977. $28, hard cover.

There are right and wrong ways to use pesticides. This book tells what pesticides to use on which crop, and how and at what rate to apply them safely.

The Distribution of Toxic Metals in Marine Ecosystems as a Result of Sewage Disposal and Natural Processes. Report No. 123. Patrick J. Whaling et al. xiv + 132 pages. Water Resources Research Institute, 124 Riddick Bldg., North Carolina State University, Raleigh, N.C. 27607. 1977. $4, paper.

Although toxic metal pollution is being abated, recovery from it is taking much longer. But before recovery can be accelerated, the metal pollution problem must be better defined. This volume is aimed at showing how to do this, and uses as a model an intensive study made in coastal North Carolina.

Air Pollution. Vol. 4, 3rd ed. Arthur C. Stern, Ed. xxii + 946 pages. Academic Press, Inc., 111 Fifth Ave., New York, N.Y. 10003. 1977. $49.50, hard cover.

This book is the fourth of five volumes, and is part of a standard reference work. It deals principally with engineering practicalities. Among subjects discussed are mist elimination; electrostatic precipitation; industries; combustion; source control; selection of devices; and related matters in abating air pollution.

Solar Collector Details. Item No. 7209. 30 pages. NC/STIC, P.O. Box 12235, Research Triangle Park, N.C. 27709. 1977. $5.75.

So you want to have a solar collector! Well, you have to know how to select and prepare your collector material. There are ways to optimize these materials and their preparation, but environmental degradation effects can occur. This booklet covers these topics.

MEETING GUIDE

September 13–16 Hollywood, Fla.
Third Symposium on Environmental Aspects of Fuel Conversion Technology. Research Triangle Institute
Write: Franklin A. Ayer, Research Triangle Institute, P.O. Box 12194, Research Triangle Park, N.C. 27709

September 16–17 Washington, D.C.
Saccharin: Scientific and Public Policy Issues. Society for Occupational and Environmental Health
Write: Society for Occupational and Environmental Health, 1714 Massachusetts Ave., N.W., Washington, D.C. 20036

September 18–21 Long Beach, Calif.
1977 Joint Power Generation Conference. American Society of Mechanical Engineers and others
Theme is "Energy—The backbone of the Economy." Environmental topics will be discussed. *Write:* Marion Churchill, Manager, Power Dept., American Society of Mechanical Engineers, 345 E. 47th St., New York, N.Y. 10017

September 19–20 St. Louis, Mo.
37th Annual AMA Congress on Occupational Health. American Medical Association and the National Institute for Occupational Safety and Health
Write: Department of Environmental, Public, and Occupational Health, American Medical Association, 535 N. Dearborn St., Chicago, Ill. 60610

September 19–20 Fort Collins, Colo.
Reclamation for Wildlife Habitat. Ecology Consultants, Inc.
Write: Dr. Russell Moore, P.O. Box 2105, Fort Collins, Colo. 80522

September 19–21 Washington, D.C.
Third Biennial Conference and Workshop on Wind Energy Conversion Systems. U.S. Energy Research & Development Administration
Write: Dr. Theodore R. Korneich, Conference Coordinator, JBF Scientific Corp., 1701 K St., N.W., Suite 905, Washington, D.C. 20006

September 20–21 Washington, D.C.
EPA/ERDA Symposium on High Temperature/Pressure Particulate Control. EPA and ERDA
Write: Mike Shackleton, Acurex Corp., Aerotherm Division, 485 Clyde Ave., Mountain View, Calif. 94042

September 21–23 Jackson, Miss.
Eighth Annual Meeting of the Southern Section of the Air Pollution Control Association
Write: Jim Haynes, Tennessee Air Pollution Control Division, 256 Capitol Hill Building, Nashville, Tenn. 37219

September 26–29 Cleveland, Ohio
Iron and Steel Exposition and Convention of Association of Iron and Steel Engineers. Association of Iron and Steel Engineers
Environmental topics will be discussed. *Write:* Association of Iron and Steel Engineers, Suite 2350, Three Gateway Center, Pittsburgh, Pa. 15222

September 28–29 Dallas, Tex.
Pollution Control Seminar for the Southern Forest Industry. U.S. EPA and the Forest Products Research Society
Write: Connie Walling, Conference Coordinator, Forest Products Research Society, 2801 Marshall Court, Madison, Wis. 53705

September 28–30 Columbus, Ohio
Second International Symposium on Polynuclear Aromatic Hydrocarbons. Battelle Columbus Laboratories
Write: Dr. Peter W. Jones, Battelle Columbus Laboratories, 505 King Ave., Columbus, Ohio 43201

September 28–30 Chicago, Ill.
Fifth Annual Illinois Energy Conference on Energy Policy Options for Illinois. The Energy Resources Center/University of Illinois at Chicago Circle and others
Write: Prof. James P. Hartnett, Director, Energy Resources Center, University of Illinois at Chicago Circle, Box 4348, Chicago, Ill. 60680

September 29–30 Dallas, Tex.
Coal Conversion: Practical and Legal Problems. Practising Law Institute and Southern Methodist University
Write: Practising Law Institute, 810 Seventh Ave., New York, N.Y. 10019

October 2–4 The Woodlands, Tex.
Alternatives to Growth '77. The Club of Rome, University of Houston and the Mitchell Energy & Development Corp.
Write: Jon Conlon, Mitchell Energy & Development Corp., 3900 One Shell Plaza, Houston, Tex. 77002, or Willem Biochel, Society for International Development, 1346 Connecticut Ave., N.W., Washington, D.C. 20036

October 2–6 Ames, Iowa
First International Conference on Iceberg Utilization. Iowa State University, the National Science Foundation, Saline Water Conversion Corp. of Saudi Arabia and the International Working Group on Iceberg Utilization
Environmental issues will be discussed. *Write:* Prof. Husseiny, Engineering Extension, 110 Marston Hall, Iowa State University, Ames, Iowa 50011

October 4–5 Williamsburg, Va.
Chemical Dispersants for the Control of Oil Spills. American Society for Testing and Materials/Committee F-20 on Spill Control Systems
Write: S. W. Bowman, American Society for Testing and Materials, 1916 Race St., Philadelphia, Pa. 19103

October 4–6 Gatlinburg, Tenn.
21st Annual ORNL Conference on Analytical Chemistry in Energy and Environmental Technology. Oak Ridge National Laboratory
Write: L. J. Brady, Analytical Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tenn. 37830

October 5–6 Minneapolis, Minn.
Reverse Osmosis and Ultrafiltration as Applied to Waste Water Treatment or Resource Recovery. Osmonics, Inc.
Registration is limited to 25. *Write:* Mrs. Patricia A. Letson, Osmonics, Inc., 15404 Industrial Road, Hopkins, Minn. 55343

October 6–7 Cincinnati, Ohio
Recirculation of Industrial Exhaust Air. National Institute for Occupational Safety and Health
Write: Franklin A. Ayer, Research Triangle Institute, P.O. Box 12194, Research Triangle

October 6–8 San Francisco, Calif.
21st Annual Western Occupational Health Conference. American Industrial Hygiene Association and others
Theme is "Carcinogens, Mutagens and Teratogens: Some Delayed Effects of the Occupational Environment." *Write:* Mary A. Zerwas, Publicity Chairperson, Stanford Research Institute, 333 Ravenswood Ave., J3096, Menlo Park, Calif. 94025

October 6–11 Philadelphia, Pa.
50th Anniversary Conference of the Water Pollution Control Federation. Water Pollution Control Federation
Write: Robert A. Canham, Water Pollution Control Federation, 3900 Wisconsin Ave., N.W., Washington, D.C. 20016

October 9–13 Seattle, Wash.
Biofouling and Corrosion in Ocean Thermal Energy Conversion. Battelle Pacific-Northwest Laboratories
Write: Dr. Robert H. Gray, Chairman, Symposium Committee, Battelle Pacific-Northwest Laboratories, P.O. Box 999, Richland, Wash. 99352

October 9–14 Easton, Md.
Energy Options for Developing Areas from the Present to 1985. Engineering Foundation
Write: Engineering Foundation, 345 E. 47th St., New York, N.Y. 10017

October 10–12 Denver, Colo.
Society of Petroleum Engineers Conference. Society of Petroleum Engineers of AIME
Theme is "Energy Strategies." *Write:* Society of Petroleum Engineers of AIME, 6200 North Central Expressway, Dallas, Tex. 75206

(continued on page 932)

October 10–12 Hampton, Va.
Noise-Con 77. NASA and the Institute of Noise Control Engineering

Write: Conference Secretariat, Noise Control Foundation, P.O. Box 3469, Arlington Branch, Poughkeepsie, N.Y. 12603

October 10–12 Columbia, Mo.
Nuclear Methods in Environmental and Energy Research. American Nuclear Society, ERDA, and the University of Missouri

Write: Dr. James R. Vogt, General Chairman, Nuclear Methods in Environmental and Energy Research, Environmental Trace Substances Research Center, University of Missouri, Route 3, Columbia, Mo. 65201

October 11–12 Cherry Hill, N.J.
Third Annual Conference on New Advances in Separation Technology. Filtration Publishing, Inc.

Write: W. F. Heneghan, Conference Chairman, 289 Greenwich Ave., Greenwich, Conn. 06850

October 11–13 Gaithersburg, Md.
Materials for Coal Conversion and Utilization. National Bureau of Standards, ERDA and Electric Power Research Institute

Write: S. J. Schneider, B308, Materials Building, National Bureau of Standards, Washington, D.C. 20234

October 11–13 Rolla, Mo.
UMR-DNR Conference on Energy. University of Missouri–Rolla

Write: Dr. J. Derald Morgan, Conference Director, Electrical Engineering Dept., University of Missouri–Rolla, Rolla, Mo. 65401

October 11–13 New Orleans, La.
AGU Conference on Oceanic Fronts. American Meterorological Society, Office of Naval Research and American Geophysical Union

Write: American Geophysical Union, 1909 K St., N.W., Washington, D.C. 20006

October 11–14 Washington, D.C.
Current Issues on Environmental Regulation of Nuclear Power Facilities. Atomic Industrial Forum, Inc.

Write: Conference Office, Atomic Industrial Forum, Inc., 7101 Wisconsin Ave., N.W., Washington, D.C. 20014

October 11–14 Lake Tahoe, Calif.
Ninth Annual Technical Meeting of the West Coast Section of the Air Pollution Control Association. Air Pollution Control Association

Write: William Krenz, South Coast Air Quality Management District, Metropolitan Zone, 434 S. San Pedro St., Los Angeles, Calif. 90013

October 12–14 Los Alamos, N.Mex.
Hazardous Solid Wastes and Their Disposal. University of California/Los Alamos Scientific Laboratory

Write: Fifth Life Sciences Symposium, University of California, Los Alamos Scientific Laboratory, P.O. Box 1663, Los Alamos, N. Mex. 87544

October 14–20 Lake Buena Vista, Fla.
National Environmental Sanitation & Maintenance Educational Conference, Exposition. Environmental Management Association

Write: Environmental Management Association, 1701 Drew St., Clearwater, Fla. 33515

Courses

September 17–December 17 Washington, D.C.
Practical Energy Conservation Techniques—Commercial Buildings Application. George Washington University

Fee: $170. *Write:* Director, Continuing Engineering Education, George Washington University, Washington, D.C. 20052

September 19–21 Houston, Tex.
Environmental Health Management. International Safety Academy

Fee: $300. *Write:* International Safety Academy, P.O. Box 19600, 10575 Katy Freeway, Houston, Tex. 77024

September 20–21 Charlotte, N.C.
Flat Line Finishing Workshop. Association of Finishing Processes of SME

Environmental topics will be discussed. Fee: $165 (nonmembers); $140 (members). *Write:* Ed Cherryholmes, AFP/SME, 20501 Ford Rd., P.O. Box 930, Dearborn, Mich. 48128

September 20–22 Rolling Meadows, Ill.
Analytical Methods and Techniques in the Petroleum, Fuel and Power Industries. Hewlett-Packard Co.

Environmental topics will be discussed. Fee: $225. *Write:* Bill Hart, Hewlett-Packard Co., Route 41, Avondale, Pa. 19311

September 22–23 Los Angeles, Calif.
Utilization of Solar Energy. The American Society of Mechanical Engineers

Fee: $200 (member); $225 (nonmember). *Write:* S. M. Greenwald, director, Professional Development Program, American Society of Mechanical Engineers, 345 E. 47th St., New York, N.Y. 10017

September 22–23 Los Angeles, Calif.
Energy Conservation. American Society of Mechanical Engineers

Fee: $200 (member)l $225 (nonmember). *Write:* S. M. Greenwald, director, Professional Development Program, American Society of Mechanical Engineers, 345 E. 47th St., New York, N.Y. 10017

September 22–23 Sewickley, Pa.
Occupational Health Update. Industrial Health Foundation, Inc.

Fee: $125 (member); $165 (nonmember). *Write:* George Reilly, Industrial Health Foundation, 5231 Centre Ave., Pittsburgh, Pa. 15232

September 26–29 Research Triangle Park, N.C.
Source Sampling for Particulate Pollutants. Air Pollution Training Institute

Fee: $140. *Write:* Registrar, Air Pollution Training Institute, MD 20, National Environmental Research Center, Research Triangle Park, N.C. 27711

September 26–29 Seattle, Wash.
Statistical Evaluation of Air Pollution Data. Air Pollution Training Institute

Fee: $88. *Write:* Registrar, Air Pollution Training Institute, MD 20, National Environmental Research Center, Research Triangle Park, N.C. 27711

September 30 Davis, Calif.
California's Environmental Quality and Business Climate: Compatibility or Chaos? University of California Extension–Davis

Fee: $45. *Write:* University of California Extension, Davis, Calif. 95616

October 1 Washington, D.C.
Residential Energy Conservation Methods & Incentives. George Washington University

Fee: $45. *Write:* Director, Continuing Engineering Education, George Washington University, Washington, D.C. 20052

October 3–7 Chicago, Ill.
Radioactive Waste Management for Nuclear Power Reactors. American Society of Mechanical Engineers

Fee: $425 (member); $475 (nonmember). *Write:* S. M. Greenwald, director, Professional Development Program, American Society of Mechanical Engineers, 345 E. 47th St., New York, N.Y. 10017

October 3–7 Washington, D.C.
Solar Heating and Cooling: Residential and Commercial Applications. George Washington University

Fee: $475. *Write:* Director, Continuing Engineering Education, George Washington University, Washington, D.C. 20052

October 9–14 Easton, Md.
Energy Options for Developing Areas—The Next 10 Years. Engineering Foundation

Fee: $265. *Write:* Engineering Foundation, 345 E. 47th St., New York, N.Y. 10017

(continued on page 936)

CLASSIFIED SECTION ■ POSITIONS OPEN

DIRECTOR

Energy and Environment Division
Lawrence Berkeley Laboratory
University of California

Applications and nominations are invited for Head of the Energy and Environment Division of the Lawrence Berkeley Laboratory. The Division is primarily funded by the Energy Research and Development Agency and has programs in:

> Conservation, combustion research and instrumentation, chemical process development, regional studies and energy policy analysis.

Candidates should have a record of distinguished achievement in energy-related or environmental research and the ability to give scientific and administrative leadership to a large and diverse division of a multi-purpose laboratory.

Applications or nominations should be submitted by October 1, 1977, to:

The Energy and Environment Search Committee
Director's Office
Lawrence Berkeley Laboratory
1 Cyclotron Road
Berkeley, California 94720

LAWRENCE BERKELEY LABORATORY
An Equal Opportunity Employer

A CONCERN FOR PEOPLE, AND THE ENVIRONMENT.

AIR QUALITY MANAGER

Our Mission is Energy . . .
. . . But Our Commitment is to a Cleaner and Safer Environment

. . . Here's your opportunity to play a key role in meeting both these objectives. We're TVA, an organization with a proud reputation for starting-up one of the most enterprising efforts in the history of power generation and energy conservation, and a focal point of national attention in the field of pollution control. New challenges arising from our efforts to set the environmental standards of the future have created this outstanding career opportunity for a professional to head-up the Air Quality Branch of our Division of Environmental Planning.

This high priority position extends overall responsibility for the planning, development, coordination, administration and technical direction of TVA's comprehensive air quality management program. For consideration candidates must possess at least a Master's degree in environmental engineering, chemical engineering or meteorology as well as a background demonstrating technical accomplishments in the supervision of air quality management programs. Professional Engineering certification is highly desirable. Strong leadership skills and a proven record for meeting project objectives are essential.

In return for your expertise you'll receive an exceptional package of compensation, complete benefits, and industry-wide recognition for your achievements. Qualified candidates are invited to submit resumes in confidence with earnings history to Employment Branch, 232 MIB, Department ES-61, Knoxville, Tennessee 37902.

An Equal Opportunity Employer

TENNESSEE VALLEY AUTHORITY

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	$59	$57	$55	$53	$51

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

SHIPPING INSTRUCTIONS: Send all material to

Environmental Science & Technology
Classified Advertising Department
25 Sylvan Rd. South, Westport, CT. 06880 (203) 226-7131

POSITION AVAILABLE

Mediator, Office of Environmental Mediation, University of Washington

The Office of Environmental Mediation, established with funds from the Ford and Rockefeller Foundations to offer mediation services in environmental conflicts, is seeking a person to serve on a mediation team which seeks resolution to a variety of environmental disputes. The applicant should have a strong background in the private or governmental sector and broad contact and acceptance with the various groups and interests involved in environmental conflict. A working knowledge of economic and environmental issues and experience with the political structure in the western U.S. is essential.

Applications, which should include a resume and three personal references, must be received by October 15, 1977. For additional information, contact:

Leah K. Patton
Office of Environmental Mediation
Institute for Environmental Studies, FM-12
University of Washington
Seattle, Washington 98195
Phone: (206) 543-6713

The University of Washington is an Affirmative Action, Equal Opportunity Employer.

■ SITUATIONS WANTED

SENIOR ENVIRONMENTAL MANAGER/SCIENTIST

broad experience, pollution control, environmental impact assessment, regulatory affairs, USA locations only, resume, references, write **Box EST-9771, ACS, 1155 16th St. N.W., Washington, D.C. 20036.**

CLASSIFIED SECTION

POSITIONS OPEN

SUPERVISORY OCEANOGRAPHER

Coast Guard Research and Development Center. Functions as Chief, Oceanography Branch. Conceives, plans, directs applied R&D programs in physical oceanography currently involved in oil spill movement prediction, iceberg drift and deterioration, probability of detection in Search and Rescue and various polar programs including polar vessel information systems. Broad progressive education with advanced degrees in physical oceanography or equivalent experience is required as well as demonstrated or potential ability to direct professional and technical personnel in theoretical, laboratory and field research. Experience in high seas oceanography, instrumentation, computer data reduction and computer modeling is preferred. Career civil service position. Salary $28,725 to $37,347. Submit SF-171, US Employment Form, to **R. MARTIN Code EST, USCG R&D Center, Avery Point, Groton, CT 06340.** Closing date: 30 September 1977 Equal Opportunity Employer.

WATER QUALITY SCIENTIST

Nalco Environmental Sciences has an immediate opening for an Associate Scientist in our chemistry section. Responsibilities include management of environmental water chemistry studies, data analysis and interpretation, and report preparation. Must have the ability to work independently and write well. Qualifications should include an M.S. or PhD in Environmental Chemistry or related field; previous work experience is desirable. Position offers a starting salary commensurate with experience, liberal company benefits including profit sharing. Send resume and salary history to: **Personnel Dept., Nalco Environmental Sciences, 1500 Frontage Road, Northbrook, Ill. 60062.** An Equal Opportunity Employer.

ENVIRONMENTAL HEALTH SCIENCES TRAINEESHIPS

A limited number of traineeships leading to a Master of Science degree are available at the School of Public Health, University of Illinois, Chicago. These traineeships support graduate study and research in environmental health disciplines, environmental management, and interrelated areas such as epidemiology, toxicology and biometry. Successful candidates will receive an annual stipend of $3900 plus tuition and fees for a period up to two years. Interested applicants should contact **Arthur H. Wolff, Professor and Director, Environmental Health Sciences, School of Public Health, University of Illinois at the Medical Center, P.O. Box 6998, Chicago, IL 60680,** telephone 312/996-8855.

FACULTY POSITION: Asst. or Assoc. Prof. to join full-time teaching faculty for major in Environmental Studies, **School of Human Ecology, Howard Univ., Washington, D.C.** Program emphasis is on man-environment interactions. Initial appt. for one year only, expected to be renewable. Candidates should have some experience in environmental field and PhD in a relevant discipline.

LABORATORY DIRECTOR—Technical and administrative responsibility for Laboratory Services Division. Excellent opportunity to build future with small, rapidly growing environmental firm. Laboratory is AIHA accredited. Qualifications include experience in environmental related and/or industrial hygiene fields. MS minimum, PhD preferred. A solid working knowledge of analytical laboratory methods required. Salary commensurate with qualifications. Send resume and salary history to: **Allen E. Galson, President, Galson Technical Services, Inc., 6601 Kirkville Road, E. Syracuse, New York 13057.**

CHEMIST
Industrial Wastes Control
$1,413—1,847

Desire Chemist with B.S. degree and at least two years experience in wastewater analysis with extensive work in gas chromatography and experience in industrial wastes control. Supervisory experience desired. Send resume to Personnel Officer, **Metropolitan Denver Sewage Disposal District No. 1, 6450 York Street, Denver, Colorado 80229.** An Equal Opportunity Employer.

professional consulting services directory

CONSULTATION AND LABORATORY SERVICES

- Radionuclide Analysis
- Environmental Studies
- Low Level Tritium Counting
- Licensing Assistance
- Bioassay
- Health Physics Services
- Whole Body Counting (Mobile)
- Emergency Medical Planning

RADIATION MANAGEMENT CORPORATION

UNIVERSITY CITY SCIENCE CENTER

3508 MARKET STREET, PHILADELPHIA, PA. 19104

Phone (215) 243-2950

SINCE 1917

HDR

HENNINGSON DURHAM & RICHARDSON

ENGINEERING•PLANNING•SYSTEMS•ECOSCIENCES

Complete Planning and Design Services for Pollution Control Facilities

Atlanta Charlotte Chicago Dallas Denver helena Los Angeles Minneapolis New Orleans Norfolk Omaha Pensacola Phoenix Seattle Santa Barbara Washington, D.C.

8404 INDIAN HILLS DRIVE
Omaha, Nebraska 68114 [402] 399-1000

Since 1885
Service to Industry

Stearns-Roger

COMPLETE ENVIRONMENTAL SERVICES:

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

ENVIRONMENTAL SCIENCES DIVISION
(303) 758-1122

P. O. Box 5888
Denver, Colorado 80217

Woodward-Clyde Consultants

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

Environmental Systems Division
Headquarters: San Francisco, CA
**Other offices in: Denver, CO*
Anchorage, AK • San Diego, CA

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

Engineering and Laboratory Services including:

- ☐ Water & Wastewater Analyses
- ☐ Characterization & Treatability
- ☐ Pilot Plant Studies
- ☐ Environmental Assessments
- ☐ Water Quality Surveys

O'BRIEN&GERE

1304 Buckley Road, Syracuse, N.Y. 13201
(315) 451-4700

SRC

CHEMICAL HAZARD ASSESSMENT
for Government and Industry

HAZARD ASSESSMENTS

- Toxic Substances
- Occupational Hazards
- Environmental Contaminants

LITERATURE REVIEWS AND EVALUATIONS
DESIGN AND DEVELOPMENT TEST PROGRAMS
ENVIRONMENTAL FATE AND TOXICITY REVIEWS

Contact Dr. Philip H. Howard
Center for Chemical Hazard Assessment
(315) 425-5134

Syracuse Research Corp., Merrill Lane, Syracuse, N.Y. 13210

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

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

professional consulting services directory

environmental science and engineering, inc.

TOTAL ENVIRONMENTAL SERVICES

P.O. BOX 13454 • GAINESVILLE, FLORIDA • 32604 • PHONE 904/372-3318

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

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

Complete Analytical Services for Environmental Studies & Pollution Control

---

Environmental Impact Analysis
Water and Wastewater Engineering
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

J. E. SIRRINE COMPANY

Engineers Since 1902 **An Employee Owned Company**

Complete Design of Environmental Facilities

USA: Greenville, SC. 29606 • Houston, TEX. 77027
Raleigh, NC. 27607 ☐ Riyadh, Saudi Arabia

IMPACT STUDY?

For heads-up help on ecostatistics call J.S. Warner, consulting biologist.
750North 50West
Logan, UT 84321
(801) 753-3549 References

AIR & WATER ANALYSIS

TOTAL SOURCE TESTING & DATA ANALYSIS
FEATURING: IN-SITU PARTICLE SIZING & RESISTIVITY MEASUREMENTS

ENVIRONMENTAL TESTING SERVICES inc.

2141 PATTERSON AVE., ROANOKE, VA., • (703) 342-3171

WESTON
ENVIRONMENTAL CONSULTANTS-DESIGNERS

Baton Rouge, LA/Cleveland, OH/Concord, NH
Decatur, GA/Houston, TX/Los Angeles, CA
Metairie, LA/Nashville, TN/Oklahoma City, OK
Richmond, VA/New York City, NY/Silver Spring, MD
West Chester, PA/Wilmette, IL

HAVENS AND EMERSON LTD.

Environmental Engineers

700 Bond Ct. Bldg, Cleveland, OH
299 Market Street, Saddle Brook, NJ
150 Technology Park, Atlanta, GA

USE THE
CONSULTANTS'
DIRECTORY

NUS CORPORATION

Environmental services, air and water pollution control engineering and consulting

4 Research Place
Rockville, Md. 20850
301/948-7010
TWX: 710-828-0540

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

Environmental Studies, Design and Construction Management

Gilbert/Commonwealth

Engineers/Consultants

Reading, Pennsylvania/Jackson, Michigan

CHARLES R VELZY ASSOCIATES, INC.
CONSULTING ENGINEERS
WATER POLLUTION CONTROL • SOLID WASTE DISPOSAL • AIR POLLUTION CONTROL • INDUSTRIAL WASTES • DRAINAGE • WATER SUPPLY
355 Main Street
Armonk, N.Y. 10504
Mineola, New York **Babylon, New York**

Environmental Quality Laboratory, Inc.
A General Development Subsidiary

- CHEMICAL & BACTERIOLOGICAL ANALYSIS
- ECOLOGICAL RESEARCH
- LAND USE & WATER RESOURSE STUDIES
- ENVIRONMENTAL IMPACT ASSESSMENT

590-D N.W. Olean Blvd., Port Charlotte, Fl. 33952 (813) 625-3137

TRUESDAIL LABORATORIES, INC.
CHEMISTS • MICROBIOLOGISTS • ENGINEERS

ESTABLISHED 1931
POLLUTION TESTING SERVICES
AIR - WATER - NOISE
4101 N. Figueroa St., Los Angeles 90065
(213) 225-1564
184 S. Hotel St., Honolulu, HA 96813

CAMP DRESSER & McKEE INC.

ONE CENTER PLAZA, BOSTON, MA 02108

ENVIRONMENTAL ENGINEERING & SCIENTIFIC CONSULTANTS

NEW YORK • WASHINGTON • DENVER • PASADENA
FT. LAUDERDALE • ORLANDO • ATLANTA • AUSTIN
WALNUT CREEK, CA • SPRINGFIELD, VA
MILWAUKEE • NEW ORLEANS

MOGUL
enviroservice®
PROGRAMS

- Water Quality Evaluation—Monitoring
- Air Testing—Ambient & Source
- Engineering—Environmental Energy & Water Conservation

SEND FOR 8-PAGE BROCHURE

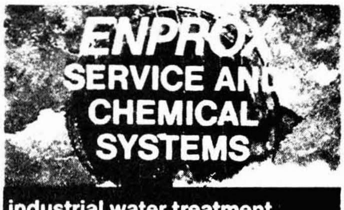
THE MOGUL CORPORATION
Chagrin Falls, Ohio 44022
(216) 247-5000
Arlington, TX ★ Charlotte, NC ★ Los Angeles, CA
Minneapolis, MN ★ Portland, OR

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) 735-8300
1 Blue Hill Plaza, Pearl River, N. Y. 10965



industrial water treatment pollution control

ENVIRONMENTAL PRODUCTS DIVISION OF OAKITE
working with industrial water 62 years

OAKITE PRODUCTS, INC.
BERKELEY HEIGHTS, N.J. 07922 • TLX 138661

PHONE **(201) 432-9385**

General Environmental Testing Laboratories, Inc.

Specializing in Water Analysis—Water Quality Investigations
Chemical Investigation, Monitoring and Sampling Services
EPA and APHA Methods
on-site testing
AA, IR, GC

181 PACIFIC AVE. JERSEY CITY, N.J. 07305

INDEX TO THE ADVERTISERS IN THIS ISSUE

Advertising management for the American Chemical Society Publications

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; 25 Sylvan Rd. South, Westport, Connecticut 06880 (Area Code 203) 226-7131

ADVERTISING SALES MANAGER

Benjamin W. Jones

SALES REPRESENTATIVES

Atlanta . . . Robert E. Kelchner, CENTCOM, LTD., Phone (Area Code 203) 226-7131

Boston . . . Anthony J. Eagan, CENTCOM, LTD., (Area Code 212) 972-9660

Chicago 60093 . . . Thomas C. Hanley, CENTCOM, LTD., 540 Frontage Rd., Northfield, Ill. (Area Code 312) 441-6383

Cleveland . . . C. James Pecoy, CENTCOM, LTD., Suite 205, 18615 Detroit Ave., Lakewood, OH 44107. (Area Code 216) 228-8050

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

Houston . . . Robert E. LaPointe, CENTCOM, LTD., (Area Code 415) 692-0949

Los Angeles 90045 . . . Clay S. Holden, CENTCOM 3142 Pacific Coast Highway, Suite 200, Torrance, CA 90505, (Area Code 213) 325-1903

New York 10017 . . . Anthony J. Eagan, CENTCOM, LTD., 60 E. 42nd Street, (Area Code 212) 972-9660

Philadelphia . . . Benjamin W. Jones, Anthony J. Eagan, CENTCOM, LTD., GSB Building, Suite 510, 1 Belmont Ave., Bala Cynwyd, Pa. 19004, (Area Code 215) 667-9666

San Francisco . . . Robert E. LaPointe, CENTCOM, LTD., Room 235, 1499 Bayshore Highway, Burlingame, CA 94010. (Area Code 415) 692-0949

Westport, Ct. 06880 . . . Anthony J. Eagan, CENTCOM, LTD., 25 Sylvan Rd. South, (Area Code 203) 226-7131

Manchester, England . . . Jill E. Loney, Technomedia Ltd., 216, Longhurst Lane, Mellor, Stockport, SK6 5PW Telephone: 061-427-5660

Reading, England . . . Malcolm Thiele, Technomedia Ltd., Wood Cottage, Shurlock Row, Reading, RG10 OQE. Telephone: 073-581-302

Paris, France . . . Patric Hale, Technomedia Ltd., 18 Rue Gounod, 92 Saint-Cloud, Paris. Telephone: 602-24-79

Tokyo, Japan . . . Haruo Moribayashi, International Media Representatives Ltd., 2-29 Toranomon 1-chome, Minato-Ku, Tokyo 105 Japan. Telephone: 502-0656

PRODUCTION DIRECTOR

Joseph P. Stenza

PRODUCTION ASSISTANT

Diane C. McGrath

October 12–14 Davis, Calif.
Introduction to Environmental Planning. University of California Extension–Davis

Fee: $300. *Write:* University of California Extension, Davis, Calif. 95616

October 13–15 Hampton, Va.
Noise-Con Seminar. Institute of Noise Control Engineering

Fee: $275. *Write:* Noise-Con 77 Conference Secretariat, P.O. Box 3469, Arlington Branch, Poughkeepsie, N.Y. 12603

Call for Papers

September 14 deadline
Fifth Energy Technology Conference and Exposition. Government Institutes, Inc.

Conference will be held February 27–March 1, 1978 at Washington, D.C. *Write:* Thomas F. P. Sullivan, Government Institutes, Inc., 4733 Bethesda Ave., N.W., Washington, D.C. 20014

September 15 deadline
1978 National Conference and Exhibition on Control of Hazardous Material Spills. U.S. Environmental Protection Agency, U.S. Coast Guard and Hazardous Material Control Research Institute

Conference will be held April 10–14, 1978 at Miami Beach, Fla. *Write:* Conference Technical Chairman, Dr. Gary Bennett, c/o Dept. of Chemical Engineering, University of Toledo, Toledo, Ohio 43606

September 15 deadline
Sixth Mineral Waste Utilization Symposium. U.S. Bureau of Mines and IIT Research Institute

Conference will be held May 2–3, 1978 at Chicago, Ill. *Write:* S. A. Bortz, IIT Research Institute, 10 West 35th St., Chicago, Ill. 60616

September 30 deadline
CLEOS '78: Conference on Laser and Electron-Optical Systems. IEEE and Optical Society of America

Conference will be held February 7–9, 1978 at San Diego, Calif. *Write:* CLEOS, c/o Optical Society of America, Suite 620, 2000 L St., N.W., Washington, D.C. 20036

October 1 deadline
World Conference and Exhibition on Energy from Biomass and Waste. Institute of Gas Technology

Conference will be held August 14–17, 1978 at Washington, D.C. *Write:* Ms. Kathy Fisher, Institute of Gas Technology, 3424 South State St., Chicago, Ill. 60616

October 1 deadline
Third Annual Illinois Private Sewage Disposal Symposium. Illinois Dept. of Public Health and Illinois Cooperative Extension Service

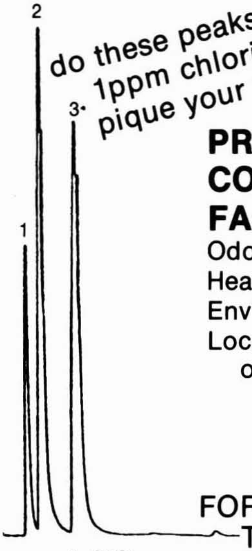
Conference will be held February 13–15, 1978 at Champaign, Ill. *Write:* Michael Neumann, Regional Engineer, Illinois Dept. of Public Health, 2125 South First St., Champaign, Ill. 61820

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	Telemetering & 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 postage stamp necessary if mailed in the United States

postage will be paid by

Environmental
Science & Technology
P. O. BOX 8639
PHILADELPHIA, PA. 19101

ENVIRONMENTAL Science & Technology

SEPTEMBER 1977

VALID THROUGH
JAN. 1978

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
185	186	187	188	189	190	191	192	193	194	195	196	197	198

Quick Search:

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

SEPTEMBER 1977

VALID THROUGH
JAN. 1978

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
185 186 187 188 189 190 191 192 193 194 195 196 197 198

Quick Search:

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

FIRST CLASS
Permit No. 25682
Philadelphia,
Pa. 19101

BUSINESS REPLY MAIL
No postage stamp necessary if mailed in the United States

postage will be paid by

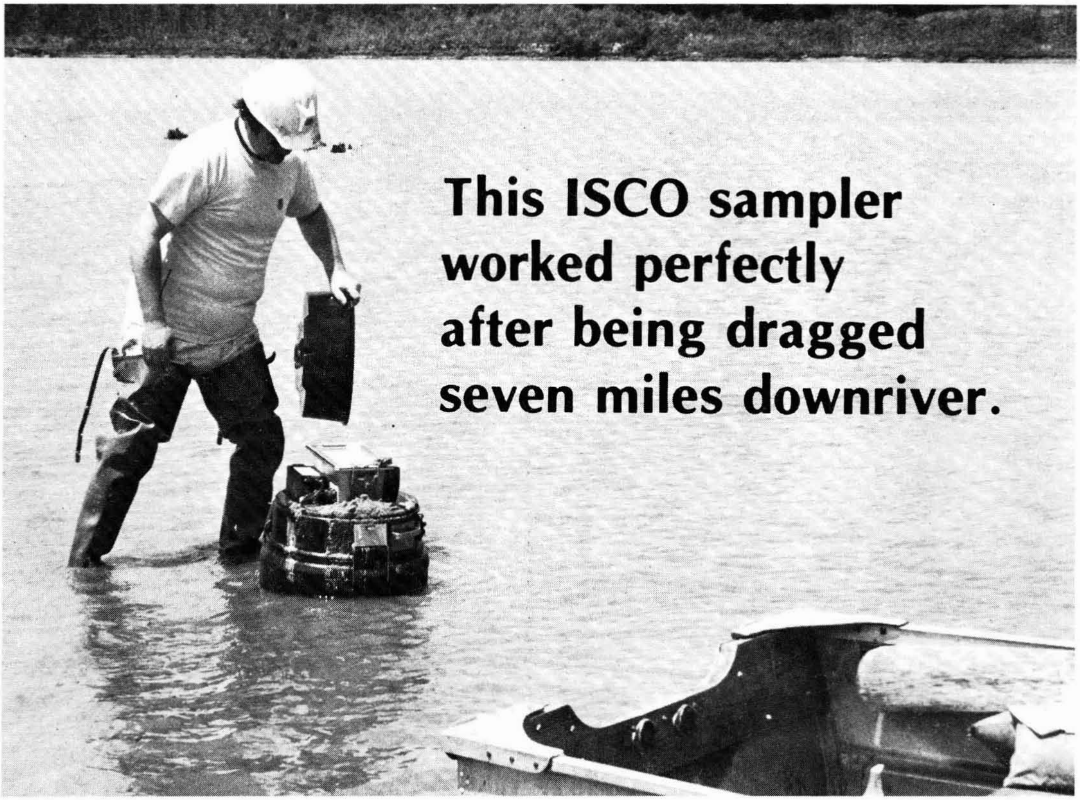
Environmental
Science & Technology
P. O. BOX 8639
PHILADELPHIA, PA. 19101

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	Telemetering & Data Acquisition
212	Waste Disposal Services
213	Water Pollution Instruments
214	Water Purification Equipment



Ruggedness doesn't show up on the specification sheet - it's proven only after many years' service, or by rigorous tests such as when we towed our Model 1680 Sampler down the muddy Platte river. Dragging over sandbars and floating upside down all the way didn't hurt it a bit: not a drop of water leaked into the watertight stainless steel case containing **all** motors, drives, and electronic components. The Nicad dry battery wasn't damaged, and the sampler passed a complete function test before it was even pulled out of the water.

Your sampling program probably won't involve the risk of losing a sampler down a river, but this is the kind of ruggedness you need to rely on for any job, whether it's a permanent outdoor installation or sampling a different manhole every day.

ISCO's versatile automatic samplers also operate on AC line power, and are available in 28 bottle sequential and 3 or 5 gallon composite models. Both can also be supplied in refrigerated versions. All have electronic digital controllers for reliable, flexible selection of sample volume and frequency.

Samplers can be controlled by either of two flow meters for flow proportioned collection. ISCO float or bubbler flow meters are not affected by temperature, and have a unique optical-electronic system which converts head height to flow rate with an accuracy of better than ± 0.2%. Flow rate vs. time may be recorded on a manhole-proof, battery operated recorder. The convenient linear strip chart puts an end to interpreting curved lines on a circular chart. If you want to save even more work, our battery operated digital printer can give you an already integrated printout of incremental and total volumes in gallons, liters, or any other unit, along with the time and date.

ISCO equipment gives you what you want, and it works when you want it. Send for our catalog or phone us today - we may be able to arrange a demonstration tomorrow.

ISCO

Box 5347 Lincoln, Nebraska 68505 Phone (402) 464-0231

CIRCLE 16 ON READER SERVICE CARD