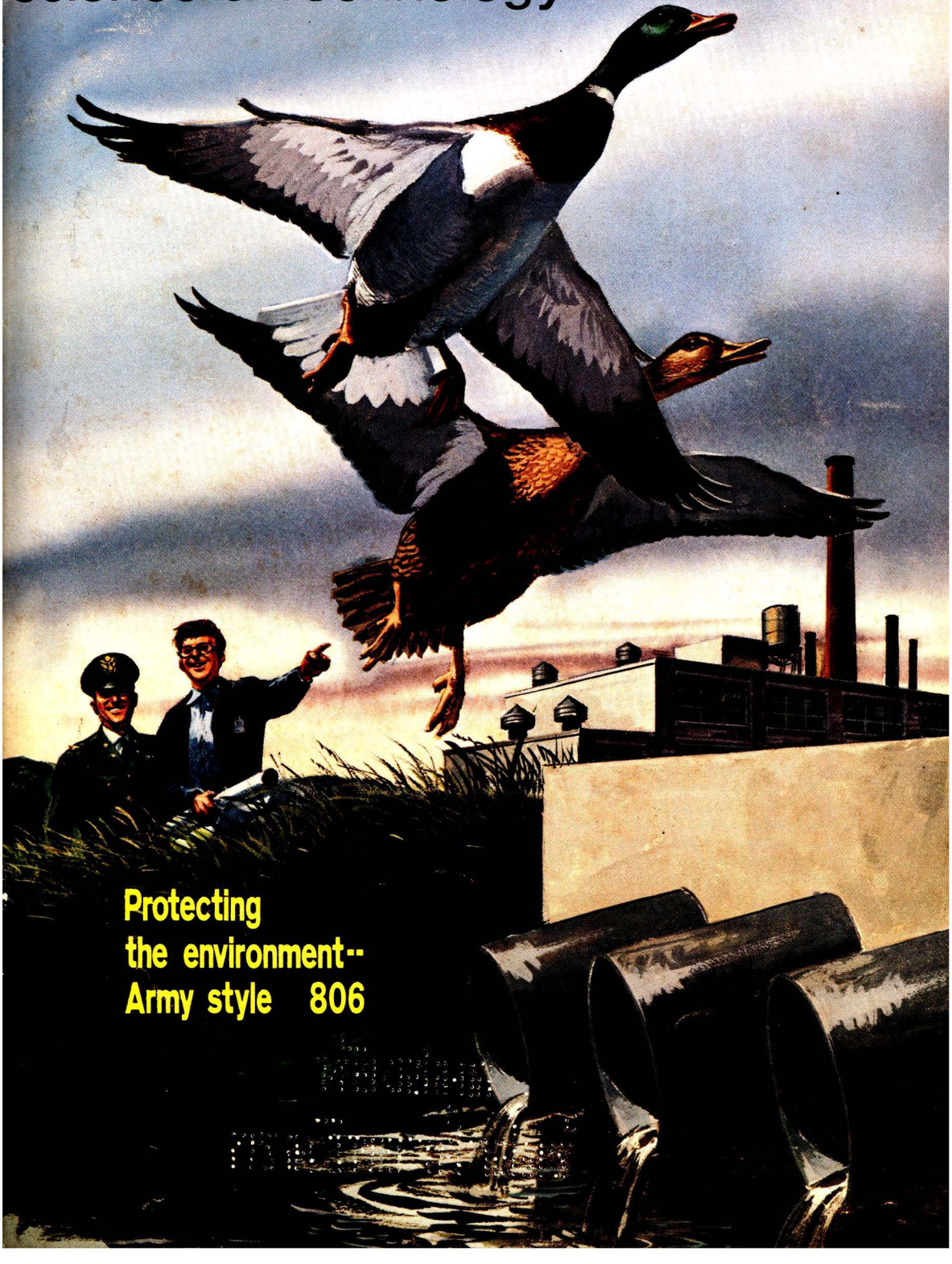
Environmental

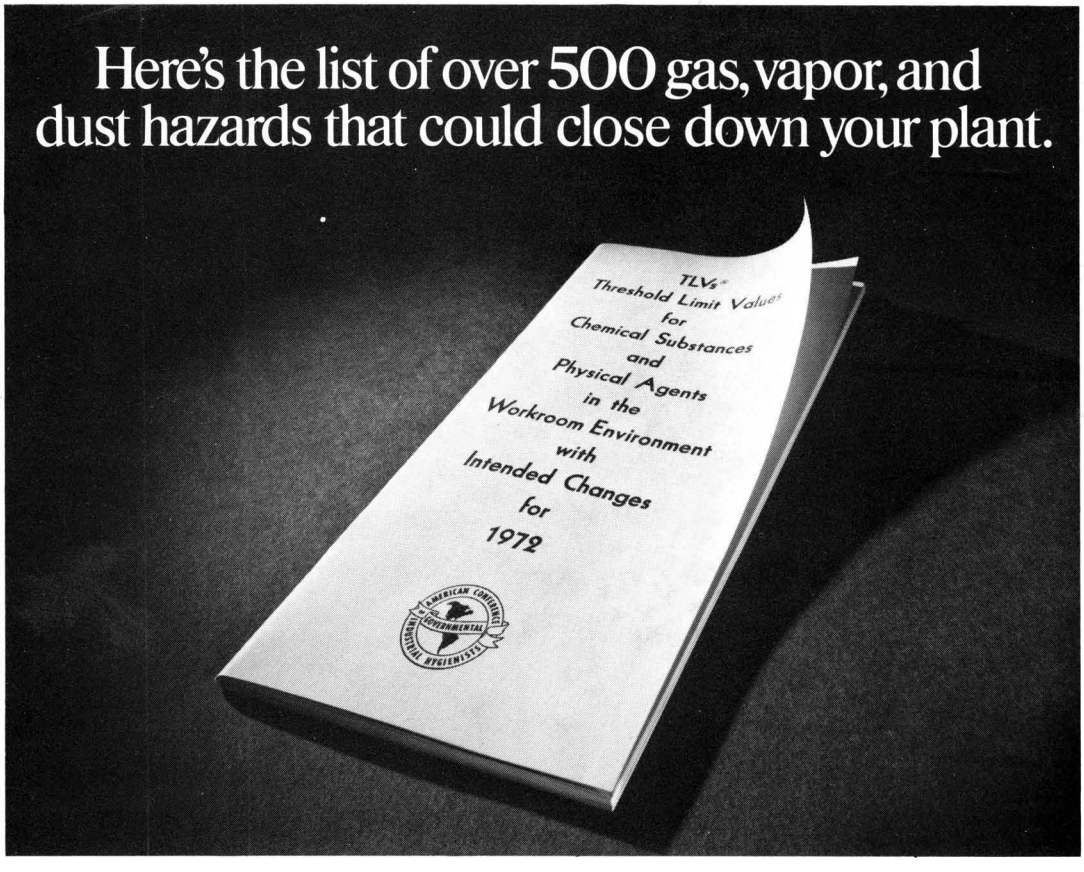
Science & Technology

SEPTEMBER 1973



Protecting
the environment--
Army style 806

Here's the list of over 500 gas, vapor, and dust hazards that could close down your plant.



MSA has the instruments that can spot check or continuously record 90% of them.

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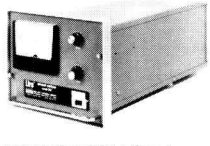
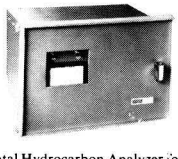


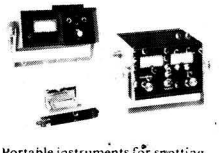
LIRA® Model 303 Infrared Analyzer for recording specific potential hazards in air, and for stack monitoring.

Toxgard for economical monitoring of toxic gases such as chlorine, hydrogen cyanide, or hydrogen sulfide.

CO Alarm Model 701 for continuous detecting and warning of presence of dangerous carbon monoxide concentrations.



Total Hydrocarbon Analyzer for low-level monitoring of hydrocarbons in air or in gas mixtures.



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EXHIBITORS

THE PRACTICAL ANSWER TO POLLUTION AND PROCESS MONITORING REQUIREMENTS

A new series of continuous monitors is available which automate proven ion electrode analytical methods. By employing sample pre-treatment procedures, these monitors offer laboratory accuracy over a wide concentration range.

Monitors for ammonia, cyanide, fluoride and chlorine are among the units offered by Orion Research, Cambridge, Massachusetts.

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If you are a subscriber, a reader, an exhibitor, a manufacturer, a consultant, an author—in fact, if you have any interest whatever in pollution control—you are invited to visit the ENVIRONMENTAL SCIENCE & TECHNOLOGY booth to browse through our literature, magazines, books, periodicals, guides, and journals—which are specifically designed and edited to be of interest to you.

Our staff at the booth will give you a most cordial welcome.

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Environmental Science & Technology

Volume 7, Number 9, September 1973

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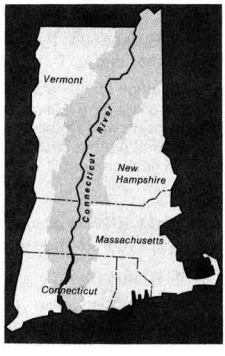

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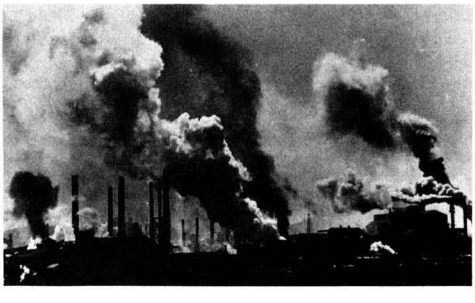
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CURRENT RESEARCH

Sources of vanadium in Puerto Rican and San Francisco Bay Area aerosols 817

C. S. Martens, J. J. Wesolowski, Robert Kaifer, Walter John, and R. C. Harriss

Atmospheric sources of vanadium are investigated by comparing its abundance and particle size distribution to that of other elements found in the atmospheres of the San Francisco Bay and Puerto Rico areas. Vanadium was found to originate from both soil and combustion sources.

Ligand photooxidation in copper(II) complexes of nitrilotriacetic acid. Implications for natural waters 820

C. H. Langford, Michael Wingham, and V. S. Sastri

Copper complexes of nitrilotriacetate are irradiated at 350 nm in a photoreactor based on a Rayonet unit. Despite the low absorptivity of the complexes at this wavelength, a significant photodecomposition of the ligand (identified products are CH_2O and iminodiacetic acid) occurs.

Fluorometric determination of selenium in water with 2,3-diaminonaphthalene 823

J. M. Rankin

A simple method for determination of selenium in clean water begins with hydrogen peroxide oxidation to convert inorganic selenium to selenite. The selenite is then reacted with 2,3-diaminonaphthalene to form an organic extractable piazselenol, naphtho-[2,3-d]-2 selena-1,3-diazole, which is determined fluorometrically. Method detects selenium at 1 ppb level.

Response of pinto bean and tobacco to ozone as conditioned by light intensity and/or humidity 824

J. A. Dunning and W. W. Heck

Pinto bean and Bel W3 tobacco are grown and exposed for 1 hr to 40 pphm of ozone at two light intensities and at two relative humidities. The interaction between relative humidity and light intensity during exposure is found to be significant, independent of species.

Volumetric methods for control of ammonia scrubbing process for removal of SO_2 from stack gases 827

T. C. Woodis Jr., J. M. Cummings Jr., and G. B. Hunter

Volumetric methods for analytical control of the ammonia scrubbing process are developed from standard analytical procedures. Results of three titrations are found to be sufficient to calculate the concentrations of ammonium bisulfite, sulfite, and sulfate in the scrubber liquor before or after the liquor is acidified with ammonium bisulfate and stripped of its SO_2.

Copper micronutrient requirement for algae 829

S. E. Manahan and M. J. Smith

A reproducible copper requirement for *Chlorella vulgaris* and *Oocystis marssonii* is demonstrated. Optimal growth is observed above 30 g/l. for Chlorella and 40 g/l. for *Oocystis*.

Chlorinated hydrocarbon insecticides in sediments of southern Lake Michigan 833

H. V. Leland, W. N. Bruce, and N. F. Shimp

Dechlorination of DDT to form DDD apparently predominates under the reducing conditions of sediments on the eastern side of the south basin of Lake Michigan. In other areas of the lake, DDT is the principal component of the t-DDT complex in sediments and DDE and DDD are major degradative products.

Rapid gas chromatographic method for determination of residual methanol in sewage 838

M. E. Fox

Rapid and specific method for the determination of low concentrations of methanol over the range of 0.5-100 ppm in sewage or other aqueous solutions involves the use of direct aqueous injection gas chromatography on a porous polymer column. Method does not require preconcentration or extraction.

Distribution of alkyl arsenicals in model ecosystem 841

A. R. Isensee, P. C. Kearney, E. A. Woolson, G. E. Jones, and V. P. Williams

Distribution of ^{14}C-labeled cacodylic acid (CA) and dimethylarsine (DMA) among aquatic organisms in a model ecosystem was studied. Amounts accumulated by the organisms show that neither substance has a high potential to biomagnify in the environment.

Dieldrin. Effects of chronic sublethal exposure on adaptation to thermal stress in freshwater fish 846

E. K. Silbergeld

Freshwater fish, of the species *Etheostoma nigrum*, were pretreated with 2.3-ppb dieldrin for 30 days and then exposed to thermal stress, applied by heating the water at a rate of 1°C/hr to a maximum of 7–9°C above ambient temperature. The pretreated fish were found to have higher mortality than those not pretreated.

Portable continuous chromatographic coulometric sulfur emission analyzer 849

R. J. Robertus and M. J. Schaer

An instrument capable of automatic continuous quantitative analysis of sulfur compounds in stack gases has been developed and tested. Gas samples can be analyzed for SO_2, H_2S, and CH_3SH once every 10 min. Concentrations of 0.1 ppm for CH_3SH, 0.2 ppm for H_2S, and 1.0 ppm for SO_2 can be detected.

NOTES

Leaves as source of phosphorus 853

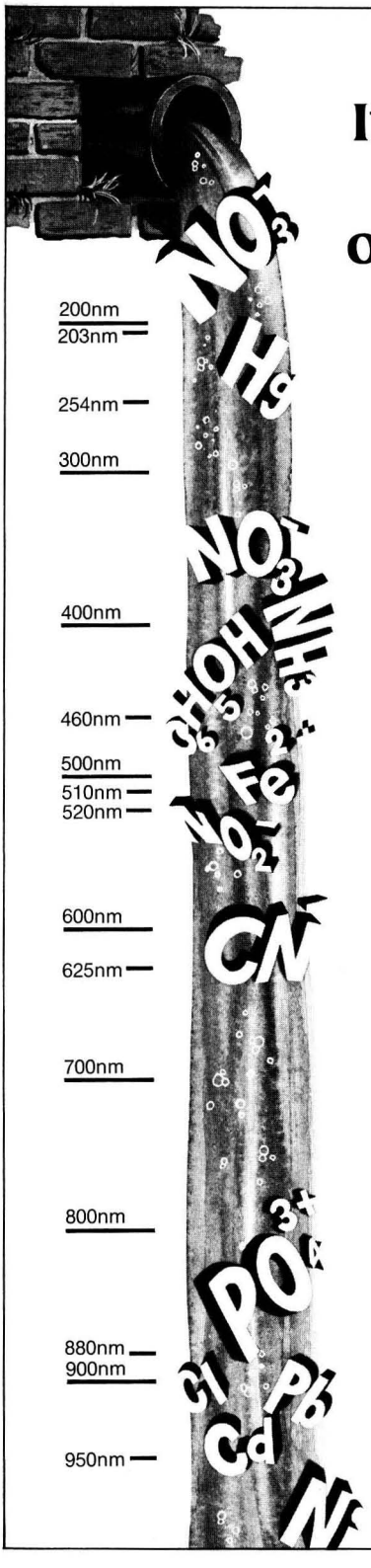
W. F. Cowen and G. F. Lee

Cut up leaves are found to release almost three times as much soluble P as intact leaves, and moisture retained on leaves after a rainstorm are found to contain significant soluble reactive P. Results of investigation point to the importance of proper leaf pickup.

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

Credits: 781, *C&EN*'s Fred H. Zerkel; 800, Penn. State Dept. of Health; 801, Jon Brenneis and *Fortune*.

Cover: Raymond Thorley, Picatinny Arsenal



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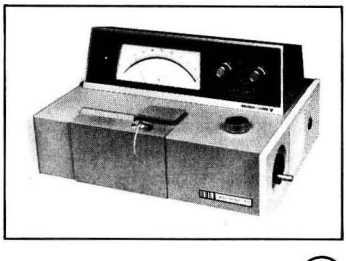

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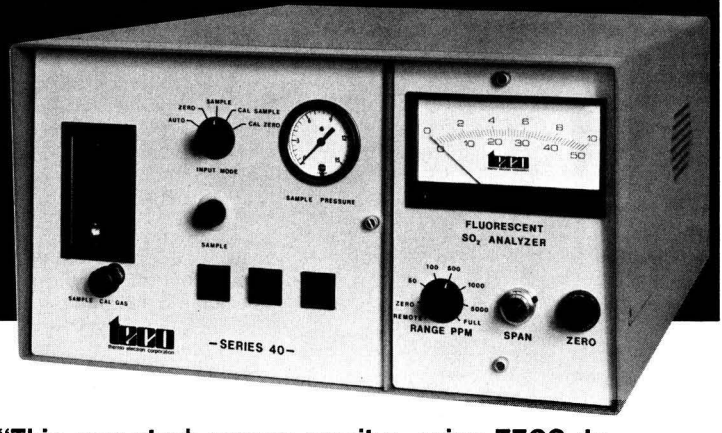

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In each paper with more than one author, the name of the author to whom inquiries should be addressed carries a numbered footnote reference.

Maintaining a water cleanup posture

On one hand we wonder if the public is convinced that water pollution cleanup is really under way. On the other, we witness the flurry of paperwork triggered by the Federal Water Pollution Control Amendments of 1972 and wonder, sometimes, how the public can be anything but convinced. But as it has been pointed out before, regulations and guidelines are only the beginning; only when enforcement actions are taken will the doubting Thomases be convinced.

As *ES&T*'s Carol Lewicke points out in this month's special report, states are making headway under the new water law, somewhat slowly, perhaps reluctantly, but nevertheless progress. Obviously, much remains to be accomplished in the ensuing years. Also, in this month's issue, is *ES&T's* first PAT report. It's aimed at publicizing the practical and available technology that is finding use either in the public or private sectors.

According to last year's annual report of the Council on Environmental Quality, the improvement in water quality on a national scale was not significant. We wonder if we will hear the same line later this month when CEQ's fourth annual report on environmental quality is released. Certainly, we hope to hear better news than last year's.

At the end of this month and the first week of October, the Water Pollution Control Federation will host its annual convention in Cleveland, Ohio. Somewhat later, the second International Pollution Control Conference and Exposition will be held in Philadelphia. More technical progress will be presented at each.

But if the public is not aware of and happy with the cleanup, then we wonder who is. Certainly, one would think that the professionals, the members of WPCF, who owe their livelihoods and professional careers to the cleanup program would be somewhat pleased with the progress. To the list we would add construction firms who are involved in the building of these waste water treatment facilities. We submit that if they had to choose between unhappy and happy, the majority of these people would choose the latter. But that, of course, is not saying they are ecstatic about the cleanup progress either.

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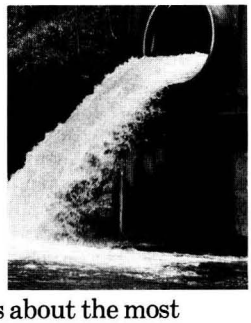

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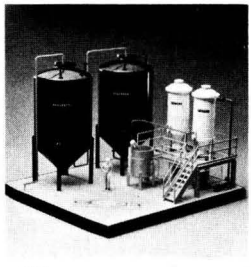

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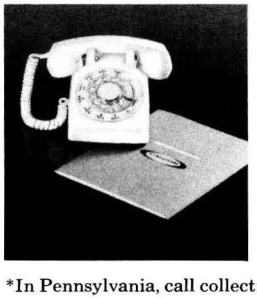

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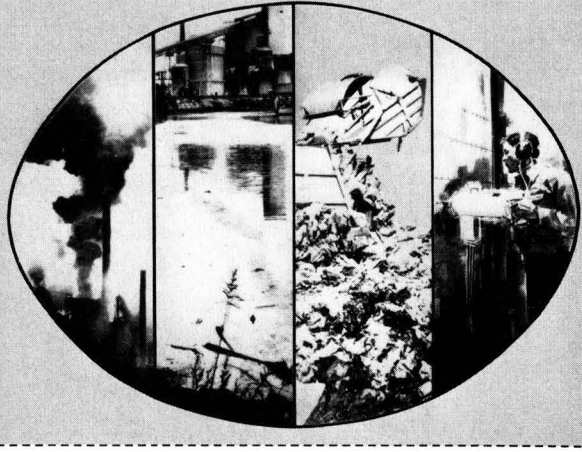

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LETTERS

Scrap iron transportation

Dear Sir: I greatly enjoyed reading the article: "Transportation: bugaboo of scrap iron recycling" (*ES&T*, May 1973, pp 408–11). However, it raised certain questions in my mind regarding the basis of the various cost comparisons.

It appears to me the real basis of the cost comparisons should be the tons of processable iron, delivered to the mill door, and not just the tons of total material moved. For example, we find that, on the average, an ore containing 51% iron is considered a fairly good iron ore. On the other hand, one ton of good scrap contains nearly one ton of usable iron (or "iron units" as it is referred to in the article). Further, the ton of iron recovered from the ore should, in a realistic comparison, also bear a proportionate share of mining, processing, and land rehabilitation costs, in addition to the shipping costs of the raw ore.

Under these conditions, the comparisons of the actual resources "use" costs seem to be somewhat different. To keep the figures simple, let us say it takes two tons of ore to give one ton of processable iron. We then find the shipping costs of 50 tons of iron produced from raw ore becomes $164 instead of the $82 used in the article for raw ore. Let us then say mine stripping costs average at least $2.00 per ton of ore. This gives us $4.00 per ton of actual iron recovered or $200 for the 50-ton example used in the article. And finally, let us consider land rehabilitation costs of the strip mining operation. It would not be unreasonable, under present EPA standards in most states, to consider this to average close to $1200 per acre for this cost. Or to put it another way, an average environmental protection cost of at least $1.00 per ton of usable iron recovered. So we then have another $50 per 50 tons of iron to add on the cost when the iron is taken from raw ore.

On the other hand, we find that 50 tons of good scrap has a shipping cost of $206. This may provide, on the average, 50 tons of usable iron. If we assume an average gathering cost of $40 per ton of scrap we have a total cost of $406 per 50 tons of usable iron delivered at the steel mill. At this point we find that the 50 tons of required iron, if taken from raw ore, has costs of $414 at the mill door. Or to summarize for the 50-ton unit involved:

	Ore	Scrap
Shipping costs	$164	$206
Mining costs	200	200 (av price, $40/ton)
Environmental costs	50	0
Totals	$414	$406

(Continued on page 774)

"D' you know what your BOD's been up to this week?"

"Of course."

"Oh yeah? So where was it on Wednesday?"

Many people measure Biological Oxygen Demand just twice a week—once Monday, once Friday. Then they rule a perfectly straight line between their two data points, and call it a week. It's an understandable practice because the standard BOD test eats time. Our automated electrolytic BOD analyzer makes the test a breeze. It reads out continuously, so come Friday you've got an honest, lumpy curve that accurately depicts deviations like initial and intermediate lag phases. One E/BOD can save you as much as $1350 per year in man-time. Better yet, it will let you know exactly what your BOD was up to on Wednesday and every day. Write for details!

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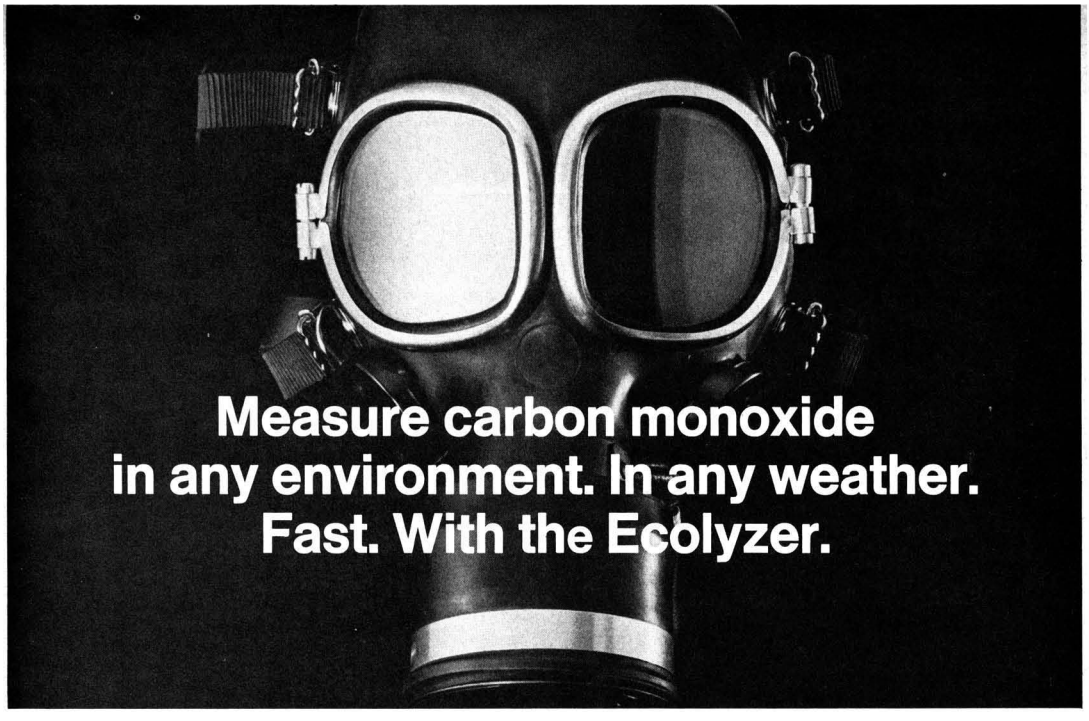

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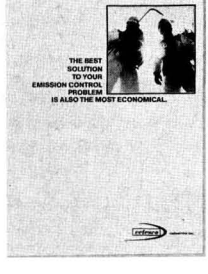

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It seems to me that when due consideration is taken of some more of the factors involved in the costs of processable iron, that recovered from scrap, may well, in many cases, be somewhat less than that of iron recovered from raw ore, freight rates not withstanding—although it would appear that lowering freight rates on scrap could well be an effective means used to provide additional incentive for the increased use of scrap, particularly in view of the effect of the depletion allowance which I have not included. The inclusion of this allowance would make the iron from raw ore a bit cheaper at the mill door, in all probability, depending on scrap price variations. Nor can there be much question but that the freight rate structure is discriminatory by the ICC's own definition of the word.

However, one does wonder if, perhaps, the apparent failure to consider all the actual costs of usable "iron units" at the mill door might not be another of the contributing factors to the fact that the Japanese seem to be able to buy scrap in the United States, pay going freight rates, ship it to Japan, process it, ship back finished products, and still make money on the product. Maybe they have discovered an "iron mine" in our own backyard that we did not realize existed and is not due entirely to labor cost differentials.

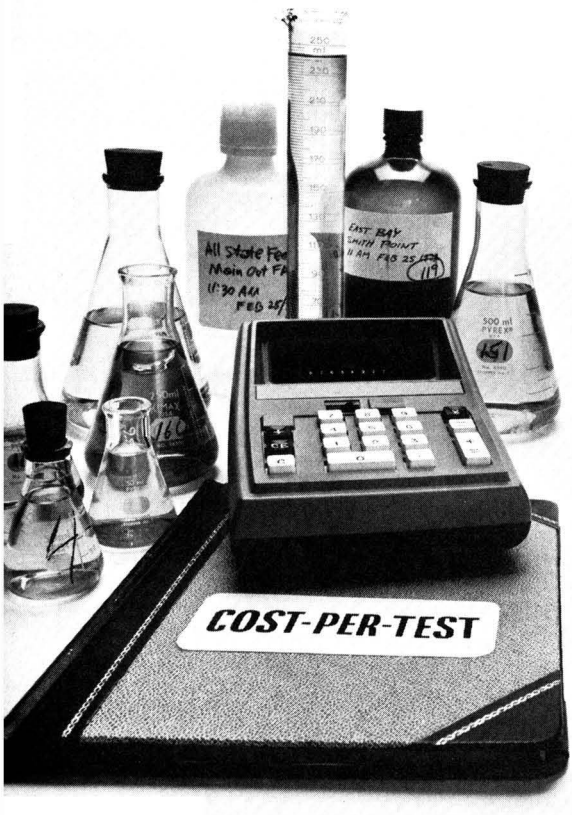
C. A. Caswell, President
Environmental Audit Corp.
Pittsburgh, Pa. 15232

Sewer line infiltration

Dear Sir: I thought the article (*ES&T*, July 1973, p 586) was excellent. However, I would like to point out that our company is also in this business and has been since the early 50's. We do no inspection but we do manufacture equipment for our own use. In 1952, we repaired an old and deteriorated sewer line for West Palm Beach, Fla. During the mid-50's, the Centriline Division of Raymond Int. started the development of a television camera and, independently of the other companies in the field, developed a packer system as well as television inspection systems. After doing several jobs, however, we found we were "before our time." The rash of people entering the business with off-the-shelf television cameras and inadequately experienced personnel supported our decision to soft-pedal this end of our business. We do, however, continue to do quite a few sewer rehabilitation jobs. These are not the run-of-the-mill type jobs discussed in your article, however, and would probably not qualify for inclusion unless there were a section on Specialist of the Specialties.

Charles M. Aiken
Raymond International Inc.
Houston, Tex. 77027

There's more to analyzing water than precision and accuracy.



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No. of Water Samples Per Day	Commercial Laboratory	Technician Manually	Technician and AutoAnalyzer
20	$7.00	$1.48	$.90
40	7.00	1.48	.45
60	7.00	1.48	.30

These cost figures are based on national averages. The AutoAnalyzer II comparison is based on being used normally—no "special" conditions.

For a copy of our nutrients in water cost-per-test kit, just circle the reader service number below.

Or, perhaps you'd like to see the complete Technicon AutoAnalyzer II cost-per-test presentation. It's a 14-minute film and it's very revealing! Just write to Technicon Industrial Systems, Tarrytown, New York 10591 on your letterhead. Our local representative will call you and set up a meeting.

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Reagent grade water for the laboratory:

why you need it, how to get it, what it costs

All water supplies contain substantial amounts of suspended and dissolved contaminants which can seriously interfere with chemical and biological test procedures.

"Reagent grade water" implies that contaminants have been removed or reduced to a level below test sensitivity; and there are several "grades" of such water. The College of American Pathologists, for example, classifies "Type I" reagent grade water as having a minimum resistivity of 10 Megohm-cm (one of several specifications).

The CAP recommends that Type I water be used for *atomic absorption spectrometry, flame photometry, enzymology, determinations of electrolytes, inorganic ions, blood gas* and *pH* and *the production of reference buffer solutions.*

Distillation, deionization, reverse osmosis and filtraton are methods commonly used to produce reagent grade water. Each has limitations and none alone can meet most of the purity standards. For example, water produced by distillation — the classical laboratory method of purification — has a resistivity approaching 0.5 Megohm-cm (single distillation) which does not meet the minimum specifications for Type I reagent grade water as specified by the CAP and the ASTM.

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*Allegheny County Health Department, Bureau of Air Pollution Control, Pittsburgh, Pennsylvania:

1938, first air sampling stations.

1945, first enforceable air control program.

1958, dustfall reduced by 84% compared to 1945.

1958, all of Allegheny County under one regulatory body; 60 station non-telemetered network established.

1968, first on-line telemetered pollution monitoring network, now including seven Philips PW9700 SO_2 monitors.

1973: Allegheny County Air Pollution Control Program meets all of the newly established criteria for award of maintenance grant and becomes one of the first agencies in the country to be awarded such a grant by the Environmental Protection Agency.

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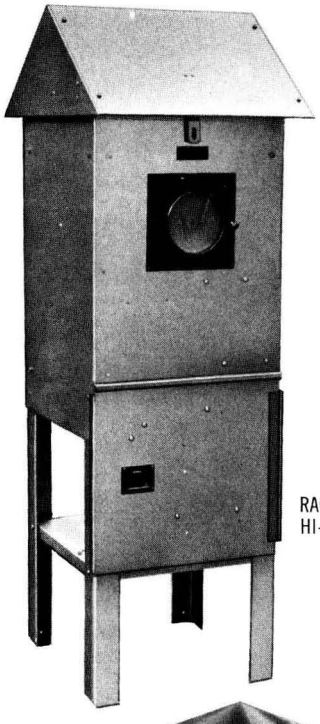

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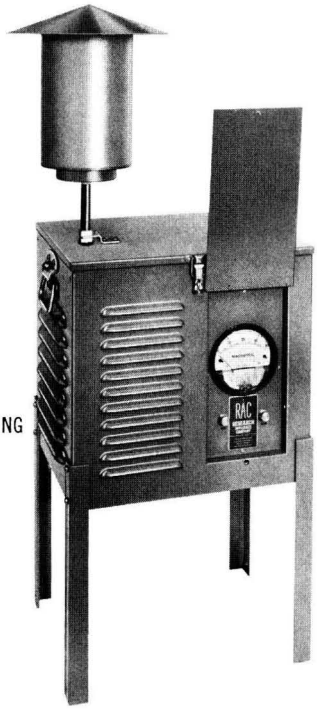

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For details, write for BULLETIN 2338-A.

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Designed and built to **EPA** specs, this instrument uses a membrane filter to collect fine particles (to 3.0 micron dia) not easily sampled by paper or glass filter media. Samples suitable for highly definitive analyses are obtained with no contamination from filter medium.

Unit operates continuously at 5.5 cfm flow rate when equipped with a 3.0 micron membrane. Its 4″ (100mm) dia filter has an 88mm effective area.

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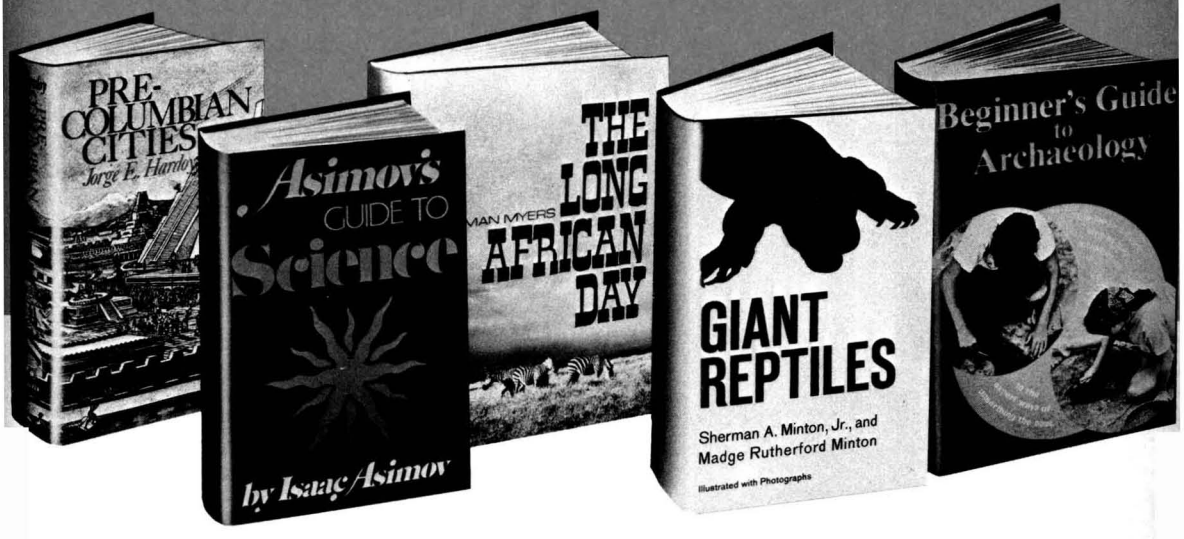

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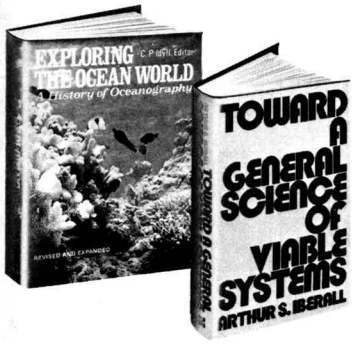

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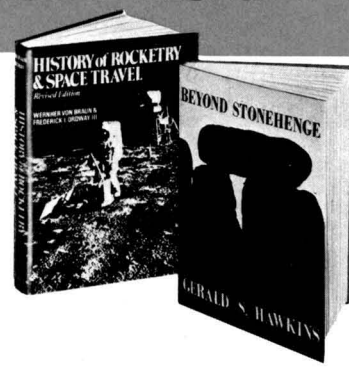

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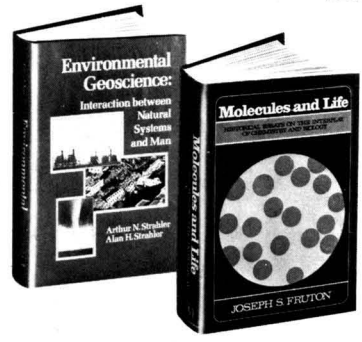

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CURRENTS

INDUSTRY

Ford has purchased nonexclusive worldwide rights to Honda Motor Company's CVCC stratified-charge engine. Under the agreement, Ford gets Honda's technical information and can make and sell engines of all sizes for all applications. Ford had been active in stratified-charge engine design with its Proco (programmed combustion) engine, but the company says Proco costs too much and is too complex. Other than Ford, only Toyota has been licensed by Honda to make the CVCC. Ford did not disclose any cost figures or details of the agreement. Chrysler and GM are understood to have been negotiating with Honda for narrower rights to the engine or pieces of the technology.

Ethyl Corp. and the EPA have come to an agreement over a squabble involving the federal Freedom of Information Act. Earlier, Ethyl had sued EPA under the Freedom of Information Act to gain access to documents relating to proposed regulations of lead antiknocks in gasoline. Under the agreement, Ethyl and the general public will be provided with medical, scientific, economic, and technological data relating to the health effects of airborne or other environmental lead. The agreement covers inspection and copying of documents prepared by EPA or received by EPA by other agencies, industries, or the general public. The agreement extends for four months after adoption of any lead regulations by EPA.

Pacific Gas and Electric Co. has opened a Diablo Canyon Nuclear Information Center about seven miles south of San Luis Obispo, Calif., on Highway 101. The Center is divided into four major areas containing displays on archeology, nuclear theater, future clock, and ecology. The displays were designed to present the power plant as part of a conscientious plan to balance the demand for energy and the requirements necessary to maintain the environment, explain the process

Nuclear information center

of nuclear fission as a source of electrical energy, demonstrate PG&E's concern for safety and the precautions used in the operation of the plant, and to dramatize how PG&E actively plans to provide for future power needs.

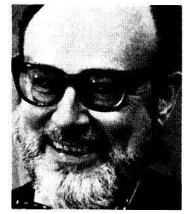
The steel industry is making only "token efforts" to increase the amount of steel scrap it obtains from sources outside its own production facilities, according to the Council on Economic Priorities (CEP). The reports says industry claims about recycling are misleading. Sixty percent of the scrap used by the industry is generated by the mills themselves, CEP says, and only 13% of new steel is composed of scrap discarded after consumer use. The American Iron and Steel Institute (AISI) disputes CEP's findings, saying that recycled scrap has accounted for more than 50% of the raw materials used to make new steel and almost half is purchased from outside sources.

Envirogenics Corp. has begun producing significant amounts of pure water from hot underground geothermal brine. An experimental distillation pilot plant produced more than 7000 gal on the first day of operation, reducing the salt content of the brine from 20,000 to less than 50 parts per million. The unit has a design capacity of 20,000–50,000 gal per day and is expected to be producing some 20,000 gal per day of water by press time. A second distillation test unit, also with the capacity of 20,000–50,000 gpd which uses a slightly different distillation method, is scheduled to begin operation some time this month.

RESEARCH

Fluorescent Whitening Agents (FWAs) have received a clean bill of environmental health from a symposium convened by the Swedish Center for Environmental Sciences and the National Swedish Environmental Protection Board in Stockholm last spring. "From all the data presented at the symposium it was apparent that the FWAs used nowadays are not mutagenic and also show no signs of any teratogenic effect," reported Hans O. Bouveng, chairman of the Stockholm symposium on fluorescent whitening agents. "Analyses of river water in Europe and elsewhere show that FWAs cause no real pollution to speak of," the chairman added. In all major rivers tested, FWA concentrations were below 0.5 μg/l.

Arthur M. Squires, professor and chairman of the Chemical Engineering Department of the City College of the City University of New York, has received the Henry H. Storch Award presented by the American Chemical Society's Division of Fuel Chemistry. The



Storch award recipient Squires

Storch Award, established in 1964, is given to a U.S. citizen who has contributed most to fundamental or engineering research on the chemistry and utilization of coal or related materials in the preceding five years. Squires heads a 15-man

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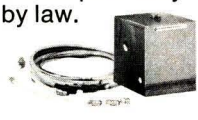

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research team working under a grant from the RANN program for converting coal into nonpolluting fuels. Squires holds patents on fuel processing and power generation.

TECHNOLOGY

The first systematic assessment of environmental damages attributable to production of three major materials—steel, aluminum, and plastics—will be undertaken by Calspan Corp. to determine whether raw materials or recycled wastes exact a higher environmental penalty. The ecological appraisal is being made under a $90,799 contract from the EPA. In the first stage of its work, Calspan is determining the extent to which some forms of present-day and proposed recycling will reduce nationwide pollution levels or whether recycling may cause more pollution than it prevents. The study will examine alternate paths to the end product.

The demonstration phase of the Accelerated Biological-Chemical (ABC) waste water treatment process is now complete, according to Environmental Quality Engineering Inc. The results show the process can produce a high quality product water from the raw municipal sewage of the North Tahoe-Truckee (Calif.) Sanitation Region. The ABC process, using high-rate activated sludge, performed exceptionally well under shock loading and transient conditions in tests for the California Water Resources Board, Environmental Quality Engineering said. Treatment resulted in consistent removal of BOD, suspended solids, and phosphorus of greater than 90% with aeration times as low as 45 min.

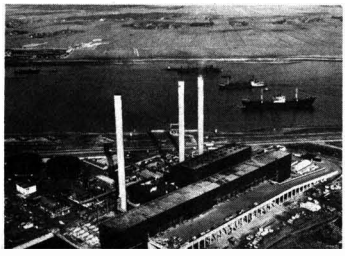
A porous pavement which permits water to drain directly through it rather than running off the road and creating pollution and soil erosion problems will be tested in Florida over the next five years. The porosity of the road surface will be achieved by using only coarse grades of aggregate, eliminating the surface sealant normally used in asphalt road construction. Conventional road building calls for an impermeable surface to prevent water from getting into the base material and weakening it. But at least two types of limestone common to Florida, and perhaps other materials as well, do not lose their strength when wet and thus can be used as a base for porous road surface.

INTERNATIONAL

West Germany and the Netherlands face serious water pollution problems which will require big increases in pollution control spending, according to a report recently released by Sira Institute, Kent, England. The two countries will double their rate of expenditure in five years to cope with the problem, the report says. Annual spending on effluent and drinking water plants is expected to grow from $575 million to $1120 million between 1972 and 1977. Spending on instrumentation alone is forecast to grow from $39.2 million to $82.5 million in the same period. The expenditures will be largest in West Germany where the investment required in both the public and private sector should top $4000 million in the years 1973 to 1977.

The world's largest incineration plant is now going full steam in the Netherlands in the highly industrialized Botlek district near Rotterdam. The 700,000 tpy incinerator installation is the major component of a $70 million complex which also includes a power station and a water distilling plant. The plant, which serves the city of Rotterdam and 23 surrounding towns and villages, was designed to dispose of 190,000 tpy of regular urban garbage as well as 440,000 tpy normal industrial waste and an additional 70,000 tpy of solid and liquid chemical waste products. The incinerator, power station, and distilled water plant are operated by state-supported N. V. Afvalverwerking Rijnmond.

New Dutch incinerator



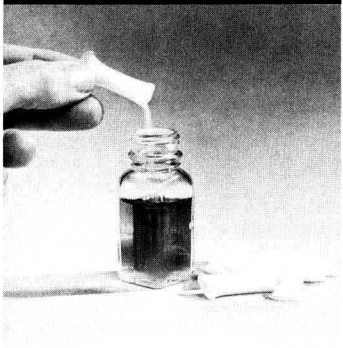
WASHINGTON

Former EPA acting administrator Robert Fri left office with high praise for his successor-designate Russell Train. Fri said Train "for many years has shown a sensitive and intelligent concern for the environment, and able leadership in this field." Besides serving as the first chairman of the President's Council on Environmental Quality, Train formerly was Undersecretary of the Interior. Back in the mid-1960's, Train founded and became the first president of the African Wildlife Leadership Foundation. Critics have complained, however, that despite a past interest in the environment, Train lacks the technological know-how to serve successfully as EPA head.

New EPA boss Train

The EPA has decided not to hold Detroit to the original timetable for reducing nitrogen oxides emitted by cars into the atmosphere. Acting director Fri, at his last official news conference, announced an interim NO_x standard for 1976 of 2.0 grams per mile. The action postpones for one year the standard of 0.4 gram per mile required under the Clean Air Act of 1970. The postponement is allowed if studies determine the standard to be unreachable. Fri noted that technology is not yet within reach to reduce nitrogen oxides to the 0.4 level and added that the nitrogen oxide health hazard is not so great as was originally feared.

Analyzing water?



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The DR-EL/2 is intended for universal water quality testing by scientist or layman. It is ideal for schools, industry, water treatment plants, laboratories, field survey work, power plants and agriculture.

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CURRENTS

EPA plans for a quieter America have been revealed. The agency announced rules for reducing noise from trucks traveling interstate highways, and outlined what it hopes to do to reduce noise at the nation's airports. Specifically, the EPA proposed that noise from trucks traveling at more than 35 miles per hour could not exceed 90 decibels at a distance 50 ft away. EPA said that between 10 and 20% of some 1 million trucks now using interstate highways emit noise levels of 110 decibels. Noise abatement cost would be between $50 and $200 per truck. As to reducing airplane noise, EPA said installing noise-absorbing padding inside airplane engines was a quick, effective way to quiet them.

The House appears to have cleared the way for oil companies to construct the $3 billion Alaskan pipeline. But the bill they passed is a curious one, and may be headed for the courts despite language in the measure designed to circumvent such a challenge. The bill, in overruling NEPA provisions to the contrary, finds that the pipeline has already satisfied federal environmental rules. It further says the courts shall not review that claim. Critics say the bill creates a very dangerous precedent. Rep. Jonathan Bingham (D-NY) predicted the bill would go to the courts despite its language. The Senate passed a similar measure after a tie-breaking vote by Vice President Agnew.

The National Water Commission's final report is recommending a major overhaul of the nation's water policies and programs. In the form of 232 specific recommendations, the 570-page document calls for: greater reliance on state and local governments and nongovernment groups to implement development programs and improve water quality; better data collection and R&D programs; modifications of laws and institutions that regulate present policies; more economy and efficiency in the use of water; and for the conservation of energy where it is related to water use. The seven-man commission will be disbanded now that its work is completed.

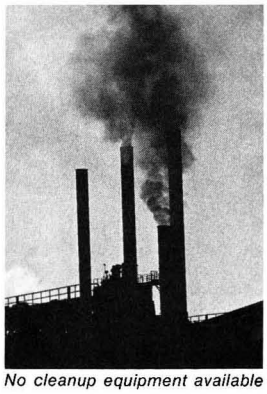
Permanent job safety and health standards for 14 industrial cancer-producing materials have been proposed by the Occupational Safety and Health Administration. The standards provide for a system of permits, without which employers would be prohibited from using the carcinogens after Dec. 31, 1975. OSHA head, John Stender, emphasized that the standards set requirements designed to protect employees rather than actually ban the use or manufacture of any of the 14 substances. Meantime, scientists at HEW have developed a new rapid method based on embryo culture, for screening potential carcinogens.

STATES

Solid waste problems are under study in Ohio and Arizona. The Akron (Ohio) City Council recently approved a $710,000 contract for a design study for energy recycle. The $20 million system, to be in operation by 1976, will burn garbage and trash, producing steam which will be used for downtown and industrial customers. In the West, the city of Scottsdale and the Salt River Pima-Maricopa Indian Community have issued a joint call for proposals to develop and construct a solid waste recycling-recovery system. The two groups are seeking to interest segments of private enterprise to join with them in developing an economically feasible resource recovery system.

The Colorado Department of Health has contracted with Automotive Testing Laboratories, Inc. (ATL) in Aurora, Colo., to conduct emission tests on 300 randomly selected vehicles to develop emission factors for Colorado, as specified in recently enacted legislation. ATL will select privately owned vehicles for the model years 1964–1973, representing by make and model 90% of the automobiles registered in the state. Under the program, which began last month and will be completed in December, those systems deemed most effective in the reduction of smog in the Denver area will be recommended to the 1974 Colorado legislature for implementation by mid-1975.

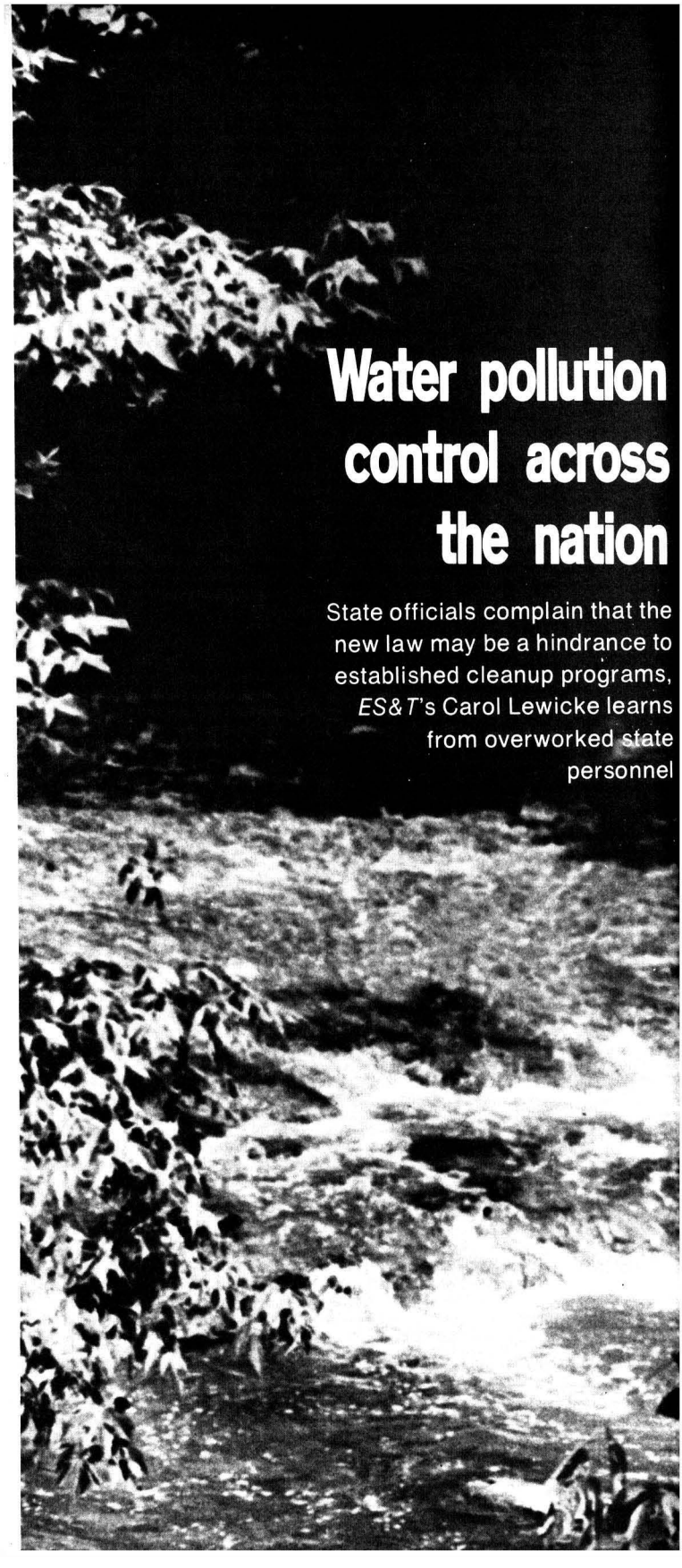
Some Oklahoma industries can't comply with air pollution regulations, according to state officials. An increased nationwide demand for air pollution abatement equipment has left manufacturers with a backlog of unfilled orders and customers without the necessary equipment for compliance, according to the state air pollution council. "Orders placed



No cleanup equipment available

now with leading companies can't be met before 1975," says Jack Gallion, air pollution control division, state department of health. Oklahoma has granted deadline extensions to companies who had not received dust control equipment as promised. This equipment is not mass produced, say officials, and installation is time consuming also.

A law recently enacted in Hawaii establishes a permanent Population Commission, thus making Hawaii the first state in the nation to establish a permanent commission on population. The action by the legislature implements one of the major recommendations of an earlier Temporary Commission on Population Stabilization which submitted its report to the 1972 session of the Legislature. Eleven commission members will be appointed in late fall. The Commission will study population migration, capacity of the state, formulate policies, and other duties to determine the optimal population capacities of the counties as well as means of controlling the number of incoming residents.



Water pollution control across the nation

State officials complain that the new law may be a hindrance to established cleanup programs, *ES&T*'s Carol Lewicke learns from overworked state personnel

Water pollution control is a headache for industrial and municipal officials. But it's a bigger headache for officials of state environmental agencies—they have the final responsibility for pollution abatement. Under federal law, state programs are the crux of the U.S. water pollution control effort. It is at this level that the day-to-day exchange of blows between state officials and their counterparts in industries and municipalities takes place.

All programs relating to water pollution and its control have been affected by the new water law, P.L. 92-500, the Federal Water Pollution Control Act Amendments of 1972. Both state and industry officials criticize the new law—many specific deadlines have been set, ways and means of achieving these deadlines are outlined, but much remains to be done.

To gain an insight into the accomplishments, problems, and frustrations each state must encounter now and in the future, *ES&T* canvassed officials from each state environmental agency. More than half of the states replied, and their comments are the basis for this report, a sequel to one published two years earlier (*ES&T*, Feb. 1971, p 120).

Basin planning requirements

Required under the previous federal law, river basin planning must now be completed by July 1, 1975. The deadline is set, but states were and are still hampered by limited funds and available manpower.

Two years ago, according to state officials, basin planning was a major state environmental problem. And it still is. It "continues to be a problem in water pollution control," explains Reginald LaRosa of Vermont's Agency of Environmental Conservation. Basin planning requirements which existed under the earlier federal law were somewhat complicated as written. Requirements were interrelated to the functional water and sewer programming requirements of the Department of Housing and Urban

Development. Under the new law, basin planning is intensified substantially with the requirements for 303e planning, 303 basin planning, 208 planning, 106 planning, and 201 planning (the numbers are references to the sections of P.L. 92-500).

"Some of the new problems associated with meeting the planning requirements of the new law revolve around the fact that funding arrangements for such planning have not been forthcoming and that the guidelines delineating what should be contained in such plans have not been fully promulgated," LaRosa continues. "In addition, some of the planning requirements are not applicable to rural states such as Vermont. In the area of administering the water pollution control program, one of our most serious problems at the present time is obtaining the completed regulations on the administration of the Federal Water Pollution Control Act" and relating them to the resources available to Vermont.

Idaho, Missouri, and Virginia officials concur; basin planning is still a major problem, especially since plans are not yet complete, adds South Carolina's R. Kenneth Tinsley of the Pollution Control Authority. Personnel in Montana's Department of Health and Environmental Sciences "are devoting about half of our efforts to planning and the needed monitoring to prepare basin planning reports."

In Colorado, basin planning has been quite limited owing to the lack of both federal and state funds. "As a result of the enactment of P. L. 92-500 and its deadline requirement, it now appears that our state legislature will provide funding for the completion of such plans," comments Frank Rozich, technical secretary of the Water Quality Control Commission.

Even at this late stage, some states still are hesitant about river basin planning. Wisconsin officials question completion of basin and related regional/metropolitan planning

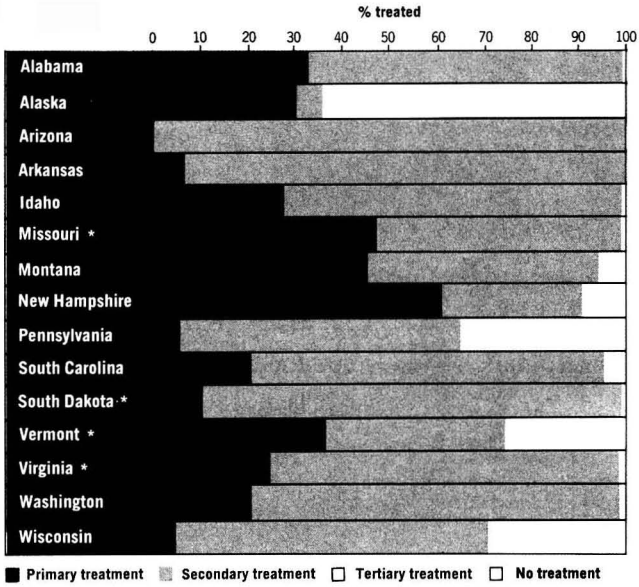
States' financial needs outstrip available funds

(Millions of dollars)

STATE	FISCAL YEARS				
	1971	1972	1973	1974	1975
Alabama		$33	$7.2		
Alaska	$3	$3	$5		
Arizona		$15	$2.7	$4	
Arkansas		$19	$7	$10	
California			$196	$261	$390
Colorado		$18	$6.3	$9.5	
Florida		$64	$72.5	$108	
Maine		$12	$19.5	$26	
Missouri	$18	$45	$33.1	$49.6	
Montana		$7.7	$3.3	$5	
New Hampshire	$3.4	$7.8	$16.6	$24.7	
New Jersey	$26	$62	$154	$231	
Pennsylvania	$58	$112.4	$108.4	$162.6	
South Carolina					
South Dakota	$9.6	$9.6	0		
Vermont		$3	$4.3		
Virginia		$44.6	$145.7	$174.8	
Wisconsin		$42.6	$34.8	$52.2	

Available Needed

Status of municipal waste water treatment in the U.S.



Note: Chart is based on approximations, and values will change as treatment is upgraded.

*Limited amount of tertiary treatment.

in time to be of value in decision making. The Alabama Water Improvement Commission hopes that federal funds will be available to the states to ease basin planning problems.

Not all states feel that river basin planning is a burden. Washington state officials say that basin planning is progressing at a satisfactory rate. And "basin planning a year ago was a major problem" according to Arkansas Department of Pollution Control and Ecology. "However, new regulations have redefined basin planning requirements or levels of planning and are somewhat more realistic than a year ago."

State river basin programs

Basin plans are an integral part of any state's water pollution control program. Some states who started under the earlier water law are well along in the process. Now, they are faced with retrofitting progress with the new law. All are laboring to meet the requirement of the new law.

Florida is developing water quality management plans for 12 river basins in accord with EPA requirements. Plans are nearly completed for six metropolitan/regional areas and will be incorporated into the basin plans.

Existing water quality data for the quality limited segments will be reviewed and analyzed by Florida officials to quantify the degree of treatment necessary to achieve water quality standards. The quantitative and subsequent load allocations will be based primarily upon modeling studies although comparative analysis and local legislation may provide adequate justification for load allocations. The basin plans will provide the necessary data for designating planning areas (Section 201). Permits issued to facilities in these areas will require a compliance schedule for the development of a 201 plan, resulting in a final implementation date.

The first of six major basin plans in Idaho were recently completed. Their program got under way only this January. The other five plans will be done in order of priority. Max Pope, Idaho's Department of Environmental and Community Services, anticipates that individual basin plans will form overall "umbrella"-type planning for an entire basin. These plans will establish priorities and define problem areas within the basin, as well as map strategies for attacking these problems. Implementation and local planning and development efforts will then fall within the scope and strategy of the basin plans for combating water pollution in any given basin within the state.

Virginia's basin planning program will be a management tool for statewide water planning. Much of the basic data for Virginia's plan has been collected and published; about 75% of water resources planning has been done. The California State Water Resources Board expects to derive receiving water standards, construction priorities, and permit priorities from its intensive basin planning program.

The basin planning program in Colorado consists, at present, of two persons; however, the state will contract for these basin plans. Therefore, Colorado will not need to retain a large staff. "Although on a limited basis," continues Rozich, "we expect basin planning to tie in with our overall water pollution control program by restricting the proliferation of small treatment plants in any one area. In other words, once regional treatment plants are located in a particular basin, we will adhere to this plan and not give any grants to anyone not complying with the plan. Of course, we could also take action via the permit program."

Vermont's basin planning is currently oriented around the requirements of the previous Federal Water Pollution Control Act. "We have been able to execute interim basin plans in all areas in which we expect to undertake construction of water pollution control facilities in the next fiscal year," says Vermont's LaRosa, although format for the basin plans is not in direct alignment with the manner of conducting the state's water pollution control program.

Missouri's basin planning program is in the very early stages, but interim plans required by EPA are completed. Officials hope that after the basin plans are fully established, "it should help us predict when cities will need to expand their sewage treatment work facilities to reduce the number of complaints and fire-fighting kind of work." Basin planning is also in the early stages in Arizona and New Hampshire.

Alabama's basin planning program relies on contract assistance because of the small state staff and required time frame for completion. Also, Arkansas is severely hampered in its basin planning program in two areas: a personnel shortage in the planning section, and no management information system capable of fulfilling planning needs. However, Arkansas has always taken a basin-wide approach to control and abatement of water pollution, and plans are under way to alleviate these problems.

New Jersey has no comprehensive water quality management plan for each of the basins in the state, but it is a goal. Now, in place of basin planning per se, three separate types of planning operations are going on: waste water facility planning, area-wide waste treatment planning which is a regional responsibility, and water quality management planning whose

purpose is to establish waste load allocations.

Basin planning is in the early stages for the Passaic and Raritan Rivers, while elsewhere in New Jersey the basin planning for the future is being developed by regional or county sewerage authorities. To receive a permit to discharge, say New Jersey officials, a waste load allocation is needed; and waste load allocations are a part of the planning process.

Interstate agreements

In view of the fact that pollution knows no boundaries, many states are members of interstate commissions—some quite able to cope with environmental problems and others hindered by lack of authority and cooperation. Vermont, for example, is a member of the New England Interstate Water Pollution Control Commission. This commission has been very effective, according to Vermont spokesmen, in coordinating the actions of the adjacent states as they relate to integrated water quality standards and criteria. The Commission also is the coordinating agency for input from individual states to the federal EPA in the development of regulations and administrative procedures for handling the 1972 admendments.

Pennsylvania is a member of a number of interstate compacts. The Delaware River Basin Commission and the Susquehanna River Basin Commission have broad water resources planning and regulatory powers. However, the need for interstate agency regulation, says Pennsylvania Department of Environmental Resources' Walter A. Lyon, in water pollution control has been greatly reduced by the new federal legislation. Other compacts such as the Ohio River Valley Water Sanitation Commission and the Interstate Commission on the Potomac River Basin work primarily in the water quality area and have limited power.

Other states cooperate with neighbors on common problems. Arkansas has interstate agreements pertaining only to wetlands. Florida cooperates with Alabama regarding water pollution in the Pensacola area. Idaho is in the process of drafting interstate memorandums of agreements for neighboring states.

Arizona, Alabama, Colorado, Missouri, Montana, South Carolina, and Wisconsin are a few of the states not involved in interstate agreements. New Hampshire officials, although members of interstate compacts, believe they are only marginally effective since many states strongly believe in control in the hands of the state. Problems may occur, say Washington Department of Ecology officials, in the area of coordination with neighboring state entities and the federal EPA. Maine has interstate ties, but "interstate problems have been minimal, and to date there has never been a need to seek remedial action under interstate agreement," explains George C. Gormley of the state Department of Environmental Protection.

The Virginia State Water Control Board has agreements for water pollution control with the Interstate Commission on the Potomac River Basin, the Ohio River Valley Water Sanitation Commission, and a tristate organization of Virginia, Maryland, and Washington, D.C., to consider water problems. So far, officials observe, these interstate agreements appear to be quite ineffective, perhaps for lack of adequate authority.

P.L. 92-500 problems

From all outward appearances, no one is completely pleased with the new law. Criticisms vary, but a number of states stand together somewhat uniformly on differences. As a start, Texas officials complain that the law applies blanket regulations to all states regardless of geography, successful ongoing programs, and population distribution and effects. In fact, their officials were told by sources on Capitol Hill that the Act was written to be too stringent. Perhaps more progress would be made in this manner, the sources observed!

The main complaints with the Act, says Donald Schiesswohl of Florida's Department of Pollution Control, are twofold—whether the nationwide goals can be met and whether sufficient federal and state funds will be available for the cleanup—e.g., waste water treatment plant construction, monitoring requirements, enforcement, and basin planning.

Vermont contests that its water pollution control program must be realigned to be in accord with methodologies outlined in the new law. "Even though we are required to revise our methodologies, we do not feel it will produce enhanced water quality beyond that which would have been accomplished under the previous procedure," argues Vermont's LaRosa. Also, the state has been unable to reorganize and reallocate resources to meet requirements of the Act due to the absence of clear-cut interpretations and definitions of requirements through regulations being promulgated by the federal EPA. "They (EPA) are currently well behind in the promulgation of certain regulations and guidelines required by the Act."

Eugene T. Jensen, Executive Secretary of the Virginia State Water Control Board, is concerned with reissuance of permits, increased manpower needs, lack of definition of phased construction grant payment [Section 203 (b)], secondary treatment guidelines creating much higher effluent limits for some community plans that would be required to meet water quality standards, movement into the NPDES (National Pollution Discharge Elimination Systems) being implemented and designed at the same time rather than being tested and developed prior to implementation, and grant holdups if prerequisites are enforced, for example, infiltration correction (*ES&T*, July 1973 p 586). Arizona, Colorado, Maine, Missouri, New Hampshire, South Dakota, Washington, and other states echo similar concerns.

In Montana, the staff responsible for programs at the state level have had to almost completely divert their efforts to meeting federal deadlines, according to the Department of Health and Environmental Sciences. The small amount of construction grant money provided in relation to the high percentage of federal grants obtainable has forced cities to delay programs. For example, one phase of one project in Montana will use the complete fiscal year 1974 allocation.

John Cain, of the Wisconsin Department of Natural Resources, admits that paper work and changing regulations have caused a virtual stoppage of the state's pollution control program. Another state official terms his major problem as "an inordinately large amount of paper work which appears to be to the accomplishment of nothing."

In contrast, however, South Carolina's Tinsley believes that the law "creates a new approach to water pollution control but creates no problems for the state which cannot be solved efficiently and systematically." California officials continue, "The fact that California has been delegated permanant authority under the 1972 Amendments reflects the fact that there are no serious problems that it creates for us. The state's Porter-Cologne Act is, in many cases, stronger than the federal legislation."

Permits and monitoring

Under the law, states must now modify their existing discharge permit program or create new ones to adhere to NPDES guidelines. Many states had permit programs before it became a national requirement, and agency officials are currently making the necessary modifications to administer NPDES permits. Connecticut, Missouri, South Carolina, Virginia, Washington, and Wisconsin were six of 18 states granted interim au-

thority by the federal EPA to issue discharge permits. Permits are issued on the basis that the effluent does not violate any water quality standards. Also, the quality of the receiving water must be maintained. Several states are processing permit applications to the point of issuance; then EPA will make the actual issuance.

Integral with enforcing pollution abatement schemes is a monitoring system. A few states, including Arizona, have no monitoring program; and a few other states have intensive monitoring systems. Unsurprisingly, the majority fall somewhere in between.

Arkansas, New Jersey, and South Dakota agree that their monitoring programs work in a reasonable way but need intensification. In Montana, the water monitoring program is just getting under way; until a year ago, about ½ man-year each year was devoted to monitoring. Now, staff and laboratory capabilities have been expanded, and most of the monitoring program is concentrated in areas where basins are being prepared.

Operating since 1966, Colorado's monitoring program consists of some 128 stream surveillance stations that are sampled at least once a month. "In next year's program," Rozich explains, "we hope to pick approximately 30 of these stations for more frequent sampling, perhaps weekly." Idaho's monitoring system contains 144 permanent stations, and spot checks and intensive studies are done as required, as does Washington state. South Carolina collects and analyzes samples from 1800 stations.

Vermont has had a monitoring program for several decades. It involves water quality evaluations of the surface waters of the state as well as a continuing monitoring program of the efficiency of operation of all waste treatment facilities, public and private. In addition, "We have an Operations and Maintenance Section which makes periodic inspections of sewage treatment facilities not only to determine their operating efficiency but also to evaluate the efforts being made to maintain and care for the facilities," explains Vermont's LaRosa.

Florida is developing a statewide monitoring system that will integrate the activities of its six regional laboratory facilities. The program will conform with EPA draft guidelines for monitoring, including permanent network stations, permit compliance monitoring, intensive surveys, groundwater monitoring, lake eutrophic conditions, and laboratory support.

In Pennsylvania, stream samples for chemical analysis and biological monitoring are collected on a routine basis. "We inspect facilities regularly and monitor effluents," Lyon explains. "We require waste dischargers to do self-monitoring and submit reports to us."

Missouri has a contract with the U.S. Geological Survey and cooperative agreement with Kansas and Illinois for sample collection from 133 stream stations. "In fiscal year 1974 we will sample 490 municipal facilities and 125 industries," explains a spokesman for the Missouri Clean Water Commission. "In fiscal 1973 the Neosho Water and Wastewater Technical School was under contract to us to sample effluents in southwest Missouri."

In Wisconsin, comprehensive surveys are completed for each river basin in the state every five years. In addition, permanent monitoring stations have been sampled monthly for the past 12 years.

Specific water pollution problems in the states

ALASKA
- **Pulp and paper mills**
- **Seafood processing**
- **Municipal wastes**
- **Accidental oil spills**

ARKANSAS
- **Municipal wastes**
- **Agricultural runoff**
- **Leaching from abandoned salt water vaporation disposal in oil production**
- **Food processing industries**

COLORADO
- **Agricultural wastes**
- **(Feedlot and irrigation return flows)**

CONNECTICUT
- **Municipal wastes**
- **Organic chemicals**
- **Pharmaceuticals**
- **Metal plating**

FLORIDA
- **Municipal wastes**
- **Urban runoff**
- **Citrus processing**
- **Phosphate mining and fertilizer production**
- **Pulp and paper mills**
- **Chemical and synthetic fiber industries**
- **Sugar production**
- **Muck farming**
- **Thermal pollution (Electric power generation)**

IDAHO
- **Mine wastes**
- **Siltation from logging operations**
- **Food processing**
- **Sugar production**

MAINE
- **Pulp and paper industry**

MISSOURI
- **Municipal wastes**
- **Meat processing**
- **Lead mining**

MONTANA
- **Sediment from erosion**
- **Mining and milling**
- **Sugar beet refining**
- **Paper and pulp milling**

NEW HAMPSHIRE
- **Municipal wastes**

NEW JERSEY
- **Municipal wastes**
- **Chemical industry**
- **Pulp and paper industry**
- **Petroleum refining**

NEW YORK
- **Combined sewer overflows**
- **Thermal pollution**
- **Lake eutrophication**

PENNSYLVANIA
- **Drainage from abandoned coal mines**
- **Petrochemical and toxic materials discharges**
- **Municipal wastes**
- **Steel industry**

SOUTH CAROLINA
- **Discharges from single cell oxidation lagoons**
- **Textile finishing industry**

SOUTH DAKOTA
- **Nonpoint sources**

VERMONT
- **Municipal wastes**
- **Dairy industry**
- **Pulp and paper industry**
- **Metal plating industries**

VIRGINIA
- **Municipal wastes**
- **Urban runoff**
- **Agricultural wastes**
- **Pulp and paper industry**

WASHINGTON
- **Forest products industry**
- **Agricultural wastes**

WISCONSIN
- **Pulp and paper industry**
- **Food processing**
- **Municipal wastes**
- **Land runoff**

Note: Most pollution sources listed are on abatement or compliance schedules.

Wetlands and coastal zones

Formerly unprotected areas, wetlands, and coastal zones are now under scrutiny to ensure that ecological balances are maintained. Dredging, dumping, and filling are being regulated to prevent widespread destruction of fragile and important ecosystems. In Maine, the State Wetlands Act gives the Department of Environmental Protection control over dredging, filling, or discharging into wetlands area. A new state zoning law is also being implemented which requires protective zoning ordinances within 250 ft of any navigable waterway in the state.

Virginia's "wetlands" law provides for protection of vital wetlands through local wetlands commissions and the state's Marine Resources Commission. The New Jersey Department of Environmental Protection, under the authority of the Wetlands Act of 1970, has banned dumping in wetlands and issues permits for any development or construction. Many states—i.e., South Carolina, Vermont, New Hampshire, Washington, and Arkansas—include wetlands in the definition of waters of the state over which they have control. Washington has a Shoreline Management Act which guides and regulates development in wetlands and coastal zones; and Arkansas is considering land use legislation to protect wetlands.

As with wetlands, many states include coastal waters as under jurisdiction of all state water pollution control laws. The State Water Control Law, upon which Virginia's pollution control program is based, provides for the protection of coastal areas from pollution. The State Water Control Board further adopted regulations to control pollution from boats. Virginia's legislature has also given localities the right to control beach erosion. The city of Virginia Beach, in cooperation with the Army Corps of Engineers, has a very active program of beach replacement and erosion control.

Florida exercises control over its coastal zone through several agencies and various acts. Beaches and shores are managed by the Department of Natural Resources. The Coastal Coordinating Council (composed of the Department of Pollution Control, the Department of Administration, the Trustees of the Internal Improvement Trust Fund, and the Department of Natural Resources) is concerned with land use and management in the coastal zone. Development in coastal areas is not regulated directly although legislation has been proposed; rather, activity has been regulated through control of dredge and fill actions, and through the Corps of Engineers and state permits. The Department of Pollution Control certifies as to effect on water quality.

New Jersey's Coastal Area Facility Act becomes effective this month. It is aimed at protection of the state's shoreline from misuse. It regulates construction and requires development applications and environmental impact statements. The Department of Environmental Protection decides on applications and a Coastal Area Review Board was created to hear appeals on these decisions.

New Jersey officials foresee a changing pattern of land use so that coastal areas are compatible with environmental constraints. New Hampshire's Water Supply and Pollution Control Commission predicts that most wetlands and coastal zones will be acquired by state or federal governments. Most state officials believe that coastal zone protection is the responsibility of both the state and federal governments, but that wetlands are a state responsibility.

Financing and fund impoundment

The majority of state officials contacted feel that the federal construction grant program has not been a disincentive to the states in the past. Alaska's Ronald Hansen in the Department of Environmental Conservation believes that it "has been one of the more effective programs of environmental protection agencies." Arkansas, Colorado, and Pennsylvania authorities agree.

What the states consider the most serious hindrances to clean water

- Insufficient funding
- Lack of federal direction on 1972 Amendments
- Lack of manpower
- Nonpoint source pollution
- High costs to properly collect and treat wastes from small communities
- Basin planning problems
- Excessive paper work
- Inability of feds to agree on trade-offs between increased federal subsidy and inflation effect on the economy
- Lack of state land use control
- Problems of small rural states to establish a clear-cut water pollution control program
- Lack of effective data management system
- The philosophy of treating symptoms of a problem rather than the problem itself

In Vermont, the small size of many communities would make it economically impossible to proceed with pollution abatement programs without substantial subsidy of the construction costs through state and federal grant funds. Even at a 90% grant level for initial construction, LaRosa explains, the repayment of the bonds for the 10% of capital investment costs plus operating costs exceeds, in many instances, $126 per family per year in small communities.

However, state officials complain that the present withholding of current funds and holding back funds already designated for these purposes have stopped some states' pollution control programs. Other officials complain that, even in former programs, not enough money was made available while new requirements were continually imposed. In Texas, 125–150 projects qualified for federal grants, but virtually no money is available for fiscal 1973 and for fiscal 1974. Texas has $70–100 million "water quality enhancement funds" that will be loaned to small municipalities "to keep the program going in spite of EPA."

EPA interim regulations governing the award of construction grants for waste treatment plants require states to set up a system of priorities to qualify for federal funding. A majority of states have done so; at press time, a few had received approval. Vermont authorities are concerned with the fact that states are required to establish a priority system which does not recognize readiness to proceed or need for financial assistance.

A majority of states are deeply affected by the impoundment of federal funds. In past years 25–30 Colorado applicants per year received federal construction grant funds; during the present year, only three communities were assisted in this respect. Vermont's potential construction has been reduced by almost 60%. "We are totally dependent upon receipt of federal funds to make the project economically viable," LaRosa explains. As of June, Vermont had received no federal grant offers from fiscal 1973 or 1974 funds. Municipal applications for these funds were submitted to EPA over the last nine-month period and are still pending in the regional office, lament Vermont spokesmen. The impoundment has cut the number of New Hampshire's possible projects in half and "slowed down the cleanup of the state's wastes," according to the Water Supply and Pollution Control Commission. Alaska officials say that sewage treatment plant construction has been stalled. A few months' delay in availability of funds in cer-

tain portions of the year can delay projects at least one year in Alaska because of the short construction period in that state.

Idaho has a construction delay of 24 months; South Carolina's funds have been cut by 50%. Alabama has received no new grants for construction in the last year. Florida, Missouri, and South Dakota projects were stalled since immediate needs far exceed the funds available. On the other hand, California's State Water Resources Control Board claims that it has been able to fund most of its projects in the highest priority class.

In most of the states polled, water pollution control does receive the majority of attention and funding. Although many states feel that funding has largely been on an adequate basis in large communities vs. small communities, several spokesmen express fears that this will not continue. "It is much more difficult for small communities to receive funds when compared with metropolitan districts that have more people and problems in a concentrated area," explains Florida's Schiesswohl. Colorado's Rozich comments that recent edicts from EPA have informed states that "We can no longer consider financial need, but that the main consideration must be on the amount of pollution discharged. Consequently, the larger the community, the more pollution."

Enforcement

Legislative authority for enforcement of environmental regulations varies from state to state. Most actions, however, are administrative. In Washington, the Department of Ecology issues civil penalties through "documents," departmental order, and standard suits by the Attorney General. In the first quarter of 1973, only 10 cases were in the hands of the Attorney General.

Virginia's State Water Control Board may issue cease-and-desist orders and emergency orders; investigate fish kills and authorize settlements; issue injunctions, mandamus, or other remedies to enforce regulations; and assess fines when necessary. Vermont can initiate civil or criminal actions against anyone who violates water quality standards or conditions of permits; however, most enforcement actions against municipalities are civil; criminal actions are taken against individuals.

South Dakota is organizing a new environmental department that will have full-time legal counsel. Pennsylvania's Department of Environmental Resources has a staff of 30 attorneys in the Office of Enforcement; the Deputy Secretary for Enforcement has substantial autonomy in initiating legal action.

The enforcement muscle in the hands of the states looks as if it is getting tougher. To comply with federal regulations, the states are beginning to take a harder look at polluters and a tougher stance on abatement.

Can the goals be achieved?

Responses were again varied when state officials were asked if the goals for clean water in the 1972 Amendments were realistically achieveable. "Yes" for Arkansas, Connecticut, Missouri, and New Hampshire; "In part" say Montana, New Jersey, and Virginia; Arizona says the state has clean water and intends to keep it that way.

Some states doubt the necessity of the no-discharge goal by 1985. "It is extremely difficult to define whether the goals of the law are achieveable until the goals themselves are more clearly defined through regulations and engineering parameters," complains one official. Another source sums it up: "The philosophy of the federal law is commendable. Some of the goals (no discharge) are unrealistic, and the time frame is much too stringent for accomplishment with available federal and state resources."

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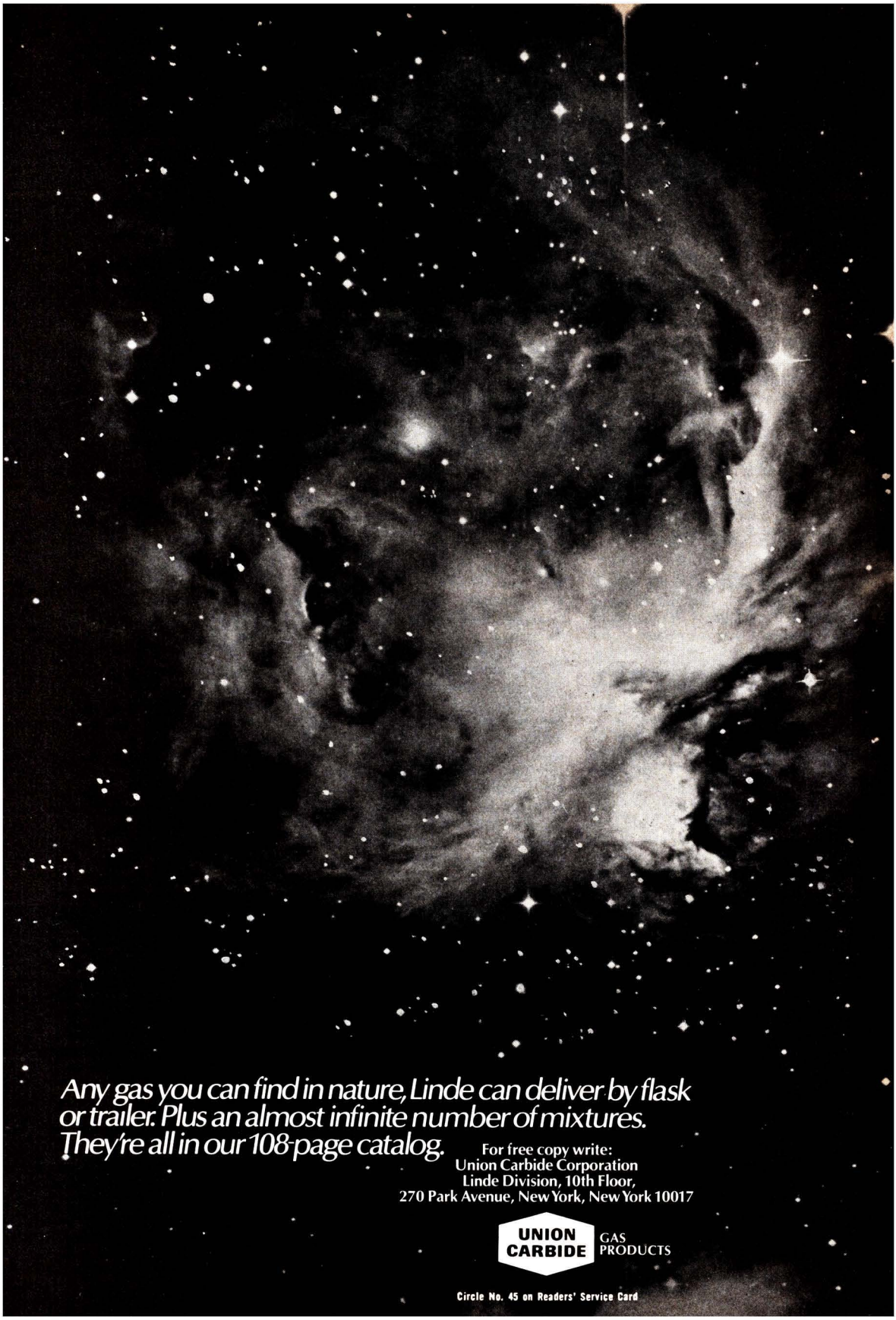
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Happenings on the Washington waterfront

EPA, it would seem, is running harder just to keep up with another flurry of deadlines; only when the paper work logjam is broken will long-overdue construction begin

Keeping up with all the tight deadlines in the new water law, P.L. 92-500, is difficult. Seemingly, there is an endless number of specifics—permits to be issued, technology to be identified, municipalities to provide secondary treatment, construction speedups, user charge regulations, the construction management (alias turn-key) for waste water treatment facilities, and sewer infiltration/inflow analyses (*ES&T*, July 1973, p 586).

Fast-tracking

The federal position on the design-construct phase of the waste water treatment facilities' construction grant program was published in the *Federal Register* of February 28. Despite this fact, not one proposal from any municipality has come into the EPA, not one proposal from any municipality that wants to try this route.

Of course, proponents for this alternative method have alleged that they could perform the construction in less time than the traditional method, which takes anywhere from four to six years. They say they can "fast-track" since more than one of the three elements of the epc (engineering, procurement, and construction) are provided concurrently. Of course, as everyone is aware, the consulting engineering profession is lined up on the other side of this issue. Everyone is also aware of the fact that in the traditional method, an engineering design is completed first, then construction firms bid on the actual construction based on the design, the contract being awarded to the lowest bidder.

But now, under EPA regulations, all publicly owned treatment works approved for a construction grant prior to June 30, 1974, must now be completed within four years of approval.

To study and evaluate the various combined design-construct contracting methods, and indeed to see whether these methods could be used in the municipal waste water construction field, EPA recently contracted for a study with Bechtel Corp., one of the leading engineering construction firms in the U.S.

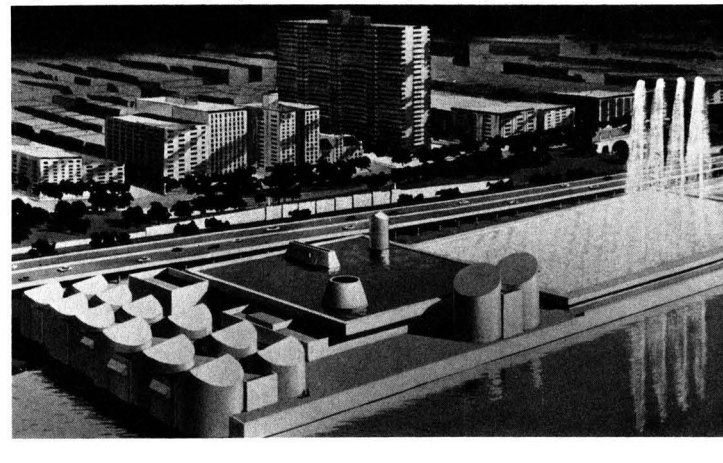
Phase One of their report, "A Study of Single Responsibility Concept as Applied to Water Pollution Control Projects," was due to EPA on August 1; basically, it was a summary of past experiences in both the public and private sectors as practiced in the engineering construction field. Then Phase Two, due by the first of this month, will provide EPA with "An Analysis of the Major Project Functions," which are necessary in approaching the single responsibility concept.

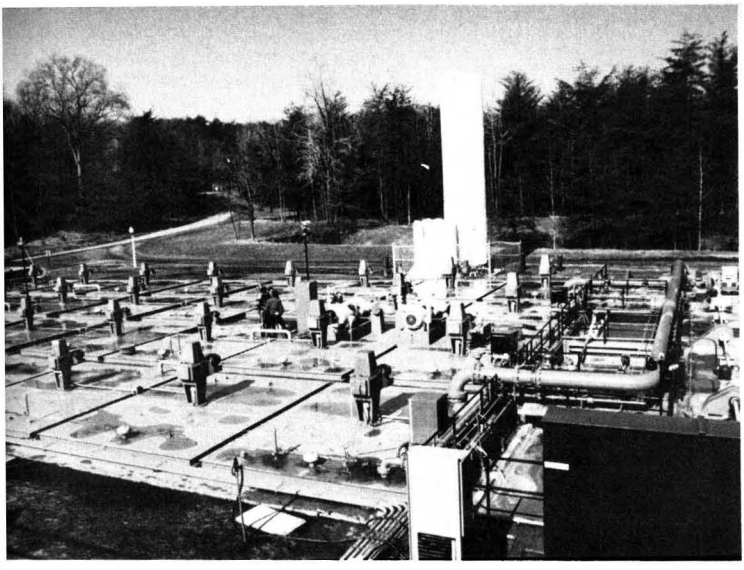
There are at least four other forms of contracting methods that provide for single responsibility:

- Engineering and Management has been successfully used in many major public and private work projects. In this case, the contractor (engineer and manager) has the design capability, and through management of the construction work, remains responsible throughout the project so that appropriate guarantees can be supported.
- Construction and Management allows strengthening of a construction contractor's (constructor and manager) capability by subcontracting process selection and engineering. This option keeps overall responsibility in the contractor's hands, again allowing for a guarantee position.
- Multiphase engineering-procurement-construction is most nearly like the "turn-key." It extends the contractor's (engineer-constructor) responsibility to include process selection. Each phase is priced separately, with increasing firmness as the scope of work becomes better defined. This option requires a contractor of broad capability, extending from pilot plant operation to construction. Joint ventures are one means of organizing this capability.
- Project management is a concept that can be carried out by owner or agent alike. In this case, single responsibility exists wherein the project manager coordinates the guarantees of the individual subcontracting parties and suppliers.

So, the assignment that Bechtel is faced with is identification of the

Rejected. NYC municipal plant never made it past design





Online. Fairfax County, Va., plant is treating sewage

methods for executing design/construct projects and recommending how these methods might be made applicable to the waste water construction field—in other words, how best to achieve a single management responsibility for the construction of waste water treatment facilities in the public sector.

There obviously are both advantages and disadvantages to the single responsibility method. The principal advantage is that it would allow the owner to perform more than one of the engineering, procurement, and construction operations at the same time and not sequentially. The main disadvantage, however, is the problem of protecting the public interest.

The second phase of the Bechtel analysis is identification of the functional elements of projects—financing, design, planning, procurement, performance optimization, and construction. In any event, Bechtel will be recommending alternative systems in the waste water treatment field; their final report is due at the end of this month.

Single responsibility

A recent example of single responsibility project execution is the World Trade Center Towers in lower Manhattan. This $550 million job was performed by the New York Port Authority as the owner and project manager. The actual project management team included one construction management firm, two A&E (architectural and engineering) firms, and 170 major construction contracts. The construction was done by overlapping design and construction, the key in this case being the in-house capability of the New York Port Authority to manage the overall project.

Several federal agencies are developing or have developed policies and procedures providing for design/construct methods using construction management concepts. These agencies rely, in part, on single responsibility contracting for facilities and include the General Services Administration, the Department of Housing and Urban Development, and the Department of Health, Education, and Welfare (HEW). This technique of single responsibility is employed by HEW in construction of hospitals and educational facilities, some of which are $50–100 million projects. For example, the University of Massachusetts campus is being built with a construction manager setup. Basically, under this HEW project, the construction manager coordinates the epc elements to "fast-track" the job.

Must be secondary

Municipal waste treatment plants are faced once again with secondary treatment. But the effluent limits, proposed in the *Federal Register* of April 30 (with comments until June 29), are now, for the first time ever, couched in terms of effluents standards. Limits are placed on BOD, suspended solids, fecal coliform bacteria, and pH. In the past, meeting the secondary treatment requirements was based on reducing the BOD by some arbitrary percentage, for example, 85%.

User charge fee schedules are required in any grant approved after March 1, 1973. The point here is that all federally funded, publicly owned treatment works must now be revenue producing and self-sufficient. In the past, mills in the New England area, for example, were tied in with the local municipality, and the town was taxed for the treatment facility. Another example is the textile industry in the southern part of the U.S. where a similar-type tax base was established. In any case, the new requirement will avoid the use of federal funds for construction that is tied in with a municipal tax base. Of course, the main intent is to have the treatment plant self-sufficient, cost effective, and revenue producing. These specifics were spelled out initially in the May 22 *Federal Register*.

Technology and permits

The EPA water program office is faced with the setting of no less than three sets of effluents standards:

- best practicable technology
- best available technology
- new source performance standards.

In contrast, the air program office is establishing only one set of standards—namely, new source performance standards for new or substantially modified sources of air pollution.

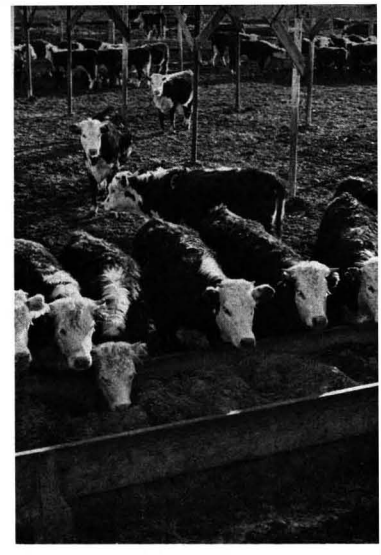
Nevertheless, in the *Federal Register* of September 18, there will be published proposals of the three levels of technological water pollution effluent control for 28 industries. Each industry earlier was the subject of a study by individual contractors. When we consider that $4 million was spent last fiscal year on the development of these effluent standards, much needed clarification is expected.

Then too, pretreatment standards will be proposed in the *Federal Register* of October 18. These standards will specify what materials must be removed from industrial effluents before they are discharged into a municipal or regional waste treatment plant.

It has been estimated that the above 28 industries cover only about half of the permits that are to be issued before the end of next year. EPA, of course, is concentrating on the priority list of 2700 dischargers identified more than a year and one half ago. That list came into being when EPA asked its 10 regional offices to identify the most difficult-to-control 250 pollution problems in each region. All told, EPA has in hand 20,000 permit applications for indirect discharge under the Refuse Act and another 3000 applications specified by P.L. 92-500. SSM

EPA readies farm antipollution guidelines

In response to 1972 pesticide and water quality requirements, the EPA is busy preparing groundwork for controlling "nonpoint source" farm pollution



The feat today still demands the strength of Hercules, but the method's no longer good enough. When this mythical hero brought the rivers Alpheus and Peneus through the stables of King Augeas of Elis, he did dispose of a large quantity of farm waste, but think of the havoc it must have caused downstream—manure from three thousand oxen, whose stalls had not been cleaned for thirty years.

In fact, such unthinking disposal methods are precisely why the U.S. Government is now concerned with abating farm pollution. As former EPA acting administrator Robert Fri has pointed out, "We all live downwind or downstream from somebody else." A farm operation may be miles from heavily populated areas, but its feedlot, fertilizer, and pesticide runoff can enter streams and affect these populations in direct and devastating ways.

With this problem of "nonpoint source" pollution in mind (this is scattered source pollution, or pollution sources other than factories or municiple facilities where output is localized and concentrated), Congress in 1972 passed the Federal Water Pollution Control Act Amendments and the Federal Pesticides Control Act. The EPA is charged with putting these regulations into effect.

Fri revealed at a meeting of the American Agricultural Editors Association in Washington recently that the agency will issue information on methods to control nonpoint sources sometime next month. He said research is already under way to provide additional data on the best procedures to use. The EPA will then send this information to the states, which will devise control programs during fiscal year 1974 and recommend, by fiscal year 1975, firm plans to control nonpoint sources. In addition to the state plans, Fri said, basinwide waste treatment plans also must include nonpoint source controls. These probably will start coming into EPA for review by fiscal year 1975, he said.

As to pesticides, Fri said, "We in EPA fully realize that chemicals will continue to be employed routinely as pest killers for the foreseeable future." He added, however, that the law "provides us with a framework for regulating the use of these biocides in a way that will serve the best interests of farmers as well as the environment in which we all find our sustenance." If this seems a little hazy, Fri left little doubt as to its meaning when he later said limits will be placed on "the places, the number and the manner of (pesticide) applications."

The problem today with animal waste is that there is too much of it, or at least more than can be economically returned to the land. Inexpensive commercial fertilizers provide from 20–100 times as much nitrogen, phosphorus, or potassium per unit weight as manure, and transportation costs alone can be significant.

With the onset of large feedlots during the 1950s and '60s, the problem has intensified. Both the number of large commercial livestock feeding operations and the average number of animals per production have risen as farmers have fought low prices by cutting costs per animal. In 1966 the number of feeder cattle removed from pastures and grasslands and confined to feedlots numbered 10 million. This was an increase of 66% during the eight years since 1958, and 120% during the 15 years since 1951.

Magnitude of waste

The magnitude of this shift can well be understood when animal waste output is compared with the equivalent human waste output. An average-sized feedlot, of 30,000 head of cattle, may produce the BOD equivalent of a city of 200,000 people and a total solids output equivalent to a city of 600,000 people. Similarly striking figures exists for hog and poultry feedlots.

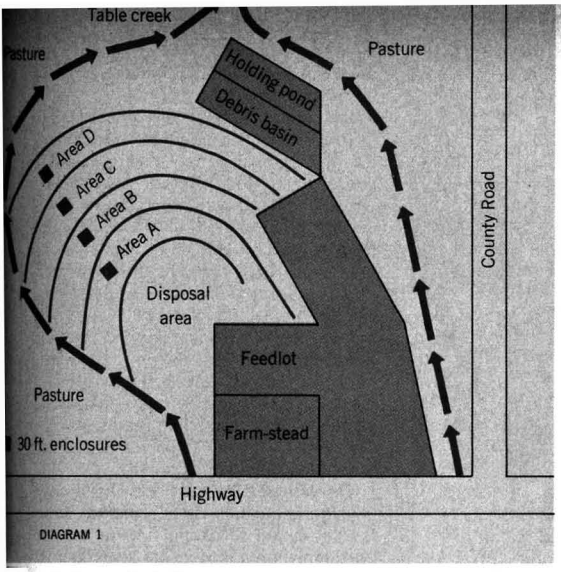
Fri says the EPA will require permits for feeding stations of 1000 or more animal units, but that some states will require them for smaller capacity feedlots. Thus, even small animal-feeding facilities will be expected to minimize discharges. Fri said the control of runoff and irrigation return flow will require a continuous, on-going effort by each farmer, rancher, and feedlot operator.

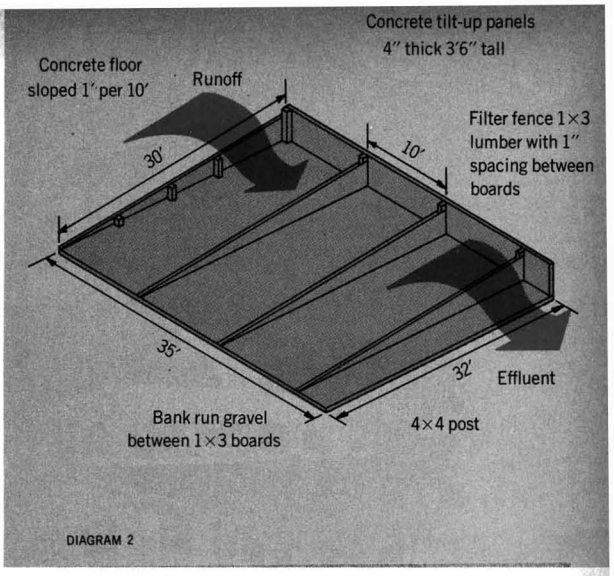
The water act itself will require comprehensive efforts of erosion, sediment, and nutrient control, including accelerated implementation of existing measures, more emphasis on upper basin areas, application of fertilizers under optimal conditions, as well as the retention of animal wastes. Fri says the key to success will be an integrated, long-range plan for on-site water management. He pointed out that an uncontrolled farm or feedlot could ruin the entire program, which, by its nature, must embrace whole watersheds to be effective.

The problem arising from excessive application of commercial fertilizers is that these concentrated nutrients can be transported into groundwater by leaching or into waterways by natural drainage and storm runoff. Nitrates in drinking water can cause a "blue-baby" condition in infants. Phosphorus has been implicated in algal blooms in U.S. waterways and lakes.

Although pesticides have been of great help in reducing the damage caused by pests that affect agricultural crops and livestock, as well as a great help in reducing pests that carry human diseases, they often have had undesirable effects on beneficial species and they have often lost their effectiveness, as pest resistance has evolved. Studies have shown that the use of pesticides is economically justified in many situations, but they also have shown that farmers may be overusing them.

As a result of the 1972 pesticide law, the EPA will be looking closely at the use of these chemicals by farmers. The act provides penalties for pesticide misuse, as well as other methods for regulating their use. For example, now, for the first time ever, intrastate shipments must be federal-





Photograph *indicates how rapidly waste can accumulate in crowded feedlot operations. In Diagram 1 the disposal area orientation to feedlot and runoff control facilities are indicated. Diagram 2 illustrates the configuration of the settling basin at the Throckmorton Purdue Agricultural Center*

ly registered and the disposal of containers regulated.

There are exceptions, however. When necessary, a state can, with EPA approval, register certain pesticides for use when they are intended for "special local needs." Fri cited an instance occurring earlier this year when the EPA permitted DDT use in Washington and Idaho for a 60-day period because the pea weevil threatened a $5 million crop. Although the agency had turned down several requests for use of the chemical since it was banned last year, it permitted its use in this case because no surrogate (substitute) method or chemical was available. The crop was saved in the nick of time, Fri noted.

"Nature's own technique"

Fri pointed to "nature's own pest control techniques" as alternatives to pesticide usage. He said EPA researchers have found a virus-based insecticide effective against several major cotton pests but harmless to animals and human beings. Such products do not require the setting of tolerance levels, he said, because they are incapable of injuring nontarget species. He noted that success also has been achieved by introducing sterilized insects where infestation is particularly heavy, as well as by using sex-attractant chemicals. If care is taken, he said, natural enemies can be introduced in some areas.

Fri said the EPA intends to be even-handed about enforcing the new pesticide law, but that the agency also intends to implement it fully over the next four years as Congress specified. "In doing so we will give full attention to professional opinion and the developing scientific consensus on what is the best approach to take," he said.

Current innovation concerning animal waste control has focused mostly upon anaerobic and aerobic biologically active systems, and the land spreading of wastes in both solid and liquid forms. Incineration, dehydration, and composting are also being studied.

Anaerobic digestion systems have proved successful in the field as well as in the laboratory, but only under some conditions. Anaerobic lagoons with a small surface area can be used where construction and groundwater conditions permit. These lagoons remove and destroy much of the organic matter. They can be combined with aerobic systems to give an effluent that is of adequate quality for discharging into rivers. Thus, the anaerobic system can accept slugs from a feedlot operation and partially degrade and gasify them. The aerobic unit can degrade the remaining soluble and particulate matter.

Aerobic units are generally shallow oxidation ponds that can have anaerobic conditions near the bottom. Although they work well, they require very large surface areas—about 20 acres for 1000 head of cattle and 5 acres for the same number of hogs. However, the amount of land needed can be reduced by using mechanical or diffused aeration systems.

Although several methods exist for controlling runoff from outdoor beef cattle feedlots, they all include three major components: a solids settling area, a temporary liquid storage area, and a disposal area. With land at a premium for most feedlot operators, this system needs to be designed so as to utilize as little land as possible.

ASAE discusses cleanup

In a paper given this summer at a meeting in Lexington, Ky., of the American Society of Agricultural Engineers, researchers J. A. Nienaber, C. B. Gilberston, T. M. McCalla, of the U.S. Department of Agriculture's Agricultural Research Service at Lincoln, Neb., and F. M. Kestner, of the University of Nebraska, reported on a system that would utilize a minimum area of one-half acre disposal area per acre of feedlot. Under their design, they found, the feedlot runoff did not impair crop production or cause pollution accumulation in the soil.

Their facility included a debris basin and holding unit installed at a 9.3-acre feedlot, which had been designed for 1000 head of cattle. The site has a 6% slope to the northwest (Diagram 1) with contour terraces at 100-ft intervals. Four half-acre terraces, on which grasses selected for potential tolerance to feedlot runoff were sown, were designated as treatment areas. Areas *A* and *C* received natural precipitation only. *B* and *D* received effluent in addition to natural precipitation.

The effluent, pumped to the area and then sprayed on the land, was applied when runoff occurred, rather than by a regular application schedule. Quantity of application per acre was based on twice the quantity of runoff from an acre of feedlot. Cattle

were allowed to graze all treatment areas except the 30-ft fenced enclosures where the sprinklers were placed, and thrived on the grasses.

John Nye, Alan Sutton, and Evan Baugh, all of Purdue University, outlined plans for primary treatment, which included a settling basin (Diagram 2) designed to allow use of solid manure-handling equipment for cleaning. This facility, built at the Throckmorton Purdue Agricultural Center, consisted of three chambers separated by porous dams, or gravel filter fences with 1½-in. conduits near the top to allow liquid movement. The three-chambered device allowed surface-settling rates of 3, 5.5, and 11 $ft^3/hr/ft^2$ of surface area for a 2-in./hr rainfall intensity.

Terence McGhee of the University of Nebraska told the meeting how feedlot runoff following settling could be simply and effectively treated for biological content. He discussed how holding ponds can provide significant reductions in waste strength, as well as retain effluent flow. He said the cost of effectively treating settled feedlot runoff with an aerobic biological system could go as low as $0.65 per head. The cost would depend upon animal density, climate, and the balance between holding pond and treatment unit size.

As to applications, N. P. Swanson, C. L. Linderman, and J. R. Ellis, all of the U.S. Department of Agriculture's Research Center in Lincoln, Neb., said land application of feedlot effluent is the most feasible means of disposal. Although some reports on such disposal have indicated decreased yield and quality of crops, increased soil salinity, and deterioration of soil structure, USDA studies show that forage quality was unimpaired when effluent was applied to perennial ryegrass and tall fescue overseeded with Ladino clover. The treatment resulted in pure stands of Ladino clover, a salt-sensitive crop, and the yields equaled or exceeded those on plots irrigated with water.

These are only some of the possible answers. What is clear is that the EPA is going to make sure something is done about farm pollution. According to Fri, the 1972 laws mark a "new chapter in the development of responsible environmentalism," which "takes us another step toward restoration of the natural bounty of the earth." Fri said it might not be possible to make the environment as uncrowded and pollution-free as it was in the days of the pioneers, but through the cooperation of all polluters, even relatively small ones such as farm operators, "we can reach a level of salubrity and amenity that would have been inconceivable a few years ago." WSF

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Corporate watchdog for the environment

The nonprofit Council on Economic Priorities keeps the public informed of industry's intentions in the environment and other social areas

"Steel industry lagging in pollution control" is a typical example of news headlines appearing throughout the U.S. several months ago. The accompanying articles publicized the results of a study of environmental controls in the steel industry. Bethlehem Steel's Sparrows Point Works on the Chesapeake Bay in Maryland was cited as the worst polluter (of those companies studied which account for 70% of industry production) for arsenic and cyanide discharges. Over 324 lb of arsenic and 5469 lb of cyanide are discharged into the Bay daily.

U.S. Steel's Gary Works on Lake Michigan emits 22,782 lb of soot and dust each hour, according to the study—40% of the particulate pollution in the city. However, on the other end of the scale, Armco Steel's Sand Springs Works in Oklahoma emits 25 lb of soot and dust per hour and recycles all the water it uses, the report states, and is adequately controlled in all categories.

The 500-page study that documented these facts was researched and written by the Council on Economic Priorities (CEP), a nonprofit professional organization headquartered in New York City.

CEP researches, compiles, and disseminates information on the extent to which corporations are exercising social responsibility in fair employment practices, environmental preservation, production of war material, social and political impact of overseas investment, and political influence. Through its projects, the Council aims to disseminate pertinent facts in these areas to:

- the general public—to promote an awareness of the policies and practices of corporations
- prospective employees—to provide information on the social responsibility of possible employers
- individual and institutional investors—to provide information on the companies in which they invest
- corporate managers—to highlight performance on questions of social responsibility and to demonstrate that social concern is in the long-term self-interest of corporations themselves.

The beginning

How did an organization with such high objective goals come into being? Executive director and founder of CEP, Alice Tepper Marlin, recalls that while she was working as a securities analyst on Wall Street, some investors would inquire about certain social attitudes of industries prior to investment. More often than not, such information could not be found. Therefore, in 1969, Ms. Marlin left her job, and with volunteers and donated offices, furnishings, and funds, founded CEP. In 1970, CEP published its first environmental study—Paper Profits, an in-depth study of pollution control in the pulp and paper industry.

The Council struggled through its first year of existence on loans and donations totaling $30,000; now CEP's annual operating budget is close to $300,000 with 20 professional staff members trained in the sciences and other technical fields. However, the Council is not yet self-sufficient. Income is derived from subscriptions to CEP studies and reports and from grants and donations; volunteers assist the staff.

Detailed research projects

The Council now publishes at least three lengthy (some 500 pages each) in-depth studies each year. A project is initially assigned to one full-time staff member, who, with the help of volunteers, gathers all information possible on the industry under study. Background data come from such sources as securities analyst information, news articles, and annual reports, to mention a few.

On environmental projects, the researcher also reads scientific and technical literature to learn the production processes, the pollution that occurs in or from these processes, the health and ecological impact of these pollutants, how such pollution can be controlled, and the effectiveness of the state-of-the-art control technology. "If the state-of-the-art technology is quite good," executive director Marlin explains, "we will use it as a criterion to rate how well the companies are doing. If the state-of-the-art technology is poor, we will also investigate research and development efforts in the industries, the industry trade association, and other companies that might be involved" to ascertain why the technology has not advanced further.

CEP researchers also read all available government agency information on the industry. And to further gain a working knowledge of the industry, CEP representatives interview persons from the government agencies involved, the industry association, leading experts in the field, consultants to industry, and consultants to the federal EPA.

From this accumulated information, the CEP researcher develops a 10–20-page questionnaire. It asks

such questions as what specific pollution control equipment is installed, what emissions and effluents are discharged and in what concentrations, and what are the plant size and production capability.

The questionnaire is then submitted to an advisory board formed for that particular study. Members are professionals from industry and government and often must remain anonymous because of their professional positions. The advisory board reviews and approves the questionnaire and also the criteria used to compare company efforts and policies. CEP also attempts to obtain the industry trade association's endorsement of the questionnaire to attest to its thoroughly researched queries.

The approved questionnaire is then mailed to the individual companies with a cover letter explaining CEP, the questions, and the project. CEP researchers also call the companies to further explain the questionnaire. If the questionnaire is completed and returned, attempts are made to interview them further, and if the questionnaire is not returned, CEP attempts to set up an interview to obtain any information. "We usually spend six to eight months trying to convince the companies to cooperate," explains Ms. Marlin.

During the study, CEP staff members visit the plants included in the study, the state pollution control authorities, EPA regional offices, community or national groups involved with that industry, universities undertaking environmental studies in that area, local boards of health, local politicians, people living near the plant, or anyone else who could provide input—all to get an accurate handle on the situation and to present the widest possible array of data and evaluations.

CEP attempts to find out why some plants are worse polluters than others. Perhaps the state agency, regulatory bodies, or legislature is either lax or strict, or pressure from local groups is heavy or nonexistent. CEP also wants to know what companies might close on economic grounds if forced to adhere to pollution controls.

Accumulated data from the myriad sources are analyzed by computer, and the study is written for publication. Usually an equivalent of three man-years over a 12–18-month period is spent on each study.

In the environmental area, CEP has published in-depth studies entitled:

- Paper Profits (1970)—pollution control in the pulp and paper industry
- The Price of Power (1972)—pollution control in the electric utility industry
- Paper Profits: Pollution Audit 1972—progress in pollution control in the pulp and paper industry since the original CEP study
- Environmental Steel: Pollution in the Iron and Steel Industry—a study of the pollution records of the seven major steel producers.

CEP plans to update all studies every two to four years, depending on the lead time necessary for changes in that particular industry. Paper Profits: Pollution Audit 1972 was the first such update.

Progress reports

Besides the in-depth studies, CEP publishes, six times annually, shorter less technical reports called Economic Priorities Reports. Some are summaries of in-depth studies as they are completed, and others are the result of short research projects. Economic Priorities Reports that do not summarize depth studies are more illustrative and general-problem oriented. "They tend to state a problem, give illustrations, and state a variety of possible solutions and inventory actions various groups have taken. They aren't really comparative studies," according to executive director Marlin.

CEP's Marlin
Minding the corporate conscience

One Economic Priorities Report, "Minding the Corporate Conscience," is an annual undertaking, however. It discusses efforts of activists to change corporate policy by focussing on proxy social issues. It is published near corporations' annual meeting time.

Industry cooperation

How does industry view the questions and reports CEP publishes? "A slim majority of the industries contacted will usully talk to us," explains Ms. Marlin. While CEP was studying the pulp and paper industry (1969–70), 22 of the 24 companies contacted cooperated with the Council; when the update was undertaken last year, all the companies provided substantial input. CEP found 13 of the 15 major utilities fully cooperative for the Price of Power study, and the remaining two reluctantly somewhat cooperative.

However, when the Council was working on environmental control in the steel industry, not one company would answer the questionnaire or talk with CEP representatives. Bethlehem Steel Co. sent CEP a comic book. The majority of the technical data used in the study was obtained from state and regional EPA offices and Corps of Engineers data.

In all its reports, CEP emphasizes objectivity and relies heavily on technical data to back up its findings. The paper industry was found to be leading many other industries in pollution control in 1972 (the time of the follow-up and two years after the original study). The study covered 24 of the largest paper companies that account for three fourths of U.S. pulping capacity.

For the electric power study, the Council centered on 15 investor-owned power companies representing 30% of the total privately owned generating capacity in the U.S. CEP found that only 45 of the 125 fossil fuel plants in the study measured up to particulate matter state-of-the-art control technology.

The steel study covered the seven largest steelmakers, a total of 47 mills, which produce 70% of the nation's steel. The study didn't find that any mills were in danger of closing because of pollution control costs alone, and CEP reported that based on Council on Environmental Quality estimates, adequate air and water pollution control in the steel industry would add perhaps $5 annually over 5 years to the price of each new automobile produced in the U.S.

Future projects

The next environmental study CEP is undertaking is pollution control in the petroleum industry which will cover refining. The "big seven" oil companies will be contacted—Atlantic Richfield Co., Standard Oil Co. (Calif.), Mobil Oil Corp., Texaco, Inc., Shell Oil Co., Union Oil Co., and Standard Oil Co. (Indiana) and perhaps a few somewhat smaller firms as well. The study is presently under way and may be completed within a year.

CEP is considering several other environmental topics as subjects for studies. Among these are the mining industry, the chemical industry, and perhaps the textile industry. CEP has not lost sight of its goals, and if the same objectivity and accuracy are upheld in the future, the Council on Economic Priorities may provide one of the best services in the U.S. CKL

Banks study basin cleanup

Consortium of banks tries to put accurate numbers on pollution cleanup costs for Connecticut River Basin

It will cost government and industry an estimated $1.3 billion by 1980 to clean up air, water, and solid waste in the Connecticut River Basin. That's the conclusion of the Connecticut River Basin Project, a consortium of banks in New Hampshire, Massachusetts, and Connecticut, serving the 14-county Connecticut River Basin.

The project, spearheaded by the Chase Manhattan Bank, N.A., of New York, and the Connecticut Bank and Trust Company of Hartford, Conn., was designed to measure the economic impact of pollution control on the basin, according to Sheldon Sixfin, technical director of environmental systems for Chase Manhattan. The idea, he says, was for Chase Manhattan to act as a catalyst to help some of the smaller regional banks assess the impact of pollution control on the economy of the four-state basin area which includes Vermont, New Hampshire, Massachusetts, and Connecticut.

The Environmental Protection Agency contributed $30,000 for the project, which was matched by an additional $40,000 raised by contributions from the various participating banks. Taking into account donated services of various bank officials, technical experts, and municipal and industrial leaders, the cost for the one-year project came to roughly $150,000, Sixfin said.

Basin characteristics

The Connecticut River Basin consists of a strip of land about 35 miles wide and 400 miles long, running from Long Island Sound nearly due north to the Canadian border. As of the 1969 census, the basin's population was roughly 1.8 million or about 1% of the national total.

The basin is approximately 36% more industrialized than the national average, but with the exception of the paper and chemical industries, most of the industry is rather clean. Based on the geographic, demographic, and economic information available from the basin, together with a forecasting model developed by Chase Econometric Associates, Inc., the bank group attempted to:

- summarize the cost and impact of pollution control for industry in the basin during the study period (up to 1980) and for municipalities
- set forth financing alternatives—again broken down to industrial and municipal segments—for meeting pollution control in the basin
- identify the special role which could be played by banks in financing the necessary pollution control measures.

Pollution abatement costs, by industry and per employee

Industry	SIC Designator	1972 employees, 1000's	Abatement costs: Total, $ million	Abatement costs: Per employee, $1000
Paper	26	16.9	170	10.1
Steam electric power	4911	.8	133	169.5
Chemicals	28	10.4	73	7.4
Primary metals	33	8.7	63	7.2
Transportation equipment	37	46.2	43	0.9
Machinery, except electrical	35	45.3	39	0.9
Fabricated metal products	34	28.4	30	1.1
All others	...	89.6	93	1.0
Basin totals		**246.3**	**644**	**2.6**

Source: Chase Manhattan Bank.

Cleanup costs

With respect to the industrial sector, most of the investment required to bring existing plants and equipment into compliance with the clean air and water laws will be made in the years up through 1975, Sixfin said. Up through 1975, personal earnings will increase as will profits by industry, and the increase won't be canceled out by a pollution-induced increase in the Consumer Price Index.

In 1976, and becoming more important through 1980, earnings will decrease significantly. In 1974, the real increase in personal earnings will be about $76.7 million or 0.8% of base line personal earnings. In 1978, however, the real decrease in personal earnings is estimated to be about $120 million or 1% of base line earnings.

But that figure is not as bad as it sounds, according to Sixfin. As a result of the spending, a cleaner basin will give rise to benefits the economic impact of which is difficult to assess. Construction of sewage treatment plants and solid waste processing units, for example, will create some jobs in both construction and maintenance. Property values should go up as they are enhanced by improved water quality, strengthening the tax base of municiplities. Then too, increased tourism and recreational opportunities as a result of a cleaner environment could bring significant profits to the basin.

All in all, for the period up to 1980, it will take an estimated $648 million (January 1972 dollars) for industrial cleanup, $457 million of which will be for air pollution control and $191 million of which will be required for water pollution control. Of the $648 million, $120 million will have to go into capital requirements for upgrading existing plants, $81 million will go for pollution control related costs on new plants, and $440 million will be eaten up by operation and maintenance costs.

Since only a few pulp and paper mills that employ some 3% of the manufacturing personnel in the basin contribute nearly 80% of the BOD of the basin's entire industrial complex (and well over the total produced by the municipalities) nearly half of the $648 million will be spent by the paper industry and steam electric power plants (see table, page 803).

In the municipal sector the study estimates that the price tag for basin cleanup will be about $703 million. Of that about $520 million will be needed for new capital improvements, while $183 million will have to be spent on operating and maintaining the plants. Capital requirements for municipal waste water treatment

facilities are pegged at $469 million, while capital costs for new solid waste disposal facilities, assuming that 50% of the basin's municipalities build such facilities, will cost about $51 million. Operating and maintenance costs for water treatment should be about $63 million, while collection and disposal costs for solid waste should be about $120 million over the study period to 1980.

Financing alternatives

The Connecticut River Basin project also examines several possible methods for financing pollution control. In the industrial sector, taxes or effluent fees may be one way of motivating companies to clean up. Pollution control bonds, tax exempt municipal bonds issued by local government authorities to finance a cleanup facility, may also be helpful. The tax exempt features of pollution control revenue bonds allow society as a whole to accept a portion of the responsibility for improving the quality of life, according to Sixfin. And commercial banks, investment bankers, and insurance companies can aid in placing those bonds, he said.

Other methods for helping industry meet the tab of pollution control within the allotted time frame include loans and small government grants or subsidies. In the case of loans, the interest is tax free and the lender can therefore offer a lower rate than would be customary for the type of risk involved.

Financing alternatives for the municipal sector may be more attractive. In the first place, there is federal and state aid from tax dollars. Federal grants can be used to cover up to 75% of eligible capital costs. While federal money is not yet readily available, banks could assist by prefinancing the 75%, expecting to be repaid by the Government rather than the municipality. Tax exempt municipal bonds, public utility financing, taxes, and user charges are other ways a municipality may raise money to combat pollution.

Private financial institutions, such as banks and insurance companies, can aid municipalities in raising the necessary funds by exploring novel financing schemes, according to Sixfin. The prefinancing device, although not an established banking practice, is one technique by which banks may be able to bridge the gap between promised money and actual construction. Similarly, banks could take a more active role in the bond market in general, including advising, trusteeships, participations, bond purchases and the development of an underwriting capability, placement outlets and secondary trading markets, according to Sixfin.

Technical subcontractors for the Connecticut River Basin Project were the Center for Environment and Man, Inc. (Hartford, Conn.), Chase Econometric Associates, Inc. (Bala Cynwyd, Pa.), and Synecology Corp. (Port Washington, N.Y.). The other banks participating in the study were the Claremont National Bank (Claremont, N.H.), The Cheshire National Bank (Keene, N.H.), The First National Bank of Franklin County (Greenfield, Mass.), First New Haven National Bank (New Haven, Conn.), The Hartford National Bank and Trust Co. (Hartford, Conn.), the Indian Head National Bank of Nashua (Nashua, N.H.), The Littleton National Bank (Littleton, N.H.), The New Britain Bank and Trust Co. (New Britain, Conn.), The Third National Bank of Hampden County (Springfield, Mass.), The Valley Bank (Springfield, Mass.), and the Western Bank and Trust Co. (West Springfield, Mass.) HMM

Cost of basinwide industrial water pollution abatement ($1000's)

	1972	1973	1974	1975	1976	1977	1978	1979	1980	TOTAL
Capital costs										
For existing plants	5,748	8,572	7,356	5,777	1,998	900	400	400	300	31,451
For growth	6,235	4,605	3,860	3,990	4,120	4,260	4,410	4,550	4,708	40,738
Total	**11,983**	**13,177**	**11,216**	**9,767**	**6,118**	**5,160**	**4,810**	**4,950**	**5,008**	**72,189**
O&M costs										
For existing plants	10,640	11,035	11,035	11,035	11,035	11,035	11,035	11,035	11,035	98,920
For growth	400	900	1,500	1,800	2,200	2,600	3,000	3,500	3,954	19,854
Total	**11,040**	**11,935**	**12,535**	**12,835**	**13,235**	**13,635**	**14,035**	**14,535**	**14,989**	**118,774**

Cost of basinwide industrial air pollution abatement ($1000's)

	1972	1973	1974	1975	1976	1977	1978	1979	1980	TOTAL
Capital costs										
For existing plants	10,041	21,910	26,292	21,910	8,764	0	0	0	0	88,917
For growth	4,095	4,125	4,110	4,250	4,395	4,545	4,695	4,855	5,020	40,090
Total	**14,136**	**26,035**	**30,402**	**26,160**	**13,159**	**4,545**	**4,695**	**4,855**	**5,020**	**129,007**
Low-sulfur fuel penalty costs										
For existing plants	13,722	15,797	14,952	15,078	15,963	15,963	15,963	15,963	15,963	139,264
For growth	132	1,200	2,285	2,437	2,610	2,790	2,976	3,169	3,368	20,967
Total	**13,854**	**16,997**	**17,237**	**17,515**	**18,573**	**18,753**	**18,939**	**19,132**	**19,331**	**160,231**
Other O&M costs										
For existing plants	6,561	9,843	13,787	17,074	18,460	18,549	18,549	18,549	18,549	139,921
For growth	577	1,169	1,786	2,424	3,086	3,767	4,473	5,201	5,962	28,445
Total	**7,138**	**11,012**	**15,573**	**19,498**	**21,546**	**22,316**	**23,022**	**23,750**	**24,511**	**168,366**
								Overall total		**648,567**

Source: Chase Manhattan Bank.

Regional agency starts up physical-chemical treatment plant

Ecodyne's design at Rosemount, Minn., represents the most advanced technology in waste water reclamation available in the U.S. today

The nation's first independent physical-chemical waste water treatment plant to process raw municipal sewage is nearing completion in Minnesota under the supervision of the Metropolitan Sewer Board of the Twin Cities Area.

As the agency charged by the Minnesota legislature, the Sewer Board operates a Metropolitan Disposal System presently consisting of 25 waste water treatment plants, a 450-mile interceptor system, and numerous support facilities. The Sewer Board System serves a region populated by nearly 2 million people, in addition to a commercial-industrial population equivalent to an additional million persons.

The $2 million advanced waste water treatment (AWT) plant at Rosemount, Minn., will go on stream as a part of the Sewer Board System this fall. Besides providing necessary waste water treatment for the Village of Rosemount, the 600,000-gpd facility will allow research of national significance to take place, and will demonstrate, on a large scale, the feasibility of using independent physical-chemical technology for municipal sewage.

Richard J. Dougherty, chief administrator of the Sewer Board, says, "This plant at Rosemount represents the most advanced technology in waste water reclamation available in the country today." He continues, "The construction and operation of this facility will, in our opinion, provide the means for meeting the 'best available technology' requirement of the 1972 Federal Water Pollution Control Act Amendment, to be achieved by 1983. Our Rosemount facility certainly will be a pathfinder to total water pollution abatement. The many potentials for improved waste water treatment with this facility really excite one's imagination."

Sewer Board's Richard Dougherty
Meeting "best available technology"

As an example of the significance the Federal Government is placing on the Rosemount AWT plant, the federal Environmental Protection Agency has joined with the Metropolitan Sewer Board under a grant in an 18-month detailed evaluation of the entire plant process. The resulting data will ultimately be available on a nationwide basis for use in design and process determination.

What it is

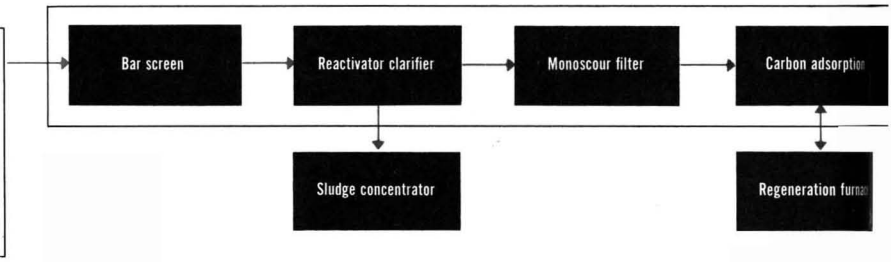
Best defined as unit processes involving physical and chemical (as opposed to biological) means of removing organic and inorganic contamination, physical-chemical treatment (p-ct) has a long history of success in industrial applications. Until recently, most physical-chemical applications treated industrial wastes. For example, a Colorado steel mill uses physical-chemical techniques to treat and recycle 36 million gallons of water per day—enough to meet the demands of a typical city of 300,000 people.

More recently, physical-chemical processes have been designed into a few municipal waste water treatment plants as an advanced waste treatment which upgrades biologically treated secondary sewage. Rosemount, however, will be the first full-scale p-ct plant treating municipal waste waters in the U.S. to employ only physical-chemical treatment methods through the entire plant. It completely replaces conventional treatment.

Past industrial successes coupled

Rosemount AWT plant

Raw sewage input, expected	
Suspended solids	300 ppm
BOD	300
COD	200–400
Ammonia nitrogen	15–35 ppm
Total phosphorus	5–15 ppm
pH	6.5–8.5



Metropolitan Sewer Board of the Twin Cities Area, Minn.

with passage of P.L. 92-500 increase the significance of Rosemount. Physical-chemical treatment can be designed to achieve high degrees of water purity to meet varying legislative standards. More importantly, it does so with predictable consistency. Consistency will be the key to meeting new standards.

The new law also may force governmental units to handle wastes previously out of their jurisdiction. Physical-chemical plants can treat nonbiodegradable wastes such as phosphates, oils, and metals.

Banister, Short, Elliot, Henderickson & Associates, consulting engineers of St. Paul, Minn., designed the Rosemount plant which features equipment manufactured by Ecodyne Corp., a large diversified company exclusively engaged in water and waste treatment and water cooling. The general contractor on the Rosemount project is Midwest Mechanical Services, Inc. of Minneapolis.

How it works

The plant is designed for a 600,000-gpd average capacity with sizable expansion possible. Raw sewage enters the plant through a 1-in. bar screen that removes large objects and trash.

After flowing by gravity through a common flume into a wet well, the sewage is divided into two separate treatment trains. The plant is designed to keep these streams separate by providing two identical process trains, each able to operate in several independent modes to permit direct simultaneous performance comparisons.

The first process component in each train is an Ecodyne (Graver) Reactivator clarifier. Each clarifier is 14 ft deep with a 25-ft diameter and is equipped with a lime and a polyelectrolyte feed system, a coagulant system for either alum or ferric chloride, and a pH adjustment system.

The clarifiers use lime to precipitate phosphates as calcium phosphate, which is drawn off as a solid. Lime also elevates pH to about 11.5 where the most efficient phosphate removal takes place. Organic solids settle from the sewage in the clarifiers reducing the BOD to 2050 ppm.

The sludge flows to a dewatering tank and from there to an Ecodyne sludge concentrator. Water from the concentrator returns to the wet well; dewatered sludge is trucked away.

Filters reduce suspended solids

After a clarifier retention time of approximately 4 hr, effluent pH is lowered from 11 to 8.5 before entering four Ecodyne Graver Monoscour filters. Two filters, each with an 8-ft diameter and a 100-ft^2 media bed, handle each section of the stream.

The dual media filters, consisting of 3 ft of anthracite over 1 ft of sand, can accommodate 4.5 gpm per ft,^{2} and have the necessary instrumentation to operate fully automatically. Here, inorganic and organic suspended solids are reduced to 3–5 ppm in filtered effluent. Backwash to clean the filters is initiated by head loss, clock, or push button.

After filtration, the effluent is pumped to a filtered water holding tank that regulates any surges that may occur in the system.

COD reduced in carbon adsorbers

From the holding tank, water is pumped to six carbon adsorption tanks, three on each stream, for removal of dissolved organics. Each adsorber contains a 12-ft carbon bed. The adsorbers operate in either an upflow or downflow mode.

In the upflow mode, the upward water velocity expands the granular carbon bed. A recycle line accommodates flow variations inherent in every sewage system to keep water velocity constant. Sensors ahead of the adsorption columns measure flow and when low flows occur, the sensors automatically open the recycle valve to pump more water through the columns.

Two of the three columns in each train operate in series. When the first column is exhausted, the second column becomes the lead column, the third column becomes the second, and the first regenerates. The adsorber removes dissolved organic compounds which are adsorbed on carbon granules to reduce organics to 5–10 ppm.

The adsorption columns are regenerated by removing carbon from the columns and transporting it through a carbon slurry line to a 3-step regeneration system. In the dewatering tank (11 ft in diameter by 22 ft deep), water is drawn off the spent carbon. A screw feeder transports the dewatered carbon to a 1700°F regeneration furnace. Organics are driven off in the absence of air to prevent a combustion reaction in the carbon.

Upon exiting the furnace, carbon is dropped into a water quench tank, then transported to a holding vessel until the next cycle.

Secondary filters remove fine solids

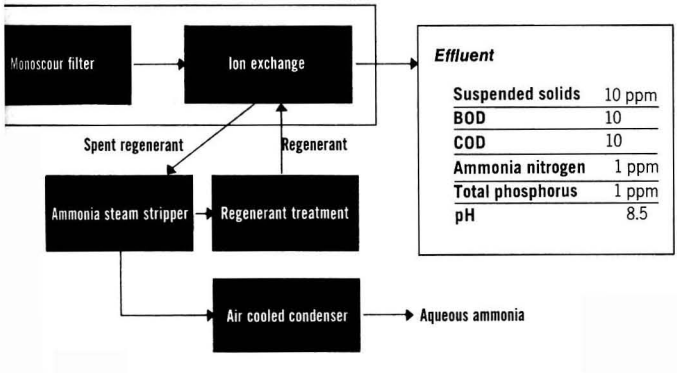
After passing through the carbon adsorption system, effluent enters a secondary set of four Ecodyne Graver Monoscour filters similar to the first to remove fine solids. These fine solids are biological species removed from the adsorption system. Effluent entering the secondary filters contains 10 ppm of suspended solids and exits the tank containing 2–4 ppm suspended solids.

Ion exchanger recovers ammonia

From secondary filters, water flows to another holding tank and then into an ion exchange vessel for ammonia removal. Each ion exchange vessel contains a natural ammonia-selective zeolite material, clinoptilolite, where sodium ions replace ammonia ions. Effluent from the ion exchange system, the last treatment step, is discharged from the plant with less than 1 ppm ammonia nitrogen.

Ammonia is recovered from the spent ion exchange regenerant in an ammonia stripper made by another Ecodyne affiliate, The Unitech Co. Steam is injected into a distillation column countercurrent with the regenerant solution to strip off the ammonia. An air-cooled plate-and-tube condenser condenses the vapor for collection in a covered tank as a 1% aqueous ammonia for sale as a fertilizer.

The Rosemount system will be placed on-line by the Metropolitan Sewer Board this fall and undoubtedly will become a model for future sewage system designs. Public cries for a cleaner environment make physical-chemical treatment a potential and attractive modern alternative to conventional plant designs.



FEATURE

Irving Forsten
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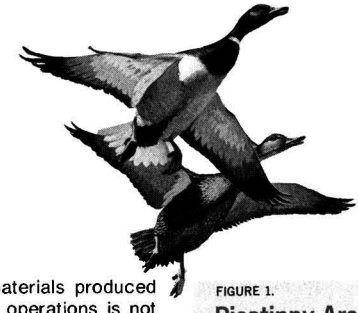
Pollution abatement in a munitions plant

Cleaning up wastes from explosives manufacture and loading operations is not easy with pollutants unique to the industry



The concept of cleaning up waste materials produced from munition manufacture and loading operations is not new. Attempts to implement abatement techniques have continued over the years. However, with the advent of a major munition plant modernization program beginning in 1968 and with the impetus given to pollution abatement through Executive Order 11507, dated February 1970, a vibrant intensive effort to eliminate objectionable pollutants from munition waste discharges got under way.

Some results were obtained rapidly. For example, in the purification process for trinitrotoluene (TNT), sellite (Na_2SO_3) is produced as part of a waste discharge and was formerly dumped into a stream. Through a simple process of aeration the sulfites were reduced to sulfates lowering chemical oxygen demand (COD) from 38 parts per million (ppm) to 20 ppm and raised the dissolved oxygen (DO) from 3.5 to 9.0 ppm, which affords a significant improvement for fish life in the stream. Most food fish require a DO level of 4 ppm, trout somewhat higher.

Filters were installed to reduce acid mist from sulfuric acid recovery plants. Neutralization facilities were installed to treat the acid waters from recovery and manufacture of nitric acid and sulfuric acid plants. Of course, many problem areas that surfaced in the course of surveying the manufacturing and loading facilities had no "off-the-shelf" ready solution.

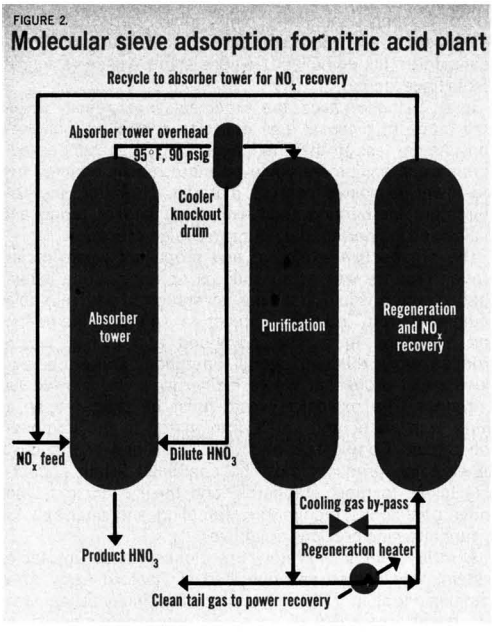
The modernization program is under the direction of the Army Material Command, Project Office for Munitions Production Base Modernization. To illustrate the extensive activity involved, the Picatinny Arsenal project is concerned with 17 Government-Owned Contractor-Operated (GOCO) plants situated in 12 different states (Figure 1). Although all pollution standards are eventually established through the Environmental Protection Agency (EPA), the state and municipality requirements must also be considered, and all abatement systems designed accordingly. Furthermore, all media of pollution must be considered—air, water, and solid wastes. Transferring a problem from one medium to another is unacceptable. Certain different media and complex technical investigations are especially concerned with problems unique to the munitions industry.

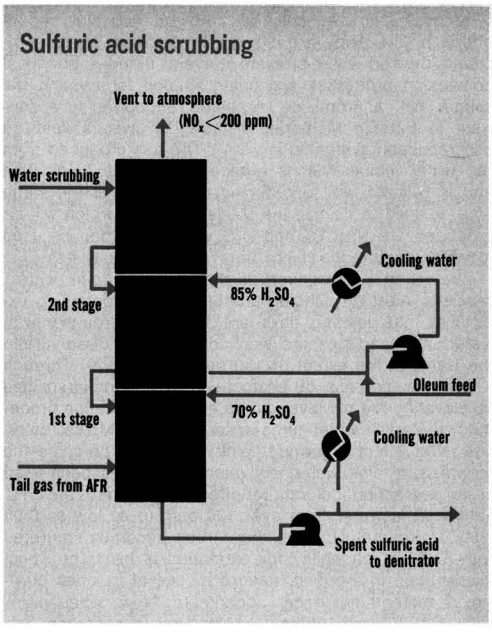
FIGURE 1.
Picatinny Arsenal related GOCO munition plants

Air pollutants from nitration processes are associated with manufacture of all classes of propellants and explosives. As examples, consider the nitration of cellulose to nitrocellulose and toluene to TNT. In both cases, abundant amounts of NO_x are released, and, in the latter case, tetranitromethane (TNM) and mononitrotulene (MNT) fumes are released through the vents of the process. In addition, manufacturing plants also produce nitric acid, a raw ingredient for the nitration processes, which, too, evolves large quantities of NO_x from stack discharge gases.

Various abatement schemes such as absorption, adsorption, catalytic combustion, and fume incineration are

FIGURE 2.





under study. Appropriate GOCO facilities are used to test in pilot plant size those processes which appear most promising.

Processes under study to abate air pollution

A prototype molecular sieve system will be installed during FY74 on a nitric acid plant at Holston AAP (Army Ammunition Plant) and evaluated in a joint effort with EPA. This installation will be extensively instrumented to demonstrate the performance and economics of molecular sieves for both Army and commercial nitric acid plant operation use. The work is progressing with procurement specifications for the molecular sieve system and instrumentation requirements completed.

The basic process diagram for the molecular sieve system is shown in Figure 2. The nitrogen oxides from the ammonia converter, after passing through a cooler-condenser, enter the bottom of the bubble cap absorber tower where they are absorbed and react to form nitric acid. The tail gas from the absorber is passed through a cooler-condenser where most of the water and some of the residual nitrogen oxides are condensed to form weak nitric acid which is recycled back to the appropriate tray of the absorber. The tail gas then goes through a molecular sieve bed where the remaining nitrogen oxides are adsorbed. The clean tail gas then passes through an expander for energy recovery. When the sieve bed is nearly saturated, it is replaced by a fresh sieve bed and regenerated by passing a clean hot gas through the bed. The nitrogen oxides driven off the bed by the hot gas are recycled to the absorber where they are used to increase the product yield. The beds are switched alternately from adsorption to regeneration to maintain a continuous process.

Two acid scrubbing systems are under investigation for the removal of NO_x from TNT acid and fume recovery tail gas. Sulfuric acid scrubbing at Radford AAP is being expanded to include prototype evaluation of scrubbing with sellite to remove tetranitromethane (TNM) from the tail gas. Volunteer AAP will evaluate a nitric acid scrubbing system for which the technology is expected to be available by the end of FY74.

Sulfuric acid scrubbing for removal of NO_x from TNT fume recovery tail gas was demonstrated with full scale equipment at Radford AAP. Based on this work, a recommendation was made to provide sulfuric acid scrubbing for several new TNT acid and fume recovery units planned as part of the modernization program.

The process for sulfuric acid scrubbing is shown in Figure 3. A three-stage scrubber (combined in a single column) will remove nitrogen oxides generated from the manufacture of TNT known as tail gas from the acid and fume recovery system. The first stage uses a recirculating scrubbing medium of about 70% sulfuric acid; the spent acid from the first stage is sent to the denitrator where the nitric portion is stripped off. The second stage uses about 85% sulfuric acid as the scrubbing medium, and acid from this stage is used as feed acid for the first stage. Oleum is added to the second stage to maintain the strength of the recirculating acid. A water-scrubbing stage is included to remove any SO_3 which might escape from the oleum in the second state. The gas to be treated enters the bottom of the column and flows countercurrently to the scrubbing media and comes out the top clean—200 ppm NO_x. (The 220 ppm emission level is intended to meet all current regulatory guidelines.)

Water pollution problems in munitions industry

A major water pollution problem stems from the manufacture and loading processes for TNT. The final manufacturing stage of TNT involves washing the trinitrated oil with a solution of sellite, which has a selective affinity for the unsymmetrical (and incidentally, unwanted) isomers of TNT. This results in a blood-colored by-product (commonly referred to as "red water") which is tapped from the mother liquid (pure form TNT) and disposed of by dumping into a convenient stream. Recently, red water was temporarily used in the manufacture of kraft paper products. However, when this isn't economically feasible because of distance to a mill, red water is burned in an incinerator. Here, aside from the NO_x emission control problem and the utilization of heat produced in the process, an ash product, Na_2SO_4, is produced.

The sulfate can be leached into the ground by rain wa-

ters causing its own pollution problem. However, recent efforts by the Army are closing the cycle to abate completely the red water problem. Several different chemical conversion processes are being studied for reusing the sulfate ash. A promising technique, supported in a contract to Battelle Memorial Institute, involves a fluidized bed reduction system (Figure 4). The ash produced from red water incineration is ground to optimize fluidization and is reacted with a reducing gas which, at the same time, is used to fluidize the solids. Products which will be produced are Na_2CO_3 and H_2S which can then be used to remanufacture the sellite, thus recycling the wastes.

Another area of concern is the so-called "pink water" problem. After the loading process of TNT-containing explosives, the loading bays are washed thoroughly with water. TNT particles are washed away and dissolve into the water to the extent of 150 ppm (by weight). Through a complex process of photochemical action, intensified by elevating the pH level during acid neutralization procedure, the wash water turns an orange or light rust color. The latter effect is termed "pink water." To preclude the formation of pink water, activated carbon has been used in an extraction column to effectively reduce the TNT contained in water from over 100 ppm to as low as 0.05 ppm. Unfortunately, once the carbon becomes saturated with TNT, its capability for extraction is lost. The spent carbon has, in the past, been disposed of by open burning, a method no longer acceptable. Now, when nitrobody (TNT) waste effluent is removed in a carbon column, and the bed becomes saturated, it is regenerated with toluene which is a solvent for the nitrobody. The contaminated toluene is transferred to storage where various techniques for extraction of the nitrobodies are being investigated. One approach is to crystallize the TNT out of solution by reducing the temperature of the mixture. The TNT can then be filtered out of the system and used in a recycle operation.

Solid waste in the munitions industry

The last medium for correction involves disposal of solid waste materials. Various forms of solid waste in munition processing exist, and every plant is faced with the problem. Furthermore, current practice is to open burn, which is objectionable by all environmental standards. The major solid waste disposal problem areas include: propellant and explosive material (past-shelf-life or from fabrication); inert, explosive contaminated wastes (cardboard shipping containers); and, finally, large bulky materials such as wood structures in obsolete buildings (candidates for demolition) where some explosive ingredients have lodged.

In all of these cases, the expedient, most readily available mode of disposal was emission-controlled incineration. As far as off-the-shelf availability was concerned, commercial equipment could be more readily adapted for the lower explosive content material. However, the requirement for burning solid explosives and/or propellant in a closed incinerator did not have design precedent.

The prospective explosive and propellant waste incineration process was established as an engineering investigation which would first take advantage of any relatable equipment from industry, subject to safety refinements, and secondly, to pursue advanced approaches which promise more efficient overall operation. Therefore, explosive and propellant waste incineration was viewed as a system. The explosive waste must be prepared as a slurry with water and safely transmitted to the combustion region. Combustion must be stable and continuous. All emission products must be contained within acceptable levels to meet standards, and the system must be under continuous monitoring (sampling and analysis) to ensure attaining previous objectives.

A rotary kiln incinerator, the closest to an available system, was piloted and operated at Radford Army Ammunition Plant in 1972. The rotary kiln incineration system has successfully disposed of propellants consisting of nitrocellulose, nitroglycerin, and nitroguanidine; aluminized propellants; and explosives TNT and HMX (cyclotetramethylenetetranitramine). A total of 63 test runs have been completed with 27,300 lb of propellants, 1065 lb of HMX, and 273 lb of TNT being burned. The nominal feed rate was 250 lb/hr of solids (a slurry of 12½% by weight solids/water) for durations of 10 min to 24 hr. Except for the HMX which tended to lump together and not burn off rapidly as did TNT, the results of the tests were good with no major problems encountered during the grinding, pumping, or incineration of the materials. An eight-channel automatic stack gas analyzer was installed on the exhaust stack of the incinerator to analyze the stack gas being emitted. A total of 14 tests have been run with the gas analyzer (10 propellants, 4 HMX), and the results show that the average emission levels are below proposed guidelines (e.g., NO_x 200 ppm guideline; 170 ppm measured).

FIGURE 4.

Na_2So_4 fluidized bed reduction system

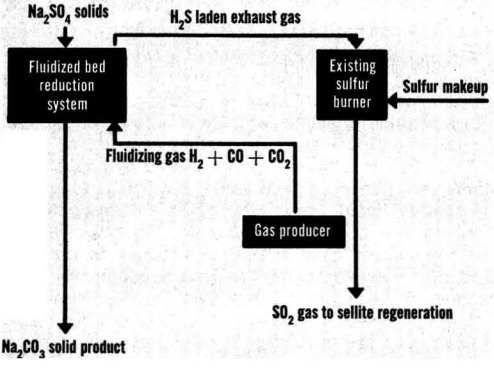
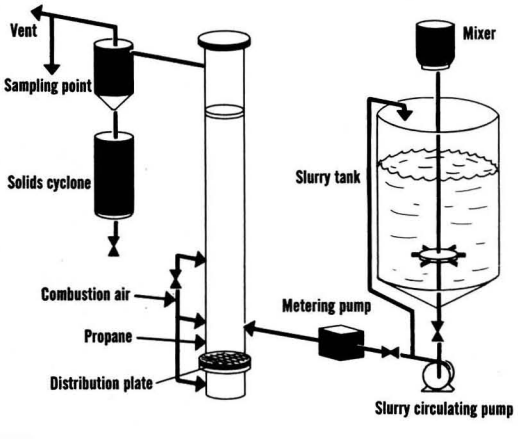


FIGURE 5.

Lab scale fluidized bed combustor



A pilot incinerator, working on an induced draft principle, was successfully operated at Picatinny Arsenal. A total of 49 tests have been completed using TNT, Composition B (60% by wt RDX to 40% TNT), RDX (cyclotrimethylenetrinitramine), and HMX slurries. Nominal flow rates of 12.75% concentration by weight of explosives in water were used to yield the design rate of 250 lb/hr explosive. Durations of individual tests ranged from 30 sec to 20 min. Prior to incineration, TNT, Composition B, and HMX were successfully ground to a uniform particle size using a ball mill grinder. Temperature and photographic data for TNT showed controlled rapid combustion occurring in the injection and combustion zones of the incinerator, with only an occasional flaming particle visible. Again, as for the case of HMX, in the rotary kiln incinerator, RDX and HMX did not exhibit the same rapidity or continuity of combustion as did TNT. Exhaust gas characterization data were obtained for tests incinerating TNT and Composition B slurries.

The demonstration of total system feasibility of the incineration of explosives was accomplished by these test programs. The future potential for a more efficient and universal system to handle all types of explosives and propellants has been shown in lab scale demonstrations of a fluidized bed combustion approach contracted as part of the overall program to Esso Research & Engineering Co. (Linden, N.J.).

A 6-in. i.d. fluid bed reactor (Figure 5) has been designed, constructed, and tested using a 10% by weight TNT slurry and a 10% by weight Composition B slurry. A total of 12 incineration tests have been completed with durations in excess of 8 hr. Exhaust gas data have been obtained for each test. Preliminary results using a catalyst with the basic bed material indicate a drastic reduction in NO_x generation well within proposed or projected regulatory standards of 220 ppm. In addition, design modification drawings to effect conversion of the Picatinny Arsenal incinerator to a fluid bed reactor have been completed. Plans call for obtaining additional data for the incineration of Composition B, TNT, and propellants and to expand the scope of work to include RDX and HMX.

As in the previous case for explosive and propellant wastes, the current method for disposing of inert wastes (such as packaging material) contaminated with explosives is through open burning. Because of the dilution effect of the inert ingredients, the explosive ingredients do not have a major impact on incinerator design. Accordingly, a commercial system (Figure 6) was modified to include safety relief features and evaluated at Joliet Army Ammunition Plant. The system has a capability of handling 600 lb/hr of waste material.

Tests were conducted using inert waste and explosive contaminated inert waste (small quantities of TNT and Composition B) to determine the optimum temperature and feed rate. In addition, an evaluation of the incinerator burning contaminated wastes was conducted by members of the Air Pollution Engineering Division, U.S. Army Environmental Hygiene Agency at Joliet (Ill.) during November 1972. The purpose of the survey was to determine if the particulate and carbon monoxide emissions from the incinerator exceeded levels prescribed by the State of Illinois. Oxides of nitrogen were also measured to provide additional information. The emissions did not exceed, and were well below, the established standards.

Incineration is also under consideration for:

- bulky explosive contaminated materials, such as large timbers, plywood, and other materials of construction
- decontamination of large metal parts prior to sale as scrap, such as process tanks, hoods, ducts, and large unloaded ordnance items
- decontamination of process operating equipment for rework or reuse.

Portions of technology available from the aforementioned programs may serve to provide much of the design data needed to pilot a system to meet this last requirement.

It would be inappropriate to convey the impression that the program is one of waste disposal, without regard to the advantages of energy conversion or recycle possibilities. In fact, in every task of the program, emphasis is placed upon avoidance of transmitting a pollution problem from one medium to another as well as maximum energy conversion and waste material utilization. In fact, waste explosive ingredients are considered for possible construction blasting material. An extensive effort by the Army's Natick Labs in Massachusetts and the Navy's Crane Indiana Ammunition Depot are investigating biological degradation of explosives (such as TNT) and propellants (such as nitrocellulose). Occurrence of microbial action has been evident, and the prospects of eventually using sewage treatment concepts are being pursued.

Instrumentation for monitoring

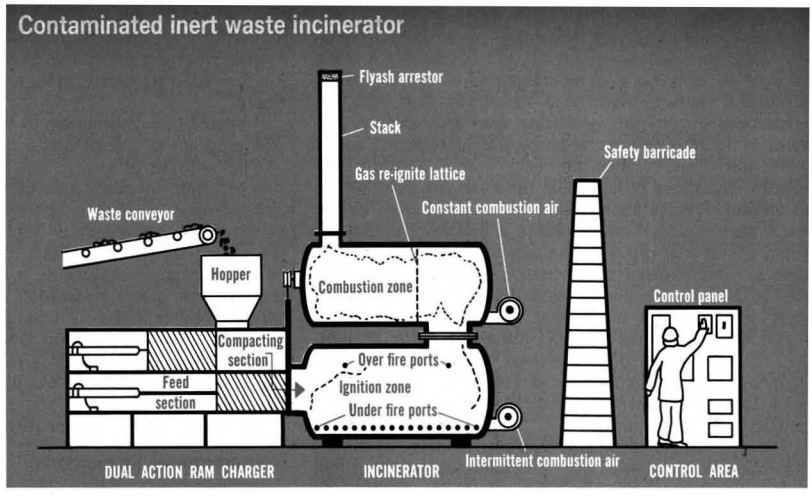
The pursuit of technical solutions to munition waste disposal problems would be meaningless without adequate instrumentation for monitoring and controlling the unique pollutants which are part of our operations. In the cases where the emissions are common to those of industry in general, commercially available instruments are used. For example, NO_x is an air pollutant arising from the manufacture of many materials besides explosives. To select the instrument most suitable for general use in ammunition plants, an evaluation program is under way to compare the performance of different types. The program includes instruments based on chemiluminescence, nondispersive infrared, electrochemical transducer, and photometric analytical principles. These instruments represent the best current state-of-the-art technology, and the completion of the program will result in a technical data package specifying the instrument that will be most suitable for use in ammunition plants.

In the cases where the emissions are peculiar to the ammunition industry (Table 1), instruments must be developed that have the necessary specificity, sensitivity, and speed of response. Although most militarily unique pollutants are explosives or propellants, some, like tetranitromethane (TNM), are by-products formed during a chemical process. Others, like acid mist and ammonia, are pollutants that are emitted in large quantities during the chemical processing associated with manufacture of explosives and propellants. None of the pollutants listed can be monitored by commercially available instruments, although for TNT pink water and for suspended nitrocellulose, it has been relatively easy to effect adaptations.

Table 1. Military unique pollutants

Air	Water
Tetranitromethane	TNT (Red & pink water)
Methyl nitrate	Nitroglycerin
Mononitrotoluene	Nitroguanidine
Nitromethane	Nitrocellulose
	Tetryl
	RDX
	HMX

For monitoring pink water, the photometric analyzer was adapted by replacing the optical filters in the standard instrument with ones that absorbed at wavelengths



appropriate to TNT. The cells were modified in the measuring and reference channels to be of the proper pathlength for the required measurement and of the proper construction for use in an aqueous medium. For monitoring nitrocellulose, a nephelometer type of turbidimeter was used to obtain the required sensitivity. The adaptation required here was to construct a calibration curve based on nitrocellulose rather than use the standard curve supplied with the instrument.

Instrument development has been initiated for the militarily unique pollutants, tetranitromethane, and nitroglycerin. For tetranitromethane, an air pollutant emitted during the manufacture of TNT, the analytical principles that will be applied are Raman spectroscopy and frequency shift caused by sorption on piezoelectric crystals. For monitoring the nitroglycerin discharged in process waste water, Raman spectroscopy and electrochemistry are being applied to instrument development. Since all of these analytical principles have been incorporated into monitoring instruments for other compounds, the transfer of technology to these specialized applications should be suitable for engineering developments.

Another area of instrument development that should be mentioned is in support of the explosive incineration program. The incineration process is applied to a water slurry of the explosive. Variation in the composition of this slurry will cause variation in incinerator performance that could produce unsafe conditions. Therefore, an instrument that can monitor the composition of this slurry and provide warning against variation is essential. A program to develop such an instrument, based on the variation in reflected light from the suspended particles, is under way with completion expected by the end of this year.

The October 1972 issue of *Environmental Science & Technology* contains an excellent initial directory for pollution control companies associated with equipment items commented upon in this article. Specific examples (Table 2) cited do not constitute an endorsement by the U.S. Government.

In attempting to discuss and illustrate the magnitude and progress of the total program, it is important to credit other organizations supporting the program. These organizations include Frankford (Pa.) and Edgewood (Md.) Arsenals; Army Environmental Hygiene Agency, Office of the Surgeon General (Washington, D.C.); Construction Engineering Research Lab, Corps of Engineers (Champlain, Ill.); Mobility Equipment Research & Development Command (Fort Belvoir, Va.); Natick Laboratories (Natick, Mass.); and Deseret Test Center (Salt Lake City, Utah). There is also interface between the Departments of the Navy and Air Force. Many industrial firms are supporting the program from technology to off-the-shelf abatement equipment, instrumentation, and control systems. EPA is charged with the responsibility for establishing standards and ensuring availability of support technology for the entire nation. Since our concern is with pollutants resulting from military munitions manufacture, a close interface exists with EPA on furnishing data for abatement systems and compliance with existing and forthcoming standards.

Table 2. Representative suppliers

Activated carbon
- Calgon Corp.
- Westvaco Corp.
- ICI America Inc.
- Barnebey-Cheney Co.

Incinerators
- Environmental Control Products Inc.
- Bartlett-Snow
- Kaiser Aluminum & Chemical Corp.
- Procedyne Corp.
- Copeland Systems, Inc.
- John Zink Co.
- Thermal Research & Engineering Co.

Instrumentation systems
- Beckman Instruments, Inc.
- Du Pont Co.
- Foxboro Co.
- Honeywell, Inc.
- Leeds & Northrup Co.

Scrubbers
- Chemico
- Vari-Systems, Inc.
- Otto H. York Co., Inc.
- Dow Chemical Corp.
- Envirotech Corp.

Molecular sieve systems
- Norton Co.
- Union Carbide Corp.

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FEATURE

Impact of aircraft exhaust emissions at airports

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Although aircraft contribute a small fraction of the air pollution burden in metropolitan areas, concentrations of some pollutants exceed standards in airport vicinities

Aircraft contribute a minor fraction of the total air pollutant burden in metropolitan areas in the U.S., but the impact of aircraft emissions is more serious in the vicinities of airports. This article concentrates on current approaches to defining and evaluating this impact. Public exposures of some pollutants at U.S. airports appear to exceed current standards, and thus, emission control measures have been proposed. Aircraft emission control regulations are likely to become more stringent with time to offset effects of increasing air traffic at airports.

Evaluation of the impact of aircraft pollutant emissions in the U.S. has been carried out in two rather distinct phases—the first phase concerned the contribution by aircraft to regional air pollutant burdens, and the second phase covered effects of aircraft emissions in the immediate vicinities of airports. The next phase of this evaluation is likely to pertain to implementation of methods for controlling the impact of aircraft emissions and evaluation of the effectiveness of these control methods.

Early and current investigations of impact

Public attention was first drawn to aircraft exhaust emissions with the introduction of commercial turbine-engine aircraft in the late 1950's. The first noticeable effects were exhaust odors at airports and visible exhaust plumes from turbine-engine aircraft. These sensory effects and the resulting complaints from the public alerted air pollution control agencies to the possibility of adverse effects from aircraft emissions, and investigations of these possible effects were initiated.

The first comprehensive studies of aircraft emissions were conducted by the Los Angeles County Air Pollution Control District (LAC-APCD) in 1960 and 1965. The results of these studies indicated that, in that time period, aircraft contributed a small but significant fraction of all pollutants emitted in Los Angeles County. Specifically, the LAC-APCD investigations indicated that aircraft contributed 1–2% of all carbon monoxide, hydrocarbon, and

nitrogen oxide emissions and approximately 10% of all particulate emissions. The indicated particulate matter fraction, however, appeared to be influenced strongly by the unique method used by LAC-APCD to measure aircraft particulate emissions.

A subsequent study, sponsored in 1968 by the National Air Pollution Control Administration (NAPCA, now a part of the U.S. Environmental Protection Agency), was concerned with the effects of aircraft emissions throughout the U.S. and methods of controlling these emissions. The results of this study indicated that aircraft contributions of all pollutant classes, including particulate matter, were 2% or less in all major metropolitan areas. Researchers predicted that this fraction would increase with increases in aircraft activity and reductions in emissions from other sources, but the aircraft fraction was not expected to become more than a minor fraction of the total in the foreseeable future.

On the other hand, the NAPCA study indicated that the local impact of aircraft emissions at airports was more serious. Emission densities by aircraft at airports were comparable to densities of the same pollutants emitted by other sources in surrounding areas, and future projections indicated that the airport environment would deteriorate rapidly with increased aircraft activity and increases in aircraft size. Also, control methods were not well defined for certain pollutants—nitrogen oxides in particular—so that a technical base for aircraft emission control did not exist at that time. The investigators recommended that more detailed analyses be conducted of the impact of aircraft emissions at airports, and that the development of emission control methods be pursued more vigorously.

In recent years, studies of air quality have been conducted at several major airports in the U.S., including John F. Kennedy International in New York and Los Angeles International in California. Air quality studies also have been conducted at other major airports of the world, including Heathrow at London, Orly at Paris, and Tokyo and Osaka International Airports. The federal EPA, which sponsored the study at the Los Angeles International Airport, subsequently sponsored a second study involving air quality analyses at several major commercial and general aviation airports in the U.S. EPA also sponsored a study involving an assessment of aircraft emission control techniques which included evaluations of both the effectiveness and costs of various approaches to emission control. On the basis of the results of these studies, EPA has concluded that the impact of aircraft emissions at airports is sufficient to warrant the promulgation of emission control regulations, and that effective control methods are now available for all classes of pollutants currently of concern from aircraft. At press time, aircraft emissions control regulations had been proposed which, if adopted, would affect all commercial and private turbine-engine and piston-engine aircraft operated in the U.S.

Table 1. Ambient air quality standards for aircraft-related pollutants

	Primary standard, health-related	Secondary standard, welfare-related
Carbon monoxide	10 mg/m^3 (9 ppm) for 8 hr[a] 40 mg/m^3 (35 ppm) for 1 hr[a]	Same as primary
Nonmethane hydrocarbons	160 μg/m^3 (0.24 ppm) for 3 hr (6–9 a.m.)[a]	Same as primary
Nitrogen dioxide	100 μg/m^3 (0.05 ppm), annual arithmetic mean	Same as primary
Sulfur dioxide	80 μg/m^3 (0.03 ppm), annual arithmetic mean 365 μg/m^3 (0.14 ppm, for 24 hr	60 μg/m^3 (0.02 ppm), annual arithmetic mean 260 μg/m^3 (0.10 ppm), for 24 hr[a] 1300 μg/m^3 (0.5 ppm), for 3 hr[a]
Particulate matter	75 μg/m^3, annual geometric mean 260 μg/m^3 for 24 hr[a]	60 μg/m^3, annual geometric mean 150 μg/m^3 for 24 hr[a]

[a] Maximum concentration, not to be exceeded more than once per year.

Impact and public and occupational health standards

The impact of air pollutants emitted by aircraft can be defined in terms of the ambient concentrations of these pollutants resulting from aircraft activities. These concentrations can be compared to existing air quality standards to obtain qualitative indications of impact. This measure of impact cannot be related in a quantitative way at the present time to the costs of air quality control or the benefits of clean air. However, the "observed vs. standard" air quality comparison can be determined readily and serves to indicate the need for implementation of air quality control methods.

Air quality standards exist at the present time which pertain to two aspects of the airport scene: public health and welfare and occupational safety and health. The public health and welfare standards pertain to the traveling public using the airport and residents of the airport vicinity. The occupational safety and health standards pertain to employees of the airport and airlines, and other business organizations operating within the airport complex.

National standards for ambient air quality have been in effect in the U.S. since April 1971 (Table 1), and plans for implementing these standards have been prepared by state air quality control agencies. The standards generally specify separate maximum allowable ambient air concentrations of each pollutant for protection of public health and public welfare, the term "welfare" being used in a narrow sense indicating property or economic well-being. The standards also specify the time intervals over which ambient pollutant concentrations are to be measured and the measurement methods to be employed. While lead and lead compounds are considered to be aircraft-related pollutants, no ambient air standards have been promulgated for these materials as yet. However, a concentration of approximately 3 μg/m^3 has been identified as a threshold level of exposure corresponding to increases in lead concentrations in the blood.

National standards governing the exposure of workers to air contaminants have been in effect in the U.S. since May 1971. These standards specify either maximum average exposures for an 8-hr workday, or "ceiling" levels for maximum instantaneous exposure. In general, the maximum concentrations allowed (Table 2) and pertaining to aircraft related pollutants are considerably higher than those specified in the ambient air standards shown in Table 1.

These standards were taken by the Federal Government from previously published standards recommended by organizations such as the American Conference of Governmental Industrial Hygienists and the American National Standards Institute. The standards are being reviewed by federal agencies and are subject to change as a result of these reviews with any changes expected to result in more stringent standards. For example, the National Institute for Occupational Safety and Health has

Table 2. Occupational safety and health standards for aircraft-related pollutants

Carbon monoxide	55 mg/m³ (50 ppm)	Time-weighted average for 8-hr day or 40-hr week
Nitrogen dioxide	9 mg/m³ (5 ppm)	Instantaneous ceiling
Sulfur dioxide	13 mg/m³ (5 ppm)	Time-weighted average for 8-hr day or 40-hr week
Lead and inorganic lead compounds	0.2 mg/m³	Time-weighted average for 8-hr day
Particulate materials:		
Inert dust (respirable)	5 mg/m³	Time—8-hr day or 40-hr week (for all particulate classes listed)
Carbon black	3.5 mg/m³	
Oil mist	5 mg/m³	

recently issued a criteria document recommending a revised carbon monoxide standard. This revised standard, if adopted, will prescribe a maximum worker exposure of 40 mg/m³ (35 ppm), determined as a time-weighted average over an 8-hr day or 40-hr week, and an instantaneous ceiling level of 220 mg/m³ (200 ppm). Furthermore, the criteria document indicates that this recommended standard is applicable to workers engaged in sedentary work, and that maximum allowable exposures of workers engaged in light or heavy work should be reduced even further.

Evaluation of impact

An airport, as a source of air pollutants, actually consists of a multitude of individual sources, some of which are in motion (aircraft, service vehicles, and automobiles) and others which are stationary (heating plants, fuel storage facilities, and aircraft maintenance facilities). The time periods over which pollutant concentrations are evaluated correspond to the time periods in the ambient air quality standards which range from one hour to one year. Consequently, the variations in local concentrations due to the movement of aircraft and ground vehicles are not of concern since the characteristic times of these movements are short compared to the air quality standard time periods. However, variations in pollutant concentrations which result from variations in aircraft and ground vehicle traffic levels must be considered since these activity levels vary over time periods comparable to those specified in the short-term air quality standards.

Variations in spatial distribution of pollutants must also be considered since the emissions from the various sources do not merge rapidly. Instead, the "plumes" from the individual sources persist over distances greater than typical airport dimensions so that pollutant concentration profiles are highly nonuniform both within the airport and outside the airport boundary.

An additional factor to be appraised in evaluating impact of emissions from aircraft activities at airports is the effect of emissions of aircraft-related pollutants by other sources in the airport vicinity. Emissions from airport surroundings create background pollutant concentrations which vary with time and with meteorological conditions. The background pollutant concentrations combine with the emissions from the airport to create higher concentrations and, as a result, greater impact than would be created by the aircraft activity alone.

The factors which most strongly affect pollutant concentrations at airports are summarized in Table 3. These factors consist of five categories of pollutant sources and the local meteorology which is the mechanism by which the pollutants from the various sources are dispersed. Each source category, as well as the meteorology, has unique time and spatial distribution characteristics which generally are variable. However, in many instances, the variabilities can be related to two primary airport variables—aircraft activity level and meteorological conditions.

Investigations of the impact of aircraft emissions conducted to date have been directed toward evaluation of effects on public health and welfare and have been reported in terms of ambient concentrations of pollutants of concern from the standpoint of public health. This type of impact evaluation is also applicable to the occupational environment, if the evaluation includes work areas within the airport complex.

Table 3. Measured pollutant concentration at Los Angeles International Airport

May–November 1970

	CO (mg/m³) 1-hr av			Particulate matter (μg/m³), 24-hr av		
Site category	Mean	Min	Max	Mean	Min	Max
Outside terminal, 2 sites	6.4	1	44	139	54	490
Inside terminal, 2 sites	10.8	1	153	Not measured		
Parking area, 1 site	5.9	1	30	121	55	502
Airport boundary, 2 sites	3.8	1	34	Not measured		

Source: LAC-APCD.

Two obvious approaches are available for evaluating pollutant concentrations at airports—direct measurement and mathematical prediction—and both approaches have been used. However, early investigations revealed that each approach used alone has substantial limitations, and thus, current practice in impact evaluation involves the use of both approaches in combination.

Direct measurement of pollutant concentrations at airports by means of on-site instrumentation is an effective approach to the evaluation of impact. The only uncertainty in the results obtained lies in the instrument errors associated with operating principles of the instruments, calibration errors, and operator errors. These sources of error generally have been reduced to acceptable levels in the ambient monitoring of air pollutants. Several evaluations of impact at airports have been based on direct measurement of pollutant concentrations.

There are, however, serious disadvantages to the direct measurement approach. Even though direct measurements provide unequivocal indications of total impact at specific locations, the relative contributions of various sources to the total impact cannot be determined. Similarly, direct measurements of pollutant concentrations cannot be extrapolated reliably to determine concentrations at other locations or at the same location at other times when conditions affecting the concentrations are different. Thus, the direct measurement method is a reliable technique for determining total pollutant concentra-

tions at specific times and locations. However, the method does not identify the sources responsible for health hazards and, thus, cannot be used alone as a basis for establishing an emission control program.

The prediction of pollutant concentrations at airports by mathematical models of emission sources and meteorological dispersion mechanisms offers advantages and disadvantages which contrast sharply with the direct measurement approach. There are no limitations to the conditions which can be simulated in the mathematical prediction approach. Airport activities can be varied to represent operational conditions typical of the past, present, or future, and meteorological conditions can be varied quite readily throughout the entire spectrum of conditions encountered during the year. Also, airport operations and meteorology can be varied independently in order to simulate combinations of conditions which may occur infrequently but represent conditions of potentially high impact. An additional advantage of mathematical modeling is that modifications in emission sources or airport activities which correspond to the application of control methods can be simulated and evaluated in terms of reduction in impact. The pollutant concentrations obtained by the mathematical prediction method also reveal clearly the relative contributions by various pollutant sources to the total concentrations existing at any point investigated.

The disadvantage of the mathematical prediction method lies in the uncertain accuracy of the results obtained. Two principal sources of error are present when the method is utilized. The first consists of inaccuracies in the simulation of the emission sources and meteorological processes that are the result of a lack of complete information on the characteristics of these factors. For example, substantial uncertainties exist as to the actual emission rates of pollutants from aircraft engines during their operation at airports. These uncertainties give rise to errors of the first type in the prediction process.

The second error source consists of inaccuracies associated with approximations used in developing mathematical models of emission sources and meteorological mechanisms. These approximations are necessary in order to create a mathematical model for which a solution can be achieved with a reasonable amount of computation. For example, the emission of pollutants from an aircraft engine is frequently represented as a set of continuous point sources, or point and line sources, distributed appropriately throughout the airport. In actuality, the initial condition of aircraft pollutants is as constituents of an exhaust plume which is distributed in space and, of course, the emission of these pollutants is not continuous. Inaccuracies in the prediction method due to approximations such as these give rise to errors of the second type. The sources of errors of both types are so numerous in the overall predictive procedure that it is very difficult even to estimate the level of accuracy of the resulting predictions. Consequently, pollutant concentrations determined purely by mathematical prediction can be regarded only as qualitatively indicative of the true concentrations existing at the airport.

The use of a combined approach to impact evaluation including both direct measurement and mathematical prediction has resulted inevitably from the realizations of the limitations of the individual methods and the complementary nature of the advantages of the methods. In the combined method, mathematical predictions are used to develop the air quality data required. By this method, data can be obtained for both actual and hypothetical airport conditions, and the contributions by aircraft and other source categories to total impact are revealed. Measured pollutant concentrations are used primarily for calibration of the mathematical models by comparison of predicted and measured data for actual airport conditions. Measured data also can be used as input information in the mathematical prediction method to represent emission sources such as airport surroundings if the analysis procedure is formulated to accept such inputs. Thus, the combined method offers the potential of providing a mathematical predictive procedure which is calibrated for the specific airport being investigated, and of providing more accurate representations of emissions from airport surroundings. As a result, the method is very likely to provide air quality data which reveal both the magnitude and sources of air pollutant impact at airports with an accuracy approaching that of data obtained by direct measurement.

Table 4. Calculated pollutant concentrations at Los Angeles International Airport

Annual average concentrations, 1970

	NO_2, $\mu g/m^3$		SO_2, $\mu g/m^3$		Particulates, $\mu g/m^3$	
	Air-craft	All sources	Air-craft	All sources	Air-craft	All sources
Outside terminal, 6 sites						
Mean	17	133	11	23	14	23
Min	16	110	10	22	12	21
Max	19	160	12	25	17	27
Airport boundary, 16 sites						
Mean	9	73	5	16	5	14
Min	6	47	3	13	3	10
Max	15	130	8	21	9	18
Airport neighborhood, 16 sites, 5 km from airport center						
Mean	3	47	1	13	2	12
Min	2	30	1	8	1	7
Max	6	99	3	35	3	30

Source: Northern Research and Engineering Corp.

Current and future impact

The impact of aircraft emissions in airport vicinities is indicated by the results of the impact investigations which have been completed. Table 3 summarizes carbon monoxide and particulate matter concentration data obtained by direct measurement at the Los Angeles International Airport during the period May to November 1970. Tables 4–6 summarize data obtained by mathematical prediction. Table 4 lists annual average concentrations of three pollutants at Los Angeles International Airport calculated for the conditions existing at the airport in 1970.

Table 5 also lists pollutants concentration data for Los Angeles International Airport calculated for 1970, but these data indicate pollutant concentrations for short time periods. The conditions selected for calculating these data were realistic conditions with the highest impact potential—that is, the combinations of aircraft activity and meteorological conditions assumed were combinations which actually are encountered occasionally during the year and which would be expected to result in the highest concentrations of pollutants. Hence, these data are termed "short-term maximum" concentrations. The time periods used in calculating these data corresponded to the averaging times specified in the air quality standard pertaining to public health and welfare.

Finally, Table 6 lists examples of predicted pollutant concentrations at four different airports for cases where the total concentrations exceeded the applicable standards. The list does not include all cases of excessive concentrations, but the examples selected were those for which the concentrations of pollutants from aircraft were the greatest at each airport.

Both the measured and predicted data indicate that

current air quality standards are being exceeded at the Los Angeles International Airport, and the predicted data indicate that excessive pollutant concentrations exist at other major U.S. airports also. However, the contributions by aircraft to the excessive concentrations are found to vary widely among the different classes of pollutants.

The carbon monoxide standards are exceeded over both the 8-hr and 1-hr averaging times in terminal areas and at sites near the airport boundaries, and aircraft contribute substantially to the concentrations at the terminals. Aircraft contributions generally are less at the airport boundaries except that aircraft contributions of CO are high at boundary sites which are near to and downwind of runways.

The hydrocarbon standard also is exceeded in terminal areas, at airport boundaries, and in neighborhood areas adjacent to airports. In some cases, the standard is exceeded by concentrations of hydrocarbons from aircraft alone.

Since the nitrogen dioxide standard is based on a one-year averaging time, the standard is considered to be applicable only to areas outside of airports where long-term exposures to NO_2 could occur. In areas adjacent to airports, the NO_2 standard is found to be exceeded. However, aircraft contributions of NO_2 are significant only in a few cases, and in no case has the aircraft contribution alone resulted in an excessive NO_2 concentration. Similarly, the particulate matter and sulfur dioxide standards are exceeded in airport vicinities, but the aircraft contributions of these pollutants generally are insignificant fractions of the total concentrations.

Thus, the principal impact of aircraft emissions on public health and welfare results from carbon monoxide and hydrocarbon emissions, and this impact extends from within the airport to residential areas adjacent to the airport. This result, indicated for the four airports investigated, is likely to be true for other major airports as well.

Concentrations of pollutants at airports are not observed to exceed current standards based upon occupational health. The pollutant of greatest concern is carbon monoxide observed in concentrations exceeding the occupational threshold limit value, and the highest CO concentrations are observed inside terminal buildings. However, these concentrations do not appear to persist over the 8-hr averaging time upon which the occupational standard is based.

Future impact

Projections of future emission rates at airports indicate that the impact of certain pollutants will continue to be of concern unless control measures are implemented. Carbon monoxide and particulate emissions are predicted to remain nearly constant so that the impact of these pollutants can be expected to persist. In addition, emissions of nitrogen oxides are expected to increase substantially

Table 5. Calculated pollutant concentrations at Los Angeles International Airport

Short-term maximum concentrations, 1970

	CO, mg/m³				THC, μg/m₃	
	8-Hr period		1-Hr period		6–9 a.m.	
	Air-craft	All sources	Air-craft	All sources	Air-craft	All sources
Outside terminal, 6 sites						
Mean	1	3	3	13	148	880
Min	1	2	0	2	0	650
Max	2	4	6	24	490	1100
Airport boundary, 16 sites						
Mean	0	1	1	12	47	390
Min	0	0	0	0	0	0
Max	1	2	6	43	270	1500
Airport neighborhood, 16 sites, 5 km						
Mean	0	1	0	5	12	290
Min	0	0	0	0	0	0
Max	0	2	4	17	170	1500

	SO, μg/m³				Particulates, μg/m³
	24-Hr period		3-Hr period		24-hr period
Outside terminal, 6 sites					
Mean	8	30	42	240	13	30
Min	5	15	20	46	9	15
Max	10	38	64	730	16	38
Airport boundary, 16 sites						
Mean	2	31	29	144	4	23
Min	0	12	0	7	0	8
Max	9	84	76	430	14	67
Airport neighborhood, 16 sites, 5 km from airport center						
Mean	0	26	8	89	1	20
Min	0	0	0	8	0	0
Max	3	84	68	240	5	70

Source: Northern Research and Engineering Corp.

Table 6. Predicted pollutant concentrations exceeding air quality standards

Pollutant	Av time	Airport	Site category	Predicted concentration (μg/m³) Aircraft	Total	Standard
CO	8 Hr	JFK	Terminal	9,000	19,000	10,000
		ORD	Terminal	3,000	12,000	10,000
	1 Hr	DCA	Boundary	45,000	59,000	40,000
		JFK	Terminal	85,000	100,000	40,000
		LAX	Boundary	0	43,000	40,000
		ORD	Terminal	21,000	41,000	40,000
NMH[a]	3 Hr, 6–9 a.m.	DCA	Boundary	310	1,300	160
		JFK	Terminal	2,600	4,000	160
		LAX	Terminal	440	870	160
		ORD	Boundary	4,500	4,700	160
NO_2	Annual	DCA	Neighborhood	2	120	100
		ORD	Neighborhood	6	130	100
SO_2	Annual, 3 hr	DCA	Neighborhood	0.6	65	60
		DCA	Boundary	25	1,700	1,300
		JFK	Terminal	14	4,900	1,300
Particulate	24 Hr	DCA	Neighborhood	0.1	220	60
		JFK	Neighborhood	18	200	60

[a] NMH = nonmethane hydrocarbons, assumed to constitute 90% of total hydrocarbon concentration.
Source: Northern Research and Engineering Corp.

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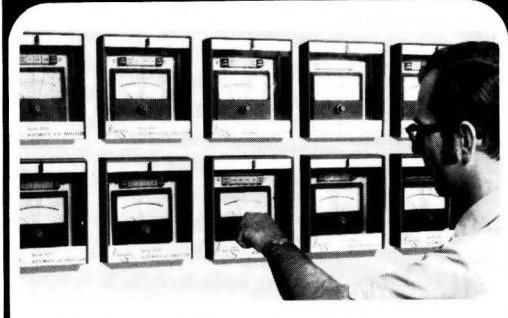

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so that the impact of this pollutant can be expected to increase proportionately. Whereas NO_2 emissions from aircraft do not appear to cause excessive exposures at the present time, they are likely to become more serious in the future.

Emission control methods have been identified with the potential of reducing the impact of aircraft emissions and preventing this impact from increasing in future years. The effectiveness of these control methods in reducing aircraft emissions and their impact has been estimated. The estimates indicate that very effective control of carbon monoxide and hydrocarbon emissions can be obtained either by modification of engines or ground operations. Reductions in emission rates by a factor of approximately 10 are predicted to be attainable, and the impact of these emissions should decrease proportionately if these control methods are utilized. Reductions in particulate emissions which are attainable also are significant. Reductions by a factor of approximately four are predicted, and these would be adequate to overcome the increases in particulate emissions anticipated as a result of increased aircraft activity. Control methods for nitrogen oxide emissions and their impact appear to be less effective, and emission reductions are attainable only by engine modifications. However, these reductions may be sufficient to maintain the impact of NO_2 emissions at approximately its current level.

Investigations of the impact of aircraft pollutant emissions at airports have provided a qualitative measure of this impact. At major U.S. airports, aircraft contribute substantially to concentrations of carbon monoxide and hydrocarbons which exceed current air quality standards based on public health and welfare. Also, aircraft emissions of nitrogen dioxide are expected to increase in the future with increases in aircraft size and activity levels, and these emissions may be responsible for excessive NO_2 concentrations in future years. Thus, a requirement exists for the control of aircraft emissions during operations at airports. Alternative approaches to the control of aircraft emissions include modification of aircraft engines and modification of aircraft ground operating procedures. If such control methods are implemented, effective control of aircraft emissions at airports can be achieved.

Additional reading

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Jones, K. H., et al., "The Federal Aircraft Emission Control Program: Standards and Their Basis," APCA 66th Annual Meeting, June 1973, APCA Paper No. 73-241.

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E. Karl Bastress *is manager of environmental research, IKOR Incorporated. He has a broad background in the analysis of nature and control of air contaminant emissions, including direct experience in the measurement of gaseous and particulate emissions from mobile and stationary sources. At IKOR, Dr. Bastress directs environmental research and consulting services to government and industry.*

CURRENT RESEARCH

Sources of Vanadium in Puerto Rican and San Francisco Bay Area Aerosols

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■ Atmospheric V sampled in the San Francisco Bay area appears to originate from both soil and combustion sources. V sampled in air flowing onto the eastern end of Puerto Rico can be associated with an Al-depleted soil source through comparisons of abundances of V, Al, Co, and Cr. Previous work (Martens and Harriss, 1973) has shown that these elements behave similarly during aerosol growth in Puerto Rican orographic clouds.

Considerable information on the abundance and particle size distribution of V has been gathered during extensive multielement investigations of the atmospheres of Puerto Rico and the San Francisco Bay area (Martens, 1972). Previous surveys of urban, industrial, and more remote locations have indicated several sources of atmospheric V including: soil (Rahn et al., 1971; John et al., 1973); oil refining and chemical manufacturing (Nifong, 1970); and fuel oil combustion (Nifong, 1970; Zoller and Gordon, 1970; Brar et al., 1970).

Our present objective is to investigate the origins of V by comparing the abundances and particle size distributions of V to that of the other elements found in the atmospheres of the San Francisco Bay and Puerto Rico areas.

Sampling and Analysis

Atmospheric sampling was carried out at nine stations in the San Francisco Bay area (Figure 1) and at four stations on the island of Puerto Rico (Figure 2). Seven of the San Francisco Bay area stations were part of the monitoring network of the Bay Area Air Pollution Control District (BAAPCD) with whose assistance samples were collected. Two other Bay area stations were set up in the Berkeley Hills and in Benicia. The stations can be described as follows: BE, Benicia station on rural hilltop 5 km from town; BK, Berkeley Lawrence Radiation Laboratory station on top of a 12-meter building at a 300-meter altitude in the Berkeley Hills overlooking the residential areas of the city; F, City of Fremont station a few kilometers east of the Nimitz Freeway in a business-residential area; P, City of Pittsburg station located less than 1 km from a utilities plant in a small business section of town; L, City of Livermore station located in a primarily residential area of a small valley immediately to the east of the hills bordering San Francisco Bay; R, City of Richmond station located in a residential area across the Bay from the city of San Francisco; RC, Redwood City station located in the center of a light industrial area near the U.S. 101 freeway on the

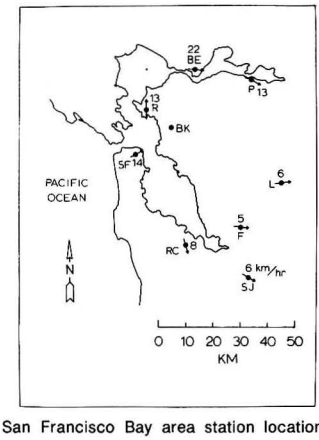

Figure 1. San Francisco Bay area station locations and wind data

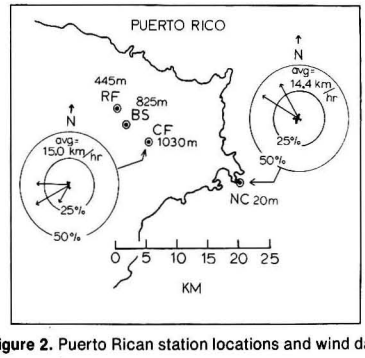

Figure 2. Puerto Rican station locations and wind data

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San Francisco peninsula; SF, City of San Francisco station located on top of the downtown approximately 40-meter high BAAPCD building; SJ, City of San Jose station located in a business–residential area.

Of the seven BAAPCD stations only SF utilized a building higher than approximately 5 meters. In general, these stations were set up to simulate environmental conditions encountered daily by persons working and living in these areas. The BK station was located on top of a 12-meter high building.

The four sampling stations on the island of Puerto Rico were located on the coastline at a Navy base (NC), just below cloudbase at a Boy Scout camp (BS), on top of Pico del Este in a cloud forest (CF), and on the leeward side of the mountain ridge in the rain forest (RF). The samplers at stations other than RF were held by ringstands 1 meter above the roofs of one- or two-story inactive buildings. The RF sampler was located on a 22-meter tower above the rain forest tree canopy.

A listing of stations, sampling periods, and total volume sampled is presented in Table I.

Aerosols were collected by seven-stage Andersen cascade impactors followed by afterfilters containing 47 mm Whatman 41 cellulose fiber paper. Vacuum was supplied by ⅓ hp vacuum pumps operated at a constant flow rate of 1 cfm (1.7 m^3/hr). Particles were impacted onto 1 mil (25 μm) polyethylene discs placed over the normal Andersen stainless steel collection discs. Details on the use of these materials can be found in Dams et al. (1972). Fifty percent cutoff diameters based on calibration of the Andersen impactor with unit density latex spheres and often used to describe the size of particles sampled by each stage (Flesch et al., 1967) are presented in Table II.

Aerosol samples were simultaneously analyzed for Al and V by nondestructive neutron activation analysis using Lawrence Livermore Laboratory's (Livermore, Calif.) 3-MW reactor. A high-resolution lithium-drifted germanium detector was used to count the samples. Details of the counting sequence can be found in Rahn et al. (1971).

Table I. Stations, Sampling Periods and Volumes

San Francisco Bay Area

Station	Sampling period	Sampling vol., m^3
BE	1200 7-13-71 to 1200 7-16-71	135
BK, F, L, P, R, RC, SF, SJ	1200 7-12-71 to 1200 7-16-71	179

Puerto Rico

Sample	Sampling period	Sampling vol., m^3
NCAI	1200 11-23-71 to 1300 11-25-71	83
NCAII	1345 11-25-71 to 1515 11-28-71	125
BSAII	0950 11-27-71 to 1400 11-30-71	74
RFAI	1015 11-23-71 to 0710 11-26-71	117
RFAII	0745 11-26-71 to 1100 11-30-71	169
CFAI	1435 11-22-71 to 0900 11-25-71	64
CFAII	1845 11-25-71 to 0830 11-30-71	125

Table II. Andersen Impactor 50% Cutoff Diameters, D_{50}

Andersen stage	D_{50}, μm
1	9.20
2	5.35
3	3.28
4	1.76
5	0.89
6	0.54
7	0.40

Results

The results of V analyses from the San Francisco Bay and Puerto Rican studies along with some results of previous studies are summarized in Table III.

Sources of V in Bay area. As a first step in understanding the source of V in the San Francisco Bay area we should examine abundances and size distributions of V at the various stations. Table III indicates that abundances range from 2.7 ng/m^3 in downtown San Francisco to 12 ng/m^3 in the much smaller city of Pittsburg. Particle size distributions of V are presented in Figure 3. It should be noted that the Pittsburg station (P) is located less than 1 km from a utilities plant which burns both natural gas and fuel oil and is also within a few miles of a complex of oil refineries.

In spite of the differences in total concentrations, the V size distributions remain roughly the same with sources of V apparently associated with both small and large particles. One possible source of large-particle V is soil dust. Rahn et al. (1971) and John et al. (1973) have associated total V at these stations with a soil dust component. Since Al was also associated with dust by the previous authors, we have therefore plotted V/Al ratios as a next step (Figure 4). It is apparent that the V/Al ratios consistently reach a minimum in the large particle fraction in a range of ratios close to that given for average crustal material (Goldschmidt, 1954; Turekian and Wedepohl, 1961).

By assuming that the entire Al concentration is associated with soil dust and subtracting from each stage in the size distributions that component of V which could be ac-

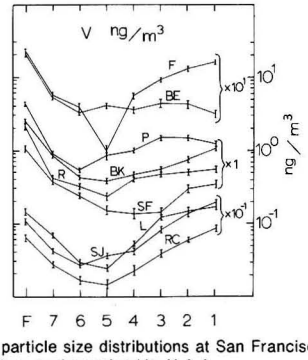

Figure 3. V particle size distributions at San Francisco Bay area station locations as determined by N.A.A.

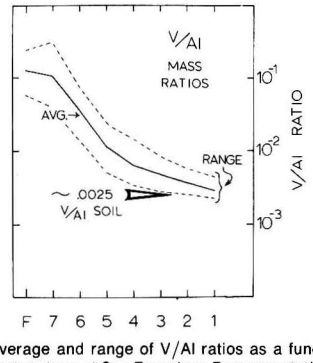

Figure 4. Average and range of V/Al ratios as a function of Andersen impactor stage at San Francisco Bay area stations

Table III. Concentrations of V Found in This Study and Selected Previous Studies

San Francisco Bay area		Puerto Rico		Previous studies		
Station	V ng/m³, 20%[a]	Sample	V ng/m³, 15%[a]	Location	Av. V, ng/m³	Authors
BE	4.9	NCAI	0.62	Pacific Ocean	0.17 ± 0.13[b]	Hoffman *et al.* (1969)
BK	6.9	NCAII	1.7	Hawaii	0.16 ± 0.11[c]	Hoffman *et al.* (1972)
F	7.6	BSAII	2.2	Niles, Michigan	2.9 ± 0.5	Rahn *et al.* (1971)
L	7.5	RFAI	1.1	NW Indiana	4.0 ± 1.0 to 18 ± 2	Harrison *et al.* (1971)
P	12	RFAII	2.7	Cambridge, Massachusetts	600[d]	Zoller and Gordon (1970)
R	5.0	CFAI	2.4	Chicago, Illinois	22[e]	Brar *et al.* (1970)
RC	3.3	CFAII	1.0			
SF	2.7					
SJ	6.7					

[a] Approximate analytical uncertainty. [b] Average of 9 samples. [c] Average of 106 samples. [d] Precision about ±10%. [e] Average of 22 metropolitan Chicago area stations; concentrations ranged from 2.2–120 ng/m³.

counted for by a soil origin, we are left with the small-particle V size distributions shown in Figure 5. Small-particle distributions of this type are often associated with combustion sources (Nifong, 1970). In the case of the Pittsburg station, many combustion sources which might emit V were noted. It appears reasonable to hypothesize that the V found during the Bay area experiment can be accounted for by the combination of a natural soil dust source contributing particles greater than 1 μm in diameter and a pollution source such as combustion of fuel oils contributing submicron particles.

V in Puerto Rico. V shows up in surprising amounts in the rather isolated Puerto Rican stations. Hoffman et al. (1969, 1972) have also found unaccountably high levels of V over the Pacific Ocean between California and Hawaii and over the island of Hawaii itself.

The V/Al ratio plotted in a manner similar to that for the San Francisco Bay area (Figure 6) seems to indicate that there are large amounts of V in Puerto Rican air not attributable to dust having average crustal abundances of Al and V. The average V/Al ratios found for aerosols at the four Puerto Rican stations are compared with those found on Hawaii by Hoffman et al. (1972) in Table IV. The ratio found for California dust and crustal material range (Turekian and Wedepohl, 1961) are also included. The Hawaiian and Puerto Rican ratios agree well but show an excess of V above or a depletion of Al below the California dust and average crustal material.

Additional data for two other elements, Cr and Co, were obtained for the NCAII and RFAII samples through long irradiation neutron activation procedures (i.e., see Dams et al., 1970). Ratios between these two elements and Al and V might serve to clarify the sources of all of them. Table V summarizes our data from Puerto Rico samples NCAII and RFAII and gives the ratios of these elements in average crustal material and in seawater.

Comparisons of the ratios in Table V indicate that: V, Co, and Cr are enriched relative to Al in comparison with average crustal abundances, and relative to each other, V, Co, and Cr show agreement with average crustal abundances.

These factors suggest that the deviation of V/Al ratios from average crustal abundances may be due to depletions in Al in soil-derived material rather than excesses of V from a special source such as pollution.

There remains an additional line of evidence that should be considered: namely, the similar behavior of Al and V in aerosols involved in orographic cloud formation

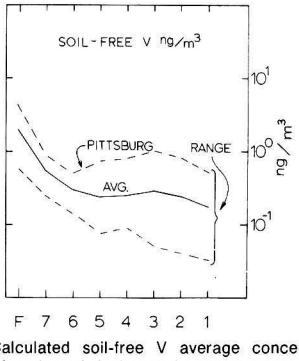

Figure 5. Calculated soil-free V average concentration and range as a function of Andersen impactor stage at Bay area stations

Note highest values found at Pittsburg, Calif.

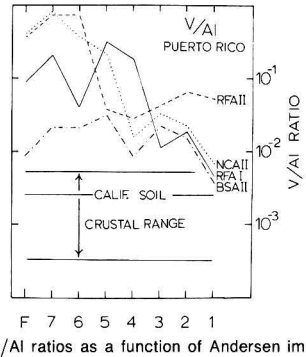

Figure 6. V/Al ratios as a function of Andersen impactor stage at Puerto Rican stations

Table IV. Comparisons of V/Al Mass Ratios for Puerto Rican and Hawaiian Aerosols, California Dust and Average Crustal Material

Puerto Rican Av				
Station	V/Al	Av Hawaiian, V/Al	California dust, V/Al	Crustal material, V/Al
NC	0.042	0.024 (Hoffman et al., 1972)	0.0025	Av (Goldschmidt, 1954), 0.0018
BS	0.011			
RF	0.089			Range (Turekian and Wedepohl, 1961), 0.0003–0.005
CF	0.021			

Table V. Multielement Ratios in Puerto Rican Aerosols, NCA II and RFA II

Sample	V/Al	Co/Al	Cr/Al	Co/Cr	V/Co	V/Cr
NCA II	0.071	0.013	0.063	0.21	5.5	1.1
RFA II	0.12	0.0086	0.068	0.13	14	1.8
Crustal av	0.0018	0.00049	0.0025	0.20	3.8	0.75
Seawater	2.0	0.10	0.050	2.0	20	40

processes in Puerto Rico (Martens and Harriss, 1973). Al and V particle size distributions out of clouds change only slightly during cloud formation indicating little incorporation of condensing water vapor. This physical evidence suggests that both elements are part of nonhygroscopic particles, probably from a soil origin. It is possible that soil dust from both local and distant sources such as the African continent (Prospero, 1972) is being sampled.

Summary and Conclusions

Both soil and combustion appear to be major contributors of V in the San Francisco Bay area atmosphere, the soil providing the larger particles and the combustion the smaller particles. V sampled in Puerto Rican experiments may be primarily from a soil source. The similar behavior of V and Al in Puerto Rican orographic clouds (Martens and Harriss, 1973) further suggests soil origin for the V, although the soil dust does not appear to have average crustal composition, especially in the case of Al which is depleted.

Acknowledgment

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Ligand Photooxidation in Copper(II) Complexes of Nitrilotriacetic Acid

Implications for Natural Waters

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The fate of aminopolycarboxylate compounds [all of which are potential detergent builders, components of some industrial wastes, and apparently products of secondary sewage treatment (Bender et al., 1971)] involves the reactions of their metal complexes because complex formation constants are so large (Ringbom, 1963). We are engaged in a study of the photochemical degradations that may occur under sunlight irradiation. Transformation of the organic molecules may be expected to be facile only when excited states of the ligand to metal charge transfer type (Balzani and Carassiti, 1970a) are accessible in the complex. This suggests that attention be given to complexes of metals from the transition group such as Cu(II), Co(II), and Fe(III). At first sight, such a restriction might discourage interest because of the low concentration of such metals, but there are two mitigating factors; first, the complex formation constants of aminopolycarboxylates with these metals are large, and second, the rapidity of ligand substitution processes in these systems (Langford and Sastri, 1972) ensures considerable "turnover."

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■ Copper complexes of nitrilotriacetate have been irradiated at 350 nm in a photoreactor based on a Rayonet unit. Despite the low absorptivity of the complexes at this wavelength, a significant photodecomposition of the ligand occurs. The identified products are CH_2O and (iminodiacetic acid). Inferentially, CO_2 must be released. The quantum yield analog function, Y, based on ferrioxalate actinometry, decreases with increasing pH linearly over the pH range 2-12. The efficiency of photodecomposition decreases with increasing concentration above $10^{-3}M$ but approaches a limiting value below about $5 \times 10^{-4}M$. The low concentration limit of the efficiency of decomposition (Y/concentration) is approximately 1.0. There is no direct evidence for the intervention of Cu(I) species although a photoredox pathway involving Cu seems the most plausible mechanism. The oxidation reaction is suggested to be general for Fe and Cu complexes of aminopolycarboxylates and α-amino acids.

Photodecarboxylation of the ethylenediaminetetraacetate (EDTA) complex of Fe(III) has been known for some time (Jones and Long, 1952), as has photodeamination of α-aminoacid complexes of Fe(III) (Balzani and Carassiti, 1970b), although neither has been studied systematically. We have recently reported facile photodecomposition of the nitrilotriacetate (NTA) complexes of Fe(III) according to the following equation (Trott et al., 1972):

$$2Fe^{III}(NTA) \longrightarrow Fe^{II} + Fe^{II}(NTA) + IDA + CH_2O + CO_2 \quad (1)$$

where IDA designates iminodiacetic acid. Since NTA is a promising detergent builder, it seems a high priority choice for investigation of aminopolycarboxylate pathways.

In the earlier work on $Fe^{III}(NTA)$ (Trott et al., 1972), a connection between laboratory experiments and natural systems was attempted, guided by an equilibrium model simulation developed by Childs (1971) of the present composition of Lake Ontario augmented by assumed NTA levels from $1 \times 10^{-7}M$ to $2 \times 10^{-4}M$ in the pH range 6-9. Although Fe(III) species bound up to 34% of the total NTA (at NTA = $3 \times 10^{-6}M$, pH = 6), at all NTA concentrations below the assumed total Cu^{II} concentration of $2 \times 10^{-6}M$ (and at all pH values), the dominant NTA species was the copper complex, accounting for nearly 80% of dissolved NTA at $10^{-6}M$ or less. This suggests that despite weaker absorption of actinic light by Cu(II) complexes and the greater barrier to the reduction Cu(II)/Cu(I), the fate of copper aminopolycarboxylates may be more significant than the fate of iron complexes in many natural waters.

In initial experiments, we prepared solutions of $Cu(NTA)^-$ by combining equimolar ($0.001M$) solutions of $Cu(NO_3)_2$ and sodium nitrilotriacetate prepared in both distilled water and water drawn from the Rideau River in Ottawa. These were adjusted to pH values from 4-8 and irradiated in closed borosilicate flasks containing air in open summer sunlight. Within three days, all irradiated samples gave strong positive indication of the presence of aldehydes with Schiff's reagent, whereas dark controls did not. Consequently, a systematic investigation was initiated.

Experimental

Reagent grade from Eastman and BDH Chemicals from Fisher Scientific, Montreal, P.Q., were used in all experiments without additional purification.

For each photolysis run, 50 ml of Cu-NTA complex was prepared from stock solutions of Cu^{2+} and H_3NTA and adjusted to the desired pH with either HCl or NaOH. The solution (10 ml) was placed in a 5-cm cylindrical spectrophotometer cell, 2 cm in diameter, and irradiated. The remainder was held as a dark control. Irradiation was carried out with 350 nm of light in a Rayonet photoreactor for 100 min. Light intensity was determined using a solution of the well-characterized chemical actimometer $Fe(C_2O_4)_3^{3-}$ at a concentration absorbing all light incident of wavelength less than 450 nm (Hatchard and Parker, 1956). Actinometry involves determination of photolytically produced Fe^{2+} using *o*-phenthroline. The actinometer value characterizes the quantity of light entering the solution for our standard geometry. Since our solutions are weakly absorbing, we do not measure conventional quantum yields but a quantum yield-related function Y = moles reaction/einsteins light entering solution. This will vary with concentration but the efficiency of photolysis, Y/concentration, will approach a limiting value at low concentration where illumination is nearly homogeneous.

The quantity of photodecomposition was estimated by determination of formaldehyde produced using the spectrophotometric procedure of Lappin and Clarke (1951). Solutions above $0.004M$ required Cu(II) removal on a cation exchange resin prior to analysis. Addition of excess CH_2O in advance in some runs established that this product was not decomposing under photolysis conditions. IDA was sought as follows: An irradiated solution was evaporated to 25% of its original volume and treated with sodium diethyldithiocarbamate to precipitate Cu(II). The dissolved Cu-dithiocarbamate complex was extracted with $CHCl_3$. The aqueous layer was then evaporated to dryness and the products were esterified with diazomethane prepared freshly from diazold. The esters were finally dissolved in a little $CHCl_3$ and thin-layer chromatography (tlc) was carried out on silica gel plates using ether as solvent. The plates were developed with $KBrO_3$ and KI. Reference chromatograms of NTA, IDA, and the dithiocarbamate were prepared.

Results and Discussion

The results of tlc indicate the presence of esters of NTA, IDA, and the dithiocarbamate. In one chromatogram there is a trailing behind the NTA spot and before the IDA spot, but it seems unlikely that any fourth substance is chromatographically detectable. Based on the detection of CH_2O and the earlier results on the iron system, we postulate the Cu(II) complex photoinitiated reaction as:

$$NTA + \tfrac{1}{2}O_2 \longrightarrow CO_2 + CH_2O + IDA \quad (2)$$

We suspect this is mediated by the photoreduction of Cu(II) to Cu(I) followed by:

$$2Cu(I) + \tfrac{1}{2}O_2 + H_2O \longrightarrow 2Cu(II) + 2OH^- \quad (3)$$

but obtained no direct evidence for Cu(I). We did not seek Cu(I) vigorously because Morimoto and DeGraff's (1972) results on malonate decomposition suggest it is hard to find (if it is present at all).

In the experimental section, Y, the parameter used by Trott et al. (1972), was defined for use as a measure of the yield of the decomposition. It was suggested that "efficiency" of decomposition be expressed as Y/concentra-

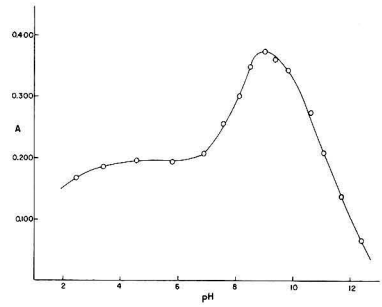

Figure 1. Y/concentration plotted against complex concentration on logarithmic scale

Experiments at 25°C, pH = 4.15. Y is quantum yield-related function defined in text

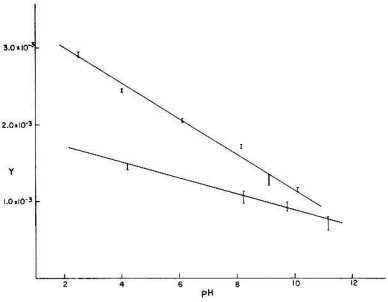

Figure 2. Photodecomposition yield as function of pH at two concentrations of complex

Note greater pH dependence at higher concentration. Upper curve is 0.01*M* Cu; lower curve is 0.004*M* Cu

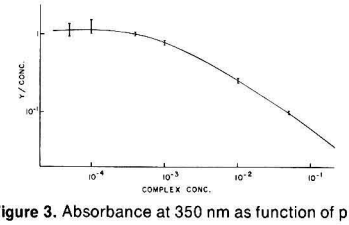

Figure 3. Absorbance at 350 nm as function of pH

Cu concentration is 0.004*M*

tion. A plot of Y/concentration vs. concentration of the complex for pH = 4.15 is shown in Figure 1. At a concentration of $5 \times 10^{-3}M$ the value is unity and it remains near unity to the lower concentrations of environmental significance. This implies that under given conditions of illumination and pH, the fraction of the complex photolyzed per unit time is constant.

We can be no more specific than to refer to copper complexes (plural) because the exact nature of hydrolytic equilibria is not known. Figure 2 shows that the photodecomposition yield decreases with increasing pH. The effect is more pronounced at the higher total complex concentration. The behavior is similar to that observed for the iron system (Trott et al., 1972) which we will report elsewhere for the chemistry of iron–ethylenediaminetetraacetic acid (EDTA) system. In the iron case, the decreased yields were attributed to formation of oxo-bridged dimeric species; a process favored by moderately high pH and high concentration. A feature of the dimers is appearance of new absorption bands in the near uv spectrum. Suggestive evidence that the copper system has behavior similar to the iron system is the variation in absorbance at 350 nm as a function of pH shown in Figure 3.

It seems that the following conclusions can be drawn. Photodecomposition of aminocarboxylate systems has been observed for complexes of Cu(II), Fe(III), and Co(III) (Endicott, 1972). In each case, the net reaction in a system open to air is, in effect, oxidation of the ligand by O_2 according to the process:

$$RHN - CH_2 - COOH + \tfrac{1}{2}O_2 \rightarrow RNH_2 + CO_2 + CH_2O \quad (4)$$

All evidence points to this reaction originating in excitation of a ligand to metal "charge transfer" (CT) excitation of the metal complex of the aminocarboxylate. The range of aminocarboxylates examined includes glycine, NTA, and EDTA. We feel this is adequate to suggest generality for the reaction. It is noteworthy that the requirement for CT absorption implies that complexes of Ca^{2+} and Mg^{2+} will probably not react in sunlight. We have sought a reaction of NTA in the presence of Mg^{2+} irradiated at 350 nm without success. However, the high complex formation constants of transition metal aminopolycarboxylates coupled with the relatively rapid "turnover" in these complexes should assure the occurrence of the photooxidations in all waters where light intensities are reasonable (a zone similar to that in which photosynthesis occurs).

A recent paper (Bada, 1971) has attempted to estimate the kinetics of amino acid decomposition in natural waters with a view to understanding amino acid lifetimes in natural waters. The paper concludes that amino acids should be remarkably stable and that the leading nonbiological reaction is the slow metal ion-catalyzed thermal oxidation in aerated waters. It is certain that metal induced photodecomposition would be faster to depths up to 10 meters (Duntley, 1963) and the role of this reaction in amino acid cycling deserves exploration.

Acknowledgment

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Fluorometric Determination of Selenium in Water with 2,3-Diaminonaphthalene[1]

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■ A simple method has been developed for determination of selenium in clean water. This method begins with hydrogen peroxide oxidation to convert inorganic selenium to selenate, followed by hydrochloric acid reduction to selenite. The selenite is then reacted with 2,3-diaminonaphthalene to form an organic extractable piazselenol, naphtho-[2,3-*d*]-2 selena-1,3-diazole, which is determined fluorometrically. The method is free from common interferences and is capable of detecting selenium at the level of 1 ppb.

The use of 2,3-diaminonaphthalene (DAN) as an analytical reagent for the determination of trace amounts of selenium was reported by Lott et al. in 1963. Since that time, fluorometric procedures based on the formation of the selenium-DAN piazselenol have been applied to the determination of selenium in biological tissue and vegetation (Allaway and Cary, 1964), lake sediments (Wiersma and Lee, 1971), and waste water effluents (Raihle, 1972).

The procedures described by Allaway and Cary (1964) and Wiersma and Lee (1971) are applicable to selenium in all its valence states, but due to the complexity of the matrices involved, they require careful digestion and separation procedures. The procedure described by Raihle (1972) employs a bromine-bromide redox buffer and is applicable to elemental selenium and selenite.

The simple procedure described here makes it possible to determine all forms of inorganic selenium in clean water, such as potable water and fresh water that receives waste effluent containing only small amounts of insoluble organic matter. The first step is hydrogen peroxide oxidation in order to destroy any organic matter present and to convert inorganic selenium to selenate. The sample is then treated with hydrochloric acid to reduce selenate to selenite (Dye et al., 1963). Finally, the selenite is reacted with DAN to form the piazselenol, which is extracted into cyclohexane and measured fluorometrically.

Nitrite, which interferes, is removed by oxidation to nitrate. Metal interferences are masked by complexation (Lott et al., 1963).

Experimental

Apparatus. All fluorometric measurements were made with an Aminco-Bowman spectrofluorometer (American Instrument Co., Inc., Silver Spring, Md.).

Reagents. All reagents were analytical reagent grade, unless otherwise specified.

A stock selenium solution (1.0 g/l.) was prepared by dissolving 1.633 grams of H_2SeO_3 in distilled deionized water and diluting to 1 liter with distilled deionized water.

A 0.1% DAN solution was prepared by dissolving 100 mg of DAN in 100 ml of 0.1*N* HCl. Prior to use, the solution was extracted with 25 ml of cyclohexane.

A masking solution was prepared using the formulation described by Lott et al. (1963).

Spectrometric-grade cyclohexane (J. T. Baker Chemical Co., Phillipsburg, N.J.) was used for all extractions.

Analytical Procedure. Treat a 50-ml sample with 2 ml of 30% H_2O_2, and boil gently for 10 min. Add 25 ml of concd HCl, and boil the solution for an additional 5 min. Remove the sample from the heat source, and adjust its volume to about 75 ml with distilled deionized water. Carefully add 20 ml of concd NH_4OH, and allow the sample to cool to room temperature. Then treat the sample with 5 ml of the masking solution, and adjust the pH to 1.8 ± 0.2 with dilute NH_4OH. After this adjustment, transfer the sample to a 125-ml separatory funnel, and add 5 ml of 0.1% DAN solution. Mix the sample by swirling, and store it in the dark for 1½ hr. Then add 10 ml of cyclohexane, and extract the piazselenol by shaking for 1 min. After discarding the aqueous phase, transfer the cyclohexane phase to a 15-ml centrifuge tube, and centrifuge for 5 min at 225 × *g*. Determine the selenium concentration in the extract fluorometrically in a 1-cm cell, using excitation and emission wavelengths of 389 and 521 nm, respectively.

Results and Discussion

Analytical Range and Precision. Calibration curves constructed by plotting the emission intensity vs. the selenium concentration were linear in the range of 0.02–1.0 μg Se. Above this level the curves bent toward the concentration axis.

Ten replicates each of a 0.5-μg and a 1.0-μg Se standard in 50 ml of distilled deionized water were analyzed. The results gave a relative standard deviation of 6.3%, with a mean value of 0.48 μg and 1.0 μg, respectively.

Interferences. Standard solutions containing 1.0 μg of

Table I. Recovery of Selenium Added (0.5 μG) to 50-Ml Samples of Potable Water

	Selenium recovered[a]	
Sample	μg	%
1	0.48	96
2	0.48	96
3	0.50	100
4	0.52	104
5	0.50	100
6	0.50	100
7	0.50	100
8	0.53	106
9	0.50	100
10	0.47	94
11	0.52	104
12	0.59	118
13	0.50	100
14	0.54	108
15	0.50	100
Av recovery, 101.9%		
Std dev, 5.9		

[a] The background selenium content of each sample was <0.01 μg.

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Table II. Recovery of Selenium Added (0.5 μG) to 50-Ml Samples of Water Receiving Waste Effluent

Sample	Particulate carbon, mg/l.	Se background, μg	Se recovered μg	Se recovered %
		Effluent		
1	4.9	<0.01	0.50	100
2	4.0	<0.01	0.55	110
3a	55.0	0.14	0.62	97
3b (filtered)	—	<0.01	0.55	110
4	1.5	<0.01	0.52	104
5	5.3	<0.01	0.50	100
		Stream		
6	2.0	<0.01	0.52	104
7	4.3	<0.01	0.54	108
8	1.1	<0.01	0.48	96
9	3.0	<0.01	0.50	100
10	1.4	<0.01	0.48	96
11	1.8	<0.01	0.51	102
12	1.9	<0.01	0.49	98
13	1.7	<0.01	0.49	98
14	1.7	<0.01	0.50	100
15	4.5	<0.01	0.52	104

Av recovery, 101.7%
Std dev, 4.6

Se in 50 ml of distilled deionized water were treated with a 500-fold excess of NO_2^{2-}, BA(II), Cd(II), Ca(II), Cr(III), Co(II), Cu(II), Fe(III), Mg(II), Mn(II), Ni(II), and Zn(II). None of these substances interfered, separately or in concert, when the solutions were carried through the analytical procedure described above.

Potable Water. Fifteen samples of potable water were collected from different sites within New York State and tested for selenium. After preliminary tests to determine the background selenium content, 50-ml portions were spiked with 0.5 μg of selenium as Se(IV) and analyzed. The results of these analyses (Table I) show an average recovery of 101.9% with a standard deviation of 5.9.

Water Receiving Waste Effluent. Three samples were collected from each of five streams receiving waste effluent. Five of the samples were collected upstream of the point at which the waste entered; five were collected downstream; and the remaining five were samples of the effluents themselves, before they entered the streams. A portion of each sample was filtered and the particulate matter collected and tested for organic carbon, using a modification of the procedures described by Van Hall et al. (1963) and Schaffer et al. (1965).

After preliminary tests, a 50-ml portion of each sample (unfiltered) was spiked with 0.5 μg of selenium as Se(IV) and analyzed. The results, given in Table II, show an average recovery of 101.7% with a standard deviation of 4.6.

Only sample 3 showed a nonnegligible background concentration of selenium. The high concentration of particulate organic carbon suggests that this was probably an organic interference. That assumption is supported by the absence of background selenium in the filtered sample.

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Response of Pinto Bean and Tobacco to Ozone as Conditioned by Light Intensity and/or Humidity

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■ Pinto bean and Bel W_3 tobacco were grown and exposed for 1 hr to 40 pphm of ozone at two light intensities and at two relative humidities. Foliar injury to pinto bean varied from 20–92% and to tobacco from 20–47% under the 16 different combinations of preexposure growth and exposure conditions used. Foliar injury showed a significant species by preexposure growth humidity by preexposure growth light interaction. Light intensity and relative humidity prior to exposure significantly affected the response of both species to ozone. Pinto bean showed a significant response to both light and relative humidity during exposure, but tobacco did not. The interaction between relative humidity and light intensity during exposure was significant, independent of species.

Relative humidity (RH) and light intensity before and during exposure to ozone are two environmental conditions that affect the response of plants to this pollutant (Heck, 1968). It is necessary to understand the interactions between these two conditions before the importance of air pollution episodes can be adequately interpreted. An increase in light intensity prior to ozone exposure decreased foliar injury (Dugger et al., 1963; Heck and Dunning, 1967), whereas increased light intensity during exposure increased foliar injury (Heck et al., 1965; Taylor et al., 1961). Several investigators reported increased foliar injury from ozone as humidity was increased, either before

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or during exposure of the plants (Cantwell, 1969; Davis, 1970; Menser, 1962; Otto and Daines, 1969; Wilhour, 1970). These studies determined the ozone-induced responses of tobacco and bean plants as affected by light intensity or RH before and during ozone exposures. The possible interactions between these two factors or between variations of a single factor prior to and during exposure were not determined.

This research was designed to study the interaction of relative humidity (hereafter referred to as humidity) and light intensity during a preexposure growth period (hereafter referred to as growth) and an exposure period on the foliar sensitivity of pinto bean and Bel W_3 tobacco. A secondary objective was to determine if the two species reacted differently to ozone stress under varied conditions. Pinto bean and Bel W_3 tobacco were chosen as the test species because of their known sensitivity to ozone (Heck and Dunning, 1967).

Methods

Plants were grown in four commercial reach-in growth chambers located in a large climate control room to ensure close control of light, humidity, and temperature. An 8-hr photoperiod was used in all experiments. Switches on paired VHO cool-white lamps permitted control of light intensity to within ±5 hectolux (hlx) for both the 215 and 430 hlx treatments. The day and night temperatures were 27° and 21°C (±0.3°), respectfully. Humidity was maintained at 80% at night and at 60 or 80% during the day by the addition of steam. Light, temperature, and humidity within the chambers were continuously recorded. Air was recirculated up through a perforated aluminum floor at a rate of 600 cfm with 10% makeup air provided through a charcoal filter.

Ozone exposures were carried out in four smaller chambers (Heck et al., 1968) that were placed, two per chamber, into two other growth chambers. Light, humidity, temperature, and ozone concentrations were independently controlled in each exposure chamber. Light was measured at the beginning of each exposure, while temperature and humidity were measured throughout the exposure using a dry and wet bulb thermistor sensing system. Temperature was controlled to within ±0.3°C and humidity to within ±5%. Air flow through each chamber was 20 cfm with no recirculation. Ozone was generated from tank oxygen by a silent electrical discharge ozonizer. Plants were exposed for 1 hr from 1–2 p.m. to 40 pphm ozone. Chamber ozone levels were monitored with a Mast ozone meter and corrected to a 2% neutral buffered KI standard.

The experimental conditions provided two light intensities (215 and 430 hlx) and two day humidities (60 and 80%). Plants from each of the four growth combinations of these variables were then exposed to ozone under the same light–humidity combinations.

Tobacco (*Nicotiana tabacum*, L.) cv. Bel W_3 was seeded in vermiculite and grown under our standard environmental conditions (day: 8 hr, 215 hlx, 27°C, 60% RH; night: 21°C, 80% RH). Tobacco seedlings were transplanted after four weeks into 15-cm plastic pots (one plant per pot) in a 1:1 (v/v) peat–perlite mix and grown for an additional 10 days under the standard growth conditions before transfer to the experimental conditions. Bean (*Phaseolus vulgaris* L.) was seeded directly into the peat–perlite mix (5 seeds per pot) and placed in the experimental chambers. Six pots each of bean and tobacco were randomly placed into each experimental growth chamber for 11 days of environmental conditioning. After 7 days the pinto bean plants were thinned to two per pot. All plants were watered daily with a half-strength nutrient solution.

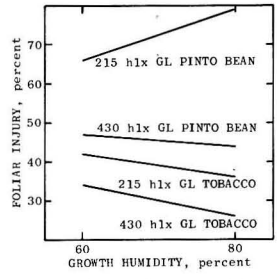

Figure 1. Interaction of growth light (GL), growth humidity (GH), and species on foliar response to ozone

Slopes for 215 hlx pinto bean and 430 hlx tobacco are significant. Each value is mean of 64 observations. LSD at 5% significance level is 5.77

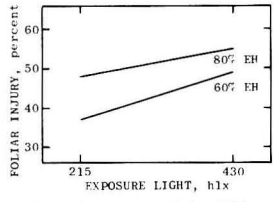

Figure 2. Interaction of exposure light (EL) and exposure humidity (EH) on foliar response to ozone as average of both species

Both slopes are significant but increase of 60% EH slope is significantly greater than increase in 80% EH slope. Each value is mean of 128 observations. LSD at 5% significance level is 4.08

On each exposure day the four most uniform pots of each species were chosen from each growth treatment. One pot per species from each growth treatment was randomly selected for placement in each exposure treatment. The eight pots thus selected for each exposure were randomly placed in each exposure chamber. They were then conditioned for 1 hr before the 1-hr exposure to ozone. Plants were left for an additional hour after exposure before transfer to a growth chamber maintained under the standard environmental conditions for development of foliar injury symptoms.

Foliar injury is the most sensitive and rapid plant response to single, short-term pollution insults. Thus, visual assessments of leaves were made three days after exposure and are reported as percent foliar injury. The data for tobacco are the average percent foliar injury to the three most severely injured leaves per plant. The data for pinto bean are the average percent leaf injury to the four primaries on the two plants in a single pot.

The factorial design was replicated 16 times and analyzed by an analysis of variance. Significant differences among means of those parameters that had a significant F test were illustrated by least significant differences (LSD) at the 5% probability level.

Results

Foliar injury to pinto bean from an acute ozone exposure was significantly affected by growth light (GL), growth humidity (GH), exposure light (EL), and exposure humidity (EH) while Bel W_3 tobacco was only affected by GL and GH. Interactions were found for: species × GL × GH, EL × EH, species × EL, and species × EH. No interactions were found between growth and exposure conditions.

Figure 1 shows the significant interaction between GL,

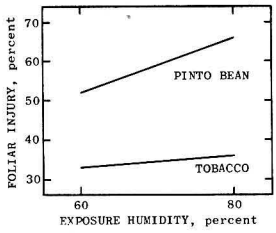

Figure 3. Interaction of exposure humidity (EH) and species on foliar response to ozone

Slope for pinto bean is significant. Each value is mean of 128 observations. LSD at 5% significance level is 4.08

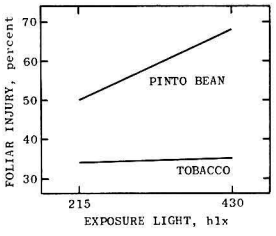

Figure 4. Interaction of exposure light (EL) and species on the foliar response to ozone

Slope for pinto bean is significant. Each value is mean of 128 observations. LSD at 5% significance level is 4.08

GH, and plant species. Pinto bean grown at 215 hlx showed a significant increase in foliar injury as GH was increased from 60 to 80%. Tobacco grown at 430 hlx showed a significant decrease in foliar injury as GH was increased from 60 to 80%. Neither pinto bean grown at 430 hlx nor tobacco grown at 215 hlx showed a significant response to a change in GH. Both species, regardless of humidity, showed greater foliar injury at the lower light intensities. This figure also shows the effects of the individual growth parameters on the foliar response of each species to ozone. Pinto bean, under the conditions used, is more sensitive to ozone than tobacco.

Figure 2 shows the significant EH × EL interaction that is independent of species. Plants exposed at either 60 or 80% RH show significantly more injury as EL is increased from 215 to 430 hlx. The increased injury in the plants exposed at 60% RH is significantly greater than the increase in plants exposed at 80% RH. Figure 3 shows the significant interaction between plant species and EH. As EH was increased from 60 to 80%, pinto bean showed a significant increase in foliar injury and tobacco did not. Figure 4 shows the significant interaction between plant species and EL. As EL was increased from 215 to 430 hlx pinto bean showed a significant increase in foliar injury and tobacco did not. No significant species × EH × EL interaction was found.

Discussion

Reasons for changes in foliar sensitivity to ozone with changes in environmental conditions have been discussed by Heck (1968). Most changes in sensitivity that occur at time of growth are probably due to a changed physiological resistance due to conditions used. Changes in sensitivity during exposure are more likely related to differences in stomatal response due to changes in leaf water potential. The lack of interactions between growth and exposure conditions, as they affect foliar response of the two species to ozone, supports the conjecture that the mechanisms of action during growth and during exposure are different.

The greater injury to both species grown at 215 hlx as compared to those grown at 430 hlx substantiates earlier reports (Dugger et al., 1963; Heck and Dunning, 1967) that increased light intensity before ozone exposure decreases injury. The increase in foliar injury in pinto bean grown at 215 hlx as humidity is increased from 60 to 80% also substantiates earlier reports (Cantwell, 1969; Davis, 1970; Menser, 1962; Otto and Daines, 1969; Wilhour, 1970). The significant decrease in foliar injury in tobacco grown at 430 hlx as humidity increased from 60 to 80% was not expected nor was the lack of a humidity effect on pinto bean (430 hlx) or tobacco (215 hlx). There is apparently some stress factor that may override the presence of additional moisture in the 80% RH growth treatment for certain species when grown under varied light conditions.

The lack of significant exposure effects on tobacco may be due to the limits of the variables used. If wider ranges of RH and light intensity were used, the foliar responses for tobacco could be significant.

It has been shown that interactions between growth or exposure conditions are important in understanding the foliar response of pinto bean and tobacco to ozone.

The marked difference in ozone injury between species suggests that care should be taken in extrapolating ozone response from one species to another.

Acknowledgment

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Volumetric Methods for Control of Ammonia Scrubbing Process for Removal of SO_2 from Stack Gases

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■ Volumetric methods for analytical control of the ammonia scrubbing process were developed from standard analytical procedures. Results of three titrations are sufficient to calculate the concentrations of ammonium bisulfite, sulfite, and sulfate in the scrubber liquor before or after the liquor is acidified with ammonium bisulfate and stripped of its SO_2. Two titrations are sufficient to determine the composition of the ammonium bisulfate that is used to strip the scrubber liquor. The only interfering ion is chloride, and this is determined by titration with silver nitrate, and a suitable correction is applied.

Ammonia scrubbing is one of the processes being studied for removal of sulfur dioxide from power plant stack gases. Sulfur dioxide is absorbed from the gas stream by an aqueous ammonia solution to form NH_4HSO_3, $(NH_4)_2SO_3$, and $(NH_4)_2SO_4$. The product liquor is acidified with molten ammonium bisulfate and stripped of its SO_2, leaving a solution that contains $(NH_4)_2SO_4$ and small amounts of NH_4HSO_3 and NH_4HSO_4. The SO_2 is processed into a commercially valuable form and some of the ammonium sulfate is crystallized from the stripped liquor and thermally decomposed to ammonium bisulfate and ammonia. The ammonia is returned to the scrubber and the ammonium bisulfate, considered to be a mixture of either NH_4HSO_4 and H_2SO_4 or NH_4HSO_4 and $(NH_4)_2SO_4$, is recycled to the acidification unit.

Analytical methods are needed to determine the sulfur compounds in the different products of the process. These methods must be reliable and simple enough to be carried out rapidly with a minimum of laboratory equipment and space.

A survey was made of methods for analysis of solutions containing ammonium sulfite, bisulfite, and sulfate. Sulfites are determined iodimetrically in acid solution (Kolthoff et al., 1969) by the reaction

$$SO_3^{2-} + I_2 + H_2O \rightarrow SO_4^{2-} + 2HI \quad (1)$$

Ammonium bisulfite can be determined iodimetrically in acid solution (Zavarov, 1960) by the reaction

$$2NH_4HSO_3 + KIO_3 + KI \rightarrow I_2 + K_2SO_4 + (NH_4)_2SO_4 + H_2O \quad (2)$$

This reaction is very rapid in highly acidic solutions but slows markedly as the acidity decreases, so that it is not a suitable basis for the determination of low concentrations of bisulfite.

Sulfates usually are determined by difference after determination of other forms of sulfur and their oxidation to sulfate and determination of total sulfur. Sulfate may be determined by precipitation and weighing as barium sulfate, but this method is time consuming and subject to serious errors (Kolthoff et al., 1969). Bare et al. (1970) determined sulfate in the presence of sulfite by complexing the sulfite with formaldehyde and titrating with barium perchlorate to the thorin end point; this method is rapid, but the end point is difficult to determine. The indirect chelometric method for sulfate of Woodis et al. (1970) gives reliable results but requires more time than is suitable for a process control method.

In this study a combination of the iodimetric procedure (Kolthoff et al., 1969) for the determination of sulfite, an alkalimetric titration for total acidity, and the AOAC formaldehyde procedure for ammonium sulfate (Assoc. Offic. Anal. Chem., 1970) were adapted to provide the information necessary to calculate the composition of the products.

Reagents

NaOH Solution, standard, 0.2*N*. Standardize against $(NH_4)_2SO_4$ (primary standard grade) after treatment with formaldehyde by titration against methyl green–phenolphthalein indicator. Denote normal factor as $N(NaOH)$.

Methyl Red–Methylene Blue Indicator. Mix thoroughly 1.250 grams of methyl red and 0.825 gram of methylene blue. Dissolve in 1 liter of 90% ethyl alcohol. Store in a dark bottle.

Methyl Green–Phenolphthalein Indicator. Add 2 volumes of 0.1% methyl green in alcohol to 1 volume of 1% phenolphthalein in alcohol and store in a dark bottle.

Analysis of Scrubber Liquor

Determination of Bisulfite and Total S. All sulfite is first oxidized to sulfate. Add 50 ml H_2O and 5 ml 30% H_2O_2 to a 250-ml Erlenmeyer flask. With stirring, transfer a sample containing no more than 1 gram of total sulfite S to the flask (the pipet tip should be beneath the surface of the liquid). Boil for 5 min, cool, transfer to a 500-ml volumetric flask, and dilute to volume. Transfer an aliquot containing no more than 100 mg of sulfate S to a 250-ml Erlenmeyer flask. Add three drops of methyl red–methylene blue indicator and titrate to the green end point with 0.2*N* NaOH. Record as volume *A* (*VA*). Add 10 ml of formaldehyde, 10 drops methyl green–phenolphthalein indicator, and, without refilling the buret, continue the titration to the first tint of purple. Correct the final buret reading for the blank on the formaldehyde and record the corrected reading as volume *B* (*VB*).

Determination of Chloride. To a 250-ml Erlenmeyer flask add 50 ml water and 5 ml 30% H_2O_2. While stirring, transfer a sample containing no more than 1 gram of sulfite S to the flask (the pipet tip should be beneath the surface of the liquid). Boil for 5 min, cool, titrate with 0.1*N* silver nitrate by procedure A of Swift et al. (1950), and record the net volume of silver nitrate as volume *C* (*VC*).

Determination of Sulfite Sulfur. Add from a buret 35 ml of 0.1*N* iodine solution to a 250-ml Erlenmeyer flask and add 10 ml of 4% HCl. Transfer an aliquot of the sample solution containing 5–10 gpl SO_3^{2-} (the tip of the pipet should be beneath the surface of the liquid) to the iodine–HCl solution. Titrate the excess iodine with 0.1*N* thiosulfate to a faint yellow, add 5 ml starch solution, and continue the titration to a colorless end point. Convert the volume to its equivalent of standard iodine solution by multiplying by the factor $N(Na_2S_2O_3)/N(I_2)$ and subtract from the initial volume of iodine solution. Record the difference as volume *D* (*VD*).

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Table I. Determination of Ammonia and Total Sulfate in Pilot Plant Ammonium Bisulfate

NH_4^+, %, determined by indicated method		SO_4^{2-}, %, determined by indicated method	
Proposed	Distillation	Proposed	Alkalimetric[a]
13.79	13.76	81.25	81.07
13.59	13.58	81.22	81.38
14.03	14.05	80.97	80.95
14.47	14.38	81.06	80.91
15.24	15.28	80.64	80.39
15.60	15.65	79.93	80.07
16.08	16.01	80.12	80.10
16.73	16.73	79.39	79.71
17.22	17.19	79.26	79.36

[a] Acid solution formed by exchange with Dowex 50 cation-exchange resin.

Calculations.

$$\text{Bisulfite S, gpl} = VA \times N(\text{NaOH}) \times 32.064/\text{ml sample} \quad (3)$$

$$\text{Total S, gpl} = VB \times N(\text{NaOH}) \times 16.032/\text{ml sample} \quad (4)$$

$$\text{Chloride correction, gpl total S} = VC \times N(AgNO_3) \times 16.032/\text{ml sample} \quad (5)$$

$$NH_4^+, \text{ gpl} = (VB - VA) \times N(\text{NaOH}) \times 18.04/\text{ml sample} \quad (6)$$

$$\text{Total sulfite S, gpl} = VD \times N(I_2) \times 16.032/\text{ml sample} \quad (7)$$

Analysis of Stripped Liquor

Oxidize the sulfite with H_2O_2 as in the analysis of the scrubber liquor and titrate the bisulfate initially present and that resulting from the oxidation of the bisulfite alkalimetrically to the mixed methyl red–methylene blue end point and record as volume *E* (*VE*). Refill the buret with 0.2*N* NaOH, add 10 ml formaldehyde and 10 drops of methyl green–phenolphthalein indicator to the sample, and titrate to the first tint of purple. Correct the titration volume for the formaldehyde blank, and record as volume *F* (*VF*).

Determine sulfite sulfur as in the analysis of the scrubber liquor and record the net volume of 0.1*N* iodine solution as volume *G* (*VG*).

Calculations.

$$NH_4HSO_3, \text{ gpl} = VG \times N(I_2) \times 49.556/\text{ml sample} \quad (8)$$

$$NH_4HSO_4 \text{ equiv of } NH_4HSO_3, \text{ gpl} = VG \times N(I_2) \times 57.555/\text{ml sample} \quad (9)$$

$$NH_4HSO_4, \text{ total in oxidized sample, gpl} = VE \times N(\text{NaOH}) \times 115.11/\text{ml sample} \quad (10)$$

$$NH_4^+, \text{ gpl} = VF \times N(\text{NaOH}) \times 18.04/\text{ml sample} \quad (11)$$

$$(NH_4)_2SO_4, \text{ gpl} = (VF - VE) \times N(\text{NaOH}) \times 66.075/\text{ml sample} \quad (12)$$

$$\text{Total S, gpl} = (VF + VE) \times N(\text{NaOH}) \times 16.032/\text{ml sample} \quad (13)$$

Correct both $(NH_4)_2SO_4$ and total S for the chloride content, as in Equation 5.

Analysis of Ammonium Bisulfate

Weigh approximately 5 grams of sample, transfer to a 250-ml beaker, add 100 ml of H_2O and boil to dissolve any insoluble salts. Transfer to a 250-ml Erlenmeyer flask, add 3 drops of methyl red–methylene blue indicator, and titrate to the green end point with 0.2*N* NaOH. Record as volume *H* (*VH*). Refill the buret with 0.2*N* NaOH, add 10 ml of formaldehyde to the sample in the Erlenmeyer flask and 10 drops of methyl green–phenolphthalein indicator, and titrate to the first tint of purple. Establish a blank on the formaldehyde, subtract from the recorded volume, and record as volume *J* (*VJ*).

If *VH* is greater than *VJ*, the solution contains NH_4HSO_4 and free H_2SO_4. Calculate NH_4HSO_4 from Equation 14 and *VJ*, and H_2SO_4 from Equation 15 and the difference between *VH* and *VJ*.

If *VJ* is greater than *VH*, the solution contains NH_4HSO_4 and $(NH_4)_2SO_4$. Calculate NH_4HSO_4 from Equation 14 and *VH*, and $(NH_4)_2SO_4$ from Equation 16 and the difference between *VJ* and *VH*.

In all samples, NH_4^+ is calculated from Equation 17 and *VJ*, and total SO_4 is calculated from Equation 18 and the sum of *VH* and *VJ*.

$$NH_4HSO_4, \% = (VH \text{ or } VJ) \times N(\text{NaOH}) \times 11.511/\text{wt sample} \quad (14)$$

$$H_2SO_4, \% = (VH - VJ) \times N(\text{NaOH}) \times 4.9032/\text{wt sample} \quad (15)$$

$$(NH_4)_2SO_4, \% = (VJ - VH) \times N(\text{NaOH}) \times 6.6075/\text{wt sample} \quad (16)$$

$$NH_4^+, \% = VJ \times N(\text{NaOH}) \times 1.804/\text{wt sample} \quad (17)$$

$$SO_4^{2-}, \% = (VH + VJ) \times N(\text{NaOH}) \times 4.803/\text{wt sample} \quad (18)$$

Discussion

In tests of methods suitable for analytical control of the ammonia scrubbing process, the iodimetric titration of sulfites and oxidation of sulfites to sulfates followed by alkalimetric titration before and after complexation of the ammonia with formaldehyde was shown to be rapid, simple, and sufficiently accurate to provide the required information. The only significant interference is that of chloride, and this is readily corrected for when the chloride is determined with silver nitrate.

Since the individual components of the sample, with the exception of total sulfite, are calculated rather than determined directly, the validity of the method rests upon the accuracy of the determinations of ammonia and sulfate. Results obtained by the proposed method and those obtained by standard methods of analysis on samples of ammonium bisulfate produced in the pilot plant are shown in Table I. The agreement of the results of the proposed method with those of the standard methods is excellent. In addition to its reliability, the proposed method requires much less time than the standard methods.

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Copper Micronutrient Requirement for Algae

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■ A reproducible copper requirement for *Chlorella vulgaris* and *Oocystis marssonii* has been demonstrated. Optimal growth was observed above 40 μg/l. for *Oocystis* and 30 μg/l. for *Chlorella*. The dependence of the growth of the two organisms on the concentration of free copper ion also was demonstrated. Techniques are discussed for preparing the high-purity media required for metal deficiency studies.

The toxicity of copper to algae has been the subject of a number of studies (Steeman Nielsen and Wium-Anderson, 1970; Hassal, 1962; Den Dooren DeJong, 1965; Whitten, 1970; Fitzgerald and Faust, 1963; Reimer and Toth, 1970) because of its widespread use for the control of algae in natural waters. In addition to being toxic at relatively high levels, copper is also an essential micronutrient for algae at very low concentrations. However, very little research has been reported on the copper requirement for algae, probably because of the extreme difficulty encountered in preparing and keeping nutrient media having copper levels of only several parts per billion.

Walker (1953) reported that copper is essential for the growth of *Chlorella pyrenoidosa* grown photoheterotrophically and that copper concentrations less than 30 μg/l. produced suboptimal growth of these algae. A similar deficiency was not demonstrable with autotrophically grown cells, probably because of copper contamination in the reagents used to prepare the media or in the CO_2–air mixture used to aerate the cultures. Similarly, a copper deficiency could not be shown in cultures of *Euglena gracilis* grown heterotrophically (Price and Vallee, 1962). In the latter two studies the algae were grown in Pyrex containers. It is extremely difficult to maintain solutions having copper in the low μg/l. range in such containers. It should also be noted that the removal of copper from distilled water is particularly difficult.

This study was undertaken to provide information on the chemical aspects of the copper micronutrient requirement of algae. The investigations were carried out in a well-defined laboratory medium so that the concentration of soluble copper species could be correlated quantitatively with algal growth. Particular attention was given to the development of techniques for the removal of trace levels of contaminant copper from the reagents used in preparing the biological media. The use of the solid state copper ion-selective electrode for determining the effectiveness of reagent cleanup procedures was investigated.

Precipitate-Free Algal Growth Medium

This study required an algal growth medium in which the concentration and nature of copper present could be known. Because of the difficulty of handling equilibrium calculations involving solid phase components, the medium had to be free of solid inorganic species. The "availability" of the metal hydroxides, carbonates, and phosphates to algal cells currently is open to question. Adsorption and coprecipitation phenomena which can occur in such systems cause additional complications that defy simple chemical definition.

The composition of the medium used in this study is given in Tables I and II. The trace element composition of the medium is similar to that used by Walker (1953). The presence of the strong chelating agent, ethylenediaminetetraacetic acid (EDTA), prevents the formation of insoluble species, particularly those containing iron, in which the nutrient metals are essentially unavailable to the algae. The EDTA also allows the maintenance of comparatively large reservoirs of trace elements that can support rapid growth. The medium contains only enough EDTA to keep the trace elements Cu, Fe, Zn, Mo, Ca, and Mn in solution. The total chelatable metal ion concentration is $1.00 \times 10^{-3} M$ and the pH is 7.00 in equilibrium with air. Metals more strongly chelated than Mg^{2+} by EDTA have their concentrations determined by the ratio $[Mg^{2+}]/[MgY^{2-}]$, where MgY^{2-} is the chelate formed from magnesium ion and the EDTA anion, Y^{4-}. Within the pH range of approximately 6–12 the equilibrium concentration of Cu^{2+} can be expressed in terms of the formal concentration of EDTA, C_Y, and the total concentration of

Table I. Contribution from Macronutrient, pH Adjusting, and Vitamin Solutions to Medium Used for Algal Growth at Constant Concentration of EDTA

From macronutrient solution

Salt	Molarity, 10^3	Mg/l. ion	Weighing form	Wt. salt, mg/l.
KNO_3	10.00	391 NO_3^-	KNO_3	1000
$MgSO_4$	5.32	129 Mg^{2+}	$MgSO_4 \cdot 7H_2O$	1311
KH_2PO_4	1.50	285 PO_4^{3-}	KH_2PO_4	204
K_2HPO_4	1.50		K_2HPO_4	261

From KOH solution

Salt	Molarity, 10^3	Mg/l. ion	Weighing form	Wt. salt, mg/l.
KOH	2.6	...	KOH	...

From vitamin solution

Vitamin	Mg/l.
Thiamine·HCl	200
Biotin	1.0
B_{12}	1.0

Table II. Contribution from Trace Element Solution to Medium Used for Algal Growth at Constant Concentration of EDTA

Component	Molarity, 10^3	Mg/l. ion	Weighing form	Wt. salt, mg/l.
$Na_2EDTA \cdot 2H_2O$	1.50	558	$Na_2EDTA \cdot 2H_2O$	558
Fe^{3+}	0.179	10.0	$Fe_2(SO_4)_3$	35.8
Ca^{2+}	0.399	16.0	$CaCO_3$	40.0
Zn^{2+}	0.331	21.6	$ZnSO_4 \cdot 7H_2O$	95.2
Mn^{2+}	0.091	5.0	$MnSO_4 \cdot H_2O$	15.0
Mo^{6+}	0.0042	0.40	$Na_2MoO_4 \cdot 2H_2O$	1.0
B^{3+}	0.092	1.00	H_3BO_3	5.70

Total chelatable trace metals = $1.00 \times 10^{-3} M$

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copper, C_{Cu}, expressed in moles/liter. The formation constant expression for the CuY^{2-} complex can be written in the following manner, if it is assumed that essentially all the copper in solution is present as CuY^{2-}:

$$[Cu^{2+}] = \frac{C_{Cu}}{[Y^{4-}]K_{f,Cu}} \quad (1)$$

where $K_{f,Cu} = 6.3 \times 10^{18}$, the formation constant of the Cu(II)–EDTA complex.

The formal concentration of Mg(II), C_{Mg}, is such that only a fraction of this ion is complexed. By the same reasoning as above, $[MgY^{2-}]$ and $[Mg^{2+}]$ are given by the following:

$$[MgY^{2-}] = C_Y - C_{TM} \quad (2)$$

$$[Mg^{2+}] = C_{Mg} + C_{TM} - C_Y \quad (3)$$

where C_{TM} is the total chelatable trace metal concentration.

When we substitute these values in the formation constant expression for the Mg–EDTA complex, concentration of the deprotonated chelating agent can be expressed as follows:

$$[Y^{4-}] = \frac{C_Y - C_{TM}}{(C_{Mg} + C_{TM} - C_Y)K_{f,Mg}} \quad (4)$$

where $K_{f,Mg} = 1.0 \times 10^9$, the formation constant of the Mg(II)–EDTA complex. By inserting Equation 4 into Equation 1 and rearranging, the final expression for free cupric ion becomes:

$$[Cu^{2+}] = \frac{K_{f,Mg}}{K_{f,Cu}} \times \frac{C_{Mg} + C_{TM} - C_Y}{C_Y - C_{TM}} \times C_{Cu} \quad (5)$$

$$= (\text{Term 1}) \times (\text{Term 2}) \times (\text{Term 3})$$

The effect of adding complexing agent under these conditions is to lower the concentration of free Cu^{2+}. A similar expression could be derived to describe the distribution of the other chelated trace metal species in the medium and their dependence on the concentration of chelate present. If the formal concentration of EDTA is varied from $1.1 \times 10^{-3}M$ to $5.1 \times 10^{-3}M$, with $C_{Mg} = 5.32 \times 10^{-3}M$ and $C_{TM} = 1.00 \times 10^{-3}M$, Term 2 ranges from 52.2–0.30 which corresponds to a 177-fold change in $[Cu^{2+}]$. The value of $[Cu^{2+}]$ is very low ($5 \times 10^{-15}M$ even at a formal concentration of $1.10 \times 10^{-3}M$ EDTA). Equation 5 is accurate to within 1% in the pH range from 6 to roughly 12. The lower pH limit is due to the dissociation of the MgY^{2-} complex and the upper limit to the precipitation of $Cu(OH)_2$.

Experimental

Reagent grade materials typically contain 10^{-4}–10^{-3}% copper. Since it was desired to study total copper concentrations as low as 1 μg/l., prior purification of the reagents used in the medium was necessary. For purification, the medium components were separated into a trace element solution and a macronutrient solution. A controlled potential electrolysis procedure was used to remove copper from a $0.200M$ solution of disodium EDTA found to be a major source of contaminant copper. A three-electrode electrolysis system was used employing a stirred 25-ml mercury pool cathode, a platinum anode, and an Orion Model 90-02 double junction electrode. The potential-controlling apparatus was a simple electronic potentiostat described by Malmstadt et al. (1963). Oxygen was removed by bubbling nitrogen through the solution before and during electrolysis. Approximately 300 ml of EDTA solution was treated each time. Normally the solutions were electrolyzed for 24 hr which reduced the level of contaminant copper to approximately 1 μg/l. The removal of copper was followed by an Orion Model 94-29A solid state cupric ion activity electrode referenced to the double-junction reference electrode.

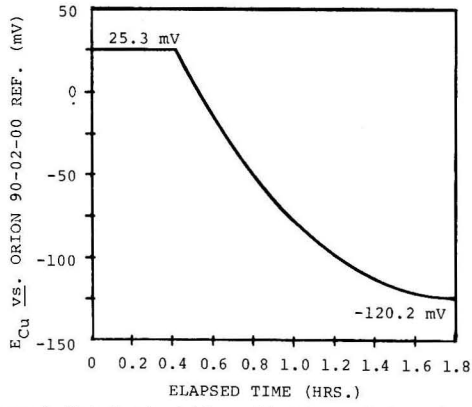

Figure 1. Plot of potential for solid state cupric ion-selective electrode vs. time elapsed during extraction of Cu^{2+} from 400 ml of tenfold concentrate of macronutrients solution initially 36.0 μg/l. in Cu(II) using 25.0 ml of 0.01% dithizone in CCl_4. Aqueous pH = 7.21

A solvent extraction procedure was both a convenient and rapid means of removing contaminant copper from the macronutrients portion of the growth medium. The selection of an extraction system to be used in conjunction with biological media, however, involves the consideration of several factors in addition to those normally considered in selecting a good extraction system. The two most important of these are the solubility of the extracting solvent and the solubility of the extracting reagent in the aqueous solution to be treated. In light of these two factors, a number of the more commonly used extraction systems are not suitable for use in biological systems. For example, the very efficient extraction of trace metals into ketone solvents with ammonium pyrrolidinecarbodithioate that is commonly used in atomic absorption analyses cannot be used since both the reagent and solvents are moderately soluble in water.

An extraction system that meets the solubility criteria is 0.01% dithizone in CCl_4. In addition, the cupric ion electrode was useful in monitoring copper levels during dithizone extractions. Not only did the cupric ion electrode offer greater sensitivity than most other methods, but it also allowed continuous monitoring during the copper removal process. A plot of electrode potential vs. time elapsed during the extraction of Cu^{2+} from a tenfold concentrate of the macronutrients component of the algal growth medium is given in Figure 1. Approximately 400 ml of aqueous solution were treated with 25 ml of 0.01% dithizone in CCl_4 in a four-neck, 500-ml boiling flask with an overhead glass stirrer to continually renew the aqueous–organic interface.

A Teflon stopcock assembly was installed in the bottom of the flask to provide for the removal of the organic phase. Typically, 2 hr were allowed for complete extraction. The pH of the tenfold concentrate of the macronutrients solution is 7.21, and at this pH, dithizone is slightly soluble in the aqueous phase. To ensure that only a very small amount of the dithizone remained in the macronutrients solution, the reagent was re-extracted from

the aqueous phase with 25 ml of redistilled carbon tetrachloride after the completion of each extraction.

Two-liter batches of a tenfold concentrate of the trace element solution were prepared from the appropriate reagent grade materials and electrochemically treated 0.200*M* Na_2EDTA. The individual components were added to the solution in the order they are given in Table II. After the addition of $Fe_2(SO_4)_3$ and $CaCO_3$, the suspended material was allowed to dissolve before additional material was added. Dissolution sometimes required as long as 2 hr at room temperature, but could be speeded up by warming.

The macronutrients solution was also prepared at a concentration ten times that in the final growth medium. The solution was prepared by adding the reagents with rapid stirring in the order they are given in Table I to approximately 300 ml of deionized, distilled water contained in a 500-ml volumetric flask. The resulting solution was then diluted to the mark. Stirring is necessary to prevent the precipitation of $Mg_3(PO_4)_2$. This solution was prepared fresh for each run and treated as described in the previous section.

A $6.50 \times 10^{-2}M$ KOH solution for pH adjustment was prepared from previously standardized about 0.8*M* ultrapure KOH (Ventron Corp., Beverly, Mass.). The 0.8*M* solution was prepared by dissolving about a 10-gram stick of the solid 75% ultrapure KOH in 200 ml of deionized, distilled water. A vitamin solution was prepared at a concentration 500 times that required in the final medium. A stock 3000 mg/l. Cu solution was prepared from anhydrous $CuSO_4$ in 0.01*N* H_2SO_4. The required standard copper solutions were prepared from the stock $CuSO_4$ solution by dilution. The appropriate volumes of the KOH, vitamin, trace element, and copper solutions were then used to prepare the final growth medium. All reagents were stored in new polyethylene bottles that were cleaned initially with HNO_3–H_2SO_4 cleaning solution and treated prior to filling with 0.05*M* Na_2EDTA in 3*M* NH_3 for 3–4 days.

Pure cultures of the two algae used in this study, *Oocystis marssonii* and *Chlorella vulgaris*, were obtained from the Starr collection of algae at Indiana University, Bloomington, Ind. The culture numbers are LB287 and LB398, respectively. Inoculum cells were maintained in copper-deficient media. Approximately 15 ml of the appropriate exponentially growing cell suspension was centrifuged and washed with a 15-ml portion of $1.00 \times 10^{-3}M$ disodium EDTA. After two additional washings in $1.00 \times 10^{-3}M$ KNO_3, the washed cells were suspended in approximately 200 ml of $1.00 \times 10^{-3}M$ KNO_3. A 10-ml portion of the resulting suspension was added to the culture medium just before dilution to final volume.

The absorbance of the cell suspension was employed as a measure of cell yield. Both *Ooocystis* and *Chlorella* are unicellular, nonfilamentous green algae which form homogeneous suspensions, thus permitting a turbidimetric determination of growth. The absorbance of an algal suspension is a function of both light scattering and absorption due to the cell pigments. For this reason, the absorbances of the cell suspension were measured at 560 nm where a minimum in the chlorophyll absorption spectrum exists for both organisms studied. It was felt that this approach would minimize the influence of the cell pigments on the measuring technique as the level of copper was varied. It was assumed that cell size remained essentially constant, and checks of the average cell size at widely varying copper levels proved to be nearly identical. The relationship between the dry weight of algal cells and absorbance was determined by diluting 1-, 2-, 3-, 4-, 5-, 6-, 7-, 8-, 9-, and 10-ml aliquots of the appropriate cell suspension to volume with fresh medium in a 10-ml volumetric flask. The absorbances of the suspensions were measured at 560 nm using a Spectronic 20 colorimeter. The dry cell weight was determined by vacuum filtering 25-ml aliquots of cell suspension through 47 mm, 0.45 μ GA-6 Metricel filters (Millipore Corp., Bedford, Mass.). Two superimposed filters, matched in weight to within 0.1 mg, were assembled in a Pyrex filter holder. Twenty-five-ml aliquots of sample were passed through both filters while carefully avoiding contact of the cell suspension with the walls of the filter holder. Both filters were, therefore, subjected to the same fluid flow, but the cell suspension was retained on the upper filter. After drying both filters, the weight of the lower filter was subtracted from that of the test filter to determine the weight of the collected cells. Triplicate analyses were made for both dry weight determinations. A linear relationship between absorbance and dry cell weight for each of the organisms was obtained. A similar plot of absorbance vs. number of cells/ml was also prepared for *Chlorella*. The plot was linear with a zero intercept. An absorbance of 0.400 represents 8.80×10^6 cells/ml.

Cultures were grown for four days in exactly 250 ml of media contained in new 500-ml polyethylene wash bottles treated as described previously. Attempts to demonstrate copper deficiencies in new Pyrex flasks treated in the same manner as polyethyleneware usually gave erratic results, presumably due to copper contamination from the glass. All operations were carried out at room temperature (25–27° C). The growing cultures were agitated continuously by means of a slow-speed shaker plate. Four 40-W Gro-Lux fluorescent lamps provided overhead illumination through a plastic light diffusing panel attached to the lamp fixture. Light intensity measurements showed, however, that only a fraction of the area under the lamps received the same intensity of illumination. Due to the high nutrient-to-cell ratio in the medium, cultures containing optimal quantities of copper for growth show a strong dependence on light intensity. Consequently, cell culturing was confined to the area receiving uniform intensity of illumination.

A CO_2–air mixture bubbled through the cultures via a Pyrex manifold served as both a carbon source and a means of pH control. The gas mixture was hydrated and washed by bubbling through a gas-mixing chamber filled with deionized, distilled water. Two additional washings were accomplished by bubbling the gas mixture through water containing a mixed bed ion exchange resin. Gas delivery to each chamber was accomplished through medium porosity gas filter candles. Gas flow rates were measured by calibrated flow meters that could be switched in or out of the delivery system by means of three-way Teflon stopcocks. The air supplied was enriched to nearly 4% CO_2 by supplying 100% CO_2 to the mixing chamber at a rate of 20 ml/min and air at the rate of 500 ml/min. After equilibration with the gas mixture, the initial medium pH is approximately 6.1 and at the end of 96 hr of optimal growth is 6.3. The pH of the medium in equilibrium with air is 7.0.

Results and Discussion

A reproducible copper requirement for both *Chlorella vulgaris* and *Oocystis marssonii* was demonstrated by employing the previously described medium at an EDTA concentration of $1.50 \times 10^{-3}M$. Figures 2 and 3 are cell yield curves obtained by adding varying amounts of cop-

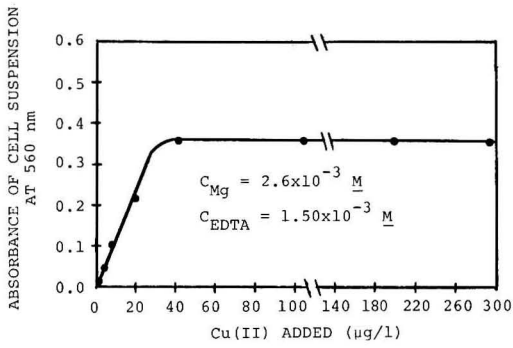

Figure 2. Cell yield curve for copper deficiency study of *Oocystis marssonii* at constant concentration of EDTA and Mg(II)

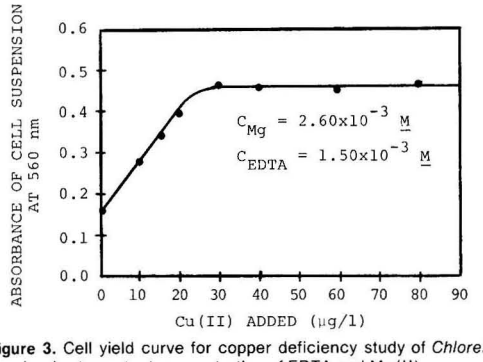

Figure 3. Cell yield curve for copper deficiency study of *Chlorella vulgaris* at constant concentration of EDTA and Mg(II)

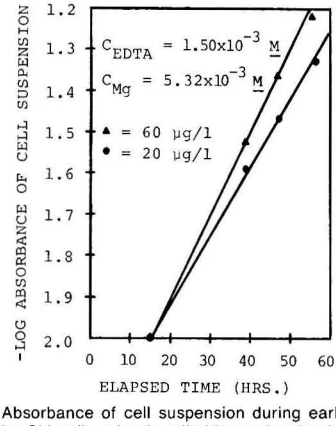

Figure 4. Absorbance of cell suspension during early portion of log phase for *Chlorella vulgaris* at limiting and optimal Cu levels

per to the copper-deficient medium while keeping the concentration of the chelating agent constant. Maximum growth is observed above 40 µg/l. Cu for *Oocystis* and 30 µg/l.for *Chlorella*. The minimum level of total copper for maximum growth of *Chlorella* is virtually identical to that obtained by Walker (1953) for *Chlorella pyrenoidosa* in a similar medium, but under conditions of photoheterotrophic rather than photoautotrophic growth. These studies suggest a reproducible copper micronutrient requirement for the green algae. It is also likely that the variation in copper requirement within this grouping is small.

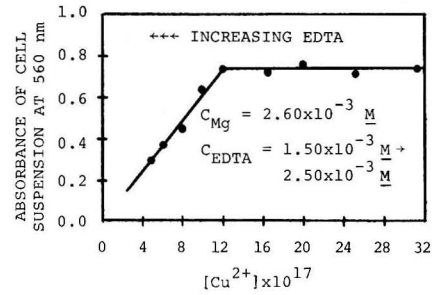

Figure 5. Cell yield vs. [Cu^{2+}] calculated for increasing EDTA levels for *Chlorella vulgaris* at constant total copper level of 30 µg/l.

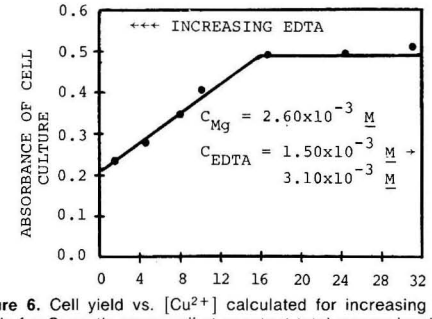

Figure 6. Cell yield vs. [Cu^{2+}] calculated for increasing EDTA levels for *Oocystis marssonii* at constant total copper level of 30 µg/l.

Additional evidence for a copper requirement by *Chlorella* is given in Figure 4 where the growth of the organism is measured as a function of time. An early portion of the log phase is shown at copper concentrations of 20 and 60 µg/l. At both concentrations the log absorbance vs. time curve is linear, but the slope of the plot at 20 µg/l. is less than that at the optimal level of 60 µg/l. Growth relationships of this type are typical of those obtained for microorganisms containing a constant, but growth-limiting concentration of nutrient. These data were taken at a somewhat suppressed light level and, therefore, the maximum rate of growth is lower than that normally achieved.

Additional information about the availability of the copper species in solution may be obtained by varying the concentration of the chelating agent in the medium. Since a level of 40 µg/l. total copper is the minimum required by *Oocystis* for optimal growth at a total EDTA concentration of $1.50 \times 10^{-3}M$, it is to be expected that an increase in the total concentration of EDTA at a constant total concentration of 40 µg/l. Cu or less would cause a corresponding decrease in the rate of algal growth. While the level of total copper and hence CuY^{2-} remains essentially constant under such conditions, the level of Cu^{2+} in the medium decreases considerably. A growth dependence of this nature would indicate the CuY^{2-} is generally unavailable for use by the organisms being studied and allow one to estimate the Cu^{2+} concentration required to support optimal growth.

In focusing attention on the copper species in solution, it must be pointed out that as the EDTA concentration is increased, the free concentrations of all the chelated trace elements in the medium decrease, as does the free Cu^{2+} concentration. If the other chelated trace elements are present in sufficient quantity, however, the decrease in

concentration of these species will not be sufficient to bring about a deficiency of the other trace elements in the medium. It is important to note that the concentration of total copper chosen is nearly growth limiting before the EDTA level is increased. When all the chelatable trace elements are present in sufficient quantity, increasing the level of chelating agent at a higher (e.g., greater than 200 μg/l.) copper level should have no effect on the growth of the organism. Furthermore, increasing the total copper concentration in solutions initially growth-limiting in Cu^{2+} and containing a high concentration of chelating agent should also increase the rate of growth if only Cu^{2+} is in fact growth-limiting.

Apparently, there is a dependence on the free Cu^{2+} level for the two algae studied as is shown in Figures 5 and 6 where the absorbances of the algal suspensions are plotted vs. $[Cu^{2+}]$ calculated from Equation 5. The total concentration of EDTA was varied from 1.50–2.50 $\times$ $10^{-3}M$ in the *Chlorella* study and from 1.50–3.10 $\times$ $10^{-3}M$ in the *Oocystis* study at a total copper concentration of 30 μg/l. A free Cu^{2+} concentration above 1.2 $\times$ $10^{-16}M$ for *Chlorella* and 1.6 $\times$ $10^{-16}M$ for *Oocystis* produces optimal growth. Maximum growth rates at high EDTA levels could be restored by increasing C_{Cu} such that $[Cu^{2+}]$ reached the level required for maximum growth as shown in Figures 5 and 6. This shows that the observed effect was due to Cu^{2+} and not due to the toxicity of EDTA or the lack of some other micronutrient metal ion.

It is likely that natural and pollutant chelating agents found in waters play a very important role in water chemistry and microbiology (Manahan, 1972). In light of the very low copper levels required for the optimal growth of algae, it is possible that much of the difference between "available concentrations" of the trace metals and their total concentrations may be explained by the presence of chelating agents. The data in this paper also suggest that the stimulatory effect of chelating agents on algal growth when added to natural waters is due to the creation of a reservoir of soluble trace metal species which allows the rapid replacement of the fraction of the hydrated metal ion depleted by biological uptake. In addition, studies designed to illustrate the required levels of hydrated metal ions required for algal growth must include the addition of a strong chelating agent so that the very low concentrations of the metal required can be studied in terms of much higher levels of the medium components.

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Chlorinated Hydrocarbon Insecticides in Sediments of Southern Lake Michigan

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■ Past usage of organochlorine insecticides in states bordering southern Lake Michigan has resulted in the presence in the lake sediments of large reservoirs of DDT, DDE, DDD, and dieldrin. Analysis of surficial sediments from different areas of southern Lake Michigan indicated high positive statistical correlations between *t*-DDT (DDT, DDE, DDD) and dieldrin concentrations in the sample and organic carbon content. The amount of organic carbon in surficial sediments was directly proportional to the clay-size fraction of sediment. Dechlorination of DDT to form DDD apparently predominates under the reducing conditions of sediments on the eastern side of the south basin of Lake Michigan. In other areas, DDT is the principal component of the *t*-DDT complex in sediments and DDE and DDD are major degradative products.

Water quality monitoring programs of the last 15 years indicate an almost continuous input of low levels of certain chlorinated hydrocarbon insecticides into lakes and rivers of the United States. Although the concentrations of the organochlorine insecticides in surface waters are minute (rarely exceeding a few μg/l.), because of the marked apolarity of these compounds (which allows storage in animal fats and plant waxes) and their resistance to enzymatic degradation, residues accumulate in plants and animals and sometimes reach high concentrations in predatory animals.

A dramatic example of biological accumulation of persistent insecticides is the presence of dieldrin and *t*-DDT (DDT, DDD, DDE) in the edible portions of many large

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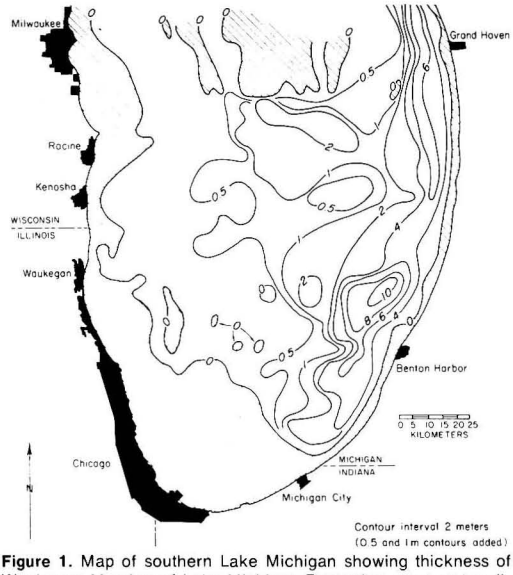

Figure 1. Map of southern Lake Michigan showing thickness of Waukegan Member of Lake Michigan Formation, youngest sediments over most of lake floor

Areas where member is absent are underlain mostly by glacial till, with or without thin cover of sand or gravel

fish of Lake Michigan at concentrations greater than the maximum levels recommended by the Food and Drug Administration in fish shipped across state borders—0.3 ppm for dieldrin and 5 ppm for *t*-DDT. The waters of the lake contain, on the average, less than 0.003 μg/l. of organochlorine insecticides (Mount, 1969). Fish in Lake Michigan contain two to seven times the concentrations of *t*-DDT and dieldrin found in fish of the other St. Lawrence Great Lakes (Reinert, 1970).

Recent findings of chlorinated biphenyls in Lake Michigan fish in amounts exceeding organochlorine insecticide concentrations (Reinert, 1972) further emphasize the importance of biological concentrating mechanisms in aquatic ecosystems. The presence of toxic, relatively stable organic products of our technological society threaten the very existence of the commercial fishery of Lake Michigan.

Although a substantial number of data have recently been obtained on organochlorine insecticides in fish of Lake Michigan, few published data exist on concentrations in the lake sediments. A mean of 14 ppb of *t*-DDT was reported in sediments of Green Bay (Hickey et al., 1966). Sediments in Grand Traverse Bay have *t*-DDT present at concentrations ranging from 10–200 ppb and lindane, heptachlor and parathion at concentrations of 1 to more than 15 ppb (Rao and Minear, 1972). The coarse sediments of Lake Michigan near the Chicago, Illinois–Gary, Indiana complex contain fewer than 100 ppb *t*-DDT (Schacht, 1972).

We here provide a profile of the extent of chlorinated hydrocarbon contamination in sediments of southern Lake Michigan. Factors affecting distribution of *t*-DDT and dieldrin in sediments of the basin and the degradation of DDT are discussed.

Experimental

Study Area. Lake Michigan is the sixth largest freshwater lake in the world, with a surface area of 58,000 km^2 and a 175,860-km^2 drainage area. Although numerous tributaries flow into Lake Michigan, none is large (they are under 140 m^3/sec), and it has the smallest drainage of the St. Lawrence Great Lakes—1560 m^3/sec at the Straits of Mackinac and a small outflow to the south through a diversion to the Chicago River.

The prominent topographic features of Lake Michigan include a deep, northern basin separated from a shallower, southern basin by ridges of bedrock and glacial till. This report considers the southern basin, which lies south of a line from Milwaukee, Wis., to Muskegon, Mich. The southern basin of Lake Michigan has a relatively smooth bottom relief. The basin is formed in the Paleozoic age bedrock, presumably by glacial erosion. The bedrock is overlain by glacial till, mostly assigned to the Wedron Formation. The till is in turn overlain by glacial lacustrine sand, silt, and clay called the Equality Formation. The Equality is overlain by the Lake Michigan Formation, which consists of soft, water-saturated clay and silty clay. The Lake Michigan Formation is divided into six members on the basis of lithology. Each member of the Lake Michigan Formation, the Equality Formation, the Wedron Formation, other tills, and bedrock may be present at the water interface in places. The most extensive surficial unit, and the one from which most samples reported here were taken, is the Waukegan Member of the Lake Michigan Formation. Glacial till is present at the water interface or under a thin cover of sand or gravel derived from erosion of the till in nearshore areas and in the southwestern corner of the lake (Figure 1). Lake floor outcrops of the other units are scattered and of small extent.

Studies of the most recent sediments in southern Lake Michigan (Lineback and Gross, 1972) indicated that the Waukegan Member is thicker along the eastern side of the lake than in the center or along the western side. The greater thickness indicates more rapid deposition during Holocene time along the eastern side than elsewhere in the southern lake basin. Most of the sediments presently being deposited in the southern lake basin are apparently derived from rivers draining southern Michigan. Cratty (1970), in a statement for the U.S. Department of Agriculture on sediment loss from the watersheds of Lake Michigan, indicated that more than half the sediment added annually to Lake Michigan is derived from tributaries or urban complexes bordering the south basin. Roughly two thirds of the annual sediment loss to the south basin is derived from watersheds in Michigan and enters through the rivers on the eastern shore.

Procedure. Lake sediments were collected with a Shipek grab (Hydroproducts, Inc., San Diego, Calif.) or a Benthos gravity corer (Benthos Inc., Falmouth, Mass.). Measurements of hydrogen-ion activity, electrode potential (Kemp and Lewis, 1968) and temperature were made immediately. Electrode potentials were measured with platinum/AgCl electrodes using a $Fe(CN)_6^{-3}/Fe(CN)_6^{-4}$ standard. Readings were taken after any initial downward drift in potential had ceased or was very slow. The sediments in every case were moist enough to provide good contact with the electrodes. These values are not amenable to rigorous physicochemical interpretation (Mortimer, 1971) and should not be considered true redox potentials. Cores and grab samples were frozen on board for subsequent analysis. Samples for laboratory analysis were thawed, carefully drained of excess water after the fine material had settled, and immediately subsampled for particle-size and insecticide determinations. A remaining portion of each sample was air-dried and used for total carbon (British Standard 1016, 1958) and inorganic carbon (Maxwell, 1968) determinations. Organic carbon was cal-

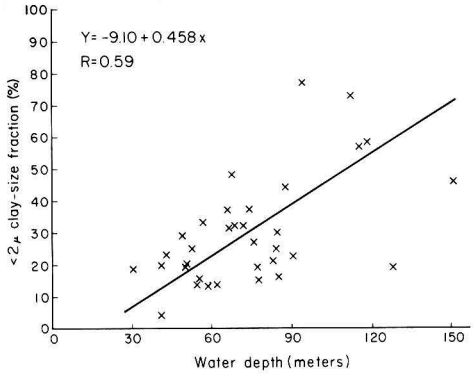

Figure 2. Percent of surficial sediments less than 2 μ vs. water depth

culated by taking the difference between the percentages of total carbon and inorganic carbon.

The sensitivity limit of the analytical procedure was 0.5 ppb for chlorinated hydrocarbon insecticides in sediments. Analysis of fortified samples yielded a 92–105% recovery, which compares favorably with Soxhlet extraction in chloroform–methanol. A moist sample (10 grams) was extracted overnight in acetone (100 grams), filtered, and the residue washed several times with hexane. To the combined filtrates, 100 ml of a mixture of diethyl ether and hexane (1:1) and 400 ml of water were added in a separatory funnel. After thorough shaking (200 times) and removal of the aqueous layer, the diethyl ether–hexane layer was washed twice with 50 ml of water to remove traces of acetone, dried over Na_2SO_4, reduced in volume, and cleaned by passage through a Florisil column. Where polychlorinated biphenyls were present in significant quantities, they were separated according to the procedure of Armour and Burke (1970). Polychlorinated biphenyls in Lake Michigan sediments have been studied (Leland et al., 1973). Measurements of chlorinated hydrocarbon insecticides were made on a Varian Aerograph 204 with a ^{63}Ni electron-capture detector and glass column (2.5 meters) containing 1.95% of QF-1 and 1.5% OV-17 on Supelcoport 100–120 mesh Chromosorb at 195°C. The injection port temperature was 225°C; the detector, 250°C.

Results and Discussion

Organic carbon content and the percent less than 2-μ clay-size material in the upper 1–3 cm of sediment at each sample location (Figure 5) were measured to determine the degree of relationship of these sediment parameters to basin morphology and distribution of organochlorine insecticides. Water depth (sample depth recovery) and percent less than 2-μ clay-size material in the uppermost sediments correlated well (Figure 2), indicating that particle-size distribution is determined in part by basin morphology. Coarser sediments are common in the relatively shallow areas of the basin and fine-grained sediments tend to be transported to deeper regions of the basin. A definite relationship (r = 0.65) between less than 2-μ clay-size material and organic carbon (Figure 3) emphasizes the importance of clay–organic interactions in transport and deposition of organic matter. The poor correlation between organic carbon and clay-size material in Lake Michigan surficial sediments reported by Shimp et al. (1971) was probably a consequence of the use of wider and more variable sediment depth intervals than were employed in the present study. A high positive correlation between the quantity of organic matter and the clay-size fraction was reported (Kemp, 1971) for the uppermost 1 cm of sediment in Lakes Erie and Ontario. In the latter two lakes, the quantity of organic carbon in sediments at the water interface is independent of depth, rate of sedimentation, and degree of eutrophication.

Several investigators have reported on the distribution of organic matter in surficial sediments of the Great Lakes, but few data exist on its chemical composition. The amounts of organic carbon in sediments at the water interface in Lake Erie and Lake Ontario vary from 0.5% in the coarse-grained nearshore zones to about 4.0% in offshore fine-grained zones. Surficial sediments are generally lower in percentage organic carbon in Lake Erie than in Lake Ontario (Kemp, 1971). The sediments at the water interface in Lake Michigan range from less than 0.2% organic carbon in nearshore sands to about 5.0% in the silty clays of the south basin (Shimp et al., 1971; Powers and Robertson, 1968). The organic carbon content is consistently higher in the uppermost 5–15 cm of the Waukegan Member than in the underlying sediments. Greater than 90% of the sedimentary organic matter is mineralized in the water column (Kemp, 1971) so the organic matter of the surficial sediments must represent complex, relatively inert molecules.

The accumulation of t-DDT in surficial sediments of southern Lake Michigan is significantly related (r = 0.60)

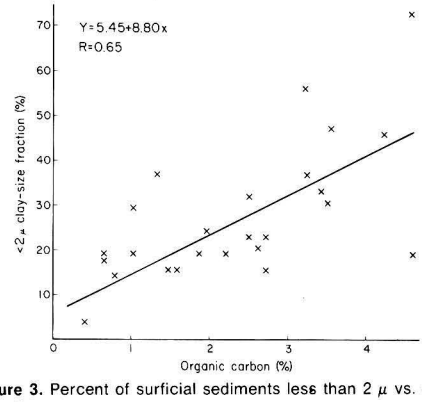

Figure 3. Percent of surficial sediments less than 2 μ vs. organic carbon

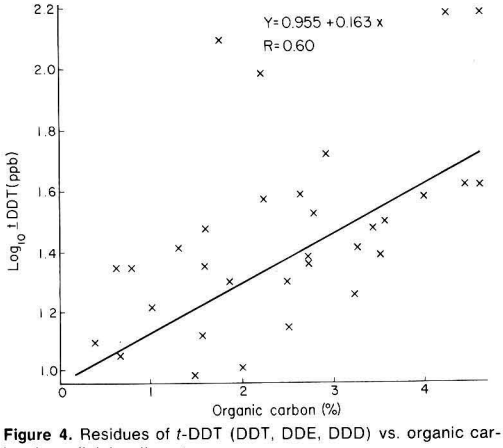

Figure 4. Residues of t-DDT (DDT, DDE, DDD) vs. organic carbon in surficial sediments

to the organic carbon content of these sediments (Figure 4). Logarithmic conversion of t-DDT concentrations is used in statistical treatment of the data because the distribution is skewed, owing to the exceptionally high concentrations of t-DDT in surficial sediments of the deepest regions of the basin (Figure 5). The accumulation of dieldrin in surficial sediments is also significantly related (r = 0.66) to organic carbon content. Data obtained on trace elements in southern Lake Michigan sediments (Shimp et al., 1970; Shimp et al., 1971; Leland et al., 1973) show similar relationships to organic carbon.

The concentrations of organochlorine insecticides in different sediment depth intervals are presented in Table I. Residues are most concentrated in the upper 2 cm of sediment at the water interface, but occur commonly at depths of 6–12 cm. The depths of accumulation of insecticides within the sediments vary considerably with location, reflecting the stratigraphic unit present at the water interface, the differences in rates of deposition, and sediment mixing due to hydrodynamic and biological activity in different regions of the basin. The principal insecticides

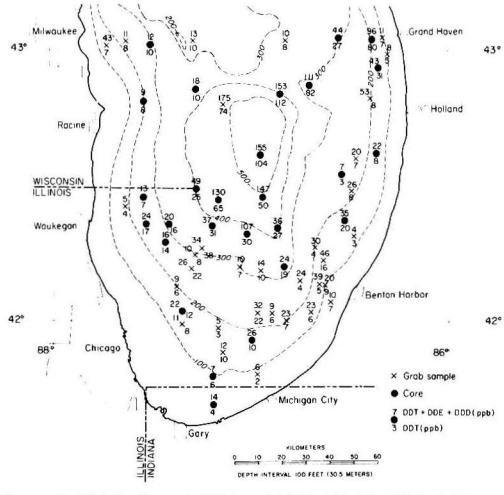

Figure 5. Distribution of DDT and t-DDT (DDT, DDE, DDD) in surficial sediments

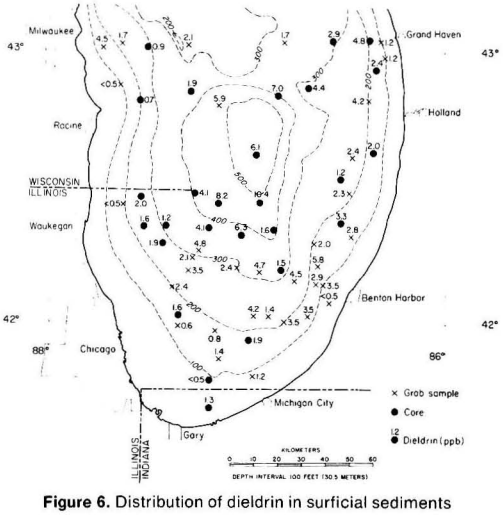

Figure 6. Distribution of dieldrin in surficial sediments

in Lake Michigan sediments are dieldrin and DDT and its degradative products. Traces of heptachlor epoxide and lindane are also present, but other common organochlorine insecticides are not found in detectable quantities. The concentrations of DDT, t-DDT, and dieldrin in the uppermost sediment interval for all stations are shown in Figures 5 and 6. The larger insecticide accumulations occur in sediments containing high amounts of organic matter which, in general, are in the Waukegan Member of the central, south-central, and eastern parts of southern Lake Michigan. Low concentrations of organochlorine insecticides occur in the sands and gravels overlying till in nearshore areas and in the southwestern part of southern Lake Michigan. Bottom currents and the absence of major tributaries on the western side of southern Lake Michigan are primary factors preventing accumulations of fine-grained sediments in these areas. The highest concentrations of t-DDT and dieldrin occur in the central, or deepest, parts of the south basin. These compounds, which are probably bound to small, finely divided particles, are presumably transported to the deepest regions of the lake by a natural sediment grading process.

Lake Michigan sediments and microbial isolates from these sediments are able to degrade DDT, as demonstrated by additions of ^{14}C-DDT to laboratory preparations (Matsumura et al., 1971; O'Connor and Armstrong, 1972). The major degradative product of DDT formed in these experiments is DDD. DDE and two polar metabolites, namely 2,2-bis(p-chlorophenyl)ethane and 2,2-bis(p-chlorophenyl)ethanol, also occur. The latter two compounds are produced upon decomposition of DDD and are not determined by the analytical procedure used in the present investigation. Decomposition of DDT and dieldrin probably occurs slowly in the sediments of southern Lake Michigan. The thermocline rarely extends much deeper than 30 meters; consequently, waters overlying the sediments at most locations sampled (Figures 5 and 6) are constantly at 4°C. Microbial degradation of DDT and dieldrin occurs very slowly at this temperature.

In general, concentrations of the DDT degradative products determined (DDD and DDE) in southern Lake Michigan sediments are not as high as the concentrations of the parent compound (Table I and Figure 5). Sediments offshore of some major tributaries (St. Joseph, Kalamazoo, and Milwaukee Rivers) are exceptions. The principal organochlorine insecticide residue in the reducing sediments of these regions is DDD, a compound formed by reductive dechlorination of DDT. DDE, a product formed by dehydrochlorination of DDT under aerobic conditions, is an equally common degradative product of DDT in sediments of the south-central and western parts of southern Lake Michigan. DDE is the major degradative product in sediments of the central part of the basin.

The percentage that DDD represents of the sum of the degradative products determined (DDD and DDE) in the uppermost sediment interval is significantly related (α = 0.05) to the electrode potential of the sediment, although the intensity of the relationship, as determined by correlation analysis (Figure 7), is weak. In the uppermost depth interval of reducing sediments, DDD is generally the principal degradative product formed. Concentrations of DDE generally exceed DDD levels in oxidizing sediments and in the deepest regions of the basin. In sediments underlying the uppermost sediment depth interval, DDD is generally either absent or present at lesser concentrations than is DDE (Table I). DDD is more susceptible to degradation than is DDT and DDE (Metcalf et al., 1971) and may be converted to more polar compounds in the older sediments. DDE, in contrast, is relatively stable

Table I. Chlorinated Hydrocarbon Insecticides (Concentrations in Parts per Billion) in Southern Lake Michigan Sediments

(Period of sampling: June to September 1969–70)

	Top interval			2–6 Cm			6–12 Cm		
Insecticide	Median	50% mid-range	No. of samples	Median	50% mid-range	No. of samples	Median	50% mid-range	No. of samples
p,p'-DDT	9.3	5.5–17	59	3.8	2.6–5.2	40	3.0	1.5–6.0	20
o,p-DDT	1.2	Tr–2.0	54	0.7	Tr–1.0	37	Tr	ND–2.3	14
p,p'-DDE	2.2	0.6–3.5	59	0.8	Tr–1.5	40	0.6	Tr–2.1	19
o,p-DDE	Tr[b]	Tr	49	ND[c]	ND	32	ND	ND–Tr	12
p,p'-DDD	3.0	1.4–10	54	0.5	Tr–2.0	37	ND	ND	12
o,p-DDD	Tr	Tr–1.8	49	ND	ND–0.5	32	ND	ND	12
Total DDT complex	18.5	10–32	59	6.3	3.9–13	40	3.4	2.2–8.1	20
Dieldrin	2.0	1.3–4.1	54	Tr	Tr–1.1	37	Tr	Tr–0.9	14
Heptachlor epoxide	Tr	Tr–0.7	54	Tr	ND–0.5	32	ND	ND	14
Lindane	Tr	Tr	45	ND	ND–Tr	30	ND	ND	14

[a] Nomenclature for insecticides are as follows: DDT, 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane. DDE, 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethylene. DDD, 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane. Dieldrin, 1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-*endo-exo*-5,8-dimethanonaphthalene. Heptachlor epoxide, 1,4,5,6,7,8,8-heptachloro-2,3-epoxy-3a,4,7,7a-tetrahydro-4,7-methanoindan. Lindane, 1,2,3,4,5,6-hexachlorocyclohexane, gamma isomer.

[b] Tr, residue present at a concentration less than 0.5 ppb.

[c] ND, no residue detected at sensitivity of test.

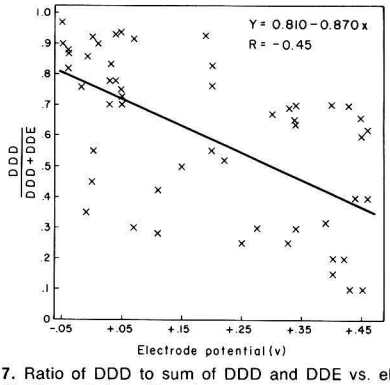

Figure 7. Ratio of DDD to sum of DDD and DDE vs. electrode potential in the surficial sediments

Electrode potentials were determined at sediment depth interval of 1 cm or below watery "floc" which exists in some areas

and degradation of this compound probably occurs extremely slowly in southern Lake Michigan sediments. The presence of DDE at levels in excess of DDD concentrations may, in some instances, simply reflect the greater chemical stability of DDE.

Records on insecticide use in the four states bordering Lake Michigan are fragmentary (Mount, 1969), and any estimates of insecticide additions via surface drainage into Lake Michigan during the past two decades based on these data are unrealistic. Insecticide usage in the watershed is not typical of usage in other regions of the United States. In the states of the cornbelt and cotton belt, most insecticides are applied to field crops, whereas Lake Michigan basin usage is perhaps 60% municipal and industrial and only 40% agricultural. Prior to 1966 the most commonly applied organochlorine insecticides in the extensive field crop and orchard areas of Michigan were DDT, dieldrin, and aldrin (which oxidizes to dieldrin). In addition to the extensive agricultural employment of these insecticides, municipalities in all states bordering Lake Michigan applied large quantities of DDT over the years for control of the lesser European elm bark beetle (the principal vector of Dutch elm disease) and mosquitoes. Federal and state agencies have used DDT extensively for control of forest pests. Published records on quantities of insecticides used for industrial operations in the Lake Michigan watershed are not available.

Results of the present study indicate that DDT, DDE, and DDD and dieldrin are distributed widely in Lake Michigan and constitute a large reservoir of stable insecticides in the sediments. The portion of this reservoir available for biological uptake is unknown, but is of great importance if benthic organisms assimilate enough insecticide from bottom sediments to contain high sublethal concentrations in their tissues. Benthic organisms comprise an important food source for many aquatic predators, and thus could contribute to the continued existence of high concentrations of organochlorine insecticides in exploitable fish of Lake Michigan for many years.

Acknowledgment

Insecticide concentrations were determined in the laboratories of the Illinois State Natural History Survey under the direction of W. N. Bruce. The authors are grateful to David L. Gross of Illinois State Geological Survey for permitting the inclusion of Figure 1. We thank Jean Wilson of the Illinois State Natural History Survey and John Schleicher and Larry Camp of the Illinois State Geological Survey for technical assistance. David Gross, Jerry Lineback, Susan Avcin, and Julia Graf of the Illinois State Geological Survey and the crew of the *R. V. Inland Seas,* Great Lakes Research Division, The University of Michigan, participated in sample collection.

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Rapid Gas Chromatographic Method for Determination of Residual Methanol in Sewage

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■ Described is a rapid and specific method for the determination of low concentrations of methanol over the range 0.5–100 ppm in sewage or other aqueous solutions. The method involves the use of direct aqueous injection gas chromatography on a porous polymer column. No preconcentration or extraction is required. The analysis time of approximately one minute per sample makes the procedure especially suited to process control applications.

Pilot plant studies on the biological denitrification of waste waters are currently in progress at the Canada Centre for Inland Waters, Burlington, Ont. (Dawson et al., 1972). An analytical method for residual methanol, which is added as a supplementary carbon source, was required.

The use of methanol as an easily assimilable supplementary carbon and energy source for the biological denitrification of municipal and industrial waste waters appears to be justified on a technical and economical basis (Smith et al., 1972). Advanced waste water treatment systems, such as denitrification, are likely to find increasing acceptance and use in the control of eutrophication of lakes and rivers. Although many substrates have been used as a carbon and energy source, research in denitrification technology in the last five years has established methanol as the prime contender for this role (Christensen and Harremoës, 1972).

Efficient and economical control of the denitrification process calls for a rapid, sensitive, and specific method for the analysis of residual methanol in plant streams and final effluent.

Analytical procedures now in use or reported in the literature are not entirely suitable with respect to convenience or specificity. In pilot plant studies at the National Environmental Research Centre, Advanced Waste Treatment Research Laboratory in Cincinnati (Smith et al., 1972), a somewhat lengthy procedure was used which involved manual steam distillation of the sample before proceeding to a colorimetric AutoAnalyzer method (Bricker and Vail, 1950). Moore and Schroeder (1970) used gas liquid chromatography with a Porapak Q column, but no details were given on the specificity, sensitivity, or convenience of the method. Until recently, the pilot plant study at the Canada Centre for Inland Waters has used total dissolved organic carbon as an approximate indication of residual available carbon (Dawson et al., 1972).

Analytical Considerations

A specific analytical method for methanol in the 0.5–100 ppm range in sewage was sought which, in addition to being quantitative, would avoid any time-consuming and error-producing cleanup, preconcentration, or extraction techniques.

The restrictions appeared to indicate direct aqueous injection gas chromatography as the method of choice. The selection of column packing material and length along with the inlet configuration and other variable operating parameters were made so as to minimize problems especially associated with direct aqueous injection techniques. A porous polymer column packing material was chosen to avoid the liquid phase stripping effects of water. The active sites on the column packing and tube walls were partially deactivated with phosphoric acid (Mahadeven and Stenroos, 1967) to prevent tailing of water and methanol. A removable glass sleeve in the injection port served to retain inorganic material and organic compounds not volatilized at the operating temperatures.

Trace components are not easily quantified when appearing on the tail of an overload solvent peak and tend to broaden when eluted before a peak due to solvent in large excess (Deans, 1971). For this work, an analytically useful compromise between these two situations was made possible by the very small magnitude of the signal produced by water in a flame ionization detector in comparison to the signal produced by similar amounts of most organic compounds. Careful choice of operating conditions allowed the water signal to appear as a very low flat-topped mound of about 50 sec duration with the methanol appearing as a sharp spike superimposed on the water base.

Experimental

Apparatus. A MicroTek GC Model 220 equipped with a removable glass demisting sleeve and hydrogen flame ionization detector was used for the study. The single column was 0.5 meter × 3.175 mm o.d. stainless steel packed with Tenax GC 60/80 mesh, batch 04900, Enka N.V., Holland, modified as follows:

The U-shaped column was packed and then saturated with 85% phosphoric acid and allowed to stand for 4 hr. Excess phosphoric acid was then removed by displacement with about 50 ml of glass-distilled water. The column was then dried with a stream of dry nitrogen.

GC Operating Conditions

Inlet temperature, 225°C
Column temperature, 70°C isothermal
Detector temperature, 225°C
Carrier gas, N_2 (Linde, U.H.P.) at 25 ml/min
Detector gases, air (Linde Zero gas) at 280 ml/min
H_2 (Linde, U.H.P.) at 40 ml/min
Sensitivity, 3.2–256 × 10^{-11} amps = full-scale deflection on a 1-mV recorder for typical concentrations in the range 0.5–100 ppm CH_3OH in sewage

Results and Discussion

Specific Nature of Response. A number of low-molecular-weight organic compounds which might be expected to possess similar retention times to methanol, Fisher Pesticide Grade, Lot 785958, on the Tenax column were tested for interference (Table I). Of particular interest were formaldehyde, BDH Reagent Grade, 37–41% solution (+11–14% methanol), and formic acid, BDH 98–100% A.R. Grade, which might be postulated as possible products arising from the oxidation of methanol. None of these compounds produced an interfering peak with methanol. Methane, which is probably the only one of these compounds likely to be found in sewage samples at significant concentrations, is completely eluted before methanol. Formaldehyde in concentrated solutions produces a broad tailing peak eluting after methanol. This broad peak may be due to polymerization of formaldehyde molecules. At ppm concentrations, formaldehyde does not produce a detectable peak under the experimental conditions. It should be noted however, that most commercially available solutions of formaldehyde contain 10–15% of methanol added as a stabilizer. For this reason formaldehyde should not be used to preserve samples for methanol analysis by gc. Other organic compounds of higher molecular weight which may be present in sewage are, for the most part, retained as a deposit in the removable glass injection port sleeve, or in some cases are eluted over such a prolonged time interval that no displacement from the base line is detectable. The column may be purged of such materials from time to time by raising the oven temperature to 250°C and cooling slowly to 70°C. This has not been necessary in this work, and no other measurable peak than the methanol peak has been observed despite the injection of hundreds of sewage effluent samples. Under less aerobic conditions methane might be produced but under extended aerobic biological oxidation, the virtually complete disappearance of very low-molecular-weight organic compounds is supported by other observers (Murphy et al., 1971).

Sample Preservation. Although the samples were passed through a 0.45 membrane filter after collection to remove suspended material, the bacterial degradation of the residual methanol continued with further storage of the sample. A typical sample originating from pilot plant denitrification columns with a residual methanol concentration of 30 ppm would lose the remainder of the residual methanol in three to five days after filtration and storage at room temperature (Table II). Standard solutions of methanol in distilled water showed no change in concentration after storage under identical conditions. A microscopic examination of a filtered sewage effluent sample showed large numbers of bacteria to be present. Acidification of the sample at the time of collection to about pH 2 with hydrochloric acid, Fisher Reagent Grade, was found to inhibit completely further loss of residual methanol (Table II).

Linear Concentration Range. Detector response to methanol was linear over the chosen range of 0.5–100 ppm CH_3OH. A plot of seven concentrations of methanol in distilled water ranging from 0.6–96 ppm vs. their corresponding peak heights produced a straight line with an intercept at the origin. The range was chosen to cover the concentrations likely to be found at the various treatment stages of the denitrification process. The linear range may be extended at either end, although a decrease in precision will be observed at levels below 0.5 ppm. Methanol feedstock solutions of about 25,000 ppm were found to be best analyzed by dilution to about 25 ppm.

Accuracy and Precision. The accuracy of the method was determined by making measurements on spiked sewage samples at various concentrations of methanol (Table III).

Table I. Retention Time of Some Low-Molecular-Weight Organic Compounds Relative to Methanol

Compound	Retention time (CH_3OH = 1)
Methane	0.2
Ethane	0.3
Propane	0.5
Methanol	1.0
n-Butane	1.3
Acetaldehyde	1.5
Ethanol	2.7
Propionaldehyde	6.7
Acetone	8.0
Formaldehyde	—[a]
Formic acid	—[b]
Methylamine	—[b]

[a] No peak observed in dilute (ppm) solutions; R_T = 2.3 in concentrated solutions.
[b] No peak observed under experimental conditions.

Table II. Sample Preservation by Acidification to pH 2

		CH_3OH ppm		
Sample	pH	0 hr	5 hr	125 hr
To reactor	7–8	35	29	0
From denitrification, Column #1	7–8	21	19	0
From denitrification, Column #2	7–8	16	13	0
To reactor	2	35	—	34
From denitrification, Column #1	2	19	—	19
From denitrification, Column #2	2	16	—	16

Table III. Accuracy of Measurements on Sewage Effluent Sample No. 3A with Different Amounts of Methanol Added

CH_3OH added, ppm	CH_3OH found, ppm	CH_3OH recovered, ppm
0	10	0
4	14	4
6	16	6
13	24	14
19	30.5	20.5

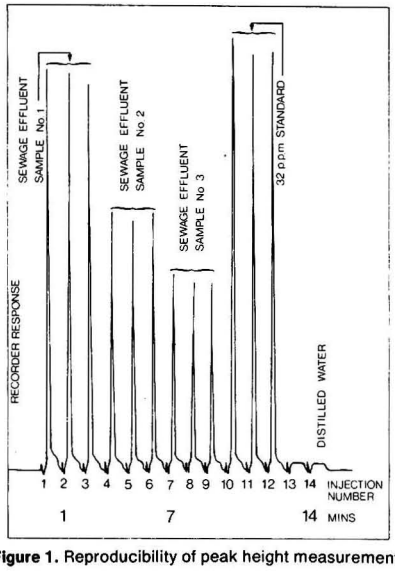

Figure 1. Reproducibility of peak height measurements

Analyses in triplicate of three sewage effluent samples and one standard methanol solution

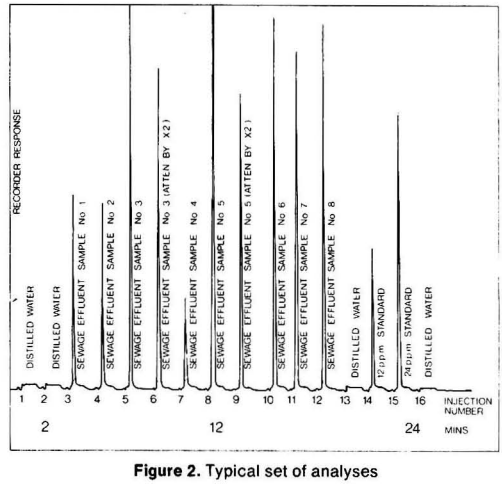

Figure 2. Typical set of analyses

Eight sewage effluent samples and appropriate standards

The precision of the method was determined from replicate analyses (10) of a sewage effluent sample at the 50-ppm level of methanol. At this level the standard deviation was 1.2 and the coefficient of variation 2.4% using peak heights. The corresponding figures using peak areas were 0.8 std dev and 1.6% coefficient of variation. These figures are close to the generally accepted optimum performance of a microliter syringe in the hands of an experienced operator. The use of peak heights was considered satisfactory for quantitative measurements. Figure 1 illustrates the repeatability on three sewage samples and one standard.

Recommended Procedure

Pass the sample (25 ml or less) through a 0.45-μ membrane filter immediately after collection. Acidify to approximately pH 2 with reagent grade hydrochloric acid (pH indicating test sticks may be used). Store the sample at room temperature in clean stoppered glass or polyethylene bottles until the analysis can be performed.

With the gas chromatographic parameters set up as indicated above, inject several 5-μl. quantities of distilled water until a small almost flat-topped water response is obtained (Figure 2). The first distilled water injection of a new set of analyses often produces a small positive peak.

Inject 5 μl. samples of sewage effluent etc. A new injection may be made as soon as the pen returns to the initial baseline (Fig. 2).

Calibrate the analyses by injecting 5 μl. each of a series of standards of methanol in distilled water of appropriate concentrations.

Measure peak heights using the top of the water "mound" following the methanol peak as the peak base line.

Inject 5 μl. of distilled water between samples occasionally to ensure that ghosting does not occur.

After approximately 100–200 samples the removable glass injection port sleeve should be removed and carefully cleaned with chromic acid followed by distilled water. The glass sleeve should then be replaced and the gc oven heated up to 250°C for 30 min and then slowly cooled to 70°C. Increased size of the water 'base' or ghosting when distilled water is injected are indications of the need to clean the glass sleeve.

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Distribution of Alkyl Arsenicals in Model Ecosystem

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■ Distribution of ^{14}C-labeled cacodylic acid (CA) and dimethylarsine (DMA) among aquatic organisms in a model ecosystem was studied. Fish, *Daphnia magna*, snails, and algae were exposed to CA and DMA for 3, 29, 32, and 32 days, respectively. Lower food chain organisms (algae and *Daphnia*) bioaccumulated more CA and DMA than did higher food chain organisms (snails and fish). Amounts accumulated indicate that CA and DMA do not show a high potential to biomagnify in the environment. An increase in biomass (primarily algae) over 32 days largely accounted for a gradual loss of CA and DMA from solution.

Heavy metals have been the subject of recent environmental controversies. Bioaccumulation of the highly toxic compound, dimethylmercury, in aquatic food chains has focused attention on metals that can be alkylated in natural systems. Methylated mercury is sufficiently fat soluble to partition into the fatty tissue of successively higher components of aquatic food chains and constitutes an imminent hazard in areas where mercury is being introduced into natural waters. Methylation of mercury by microorganisms occurs in the sediment of rivers and lakes (Jernelov, 1969). Microorganisms capable of methylating mercury (Jensen and Jernelov, 1968) and the metabolic pathway have been described (*Chem. Eng. News*, 1971).

Arsenic is distributed widely in the environment and is a constituent of some pesticides. Three alkylated arsenical herbicides, monosodium methanearsonate (MSMA), disodium methanearsonate (DSMA), and hydroxydimethylarsine oxide (cacodylic acid) find wide application in selective and general weed control programs. During 1971 the estimated U.S. production of these three arsenical compounds was 16.8×10^6 kg (Lawless et al., 1972). Cacodylic acid (CA) can be degraded oxidatively to CO_2 and AsO_4^{-3} in aerobic soils and reductively to a volatile organoarsenical, probably dimethylarsine (DMA), in aerobic and anerobic soils (Woolson and Kearney, 1973). The reductive microbial pathway starting with As_2O_3 involves a series of reductive and methylation steps, and includes methanearsonate and CA as intermediates in the formation of DMA (McBride and Wolfe, 1971). DMA has a pungent garlic-like odor characteristic of several alkyl arsines. The apparent similarity between dimethylmercury and DMA suggested the latter might undergo bioaccumulation in aquatic food chains.

The present paper examines the distribution of CA and DMA among several aquatic organisms in a simple microecosystem. Although emphasis is placed on dimethyl arsenicals, the results can be expanded to include their precursors—i.e., arsenate and arsenite—since they all are apparently related by a common metabolic pathway. Also, the operation, capabilities, and limitations of the model ecosystem are described. It is important to make these clarifications since the model ecosystem, in one form or another, may become a major tool to indicate the likelihood of organic compounds bioaccumulating in the environment.

Bioaccumulation and *biomagnification* are two terms frequently used to describe biological uptake of a compound from the environment. In this paper *bioaccumulation* is used to indicate how extensively an organism accumulates a compound from its surrounding environment by all processes (e.g., absorption, adsorption, ingestion, etc.). *Biomagnification* indicates that a compound is concentrated through the consumption of lower by higher food chain organisms with a net increase in tissue concentration. Under certain conditions, particularly in the terrestrial environment, the two terms could accurately describe the same process and could therefore be used interchangeably. Their distinction becomes apparent, however, in the aquatic environment. For example, all aquatic organisms will "bioaccumulate" some finite quantity of any compound from solution but the amount accumulated does not necessarily indicate that biomagnification has occurred.

Experimental

Preparation of ^{14}C-Cacodylic Acid and Dimethylarsine. ^{14}C-CA was prepared by reacting dichloromethylarsine with ^{14}C-methyl iodide (Woolson and Kearney, 1973). After purification by preparatory thin-layer chromatography (tlc) on cellulose-coated plates developed with a solution of methanol:$10^{-3}N$ NH_4OH (8:2 v/v), a yield of 56 μCi ^{14}C-CA was obtained (specific activity 2.7 mCi/m*M*; R_f 0.70 for CA). Prior to purification, two impurities comprising about 3.3% of the reaction mixture (based on total ^{14}C) were detected at R_f 0.55 and 0.46. DMA was prepared by reducing CA as described by Woolson et al. (1971). This procedure was modified by increasing the HCl concentration twofold. Gaseous DMA was generated in an all-glass system and swept with a stream of nitrogen into a solution of 5% HgCl in 10% HCl. The white precipitate was analyzed commercially and contained a C:As ratio of 2.09:1.00.

Description and Operation of Ecosystems. A modified version of Metcalf's et al. (1971) ecosystem was used in this study. The basic units are glass aquariums 25.4 × 5.2 × 17.8 cm filled with 4 liters of "standard reference water" (Freeman, 1953). This reference water was modified by increasing the NH_4NO_3 and K_2HPO_4 concentration fivefold to obtain satisfactory algae growth. The terrestrial phase of Metcalf's et al. (1970) system was omitted, since the compounds tested in this study are either used or supposedly form in water.

All experiments were carried out in the greenhouse with the tanks placed in a shallow water bath maintained at 22 ± 1°C. This temperature was selected since one of the food chain organisms, *Daphnia magna*, requires a temperature of about 21°C for optimal growth. All tanks were aerated with compressed air. Distilled water was added as needed to replace evaporation losses.

Cultures of *Daphnia magna*, *Oedogonium cardiacum* algae, and *Physa* snails were maintained in "standard reference water." *Daphnia* was reared on baking yeast and

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Table I. Recovery of ^{14}C in Biomass from Solutions Containing ^{14}C-Labeled Cacodylic Acid, Dimethylarsine (Oxygen), and Dimethylarsine (Nitrogen)[a]

	Algae	Snails	*Daphnia*	Fish	Total
	Cacodylic Acid				
% recovery of ^{14}C lost from solution	67.00	2.90	0.45	0.06	70.41
% recovery of ^{14}C initially added	28.21	1.16	0.18	0.02	29.57
% of total biomass[b] weight	74.10	21.54	1.16	3.20	100.00
	Dimethylarsine (Oxygen)				
% recovery of ^{14}C lost from solution	72.18	4.93	0.37	0.06	77.54
% recovery of ^{14}C initially added	31.97	2.17	0.16	0.03	34.33
% of total biomass[b] weight	72.44	23.56	0.49	3.51	100.00
	Dimethylarsine (Nitrogen)				
% recovery of ^{14}C lost from solution	87.87	8.46	0.43	0.07	96.83
% recovery of ^{14}C initially added	28.82	2.75	0.14	0.02	31.73
% of total biomass[b] weight	66.98	30.78	0.92	1.32	100.00

[a] Biomass indicates sum of all living organic material in the system; principally algae, snails, *Daphnia*, and fish. All data average of 2 replications. Exposure time: 32 days for algae, snails and *Daphnia*; 3 days for fish. CA, DMA-O, and DMA-N solution concentrations were 10.6, 7.0, and 7.0 ppb after 1 day and 6.1, 3.9, 4.7 ppb after 32 days, respectively.
[b] Shows relative contribution of the four organisms to the total harvested biomass.

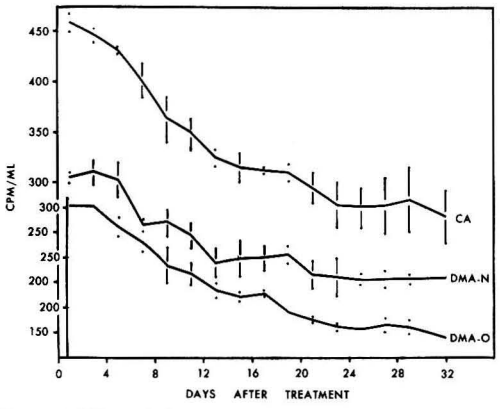

Figure 1. Effect of time on the solution concentration of CA, DMA-O, and DMA-N (expressed as cpm/ml solution)

Average of 2 replications. Inner scale for DMA-O only

Physa on carrots and lettuce. Mosquito fish, *Gambusia affinis*, obtained from a local distributor, completed the food chain. These organisms are representative of several trophic levels naturally found in the aquatic environment. In addition, small organisms such as these can be confined in correspondingly small aquariums, thereby simplifying the physical operation of the experiment.

The aquatic organisms represent parts of two food chains: water → algae → snails and water → diatoms, protozoa, and rotifers → *Daphnia* → fish. These chains overlap somewhat since snail excreta probably provided some of the food for diatoms, protozoa, rotifers, and *Daphnia*. The concentration of CA and DMA in the organisms was expressed as bioaccumulation ratio, calculated by dividing counts per minute (cpm)/mg dry tissue of algae, snails, *Daphnia*, or fish by cpm/mg of water in the tank.

The ecosystems were prepared by adding 4 liters of "standard reference water," 10 snails, a few strands of algae, about 30 *Daphnia*, and a few ml of old aquarium water to each of 8 tanks. The old aquarium water contained various diatoms, protozoa, and rotifers. Five days later duplicate tanks were treated with CA, DMA-N, and DMA-O as described below. The two remaining untreated tanks served as controls. Two 1-ml water samples were taken from each tank at two-day intervals, starting one day after the compound was added, and the radioactivity was determined by standard liquid scintillation methods. After 29 days' exposure to CA, DMA-O, and DMA-N, one sample (20–30 organisms per sample) of *Daphnia* was taken from each tank (for analysis of radioactivity), and two fish were added. The experiment was terminated three days later since the fish had consumed all remaining *Daphnia*. Fish, *Daphnia*, snails, and algae were therefore exposed for 3, 29, 32, and 32 days, respectively. Two samples of algae (50–100 mg dry wt), two fish, and four snails were harvested from each tank. The algae and *Daphnia* were washed in distilled water, dried at 60°C, ground and combusted in a stream of oxygen. The $^{14}CO_2$ was dried by passing through a column of anhydrous $CaSO_4$ and trapped in 10 ml of monoethanolamine/2-methoxyethanol (1:7 by volume). A 5-ml aliquot of the trapping solution was assayed for radioactivity by standard liquid scintillation methods. The fish and snails were homogenized in methanol and then filtered. The filtrate was concentrated to 10 ml and radioactivity determined by liquid scintillation methods. The tissue was dried (at 60°C overnight), weighed, and combusted as described above. Algae, snails, *Daphnia*, and fish contained 65.7, 72.4, 84.9, and 75.6% water, respectively.

Ecosystem Assessment of CA and DMA. ^{14}C-CA was added directly to aquarium tanks containing 4 liters of "standard reference water." The ^{14}C-DMA was adsorbed to moist Lakeland sandy loam soil and then added to the aquariums. Soil served as a convenient way of adsorbing and transporting the generated DMA. Adsorption was accomplished by placing 10 grams of soil, moistened to field capacity in a fritted glass thimble (soil depth 2.3 cm), and passing DMA (generated as described above) through the soil for 3 hr. Generated DMA was swept through the soil with N_2 or O_2 and was designated DMA-N and DMA-O, respectively. The sweep gas was finally bubbled through 95% ethanol to trap any remaining DMA. Immediately after generation, the soil was submerged in aquarium tanks. Ten grams of untreated soil were also added to the CA and control tanks. Water and organisms from control and treatment tanks were identically sampled, prepared, and analyzed as described above. Radioactivity in the control samples equaled or slightly exceeded background radioactivity and was therefore subtracted as background from the respective treatment samples. In addition, snail extracts were concentrated and chromatographed on silica gel plates using as solvents MeOH:NH_4OH:10% TCA:H_2O (50:15:5:30 v/v) or 1-PrOH:NH_4OH (7.3 v/v). The tlc plates were radioautographed or scraped for scintillation counting.

A second, shorter duration experiment was performed to determine the relative contribution of uptake from solu-

Table II. Accumulation of ^{14}C-Labeled Cacodylic Acid and Dimethylarsine (Generated in Oxygen or Nitrogen) by Algae, Snails, *Daphnia*, and Fish

Treatment		Solution concentration, ppb[a] 1 day	32 days	Algae	Snails[b] 1st harvest	2nd harvest	*Daphnia*	Fish
Cacodylic acid	BR[c]	10.6	6.1	1635 ± 358[d]	419 ± 21	110 ± 16	1658 ± 463	21 ± 6
	Ppm[a]			9.82 ± 1.18	2.60 ± 0.04	0.69 ± 0.13	16.40 ± 10.00	0.32 ± 0.07
Dimethylarsine (oxygen)	BR[c]	7.0	3.9	1605 ± 155	446 ± 21	176 ± 23	2175 ± 290	19 ± 7
	Ppm[a]			6.26 ± 0.60	1.74 ± 0.08	0.69 ± 0.09	10.35 ± 3.11	0.07 ± 0.02
Dimethylarsine (nitrogen)	BR[c]	7.0	4.7	1248 ± 140	299 ± 12	129 ± 13	736 ± 104	49 ± 24
	Ppm[a]			5.92 ± 0.66	1.41 ± 0.06	0.61 ± 0.08	5.23 ± 0.68	0.17 ± 0.05

[a] Based on total ^{14}C activity, expressed as parent compound, at 32 days. Fish exposed for 3 days.
[b] First harvest, half of snails harvested at 32 days. Second harvest, half of snails placed in untreated solution and harvested 16 days later.
[c] Bioaccumulation (ratio) calculated by dividing cpm/mg tissue by cpm/mg of solution.
[d] Standard error of the mean for 2 replications.

tion vs. ingestion of one food chain organism by another in the accumulation of CA. Solutions containing 0.1, 1.0, and 10.0 ppm labeled CA were prepared in triplicate. About 500 mg algae (fresh wt) and 300 *Daphnia* were added to each tank, exposed for two days, then removed and washed. A sample was taken for analysis, and the remaining algae and *Daphnia* were placed in separate solutions not containing CA. (A preliminary experiment revealed that algae and *Daphnia* had reached a plateau concentration of CA after two days' exposure.) Two fish were added to the untreated solutions containing *Daphnia*, and 4 snails were added to the untreated solutions containing algae. Two fish and 4 snails were also added to the treated solutions from which algae and *Daphnia* had been removed. All fish were harvested after two days (time required for the fish to eat all *Daphnia*); two snails were harvested from tanks after seven days. All tissue was prepared and analyzed as described above.

Results and Discussion

All organisms in both control and treated tanks prospered during the exposure period, indicating that the concentration of CA and DMA used were not toxic. After 29 days, *Daphnia* had increased in population from about 30 to over 100. Numerous clusters of snail eggs had been laid on the tank walls, and algae had undergone at least a tenfold increase in mass.

Solution concentrations, 24 hr after adding CA or DMA, were 10.6, 7.0, and 7.0 ppb CA, DMA-O, and DMA-N, respectively, based on activity of the parent compound. These concentrations represent 92.0, 60.8, and 61.2%, respectively, of the original activity placed in solution or in the generation flask. The 8% loss of CA activity in water was probably due to initial adsorption to algae or other organisms (Table I). The quantity of DMA found in the tanks probably represents nearly all of the DMA adsorbed to the soil. The ethanol trap always contained 30–50% of the total activity found in the soil plus ethanol trap. Also, conversion of CA to DMA (in the generation flask) never exceeded 90% efficiency. Therefore, it seems likely that the remaining DMA activity (39%) was present either in the ethanol trap or generation flask or was adsorbed to algae. Any DMA that remained adsorbed to soil (in the tanks) probably did not exceed more than a few percent.

The solution concentration (expressed as cpm/ml) of CA, DMA-O, and DMA-N decreased with time (Figure 1). After 32 days the CA, DMA-O, and DMA-N solutions had lost approximately 42, 44, and 33% of the initial activity (measured at 24 hr), respectively. Seventy to 97% of this lost activity was accounted for in the biomass (sum of all living and dead organic material) (Table I). No attempt was made to remove quantitatively all organic material from the tanks, which may have contained the unrecovered activity. It was also possible that some activity was lost by volatilization of DMA and as $^{14}CO_2$. Algae accounted for 67–74% of the total biomass (by weight), 91–95% of the activity contained in the biomass, and 28–32% of the activity added at the beginning of the experiment. Therefore, in this system, algae constituted the primary sink in which CA, DMA-O, and DMA-N accumulated.

The four organisms examined in this ecosystem exhibited different abilities to bioaccumulate CA, DMA-O, and DMA-N (Table II). Similar species differences have been observed with DDT accumulation from water (Johnson et al., 1971). Organisms that represented the higher link in the food chain (snails and fish) had smaller bioaccumulation ratios than lower link organisms (algae and *Daphnia*, respectively), indicating that CA and DMA did not biomagnify between food chain organisms. Snails that had been placed in distilled water for 16 days after exposure had bioaccumulation ratios ¼–½ as large as snails harvested at the end of the experiment. Failure of snails to retain activity when placed in untreated water indicated that much of the CA and DMA was not incorporated in tissue but apparently was weakly held and available for desorption. Adsorption probably contributes to the accumulated activity in all organisms and may account for some of the activity lost from snails. In addition, algae and *Daphnia* probably had higher surface area to mass ratios than snails or fish and therefore could adsorb more CA and DMA than snails or fish. Thus, the large differences in bioaccumulation ratio for the organisms may be due in largest part to adsorption.

The relatively large bioaccumulation ratios that were obtained for algae and *Daphnia* raise the question, "What bioaccumulation ratio is excessive or abnormally high, thereby indicating a potential hazard to the environment?" This question cannot be firmly answered since one bioaccumulation ratio has not yet been chosen (or may never be chosen) which will indicate that a hazard to the environment does or does not occur. The question may be somewhat resolved, however, by comparing bioaccumulation ratios for different compounds. Johnson et al. (1971) found that in 3 days *Daphnia magna* accumulated 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane (DDT) and 1,2,3,4,10,10-hexachloro-1,4,4*a*,5,8,8*a*-hexahydro-1,4-*endo*,*exo*-5,8-dimethanonaphthalene (aldrin) 1.14

Table III. Distribution of Mobile and Origin CA, DMA-O, and DMA-N Snail Extract Activity Expressed as a Percent of Total Activity Spotted[a]

		Mobile spot[b]			Origin spot[b]		
R_f	CA std	CA	DMA-O	DMA-N	CA	DMA-O	DMA-N
0.91–1.00		0	0	0	0	0	0
0.81–0.90			1.7	4.8			
0.71–0.8[c]		4.3	4.2	13.6	6.2	52.8	87.2
0.61–0.70							
0.51–0.60		0	0	0	12.2	2.4	1.2
0.41–0.50		8.6	6.0	2.8	22.0	11.9	3.2
0.31–0.40							
0.21–0.30	100.0	8.1	6.6	6.0	25.6	13.3	5.9
0.11–0.20		35.2	32.4	43.3	17.6	14.6	1.3
0.00–0.10		38.2	46.3	21.5	12.1	2.8	0.7
Origin spot		5.6	2.8	8.0	4.3	2.2	0.5

[a] Tlc system 1-PrOH:NH_4OH (7:3, v/v).
[b] Mobile and origin spots removed from chromagraph shown in Figure 2.
[c] All activity above origin spot to R_f 0.10.

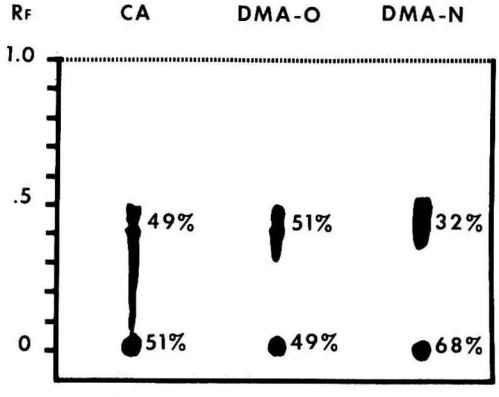

Figure 2. Radioautograph of MeOH extracts from snails exposed for 32 days to solutions containing CA, DMA-O, and DMA-N

Tlc system MeOH:NH_4OH:10% TCA:H_2O (50:15:5:30 v/v). R_f standard CA 0.65

$\times 10^5$ and 1.41×10^5 times the water content at time of sampling, respectively. Our own studies show that *Daphnia magna* accumulate 7-oxabicyclo[2.2.1]heptane-2,3-dicarboxylic acid (endothall) and (2,4,5-trichlorophenoxy) acetic acid [2,4,5-T) 150 and 217 times the water content at time of sampling, respectively (unpublished research). Therefore, *Daphnia magna* accumulated CA, DMA-O, and DMA-N about ten times more than endothall or 2,4,5-T, but only $\frac{1}{50}$–$\frac{1}{70}$ as great as DDT or aldrin. On a comparative basis, therefore, the bioaccumulation ratios for CA and DMA are not excessively high.

The similar behavior of CA and DMA in solution (disappearance of activity and accumulation in each organism) raises the question of compound identity. DMA is readily oxidized to a number of compounds when exposed to O_2. Products of oxidation include partially and completely demethylated compounds under restricted O_2 supply (Dehn and Wilcox, 1906). As the O_2 supply becomes greater, a dimer $[(CH_3)2As]_2$ forms, followed by dimethylarsenoxide, $[(CH_3)_2As]_2O$, and cacodylic acid. Therefore, in this experiment, much of the DMA generated in O_2 presumably was converted to CA. The rate of conversion is unknown so the ratio of DMA to CA in the soil after generation in O_2 is also unknown. Most of DMA generated in N_2 was probably adsorbed to the soil and likely did not oxidize to CA during generation. However, since the aquarium was aerated, oxidizing conditions would exist that might convert DMA-N to CA after it was placed in the water.

Snail extracts were therefore analyzed by tlc to determine if DMA had converted back to CA (Figure 2 and Table III). Extracts from all three compounds had similar R_f values, but differed enough with respect to tailing and ratios of mobile and nonmobile activity, to indicate that several different chemical species were present (Figure 2). The mobile and nonmobile spots were then removed and rerun using a different tlc system (Table III). For CA, the mobile spot included all activity above an R_f of about 0.08. Most of the mobile and CA origin activity had R_f values slightly less than the R_f value obtained for the CA standard. On the other hand, 53% and 87% of the DMA-O and DMA-N origin activity, respectively, had R_f values from 0.61 to 0.90. Neither the identity of the nonmobile DMA spots nor the metabolites (Figure 2) are presently known. Therefore this tlc data indicates only that snail extracts from DMA treatments contained substantial quantities of compound(s) unlike those found in the snail extracts from CA.

A second experiment was carried out to determine the relative importance of absorption from solution vs. consumption of one organism by another on the distribution of CA among food chain elements. Fish and snails accumulated 2–10 times more CA from solution than they obtained by consuming CA-treated *Daphnia* or algae (Table IV). Only a limited quantity of *Daphnia* were available to the fish, suggesting that a larger supply would have resulted in more accumulation. By contrast, snails did not have a limited food supply (algae), but after 7 days also accumulated less CA from algae than from treated solution. For these exposure periods, accumulation from solution appeared to be more important than consumption of one food chain organism by another, particularly for the algae-snail part of the food chain. Longer feeding periods may have resulted in the accumulation of similar amounts of CA between fish and snails exposed to CA-treated solutions and fish and snails supplied CA-treated food. The results generally agree with the thesis that biological magnification in the aquatic environment is primarily related to exchange equilibrium between aquatic organisms and water rather than from one food chain organism to another (Hamelink et al., 1971).

The concentrations of CA in fish treated for 2 days

Table IV. Tissue Content (Ppm) of ^{14}C-Cacodylic Acid in Algae, *Daphnia*, Fish, and Snails after Various Exposure Times, Rates, and Treatments[a]

Treatment ppm[b]	Algae[c]	*Daphnia*[c]	Fish w *Daphnia*[d]	Fish w/o *Daphnia*[d]	Snails w algae[e]	Snails w/o algae[e]
0.1	4.5 (45)[f]	3.9 (39)	0.09 (0.9)	0.14 (1.4)	0.9 (9)	2.0 (20)
1.0	17.0 (17)	41.6 (42)	0.36 (0.4)	0.92 (0.9)	2.3 (2.3)	8.5 (68.5)
10.0	71.4 (7)	254.0 (25)	6.71 (0.7)	11.20 (1.1)	7.3 (0.7)	68.3 (6.8)

[a] Average of 3 replications.
[b] Solution concentrations of ^{14}C-labeled cacodylic acid.
[c] Samples taken after two-day exposure.
[d] w *Daphnia*—fish placed in untreated solution containing CA-treated *Daphnia*. Without *Daphnia*, fish placed in CA-treated solution not containing *Daphnia*. All fish harvested after two days.
[e] w *Algae*—snails placed in untreated solution containing CA-treated algae. Without algae, snails placed in CA-treated solution not containing algae. All snails harvested after 7 days.
[f] Bioaccumulation ratios given in parentheses.

(Table IV) agree well with the amount of arsenic that was accumulated by fish in pools treated with sodium arsenite for 16 weeks (Gilderhus, 1966). He found that fish accumulated 1–6 times as much arsenic as was present in solution (0.5–9.0 ppm). Different species and ages of fish accumulated similar quantities of both organic and inorganic arsenical compounds when exposed to vastly different exposure times and experimental conditions.

Hamelink et al. (1971) have shown that pesticide magnification of chlorinated hydrocarbons by several organisms was inversely related to the water solubility and concentration of the compound. In our study, the highest bioaccumulation ratios were obtained at the lowest solution concentrations of CA (Tables II and IV). Therefore, solution concentration of water-soluble compounds should be carefully chosen to represent residue levels that would likely occur in the environment. Use of nonrepresentative rates may result in erroneously high or low bioaccumulation ratios which would be of no value in extrapolating laboratory results to actual environmental conditions.

The high variability between replications seems to be an inherent complication of the ecosystem and somewhat limits interpretation of the data (Table II). The general complexity (multiorganism rather than the more usual one organism experiment) of the system may be responsible for the variation. The number of samples per replication did not greatly influence variability, but an increase in the number of replications may improve the reliability of the results.

Despite the variability in results, the ecosystem is a useful tool for indicating the likely behavior of compounds in the environment.

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Dieldrin. Effects of Chronic Sublethal Exposure on Adaptation to Thermal Stress in Freshwater Fish

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■ The freshwater fish, *Etheostoma nigrum*, were pretreated with 2.3 ppb dieldrin for 30 days and then exposed to thermal stress, applied by heating the water at a rate of 1°C/hr to a maximum of 7–9°C above ambient temperature. Pretreated fish had significantly higher mortality than fish not pretreated with dieldrin but also exposed to the same thermal stress. Measurements of blood glucose, feeding, growth, oxygen consumption, opercular movement, whole body lipid content, and liver condition were made throughout the experiment. Pretreated fish demonstrated significant changes in all of the above parameters except opercular movement during the first 15 days of exposure to dieldrin. After 15 days, pretreated fish were found to have adapted to dieldrin exposure, as indicated by significant reversals of the above changes (except for liver damage, which was not reversed but progressed over time). In the adapted state, the pretreated fish remained different from untreated fish, in terms of these parameters. These differences provide grounds for predicting differential response to sublethal thermal stress for the pretreated and untreated fish. Such response is discussed as it may relate to the effects of chronic sublethal exposure to dieldrin.

The toxicity of a compound to organisms has been shown to be changed by alterations in the organism's environment. Increases in water temperature, for example, lower the LC_{50} of insecticides and ionizing radiation for aquatic organisms (Macek et al., 1969, Blaylock and Mitchell, 1969). The effect of exposure to a specific toxicant on the susceptibility of organisms to environmental change has not been extensively studied. In one experiment, pretreatment with ABS (alkyl benzene sulfonate) detergent did not affect the abilities of bluegills (*Lepomis macrochirus*) to survive increases in water temperature (Cairns and Scheier, 1964). In another study, pretreatment with DDT potentiated the effects of lowered water temperature on brook trout (*Salvelinus fontinalis*), demonstrated by a rise in the temperature at which cold block occurred (Anderson and Peterson, 1969).

Knowledge of the interactions between intoxicating compounds and environmental change is important for predicting the effects of altering ecosystems already containing xenobiotic compounds. Organochlorine insecticides are probably the most extensive and persistent additives to the world environment (Miller and Berg, 1969; Rudd, 1966). The general nature of insecticide toxicology (O'Brien, 1967; Kraybill, 1969) suggests that chronic exposure to insecticides may indeed be equivalent to pretreatment for many organisms, including perhaps man (USDHEW, 1969; Deichmann and MacDonald, 1971).

To investigate the concept of insecticide pretreatment and its interactions with subsequent environmental changes, the following study was conducted. A fish population was pretreated by exposure to the cyclodiene organochlorine insecticide dieldrin (hexachloroepoxy-*endo,exo*-dimethanonaphthalene). The level of exposure used was well below the mean lethal concentration for the species of fish studied and within the range of dieldrin residues detected in United States watersheds (Henderson et al., 1971). After 30 days of dieldrin exposure, the fish were exposed to sublethal thermal stress, at a rate and amount within natural fluctuations for the watershed from which they were collected. The thermal change exerted was within the limit of 10°C above maximum ambient levels suggested by the U.S. Department of Interior in 1968 (USDI, 1968).

Experimental

Two experiments were run, one in June and one in September 1971. Mature darters (*Etheostoma nigrum*) were selected from fish captured by seine in the White Clay Creek in southern Chester County, Pennsylvania. The darter is a small Percid, weighing at maturity between 1.5 and 6.0 grams, with habitat preference and tolerance of environmental change similar to those of brown trout and other important freshwater fish (Love, 1970). Organochlorine insecticides are not known to have been used on the watershed of the upper White Clay Creek for at least four years, largely because of cooperation by local residents with the ecological research of the Academy of Natural Sciences of Philadelphia. The organochlorine insecticides —lindane, *o,p'*-DDD, *o,p'*-DDE, *p,p'*-DDD, *p,p'*-DDE, and *p,p'*-DDT—were detected in stream water samples analyzed with electron capture gas chromatography, but the total concentrations of all these insecticides was below

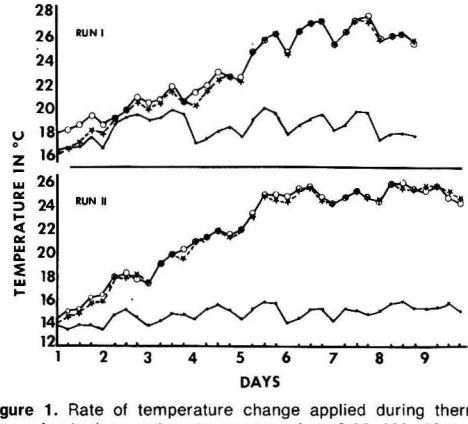

Figure 1. Rate of temperature change applied during thermal stress for both experiments, measured at 8:00 AM, 12 noon, 4:00 PM, and 8:00 PM every day

Lower solid lines and closed circles indicate water temperature of untreated, unstressed groups; upper solid lines and open circles, water temperature of thermally stressed untreated groups; dotted lines and stars, water temperature of pretreated stressed groups

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Table I. Water Temperatures in White Clay Creek for 1971[a]

Month	Day	Minimum	Maximum
May	1	7.0	16.9
	10	9.8	18.9
	20	13.0	19.5
June	1	11.6	18.7
	10	14.2	20.9
	20	15.2	20.4
July	1	17.9	22.9
	10	17.4	22.5
	20	16.7	19.4
August	1	17.8	21.3
	10	16.8	21.8
	20	15.8	20.1
September	1	15.7	17.5
	10	17.2	20.3
	20	16.7	19.1

[a] Recorded continuously at the site where most of the fish used in this research were collected.

Table II. Comparison of Mortality Rates by Treatment

	Deaths/total population/days	
Treatment	Experiment I	Experiment II
Controls[a]	17/120/30	13/120/30
Dieldrin	23/60/30	21/60/30
Thermal stress	4/20/10	2/25/10
Dieldrin and thermal	15/18/10	12/16/10
Controls[b]	1/22/10	2/24/10

[a] During days 1–30. [b] During thermal stress period.

1 ppb at any one time. Fish from the creek contained residues of lindane, dieldrin, DDT, and its analogs. The residue levels were similar to those found in fish from nonagricultural watersheds throughout the United States (Henderson et al., 1971; Morris and Johnson, 1971).

In each experiment, 180 fish were selected and randomly divided into 3 equal groups: fish exposed to dieldrin, fish not exposed to dieldrin but exposed to thermal stress, and fish not exposed to dieldrin or thermal stress. The experimental design partitioned out the effects of confinement and experimental handling from effects of the insecticide and thermal stress. Each group of fish was subdivided into 2 subgroups and held in tanks filled with recirculated stream water. The tanks were made of marine plywood sealed with three coats of Fiberglas. The design provided a riffle area by means of a 3-ft inclined plane and a pool in a 1 × 2-ft area. The amount of water per fish was 10 liters. Except for the addition of insecticide and thermal stress, all parameters of water quality—trace metals, pH, nitrogen, temperature, and dissolved oxygen —were the same for all groups and the same as the White Clay Creek. Dissolved oxygen concentrations were always at saturation. Fish were fed live caddisfly larvae collected daily from the White Clay Creek. Stomach analyses of wild darters had shown caddisflies to be the major part of their diet. Food was supplied at 3% of the biomass in each subgroup, which has been found to support average growth rates estimated for the species (Silbergeld, 1972).

Sixty fish were exposed to a mean concentration of 2.3 ppb dieldrin (range 2.0–4.0 ppb), less than one-fourth the LC_{50} for the species (96-hr test) (Silbergeld, 1972). Concentrations were monitored every other day by gas chromatography; the day-to-day variation was attributed to adsorption onto surfaces and to uptake by algae and fish in the tanks. Technical grade dieldrin was dissolved in pesticide quality acetone and added to the water. Controls were exposed to equal amounts of acetone only. After 30 days, the exposed fish and one group of 60 unexposed fish were subjected to increases in water temperature. Thermal stress was applied at a rate of 1°C a day, with fluctuations following natural diurnal variations (Figure 1). Total increase in water temperature was about 7°C above ambient for the White Clay Creek. Temperature variation for the Creek during the summer and fall of 1971 is shown in Table I. On several occasions, water temperatures increased over 9° in one day, and the diurnal temperature pulse during the summer is usually about 5°C (Vannote, 1971). Experimentally elevated temperatures were maintained for four days after achievement of maximum elevation. The experiments were terminated on the tenth day of thermal stress to retain live fish in all groups for the analyses described below.

Several indicators of metabolism and condition were measured during the pretreatment period, after the application of thermal stress, and at the end of the experiments. These were: growth rate, measured every 5 days as percent change in weight; feeding rate, the proportion of food provided which the fish ate during the same 5 days; whole blood glucose levels, measured every 5 days by a micromodification of the method of Chavin and Young (1970); oxygen consumption by the live fish, measured every 10 days; rate of opercular movement, measured in conjunction with oxygen consumption; whole body lipid content, measured every 5 days by an adaptation of the method of Dambergs; condition of the liver, defined as the ratio of liver weight to whole body weight; and liver histology, the incidence of hemorrhage, pyknosis, necrosis, and lipidosis.

Results

The incidence of mortality by comparison of mortality rates clearly shows the impact of dieldrin on the ability of fish to survive thermal stress (Table II). During the pretreatment period, an average of 12.5% (13–17) of control fish died in both experiments. This mortality may be attributable to confinement and possibly to a diet restricted to caddisfly larvae. During the same period, 36.7% (21–23) of the fish exposed to dieldrin died. This is only slightly higher than the number expected from prior tests for LC_{50}. During the 10 days of thermal stress, 4.4% (1–2) of control fish died. The decline in control mortality from the first 30 days probably results from adjustment to experimental conditions. During thermal stress, 13% (2–4) of the fish exposed to thermal stress died. This is not significantly different from the mortality of the group during the first 30 days. It is, however, significantly higher than the mortality for the controls during the same period. Finally, of the fish pretreated with dieldrin and then exposed to thermal stress, 76.5% (12–15) died during the time they were subjected to thermal stress. The mortality of this population was significantly higher than either that of the same group exposed only to dieldrin or that of the group exposed only to thermal stress.

The time course of deaths is important in understanding the results of the measurements mentioned above. During the pretreatment period, the incidence of mortality is shown in Table III. Nearly half the deaths in the pretreated group (43.5% in the first experiment and 52.4% in the second) occurred between days 11 and 15.

Between days 11 and 15, the greatest alteration occurred in many metabolic and condition measurements of pretreated fish. Whole blood glucose levels peaked at day 10 (Figure 2). By day 15, the levels of blood glucose in

Table III. Comparison of Incidence of Mortality, Days 1 Through 30, for Pretreated Fish and Controls

	Number dead						
	Days						
Treatment	1–5	6–10	11–15	16–20	21–25	26–30	Total
Controls, Experiment I	2	2	4	4	3	2	17
Experiment II	1	2	1	1	2	6	13
Dieldrin, Experiment I	0	4	10	0	3	6	23
Experiment II	2	4	11	3	1	0	21

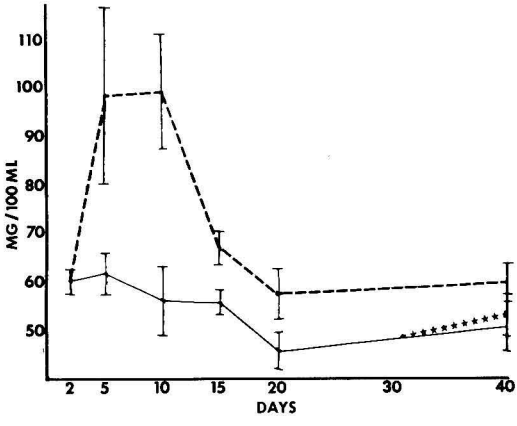

Figure 2. Means and standard deviations of blood glucose levels, in mg/100 ml

Solid line indicates controls; dotted line, fish pretreated with dieldrin; starred line, fish exposed to thermal stress with no pretreatment

pretreated fish fell to approximately initial levels for all fish. The mean level of the pretreated fish was still significantly higher than the mean for controls. Blood glucose levels in controls declined over the experiment toward the mean of 37 mg/100 ml found in wild fish. The elevation in initial values probably resulted from the stress of confinement, as fish have the same adrenal-pituitary-glucocorticoid stress reaction as mammals (Chester Jones, 1960). The biphasic pattern of response to dieldrin was also seen in oxygen consumption. Until day 15, pretreated fish consumed significantly less oxygen per gram of body weight than did controls. After day 15, the consumption of oxygen by pretreated fish increased, but remained significantly different in slope and intercept from the consumption of oxygen by controls (significance determined by comparison of correlation coefficients, mg oxygen consumed/gram of fish/hour regressed against the whole body weight of the fish; all differences significant at $p < 0.005$). Growth and feeding measurements also demonstrated that the period between days 11 and 15 represented an important change in the response of the fish to dieldrin. After day 15, exposed fish ate 75% of the food offered. Control fish maintained the initial feeding rate for all fish of 92%. Exposed fish gained over 50% of their total weight gain during days 15–30, while controls gained about 20% of the amount gained by exposed fish. Control fish showed no difference in weight change patterns before and after day 15. Body lipid composition showed a related pattern: pretreated fish surviving days 1–15 had a mean lipid content of 1.76% of total body weight, while those surviving the remainder of the experimental period had a mean lipid content of 5.18%. The condition of livers and liver histology showed a consistent trend toward enlargement and pathology. The degradation in liver condition was first seen on the fifth day of dieldrin pretreatment and was not reversed.

The thermal stress used in this study was below the lethal dose in rate of application and maximum elevation. However, unexposed fish were affected, as were the exposed fish. First, the stress produced an increase in mortality over that for controls during the same period, 13% as compared to 4.4% of the controls. Second, fish exposed to thermal stress had blood glucose levels slightly higher than those of controls (Figure 2). This difference, however, was not significant; only the difference between pretreated and control fish was significant. Third, fish exposed to thermal stress had depressed mean whole body lipid content, 3.1% of body weight as compared to 5.3% in controls. Fourth, thermal stress caused an elevation in oxygen consumption. Fish pretreated with dieldrin and thermally stressed fish had elevated oxygen consumption compared to controls. Fish not pretreated with dieldrin responded to thermal stress more sensitively than did pretreated fish.

Discussion

The results suggest that adaptation to low-level chronic dieldrin exposure is achieved by fish only at the cost of flexibility in the face of general environmental stresses. Over 75% of the fish pretreated with sublethal amounts of insecticide did not survive exposure to sublethal increases in temperature.

Changes in indicators of metabolism and condition provide a basis for predicting this disability. Pretreated fish showed an adjustment, in terms of metabolic responses, to dieldrin exposure after 15 days. They remained significantly different from unexposed fish in levels of blood glucose, oxygen consumption, feeding, growth, and lipid content. Damage to the livers of exposed fish, on the other hand, increased without remission over the experiment. This is consistent with many types of toxicant-induced liver injury, which are cumulative over the period of exposure (Jubb and Kennedy, 1970; Harr et al., 1970).

The precise mechanism of cyclodiene organochlorine insecticide toxicity is not known (O'Brien and Yamamoto, 1970). Recent work has shown that dieldrin affects ATPases (Cutkomp et al., 1971), electron transport systems (Colvin and Phillips, 1968), smooth endoplasmic reticulum (Hutterer et al., 1968), serum glutamic oxaloacetic transaminase (Lane and Scura, 1970), and nerve endings (Matsumura and Hayaishi, 1966).

The means by which fish adapt to changes in water temperature have been extensively studied (Fry and Hochachka, 1970; Moon, 1970). Because fish are relatively unable to maintain core temperatures different from environmental temperature, adaptation to thermal change involves the existence of flexibility in metabolism. Specifically, temperature acclimation in fish is known to involve changes in the optimal temperature for enzyme-substrate affinity in a number of important enzyme-isozyme systems. Accommodation of chronic dieldrin exposure by fish may affect the flexibility required for acclimation to temperature change. For example, the ability to change oxygen consumption in response to changes in water temperature is an important part of metabolic adjustment in fish (Moon, 1970; Beamish and Mookherjii, 1964). Dieldrin depressed the amount of oxygen consumed in this study. Under thermal stress, fish not pretreated with dieldrin increased oxygen consumption and survived. Pretreated fish

did not increase oxygen consumption in response to thermal stress as much as unexposed fish did. The indications are that the response of fish oxygen metabolism to thermal change was impaired by dieldrin pretreatment. Unexposed fish, stressed thermally, depleted stores of body lipids and survived; pretreated fish, with already lowered body lipid stores, may not have had equivalent amounts of expendable lipids to meet increases in metabolic demand due to thermal stress. Damage to the liver from dieldrin pretreatment may have affected many pathways of metabolism, upon which thermal stress placed additional demands. The effects of dieldrin on the ability of fish to change isozymes optimally in response to temperature change is not known (Fry, 1971) but may play a significant role in reducing adaptability which involves isozyme substitution.

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Portable Continuous Chromatographic Coulometric Sulfur Emission Analyzer

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■ An instrument capable of automatic continuous quantitative analysis of sulfur compounds in stack gases has been developed and tested for a one-month period in a kraft paper mill. The instrument is portable and uses a chromatograph column for separation and a bromine titration cell for detection of the sulfur compounds. Gas samples can be analyzed for SO_2, H_2S, and CH_3SH once every 10 min. Concentrations of 0.1 ppm for CH_3SH, 0.2 ppm for H_2S, and 1.0 ppm for SO_2 can be detected. A multistack sampling accessory for the unit has been built and successfully tested.

Several articles have been published (Blosser and Cooper, 1968; Thoen et al., 1968; Walther and Amberg, 1970; Sarkenen et al., 1970) proposing means of reducing sulfur emissions from the recovery operation. Regardless of the method used, the stack gases must be analyzed to determine the effectiveness of the measures taken. There are many ways of analyzing stack gases (Adams, 1967; Kessler, 1969; Walther and Amberg, 1967). The trend has

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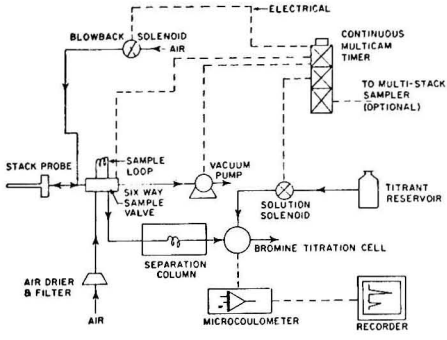

Figure 1. Sampling system schematic

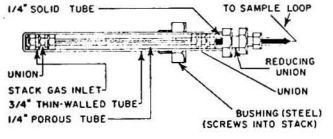

Figure 2. Stack sampling probe

been toward coulometric titration cells. This technique uses electrolytically generated bromine to react with, and give a measure of, sulfur compounds in gaseous effluents. The coulometric detectors offer specificity, sensitivity, and capability for long-term continuous readout.

If effects of operating variables on pollutant levels are known, steps can be taken to adjust them to minimize emissions. The primary problem then becomes development of a continuous analyzer to get the necessary emission data. Portability of the analyzer should be a prerequisite; reasonable cost a desirable goal.

Development of Continuous Sulfur Analyzer

Design of Instrument. The two major problems in the design are the separation technique to be used and the type of detector to be employed. Various possibilities for each of these items have been discussed in the literature (Adams, 1967; Adams and Koppe, 1967; Adams et al., 1968; Kessler, 1969). Because chromatograph columns are simple in design and relatively maintenance free, one was chosen as the separation device. This was preferred over selective prefilters (Adams, 1967) (which require such items as additional valves to route the gas stream) or scrubbing solutions which are inherently cumbersome.

Recent literature articles indicate that the bromine titration cell and flame photometric detectors (Adams, 1967; Zado and Juvet, 1966) are the best of presently known detectors for sulfur compounds. Adams et al. (1968) have reported sensitivities in the parts-per-billion range for H_2S using the bromine titration cell. The flame photometric detector is slightly less sensitive to sulfur compounds and has the disadvantages of requiring precision optics and a supply for hydrogen. Portability considerations thus eliminated this type of detector. The schematic diagram in Figure 1 shows the layout of the chosen sampling system.

Operation. The sequence of events taking place during the analytical process is controlled by a continuous multicam timer set for a cycle time of 10 min.

The vacuum pump is switched on and draws a gas sample from the stack into a sample loop attached to a six-way linear sampling valve. Simultaneously, carrier gas is passing through a chromatograph column into the detector. Both the sample loop and column are in a constant temperature oven.

Six minutes later the vacuum pump is switched off, the six-way valve closes, and the carrier gas sweeps the gas sample into the chromatograph column. The column separates the various sulfur compounds and admits them one-by-one into the detector. The detector (plus associated electronics) will give a peak on a strip chart recorder for each sulfur compound passing through it. The area underneath a peak is directly related to the concentration of that compound. The area thus depends on the size of the sample being analyzed.

While a sample is being analyzed, two ports on the six-way sample valve are closed to any gas flow. This permits a blowback phase where compressed air is forced through the probe to clean off solid particles clinging to it and to blow out any water that may have condensed in the tubing between probe and instrument. This blowback lasts about 4 min during each cycle.

At the beginning of each cycle, a solenoid valve opens and allows a small amount of electrolyte (less than 1 ml) to flow into the detector.

Probe Design. Many of the gas streams to be analyzed in a kraft mill have a high solid content. This is particularly true of gases just out of the furnace before they are scrubbed. Any solid material entering either the chromatograph column or the detector would cause unpredictable but always undesirable results. The probe must allow no solids to enter the tubing to the instrument. (A separate glass wool filter is incorporated in the instrument itself as a safety feature.)

A design which has worked quite well is shown in Figure 2. This probe uses a ¼-in. o.d. porous (100-μ) stainless steel (316) tube as the filter media. Lengths will vary depending on the nature of the sampling port. The porous tube is encased in a thin-walled ¾-in. o.d. stainless steel tube. A ½-in. hole is drilled in the wall of the casing near the end of the probe to serve as the inlet for stack gases. This hole is pointed to the downstream side of the stack so that solid particles are not forced against the porous tube by the flowing stack gases. Connections to the instrument are made using ⅛-in. polypropylene tubing and nylon Swagelok fittings.

The uniqueness of the probe lies in maintenance requirements and easy adaptability to a wide variety of sampling ports. This particular probe design was less fragile than a porous ceramic unit purchased and used in the beginning of the study. It was also much easier to clean than the ceramic device and required less frequent cleanings—once every four or five days for the stainless probe vs. once each day for the ceramic unit. Glass wool was used as a filtering medium in earlier work and was even less satisfactory than the ceramic filter.

All parts of the probe are made from readily available materials. Consequently a probe of nearly any length can be constructed by plant personnel and fitted through small or large openings in a stack depending on local needs.

Separation Chamber. The column used in the plant test of the instrument was a ¼-in. Teflon tube filled with Porapak Q-S 100-120 mesh. The sample loop—a Teflon tube of about 10 ml volume—and column are both enclosed in an insulated chamber maintained at constant temperature by an on-off controller. Keeping the sample loop in the constant temperature chamber ensures that a reproducible amount of gas is always being analyzed.

Detection Cell. Because of its high sensitivity and selectivity for sulfur compounds, the bromine titration cell was chosen as the director for the analyzer being described.

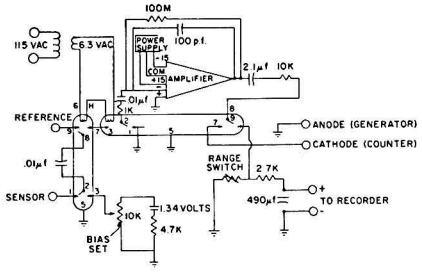

Figure 3. Microcoulometer schematic

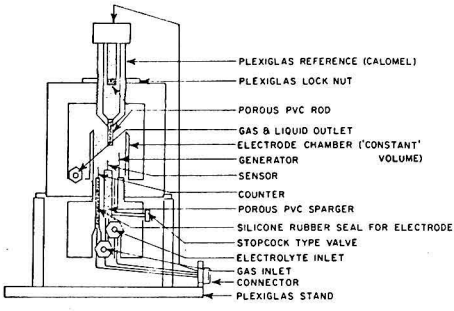

Figure 4. Mark VI detection cell

Sulfur gases separated by the packed column enter the detection cell through a porous (glass or polyvinyl chloride) rod. During in-plant tests, only SO_2, H_2S, and CH_3SH were analyzed. The primary overall electrochemical reaction for H_2S was taken to be:

$$4H_2O + 4Br_2 + H_2S = 8Br^- + SO_4^{2-} + 10H^+$$

with similar reactions occurring for SO_2 and CH_3SH. (Other later studies by the authors' associates have indicated the presence of elemental sulfur in very small quantities after prolonged use of a given amount of electrolyte.) The fact that the reported reaction may not be the only one occurring does not negate any of the results because performance of the detector was based on calibrations rather than calculations of voltages from the theoretical reactions. The change in bromine concentration gives a quantitative measure of the amount of sulfur compounds entering the cell. As soon as the bromine concentration changes, the change is a potential difference which is then an input to an amplifier of the microcoulometer. The amplifier instantaneously supplies a voltage to the generator/counter electrode pair. The balancing voltage supplied by the amplifier appears as a current-time peak on the recorder. Concentration of the sulfur compound entering the cell can be determined from the area under the peak. A circuit diagram for the microcoulometer used is shown in Figure 3. The amplifier was a solid state general-purpose model. The Range Switch was an external adjustment to attenuate the recorder response. The circuit is a simplified version of one used in an instrument sold by Dohrmann Instrument Co.

For a portable instrument possibly subject to rough treatment, a glass detection cell was considered undesirable. Different types and styles of cells were built. The most successful design—dubbed Mark VI—is shown in Figure 4. This cell was developed after the following observations were made:

Plexiglas was inert to all reactants involved, durable, easy to machine, and transparent. It was used for all parts of the cell.

Keeping all electrodes in the same compartment did not detrimentally affect the cell's performance. (The first models had the reference and counter electrodes in separate compartments.)

Good mixing in the electrode chamber was essential for reproducible results. This was best accomplished using a porous rod at the carrier gas entrance in the cell. External (e.g., magnetic) stirrers were ruled out because of the added cost and bulk.

A tall, thin electrode chamber was better than a short large diameter one because good mixing was nearly impossible to obtain in the latter. The electrode compartment in Mark VI was $^{11}/_{16}$-in. in diameter by 1-in. high.

Keeping the cell sealed (except for the gas outlet port) from the ambient air resulted in a large reduction of noise levels on the recorder.

Diameter of the platinum wire electrodes showed little effect on the cell's performance. This was somewhat puzzling, because changing the lengths did alter the detector's response. In general, shortening the electrode (to $^1/_8$-in.) reduced noise. A longer generator ($^3/_4$-1 in.) gave smooth rather than jagged peaks. Why changing diameters had no effect cannot be explained.

A calomel reference electrode was less sensitive to vibration than the $P_t|Hg\text{-}Hg_2Br_2$ reference suggested in several literature sources. A commercial-type calomel reference is preferred over the type shown in Figure 4.

Using a concentric cylinder arrangement in Mark VI eliminated the problems of condensed vapors on the cell walls falling back into the electrode chamber and causing high noise levels.

Properly dried and filtered compressed air could be used to replace nitrogen as a carrier gas. No change in cell response was detected when the change was made.

Adding about 1 ml of electrolyte during each 10-min cycle was sufficient to keep the cell's performance stable for the entire five week in-plant test period.

Lower detection limits for the instrument using a sample size of 70 ml and no separation column were about 0.1 ppm for CH_3SH, 0.2 ppm for H_2S, and 1 ppm for SO_2.

Recorder. Inexpensive noncontinuous, low-impedance recorders were tried but proved unsatisfactory because they overloaded the microcoulometer circuit. The noncontinuous trace made data interpretation quite difficult. A small potentiometric recorder with a continuous trace is essential.

Calibration Device. Several devices are available for preparing gas samples of low concentrations. These include Mylar bags, spinning syringes, screw-driven syringes, and permeation tubes. For the concentration ranges of interest in the study, the spinning syringe was felt to be most satisfactory. A fan was used as the air source for spinning the syringe. This ensured a constant spinning rate from one use to the next; thus the plunger would fall at a constant rate and give reproducible concentrations each time.

Plant Tests

After the instrument had been built and successfully tested in the laboratory, it was taken to a kraft paper mill for some in-plant tests on a recovery furnace firing unoxidized black liquor and using a direct contact venturi evaporator for final black liquor concentration.

A multistack sampler was operated successfully for about 18 hr. Despite the shortness of this test, it did demonstrate that the idea was sound. Basically the multistack sampler consists of three midget two-way solenoid valves (if set up for three stacks) plus a 24-position stepping

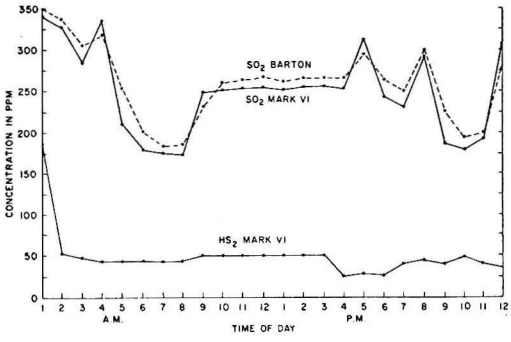

Figure 5. Comparison with a Barton titrator

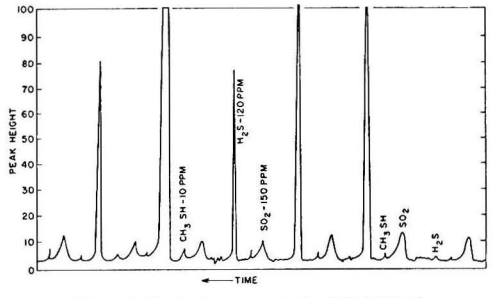

Figure 6. Recorder response for 1-hr interval

relay switch. The unit merely "plugs in" to the main analyzer. A cam timer in the main unit activates the rotating switch once during each cycle. This switch then opens one and only one of the midget valves. It remains open for one complete cycle—i.e., for both the sample drawing and blowback phases. At the beginning of the next cycle the switch advances and a different solenoid valve opens and the previous one closes. Note: When sampling from three different locations, a sample will be extracted from a given stack only once every 30 min—assuming the cycle time is still set for 10 min.

The three points sampled were just before the black liquor venturi scrubber, after the venturi scrubber, and after the secondary brine scrubber. During the test period only the gases before the black liquor venturi were analyzed simultaneously by the Mark VI and by the commercial Barton coulometric titrator, used in many paper mills throughout the country. The sample stream to the Barton was first passed through scrubbing solutions to remove H_2S and any mercaptans. A comparison of the results for the two titrators is shown in Figure 5. Notice that only SO_2 was measured by the Barton whereas both H_2S and SO_2 were detected in the Mark VI. Data points shown are somewhat "smoothed" for both analyzers. Each Mark VI data point represents a simple average of six samples (each 10 ml in volume) analyzed in a 1-hr interval. The Barton data were time-averaged readings of a continuous trace over the same hour interval. These averaging procedures account for some of the discrepancies in the values shown.

The only serious shortcoming of the instrument being described can best be explained by examining Figure 6. Although H_2S and SO_2 levels were about the same, H_2S peak areas were much larger. This was caused by SO_2 absorption on the packing material. As a result, in areas of high H_2S (>200 ppm) concentration, detector output had to be attenuated to keep these peaks on scale. This meant that SO_2 concentrations as high as 25 ppm in the same sample might go undetected.

The solution to this problem requires support material which does not absorb SO_2. Stevens et al. (1969) reported that a packing material of poly *m*-phenyl ether on a powdered perfluoroethylene support was satisfactory for separations in the parts-per-billion range. At the time of this study such a column was not commercially available, and attempts to fabricate one were unsuccessful.

Conclusions

The portable continuous chromatographic sulfur analyzer developed in this study successfully survived a five-week plant site test even though the instrument was near the venturi scrubber and subject to rather harsh weather conditions at times. It easily separated the H_2S and SO_2 in concentrations found in the stack gas. Periodically some CH_3SH peaks appeared on the recorder. The only maintenance required was replenishing the recorder chart paper from time to time, cleaning the probe every four or five days (if in high solids content area), and filling the electrolyte reservoir every three or four weeks. After three weeks of continuous use the instrument was recalibrated. The curves for both SO_2 and H_2S agreed within ±5% with the initial calibrations. This reproducibility and reliability were significantly better than the Barton cell in use during the same test period. Cell sensitivity was, however, not so good as the Barton for concentrations below 10 ppm.

The main improvement needed is a different separation column which does not absorb appreciable amounts of SO_2. H_2S and SO_2 samples of the same concentration will then give more nearly equal peak areas.

The analytical system described in this report was housed in a wood paneled cabinet with the recorder built in. It measured 24 × 30 × 18-in. and weighed less than 50 lb. Materials cost, including the recorder and probe (but excluding the vacuum pump), was about $2000. The three-stack sampling accessory cost $200 in parts and could be connected in about 5 min to the instrument shown. It was also housed in a wooden cabinet measuring 12 × 18 × 4 in. and weighed under 10 lb.

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NOTES

Leaves as Source of Phosphorus

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■ Oak and poplar leaves were leached with distilled water in laboratory columns to simulate the release of soluble phosphorus (P) forms to urban runoff. Most of the soluble phosphorus leached was reactive in a molybdenum blue analysis. The leaves tested yielded 54–230 μg P/g of leaves. Consecutive leachings of an oak leaf sample yielded soluble P in amounts related to the effective soaking period between leachings and to the number of preceding leachings. Cut up leaves released almost three times as much soluble P as intact leaves. Leaves collected from the littoral zone of Lake Mendota leached less P than control leaves collected on the shore nearby. The moisture retained on leaves after a rainstorm contained significant soluble reactive P. The results of this investigation point to the importance of proper leaf pickup and control in order to minimize the phosphorus content of urban drainage during the fall of the year.

Recent studies by Kluesener (1971) on the nutrient sources for Lake Wingra, Madison, Wis., have shown that urban land runoff transported 0.57 lb of P/acre/year of dissolved reactive P and 0.98 lb of P/acre/year of total P to the lake. The runoff contained unusually high levels of dissolved reactive P in November and May. The high May level was attributed by Kluesener to the leaching of tree seeds and flowers in the streets by runoff water; lawn and garden fertilizer applications in the spring were discounted because they were applied on pervious surfaces where runoff yields were negligible. The high November levels were thought to result from the leaching of piles of leaves in street gutters by the runoff.

The concentrations of phosphorus found by Kluesener (1971) for urban drainage in Madison were similar to those found by Weibel et al. (1964) for Cincinnati, Ohio. Storm water runoff in Cincinnati carried a total soluble phosphorus load of 0.94 lb of P/acre/year (Weibel, 1969). The potential significance of plant materials as a source of phosphorus in runoff waters has been investigated by Timmons et al. (1970). They found that plant materials such as alfalfa or bluegrass may contribute significant amounts of phosphorus to agricultural runoff. This report presents the results of a follow-up study to assess the potential of leaves as a source of phosphorus to urban runoff.

Experimental Procedures

Initial studies were made on oak and poplar leaves collected from Madison, Wis., in October 1971. Later studies were performed on oak leaves collected in November 1971; these samples were collected on the shore of Lake Mendota or from the nearby littoral zone on the lake, under the water. The sample collected on shore was split into two groups, one for a consecutive leaching experiment with intact leaves, the other for a leaching study with cut up leaves. Oak leaves were also collected in November after a rainstorm (12 hr before collection), so that the leaves were still moist.

Leaf samples were leached by soaking the leaves in glass chromatography columns for 1 hr. in 250–300 ml of distilled water, followed by percolation of 700–750 ml of distilled water through the column. The water volume was maintained at 250–300 ml in the columns during the percolations. After 1.5 hr of percolation at about 8.4 ml/min, the columns were drained into the effluent collection vessels to give a total leachate volume of 1000 ± 60 ml. Rain-soaked leaves were washed quickly (3–4 min) with 300 ml of distilled water in a column to collect the surface moisture from the leaves without additional leaching by the wash water.

Leaf leachates were analyzed for color with a Hellige Aquatestor. Phosphorus was determined after filtration through a 0.45-μ pore size Millipore filter. Dissolved reactive P was measured colorimetrically with the John (1970) modification of the Murphy and Riley molybdenum blue procedure, and total soluble P was measured by the same method after persulfate digestion (Standard Methods, 1971). Soluble unreactive P was computed by the difference between total soluble and dissolved reactive P. Total P in leaf tissue was measured following nitric acid predigestion and nitric-sulfuric-perchloric acid (10:1:4 by volume) digestion.

Results

Table I shows the yield of soluble P leached from oak and poplar leaves collected in October 1971. Although the two types of leaves released different percentages of their total P to the water, the compositions of soluble P forms in the leachates were approximately the same for both types. Soluble unreactive P was 14% of total soluble P from poplar leaves and 18% of total soluble P from oak leaves.

The results from consecutive leachings of a November

Table I. Soluble P Leached from Oak and Poplar Leaves

Leaves	Soluble P leached, μg/g of leaves			Soluble total P leached % total P in leaves
	Reactive	Unreactive	Total	
Oak[a]	44	10	54	5.4
Poplar[b]	120	20	140	21

[a] 7.86 grams, air-dry wt; leachate vol 960 ml; total P in leaves, 1000 μg/g.
[b] 9.32 grams, air-dry wt; leachate vol 950 ml; total P in leaves, 675 μg/g.

Table II. Consecutive Leaching of Oak Leaves

Leaching no.[a]	Soaking period prior to percolation, hr	Leachate color, units	Soluble P leached, μg/g of leaves	
			Reactive	Total
1	1	15	230	230
2	2.5	15	160	160
3	22.5	30	270	270
4	1	5	74	74

[a] 7.47 leaves, oven-dry wt; leachate vol: no. 1 = 1007 ml; no. 2 = 1055 ml, no. 3 = 1000 ml, no. 4 = 1000 ml.

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1971 oak leaf sample are given in Table II. No soluble unreactive P was found in any of the leachates. Soluble P yields were high in the first leaching and also in the third leaching, which had a long soaking period before it. The second and fourth leachings, which had relatively short soaking periods, yielded less phosphorus than did the other two leachings. Even though the first and fourth leachings had the same soaking period, the fourth showed significantly less phosphorus release. Apparently, the pool of leachable phosphorus had been reduced by the three previous leachings. Leachate color appeared to be somewhat related to the soluble phosphorus yields.

Oak leaves collected from the littoral zone of Lake Mendota leached relatively small amounts of soluble P compared to the control leaves collected on the shore nearby (Table II, leaching no. 1). Table III shows the yields from duplicate leachings of the Lake Mendota leaves, which might have been soaking for as long as a month in the lake water. A total soluble P range of 88–99 μg P/g of leaves was found, compared to 230 μg P/g for the control sample. The soluble unreactive P was probably not significant.

In contrast to the Lake Mendota leaves, oak leaves cut into small pieces leached 650 μg P/g of leaves, almost three times the level for intact leaves (230 μg P/g). All the soluble phosphorus leached from the cut leaves was reactive P. The leachate color was 180 units from the cut leaves, compared to 15 units from the intact leaves (Table II, leaching no. 1).

Wet oak leaves collected in November after a rainstorm contained 23 μg P/g of leaves as dissolved reactive P in the layer of moisture retained on their surfaces. The leaves had been soaking in their surface moisture for about 12 hr prior to collection.

Discussion

The column percolation procedure simulates conditions in nature where leaves are leached by precipitation for 2.5 hr. The resulting surface moisture on the leaves contains extracted soluble reactive phosphorus which can be carried away by overland flows of runoff. The concentrations of soluble P in the runoff should decrease as the number of antecedent leaching events increase, as demonstrated by leachings no. 1 and no. 4 in Table II. The concentration of soluble P in the runoff should be increased as the length of antecedent soaking periods increases, as shown by leaching no. 3 in Table II. In addition, any physical damage to the leaves would tend to increase their contribution to runoff phosphorus loads. Exposure of vein surfaces by cutting the leaves was shown to result in large amounts of leachable P compared to tests with intact leaves. Timmons et al. (1970) reported that the drying and freezing of bluegrass or alfalfa greatly enhanced the release of soluble P in laboratory leaching studies similar to those presented here. The burning of leaves in street gutters would be an extreme case of physical damage, and this treatment would be expected to result in almost quantitative yields of total leaf phosphorus to runoff.

Table III. Leaching of Lake Mendota Oak Leaves

Sample	Leachate color, units	Soluble-P in leachate, μg/g of leaves		
		Reactive	Unreactive	Total
A[a]	20	84	4	88
B[b]	25	97	2	99

[a] 3.29 grams, oven-dry wt; leachate vol = 990 ml.
[b] 4.66 grams, oven-dry wt; leachate vol = 1000 ml.

It is clear that even intact leaves may potentially fertilize many liters of runoff water above the critical concentrations of phosphorus often cited as causing excessive growths of algae or aquatic plants in natural waters. The results of these studies may be of particular importance to the urban environment since they may account in part for the relatively high concentrations of phosphorus found in urban drainage (Weibel, 1969; Kluesener, 1971). Tree seeds may also contribute to the high concentrations; preliminary leaching studies with elm seeds by the procedures given above showed that 350 μg P/g dissolved reactive P, 70 μg P/g dissolved unreactive P, and 420 μg P/g total soluble P was leached from seeds containing 5100 μg P/g total P.

It is apparent from these results that municipalities should initiate a program of rapid leaf pickup during the autumn leaf litter period in order to minimize nutrient transport to lakes and streams from urban runoff. Burning and storing of leaves in the gutter prior to pickup should be prohibited. Property owners should store leaves and other plant debris in such a way as to avoid contact with precipitation which could ultimately result in urban runoff.

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INDUSTRY TRENDS

The Ben Holt Co. (Pasadena, Calif.) has been awarded a $115,000 contract by EPA to prepare a manual to serve as an air pollution field surveillance and enforcement guide for petroleum refineries and natural gas processing plants.

Baker Commodities, Inc. (Los Angeles, Calif.) has purchased a majority interest in Pollution Control Engineering, Inc. of Downey, Calif. Baker Commodities is a rendering firm, and Pollution Control Engineering specializes in engineering and installation of water treatment systems.

American Air Filter Co., Inc. (Louisville, Ky.) has signed an agreement to acquire General Dynamic's Dynapure oil mist collector line for cash. Dynapure products are designed for collecting unwanted mist from individual process machines in the metal, food, and textile manufacturing industries. Sales of Dynapure products are less than $1 million annually.

Neptune Meter Co. (Atlanta, Ga.) has acquired Del-Pak Corp. (Corvallis, Ore.), a marketer of waste water treatment equipment. Purchase was in exchange for Neptune common stock. Del-Pak will be integrated into the operations of Neptune Micro-FLOC, Inc.

SCA Services, Inc. (Boston, Mass.) has been awarded a four-year, $2.5-million waste service contract by the city of Fort Pierce, Fla. Beginning this October, SCA will collect all of the residential and commercial waste generated by the city's 35,000 people.

Arthur G. McKee & Co. has been awarded a multimillion dollar contract by Kennecott Copper Corp.'s Utah Div. for pollution control facilities at Kennecott's Utah smelter plant in Magna, Utah. The environmental control effort poses several technical challenges since the plant has a variety of emission sources amidst mountainous terrain coupled with frequent downdrafts. In addition, work must be scheduled to permit the smelter to remain in operation during the construction phase of the project.

Combustion Engineering, Inc. has been awarded a $16-million contract to design, fabricate, and erect a 450-MW steam generator by Columbus and Southern Ohio Electric Co. The unit will be designated generator 6 in C&SOE's Conesville, Ohio, generation station. The unit, scheduled to begin operation in 1977, will burn pulverized coal and generate in excess of 300 million lb of steam/hr.

Columbia Cement Co. has completed installation of electrostatic precipitators for the control of particulate emissions at its Zanesville, Ohio, portland cement plant. Precipitators replace mechanical particulate collections devices installed in 1958. The $2.3 million project began 18 months ago.

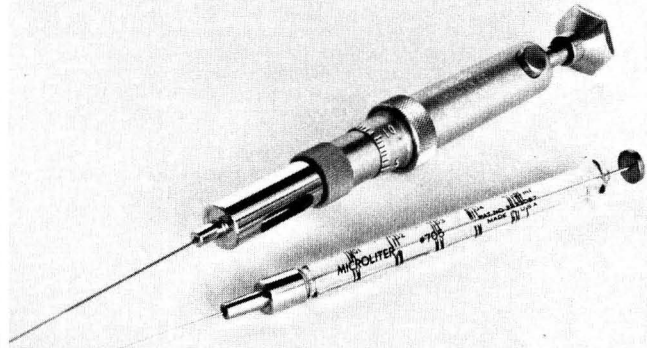
Dearborn Chemical Div., Chemed Corp., has organized Environmental Assessment Associates to provide environmental impact studies. The organization consists of a network of scientific teams qualified to make in-depth studies and environmental assessments of engineering projects for consulting engineers, governmental bodies, and conservation groups.

Roy F. Weston, Inc. and Hach Chemical Co. have agreed in principle to merge Weston and Stack, Inc., into Hach for an undisclosed amount of cash. Hach will be purchasing the assets and assuming liabilities of the business, including the lease obligation for the present operating facilities in Malvern, Pa. Weston and Stack has sales of approximately $600,000 for the year ending December 31, 1972.

International Plastics, Inc. (Colwich, Kan.) has formed a new company, Micro-Por, Inc., as a wholly owned subsidiary to manufacture and market its patent-protected microporous tubing, sheet, and rod from thermoplastic material. Products are used in reverse osmosis and water treatment, aeration, and oxygenation.

Wilputte Corp. (Pittsburgh, Pa.) has been awarded a contract in excess of a million dollars for engineering and materials supply for a waste effluent control system to be installed at the Coke Oven Div. of Bethlehem Steel Corp.'s Sparrows Point, Md., plant. The process will use a closed recirculated wash oil system to cool coke oven gas, thereby eliminating the discharge of contaminated salt water. The facility is expected to be operational by spring of 1974.

Syringes for your carbon analyzer



We've designed two syringes to introduce samples into a carbonaceous analyzer. The special metal luer fits the inlet perfectly. Both are 50 μl capacities, one has a push-button action with spring-loaded plunger. Write for literature to Hamilton Company, P.O. Box 17500, Reno, Nevada 89510.

HAMILTON

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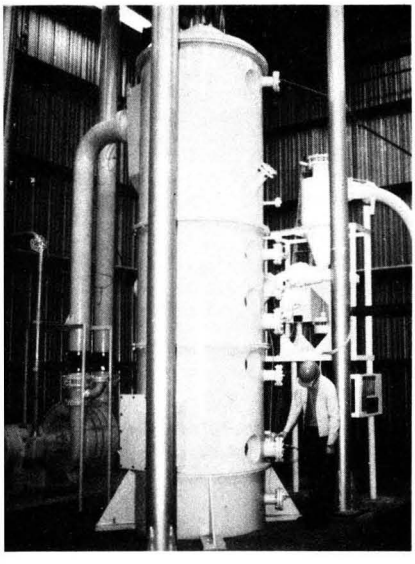
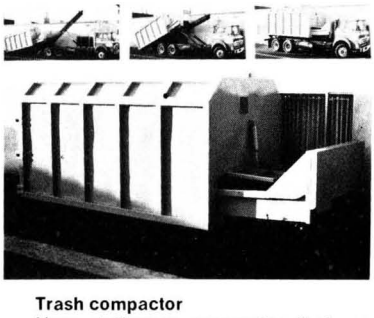
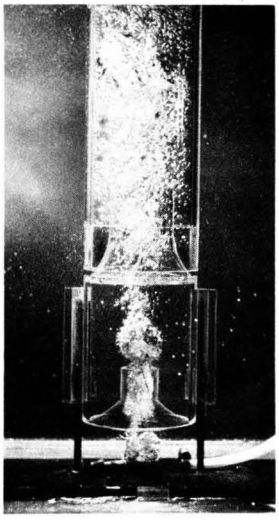
NEW PRODUCTS



Sludge disposal unit
LSW system uses solid waste as a fuel to dispose of undewatered sewage sludge. It can also use conventional liquid fuels or coal to supplement combustion of dewatered sewage sludge. The unit incorporates a fluid bed combustor coupled with a hot, dry gas cleanup system. Units are available in six sizes. Combustion Power Co., Inc. **101**



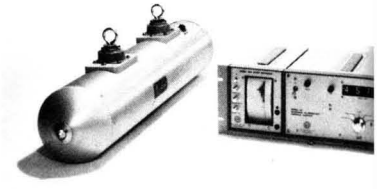
Trash compactor
New stationary compactor features built-in compactor instead of traditional separate roll-off container. Rugged and lightweight, it requires little janitorial or mechanical maintenance, and is installed with a weather-proof power unit. It is available in several models of different cubic yard capacities. Mexon Industries, Inc. **102**

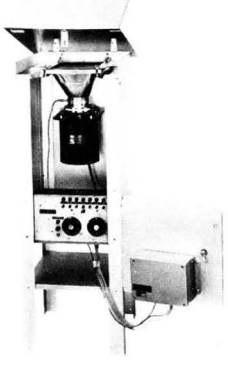


Waste water treatment system
New, high-efficiency aerobic waste water treatment system, known as the Atara-Cascade Method, incorporates aerator/mixers to produce five zones of aeration. Stacked venturi sections increase turbulence as pumpage travels upward and assure maximum oxygenation efficiency. Mixing action surrounding the units is actually two to five times as great as primary pumpage through the units themselves. Ralph B. Carter Co. **103**

Mobile bed contractor
Mobile bed contractor scrubber removes sulfur dioxide and particulate matter from boiler flue gases and other process gas absorption applications. A single unit is capable of more than 80% gas volume turndown without reduction in efficiency, and can operate with water rates of up to 50 gal per thousand cfm, as required by the application. American Air Filter Co., Inc. **104**

Particle counter
Automatic fluorescent particle counter detects and counts in real time fluorescent zinc sulfide particles in air or water environments. Its high sampling rate, sensitivity, and real time readout make it ideal for plume tracking from aircraft or for shipboard study of underwater current or pollution movement patterns. Mee Industries Inc. **105**





Air sampler
An extremely accurate and reliable high-volume air sampler gives accurate collection of suspended particulates exceeding EPA specifications. A constant rate of air flow is maintained by an electronic probe. Air flow, adjustable from 30–50 scf per minute, is controlled at constant standard conditions of 25°C and 760 mm mercury pressure within ±1 scfm. General Metal Works, Inc. **106**

(Continued on page 858)

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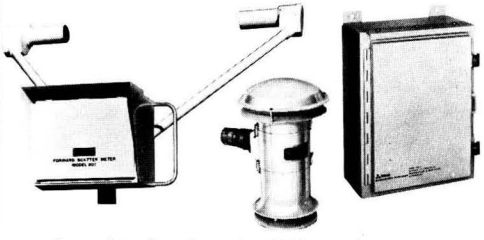
THE
METEOROLOGICAL MONITORING
SYSTEM
that measures dew point, visibility or particle sampling to meet Federal Regulations



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MODEL 207 FORWARD SCATTER METER measures visual range 50 to 5,000 ft/200 to 20,000 ft •accurate in rain, snow •large sampling volume •simple field calibration •single point installation

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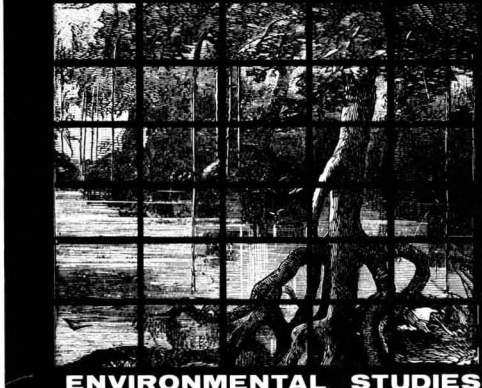

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It's inverted to let you study living specimens in culture bottles, test tubes (with optional holder) or Petri dishes. Inexpensive phase contrast accessories make "invisible" specimens visible without staining.

And the CK comes with the same Olympus optics as our laboratory research microscopes (Achromatic 4X, 10X and 20X objectives; comfortable, high-eyepoint, wide-field 10X eyepieces).

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Olympus CK
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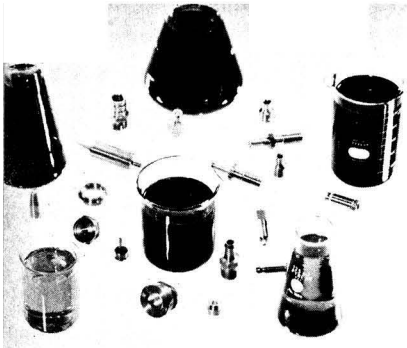
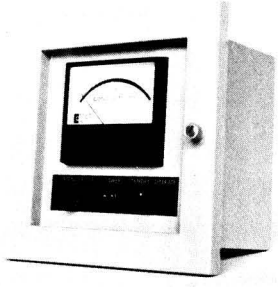


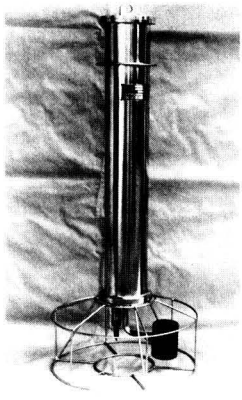
Antimist oils
Complete line of six antimist cutting oils can effectively reduce objectionable oil mist, lower housekeeping costs, and help avoid violation of established OSHA limits on oil mist concentration in plant air. The oils meet the requirements of a wide range of machining operations on most metals by providing a variety of viscosity, antiweld, and lubricity characteristics. Mobil Oil Corp. **108**

Sewer Cleaner
Sewer cleaner for small cleaning operations is easily maneuverable and does not require a large truck. Engineered with industry and smaller communities in mind, it will deliver 35 gpm at 1250 psi. The unit propels the scouring nozzle through sewers, and the hydraulic pressure scours clean with minimal investment in maintenance. FMC Corp. **107**



Process analyzer
Weatherized process analyzer can be mounted indoors or out. Its sensor can be in-line or submersible and can be located near the analyzer or more than one third of a mile away. Ultrasonic cleaning is offered as an option. Enviro Control, Inc. **109**

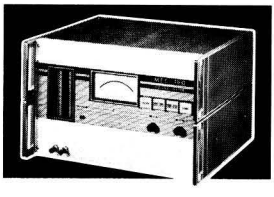
Water monitoring system
Complete environmental monitoring system features self-contained digital magnetic tape recording. Ultrastable sensors measure conductivity, salinity, temperature, depth, dissolved oxygen, pH, and turbidity. Data are recorded on magnetic tape cassettes, using standard ASCII code to facilitate data recovery via teletypewriter, paper tape punch, or computer. InterOcean Systems, Inc. **112**



Chemical dispersant
New chemical dispersant minimizes calcium and iron deposits in the piping and heat exchange equipment of cooling towers and other industrial process systems. Trademarked Tolsperse 110, the chemical dispersant

NEW LOW COST
OZONE METER

Meets the latest Environmental Protection Agency requirements.



- Measures ozone specifically by chemiluminescent reaction detection principle.
- Various models cover ranges from 1 p.p.b. to 10,000 p.p.m. (i.e. up to 1.0% ozone)

Model 1110
$2,250

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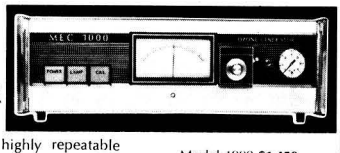

- Provides sustained, highly repeatable stream of ozonized air for calibration of ozone oxidant meters.
- Exceptionally stable—eliminates tedious wet chemistry determinations up to 3 months.
- 0 to 10,000 p.p.b. ozone output

Model 1000 **$1,450**
Model 1010 **$1,050**
Model 1020 **$600**

Send for brochure. Contact Factory for literature describing new series NO, NO_2 and NO_x chemiluminescent meters.

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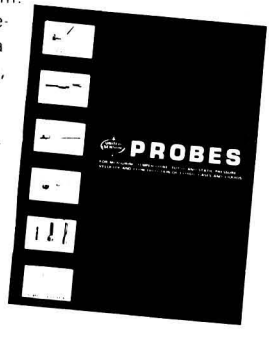

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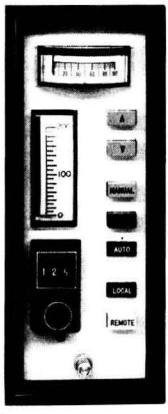
is a formulation of organic polyphosphonates and dispersing and wetting agents. It is fed into the makeup water line by a feed pump prior to discharge into the cooling tower. Petrolite Corp. **111**



Waste water controller
New proportional floating controller for use in waste water control systems includes a direct-reading digital set point and a full-scale measurement input meter. Benefits include color-coded push buttons for remote/local set point operation, automanual transfer, and manual operation of the final control element. The model is designed not only for such variables as flow, level or pressure, but also for the more difficult flows that involve dead time or long transport lag. Envirotech **113**

Turbomix afterburner
Turbomix afterburner is designed to combust hydrocarbon material to meet or surpass requirements of local air pollution authorities. The unit is designed especially for printing, metal decorating, metal finishing, and paint ovens in manufacturing plants. Field tests show it is capable of up to 95% hydrocarbon removal and complete odor elimination at exhaust temperatures as low as 1200°F. TEC Systems Inc. **110**

P.A.S. Bio-Matic
P.A.S. Bio-Matic is completely integrated system that offers maximum flexibility for the diverse requirements of industrial plants, municipalities, government agencies, consulting engineers, and research institutions. It assures automatic, continuous, and virtually clogless operation through specially designed systems for influent feed, sludge return, and sludge wasting. Flow rate accuracy is maintained within ±1%. Princeton Aqua Science. **117**

Heavy metals analyzer
Chemical analyzer is capable of an accurate test for cadmium over the range 0–1 ppm. It can test for lead, copper, chromium, silver, and manganese. All told, the instrument can perform more than 60 different tests —from acidity to zinc. Each instrument is permanently precalibrated, thereby eliminating the need for standard solutions. Delta Scientific Corp. **114**

Water pollution sampler
Portable, pressure-operated sampler model employs fluidic and pneumatic circuitry to control its timing circuits. Designed for many years of maintenance-free operation, the sampler can satisfy almost every type of sampling. Sampler is explosion-proof and ideally suited for use in hazardous areas. BVS **115**

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can help with your air quality program

Portable Model 206
IKOR Air Quality Monitor

One recent example of IKOR'S approach to environmental problem solving is the new and unique IKOR Air Quality Monitor. This instrument* measures and records particulate emission instantly and continuously. It tells you *what* happens *while* it happens. Particulate emission mass flow range: .001–100 grains/SCF. Particulate size detection range: 0.1–100 microns. Lightweight, portable Model 206 or permanently installed Model 509. Write for more information: **IKOR Incorporated**
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*Pats. Pending

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NEW LITERATURE

Spectrophotometer. Brochure explains all available accessories for Model 180 Infrared Spectrophotometer. Includes explanations of microsample handling techniques and explains each accessory's capabilities. Includes an optical schematic of each and lists all available versions of the accessories by code number. Perkin-Elmer Corp. **168**

Solid waste. New 12-page full-color brochure describes broad line of solid waste collection vehicles for residential, commercial, and industrial pickup. The complete line of solid waste systems also includes stationary compactors, detachable and roll-off container systems, transfer trailers, pulverizers, and transfer stations. The Heil Co. **169**

Compactor. Catalog sheet spotlights Tubar Trashbasher compactor with a patented end gate feature that double rams refuse at 99,000 lb force. The illustrations and complete specifications—dimensional data, capacity and force data, hydraulic system data, electrical data, and mechanical data—provide details on operation of the unit which compresses many difficult large mass objects that ordinary compactors cannot handle. Tubar Waste Systems, Div. of Uhrden, Inc. **170**

Treatment plant. Bulletin contains information on the economics of installing a concrete Rib-Wall interim waste water treatment plant. Notes typical installations of the treatments plants which offer capacities from 3500 to 40,000 gpd, and 94% plus BOD removal with the extended aeration system. Answers questions commonly asked in relation to installation time, service policy, advantages, and the economics of owning one. Marolf, Inc. **171**

Blower. Bulletin M357 presents complete application, performance, and installation information on the new Model M357 belt-driven multistage blower. Unit is well suited to a wide range of applications, including drawing vacuum on tape transfer buffer columns, cooling capstan and reel driven motors, air sampling, fume collection, combustion air, and document hold-down. Rotron, Inc. **172**

Infiltration. Leaflet describes sealing leaking sewage joints internally with televisual inspection and internal pressure chemical grouting. Video Pipe Grouting, Inc. **186**

Air pollution. Booklet covers company's gaseous source sampling service. Among services described and illustrated are sampling and analysis of stacks, roof monitors and vents; sampling of ambient air at various distances and directions from pollution sources; and preparation of detailed reports for submission to regulatory agencies. Nalco Chemical Co. **187**

Acoustics products. Catalog includes a selection of acoustics products including five sound level meters. Describes noise measuring kits consisting of a noise level meter, acoustic coupler calibrator, windscreen, screwdriver, extra batteries, and a molded carrying case. Also contains photographs and brief description of each of the devices. Pulsar Instruments, Inc. **188**

Air sampler. Brochure describes complete line of high-volume high-sampling equipment utilized throughout government and industry. Also covers accessory equipment including filter holder, filter paper cartridges, transformers, timers, and programmers. Described in detail the "Brushless Hi-Vol," the newest addition to the line that provides continuous maintenance free sampling. Lists application and dimensional information. General Metal Works, Inc. **189**

Survey. Publication covers survey of instruments and techniques helpful for monitoring water and air pollution. Articles focus on packaged laboratories for water and waste water analysis, "how-to" information on automatic EPA titrations, a report on the instruments and services geared for specific environmental applications, and a direct-reading spectrometer that analyzes for more than 20 metals simultaneously. Fisher Scientific Co. **190**

Disintegrator. Literature covers a flexible replacement disintegrator for waste water collection systems that is hydraulically powered from a remote power pack and submersible. Illustrates and describes how a highly abrasive rotor grinds sewage solids to small particles, thereby permitting more economical pumps and circulatory equipment. BIF SaniTrol, a Unit of General Signal **191**

Environmental impact. New booklet, "Assessing Environmental Impact," offered as a methodical guide for managing the volume of necessary data required in the preparation of environmental impact statements, reports and drafts under federal and California law. Environmental Research & Counsel **192**

Sewage bulletin. Technical publication describes the new NeverClog sewage ejector which is a self-contained pumping station which collects sewage from apartments, office buildings, factories, hospitals, shopping centers, schools, and all kinds of public buildings. WEMCO, Div. of Envirotech Corp. **193**

Liners. Booklet details the physical and general properties of the broadest range of lining materials on the market. Includes test data on supported and unsupported Polyliner, Hydroliner, Dri-Liner, and three formulations of Vinaliner. Goodyear Tire and Rubber Co. **194**

Pump bulletin. Fifteen different models of pumps for abrasive slurries, pulpy wastes, and other liquid-solid mixtures are detailed in new bulletin. Described are many horizontal, vertical, and vertical cantilever pumps. Discussion of the closed loop slurry test laboratory notes how to determine friction losses, critical carrying velocities, and general behavior of slurries in advance. Morris Pump, Inc. **195**

Gages. Bulletin describes porcelain enameled iron staff gages used to provide quick visual reading of water level in open channels. Covers characterists and style for the gages. Leupold & Stevens, Inc. **196**

Analysis. Bulletin, "Chemistry of Metal Surfaces," describes passivation and corrosion analyses of metal surfaces using electron spectroscopy. Contains application data and explains how rates of oxidation are determined by using Model 650 Electron Spectrometer. Also discussed is the ability to observe the top few atomic layers to readily monitor changes in layer thickness. Du Pont Co. **197**

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BOOKS

Making Polyethylene More Disposable. Irene Kiefer. 24 pages. U.S. Environmental Protection Agency. For sale by the U.S. Government Printing Office, Washington, D.C. 20402. 1973. $0.35, paper.

Discusses the unique problems in disposing of large concentrations of polyethylene. Based on "Feasibility Study of the Disposal of Polyethylene Plastic Waste" by Kurt Gutfreund, this report concludes that the RFNA method, which uses two-component systems containing nitric acid to oxidize and nitrate the polymer, is an especially useful one. The resulting nitrogen-containing polyethylene can be used as fertilizers and soil conditioners.

Land Use and Water Resources in Temperate and Tropical Climates. H. C. Pereira. xiv + 246 pages. Cambridge University Press, 32 East 57th St., New York, N.Y. 10022. 1973. $14.95, hard cover; $5.95, paper.

Summarizes in plain language the information available at present to guide decisions on policy for land-use management in watersheds. Methods available for measuring the hydrological effects of land-use changes are described. Results both of research and of recorded experiences are discussed in their relevance to temperate and to tropical environments.

Environmental Radioactivity. Merril Eisenbud. 2d ed. xii + 542 pages. Academic Press, Inc., 111 Fifth Ave., New York, N.Y. 10003. 1973. $29.50, hard cover.

Written both as text and handbook for anyone concerned with civilian and/or military applications of nuclear energy. Book shows how radioactive substances introduced into the air, water, and soil become involved in ecological processes that eventually affect man and all other biological forms. Provides detailed coverage of the various aspects of environmental radioactivity.

Clean Air—Sparkling Water: The Fight Against Pollution. Dorothy E. Shuttlesworth. 95 pages. Doubleday & Co., Inc., 277 Park Ave., New York, N.Y. 10017. 1973. $0.95, paper.

Tells, with pictures and simple language, what can be done and must be done to fight pollution. Book provides historical look at what happened to our air and water as cities and towns began to grow in number and size. Concludes that the fight can be won only if skillful scientists, watchful lawmakers, and people everywhere do their best in the battle against despoilment.

Occupational Safety and Health: A Policy Analysis. iv + 53 pages, six appendixes. David L. Mallino, Shaun M. Werner, Eds. Government Research Corp., 1930 M St., N.W., Washington, D.C. 20036. 1973. $12, paper.

Probes the policy behind the work safety and health standards of the 1970 Occupational Safety and Health Act. The author outlines the legal basis of the federal standards, details the administrative and organization responsibilities for federal standards-setting, and analyzes the adequacy of existing OSHA standards. He further pinpoints problem areas and recommends improvements.

Bioassay Techniques and Environmental Chemistry. Gary E. Glass, Ed. xi + 499 pages. Ann Arbor Science Publishers, Inc., P.O. Box 1425, Ann Arbor, Mich. 48106. 1973. $18, hard cover.

Describes bioassay techniques completely for a wide variety of organisms and conditions. The "state of the art" is described as it applies to environmental problem solving using biological and chemical indicators. Stresses that living organisms must be studied as indicators of the stresses and effects that pollutants bring about.

Health Effects of Environmental Pollutants. George L. Waldbott. x + 316 pages. C. V. Mosby Co., 11830 Westline Industrial Dr., St. Louis, Mo. 63141. 1973. $7.50, paper.

Explores the possibility humans are suffering health damage from polluted air that is not being discovered by the scientific community. Book points out that a number of circumstances render damage caused by polluted ambient air difficult to identify with its sources. The point is made that air-pollutant diseases develop slowly and inconspicuously.

Safe Use of Pesticides: Twentieth Report of the WHO Expert Committee on Insecticides. 54 pages. World Health Organization, 1211 Geneva 27, Switzerland. 1973. $1.00, paper.

Part I of this report reviews the hazards of insecticides used in public health, with particular emphasis on DDT and dichloros. Results are presented of recent animal studies and extensive observations carried out in men exposed to these insecticides. Parts II and III review molluscicides and rodenticides used in public health.

Biological Indicators of Environmental Quality: A Bibliography of Abstracts. William A. Thomas, Gerald Goldstein, and William H. Wilcox. x + 254 pages. Ann Arbor Science Publishers, Inc., P.O. Box 1425, Ann Arbor, Mich. 48106. 1973. $16.50, hard cover.

Selected abstracts emphasize the practical aspects of interpreting the biological manifestations of deteriorated environmental conditions. Abstracts are organized so that users can focus attention at any level of biological organization from the molecule to the community. Book is a time-saver, especially since primary journals or sets of journals specializing in biological indicators are lacking.

Proceedings of the 1972 International Conference on Nuclear Solutions to World Energy Problems. American Nuclear Society and Atomic Industrial Forum. ix + 358 pages. American Nuclear Society, 244 E. Odgen Ave., Hinsdale, Ill. 60521. 1973. $32, hard cover.

International Conference publication covers the presentations and summaries of discussions of five plenary sessions and two special sessions held Nov. 12–17, 1972, in Washington, D.C. Plenary sessions topics are: Nuclear Energy and the Quality of Life, Fast Breeder Reactor Types, Fuel Cycle, and Thermal Power Reactor System. Special session topics include Fusion Reactor Engineering and Workable International Safeguards.

The New Way of the Wilderness. Rev. ed. Calvin Rutstrum. viii + 280 pages. The Macmillan Co., 866 Third Ave., New York, N.Y. 10022. 1973. $2.95, paper.

Written for the "red-blooded" person who feels the call of the wild. Author tells how to exist in an unmapped wilderness with no outfit other than back pack, canoe pack, pack horse, or dog sled pack. He points out the easiest way to do things and the way to get real pleasures and benefits that such life alone can bestow.

MEETING GUIDE

September 20–21 New York, N.Y.
Real Estate and the Environment. Practising Law Institute

Contact: Nancy B. Hinman, Practising Law Institute, 1133 Avenue of the Americas, New York, N.Y. 10036

September 23–26 Tulsa, Okla.
National Forum on Growth with Environmental Quality. Metropolitan Tulsa Chamber of Commerce and others

Will question America's ability to strike a balance between ecological and conservation interests and continued economic growth. *Contact:* Bruce Carnett, Manager, Public Relations, Metropolitan Tulsa Chamber of Commerce, 616 S. Boston Ave., Tulsa, Okla. 74119

September 24–27 Denver, Colo.
Intersociety Conference on Transportation. ASME

Contact: Marion Churchill, Manager, Conferences & Divisions, ASME, 345 E. 47 St., New York, N.Y. 10017

September 24–28 Las Vegas, Nev.
Symposium on Noble Gases. EPA and the University of Nevada

Contact: A. Alan Moghissi, Chairman, Program Committee, Noble Gases Symposium, U.S. EPA, P.O. Box 15027, Las Vegas, Nev. 89114

September 24–28 Chicago, Ill.
Water for the Human Environment. International Water Resources Association

The First World Congress on Water Resources. *Contact:* G. M. Karadi, Secretary General IWRA, Science Complex Bldg., Univ. of Wis., Milwaukee, Wis. 53201

September 25–28 San Francisco, Calif.
Geothermal Resources Council. 1973 General Meeting

Contact: GRC, P.O. Box 1033, Davis, Calif. 95616

September 25–28 Boston, Mass.
3rd Urban Technology Conference. American Institute of Aeronautics and Astronautics and Public Technology Inc.

Will explore ways in which existing technology can be brought to bear on the many crises facing cities. *Contact:* Philip D. Schaub, Director of Communications, AIAA, 1290 Sixth Ave., New York, N.Y. 10019

September 26–28 Waitsfield, Vt.
Rural Environmental Engineering: A Conference on Water Pollution Control Technology in Low-Density Areas. University of Vermont and University of Maine

Write: William J. Jewell, Department of Civil Engineering, University of Vermont, Burlington, Vt. 05401

September 26–30 New Orleans, La.
International Symposium on Underground Waste Management and Artificial Recharge. American Association of Petroleum Geologists and others

Includes technical papers and field trips. *Contact:* Leslie Bowling, General Chairman, 1417 NBC Bldg., New Orleans, La. 70112 or the American Association of Petroleum Geologists, Box 979, Tulsa, Okla. 74101

September 28–October 5 Cleveland, Ohio
Water Pollution Control Federation. 46th Annual Conference

For details: R. A. Canham, WPCF, 3900 Wisconsin Ave., N.W., Washington, D.C. 20016

September 30–October 3 Hot Springs, Ark.
Soil Conservation Society. 28th Annual Meeting

Theme is "Plants, Animals, and Man." *Write:* Soil Conservation Society of America, 7515 Northeast Ankeny Rd., Ankeny, Iowa 50021

September 30–October 5 Vail, Colo.
Earth Sciences and Environmental Policy Making. Geological Society of America

Attendance limited by invitation. *Write:* Bruce B. Hanshaw, Water Resources Div., U.S. Geological Survey, Federal Center, Denver, Colo. 80225

October 1–2 Cincinnati, Ohio
Secondary Fiber Pulping Conference. Technical Association of the Pulp and Paper Industry

Contact: H. O. Teeple, TAPPI, One Dunwoody Park, Suite 130, Atlanta, Ga. 30341

October 1–3 Ottawa, Canada
International Conference on Land for Waste Management. Canadian Society of Soil Science

Will cover waste disposal and utilization in soils, evaluating such systems, and identifying problem areas. *Write:* M. K. Ward, Executive Secretary, International Conference on Land for Waste Management, National Research Council, Ottawa, Ont., Canada K1A OR6

October 1–4 San Antonio, Tex.
Second International Conference on Pressure Vessel Technology. ASME

Covers impact of new installations upon the environment. *Write:* ASME, 345 E. 47 St., New York, N.Y. 10017

October 2–5 Orlando, Fla.
Symposium on Remote Sensing in Oceanography. International Society for Photogrammetry

Will cover offshore, coastal, and estuarine areas. *Contact:* Paul G. Teleki, Coastal Engineering Research Center, 5201 Little Falls Rd., N.W., Washington, D.C. 20016

October 3–5 Las Vegas, Nev.
APCA West Coast Section. Seventh Technical Meeting

Sessions on the automobile, energy, environmental impact reports, and instrumentation. *Write:* Elliott H. Harris, Southern California Gas Co., Box 3249 Terminal Annex, Los Angeles, Calif. 90051

October 6–10 Clearwater, Fla.
Annual International Environmental Sanitation & Maintenance Management Educational Conference/Exposition. Environmental Management Association

Related to environmental sanitation maintenance industry. *Write:* Environmental Management Assoc., 1710 Drew St., Clearwater, Fla. 33515

October 7–12 Boston, Mass.
International Symposium on Fine Particles. Electrochemical Society

Write: W. E. Kuhn, 498 Rhodes Hall, Univ. of Cincinnati, Cincinnati, Ohio 45221

October 8–10 Newark, Del.
National Association of Sea Grant Program Institutions. Annual Meeting

Covers coastal zone management, mariculture, energy from the sea, and other topics. *Write:* Anne B. Ritchey, Marine Information Coordinator, College of Marine Studies, University of Delaware, Newark, Del. 19711

October 9–10 Pittsburgh, Pa.
Industrial Health Foundation. 38th Annual Meeting

Write: Daniel C. Braun, IHF, 5231 Centre Ave., Pittsburgh, Pa. 15232

October 9–12 Washington, D.C.
Association of Official Analytical Chemists. 87th Annual Meeting

Papers on analysis of pesticides, food additives, and related subjects. *Contact:* L. G. Ensminger, Executive Secretary, AOAC, Box 540, Benjamin Franklin Station, Washington, D.C. 20044

October 9–13 Boston, Mass.
NLC Training Seminar/The Energy Crisis and the State Legislative Process. Council of State Governments

For states east of Mississippi. *Contact:* Council of State Governments. Iron Works Pike, Lexington, Ky. 40505

October 12 New York, N.Y.
Libraries, Information, and the Environment Conference. American Society for Information Science and Special Libraries Association

Contact: Carmela Carbone, Engineering Societies Library, 345 E. 47th St., New York, N.Y. 10017

October 15–16 Washington, D.C.
Inside EPA. Practising Law Institute

Contact: Practising Law Institute, 1133 Avenue of the Americas, New York, N.Y. 10036

October 15–17 Washington, D.C.
1973 National Noise Control Engineering Conference and Equipment Exposition. Institute of Noise Control Engineering and others

Will cover noise legislation, environmental and product noise, and related topics. *Contact:* NOISE-CON 73, National Bureau of Standards, 233,A147, Washington, D.C. 20234

October 15–18 Houston, Tex.
Instrument Society of America, 28th International Conference and Exhibit

Second Joint Environmental Instrumentation & Control Symposium will be held concurrently with the Conference. *Write:* Philip N. Meade, Exhibit Director, ISA, 400 Stanwix St., Pittsburgh, Pa. 15222

October 17–18 Washington, D.C.
Health Industries Association. Biennial Technical Symposium

Covers sterile disposable devices in conjunction with waste management, standards, and related areas. *Write:* Sterile Disposable Device Committee, 1225 Connecticut Ave., N.W., Suite 314, Washington, D.C. 20036

October 21–26 North Hollywood, Calif.
Geology, Seismicity-Environmental Impact. Association of Engineering Geologists

Includes topics in geology, seismology, sanitary engineering, environmental quality, and others. *Write:* Charles A. Yelverton, Chairman. 16th Annual Meeting AEG, Suite 506, 201 S. Lake Ave., Pasadena, Calif. 91101

October 21–26 Seattle, Wash.
Ninth American Water Resources Conference. American Water Resources Association

Theme is "The Changing Environment for Water Resources." *Contact:* Shirley Vinson, American Water Resources Assoc., 206 E. University Ave., Urbana, Ill. 61801

October 22–24 Atlanta, Ga.
1973 Alkaline Pulping Conference. Technical Association of the Pulp and Paper Industry

Includes session on water reuse. *Write:* H. O. Teeple, TAPPI, One Dunwoody Park, Atlanta, Ga. 30341

October 22–25 Philadelphia, Pa.
Second International Pollution Engineering Congress and Exposition. Clapp & Pollak, Inc.

Covers all forms of pollution and practical techniques to reduce such pollution. *Contact:* Clapp & Poliak, Inc., 245 Park Ave., New York, N.Y. 10017

October 23–27 Kansas City, Mo.
NLC Training Seminar/The Energy Crisis & The State Legislative Process. Council of State Governments

For states west of Mississippi. *Contact:* Council of State Governments, Iron Works Pike, Lexington, Ky. 40505

October 25–26 Oxford, Ohio
Conference on Energy and the Environment. Southwestern AIChE Sections

Write: Anthony J. Buonicore, FTD/PDTN, USAF Systems Command, Wright-Patterson AFB, Dayton, Ohio 45433

October 29–November 1 New York, N.Y.
ASCE Annual and National Environmental Engineering Meeting and Exposition. American Society of Civil Engineers

Write: American Society of Civil Engineers, 345 E. 47th St., New York, N.Y. 10017

Courses

September 29–30 Cleveland, Ohio
Pretreatment of Industrial Wastewaters for Discharge into Municipal Sewers. Associated Water and Air Resource Engineers

Fee: $150. *Write:* W. Wesley Eckenfelder, Jr., AWARE, Inc., 2002 Richard Jones Rd., Suite C-305, Nashville, Tenn. 37215

September 25–28 New Brunswick, N.J.
Fuel Oil Combustion. Rutgers University and N.J. Dept. of Environmental Protection

Also other courses offered in air pollution control. *Write:* Donald A. Deieso, Dept. of Environmental Sciences, Rutgers Univ., New Brunswick, N.J. 08903

October 4–5 Milwaukee, Wis.
Exhaust Emission Control. University of Wisconsin-Extension

Also course on "Steam Power Plant Operations" on October 25–26. Fee: $100. *Contact:* John M. Leaman, Program Director, Department of Engineering, University of Wisconsin-Extension, 600 W. Kilbourn Ave., Milwaukee, Wis. 53203

October 8–12 Milwaukee, Wis.
Evaluating Environmental Impact of Transportation Projects. University of Wisconsin-Extension

Fee: $300. *Contact:* Civic Center Campus, University of Wisconsin-Milwaukee, 600 W. Kilbourn Ave., Milwaukee, Wis. 53203

October 11–14 Washington, D.C.
Techniques of Noise Control. Institute of Noise Control Engineering

Contact: William W. Lang, Institute of Noise Control Engineering, P.O. Box 3206, Arlington Branch, Poughkeepsie, N.Y. 12603

October 16–18 New York, N.Y.
Pollution Control Seminar. New York University

Write: William A. Kulok, Program Director, Dept. 37M, 600 Third Ave., New York, N.Y. 10016

International

October 2–6 Grenoble, France
National Exhibition of Antipollution Techniques. French Government.

Contact: Jacques Ch. Deloy, Commissary of the Exhibition, 38029 Grenoble, Cedex, France

October 4–10 Nice, France
International Symposium on the Chemistry of Sea/Air Particulate Exchange Process. UNESCO and others

Contact: Robert A. Duce, Graduate School of Oceanography, University of Rhode Island, Kingston, R.I. 02881

October 8–12 Düsseldorf, Germany
Third International Clean Air Congress. International Union of Air Pollution Prevention Associations

For details: Air Pollution Control Association, 4400 Fifth Ave., Pittsburgh, Pa. 15213

Oct. 8–14 Duesseldorf, Germany
International Exhibition and Congress on Engineering in Environmental Protection. Association of German Machine Tool Builders and others

Write: German-American Chamber of Commerce, Inc., 666 5th Ave., New York, N.Y. 10019

October 9–14 Rouen, France
Second International Show for the Protection of Nature and Environment. French Ministries and other organizations.

Write: PROTECNA-C.O.M.E.T., Parc Expo du Madrillet, 76120 Le Grand-Quevilly, France

Oct. 24–25 Brussels, Belgium
Environmental Chemistry: Know-How and Chemicals in 1973–78 Symposium. International Business Contact Club

Representatives from 20 countries attending. *Write:* International Business Contact Club, Administration, Nieuwelaan 65, B-1820, Strombeek, Belgium

(Continued on page 864)

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ENVIRONMENTAL ENGINEERING Assistant or Associate Professor in Mechanical Engineering. Recent Ph.D. in Engineering or Science with experience in Environmental engineering. Applications are sought from persons having expertise in areas of environmental engineering such as noise, combustion-produced pollutants, chemical kinetics or trace elements control. Equal opportunity is provided through an Affirmative Action Program. Applicants should submit curriculum vitae by October 15, 1973 to Dr. F. W. Smith, Department of Mechanical Engineering, Colorado State University, Fort Collins, Colorado 80521. Phone 303-491-6558.

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MEETING GUIDE *(Continued)*

November 5–9 Warsaw, Poland
Symposium on Environmental Surveillance Around Nuclear Installations. International Atomic Energy Agency
Write: John H. Kane, Special Assistant for Conferences, Office of Information Services, Atomic Energy Commission, Washington, D.C. 20545

November 27–29 Eastbourne, England
Fuel and the Environment International Conference. Institute of Fuel
Contact: Conference Secretary, Institute of Fuel, 18 Devonshire St., London, England W1N 2AU

November 28–30 Rüschlikon, Switzerland
International Symposium on Recycling and Corporate Goals: A New Environmental Technology or a New Economic Priority. Gottlieb Duttweiler Institute
Contact: Rudolf Brun, Gottlieb Duttweiler Institute, CH-8803 Rüschlikon, Switzerland

December 17–21 Sanremo, Italy
International Association for Water Pollution Research. Second International Congress
Write: Istituto di Ingegneria Sanitaria del Politecnico, Piazza Leonardo da Vinci 32, 20133 Milano, Italy

May 20–25, 1974 Dublin, Ireland
Seventh World Congress on Occupational Safety and Health. World Congress.
For more information: World Congress Secretary, Ansley House, Dublin 4, Ireland

June 24–28, 1974 Ottawa, Canada
IXth IUPAC Conference on the Chemistry of Natural Products. IUPAC.
Contact: M. K. Ward, Executive Secretary, IXth International Symposium on the Chemistry of Natural Products, c/o National Research Council of Canada, Ottawa, K1A OR6, Canada

Sept. 8–14, 1974 The Hague, The Netherlands
First International Congress of Ecology. International Union of Biological Sciences and others
Contact: Human Adaptability Coordinating Office, 513 Social Science Bldg., University Park, Pa. 16802

September 9–12, 1974 Paris, France
Symposia on Effects of Man on the Hydrological Cycle and on Flash Floods. UNESCO and others
Write: U.S. National Committee, International Hydrological Decade, National Academy of Sciences, 2101 Constitution Ave., Washington, D.C. 20418

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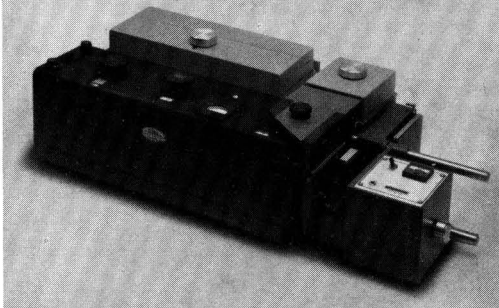

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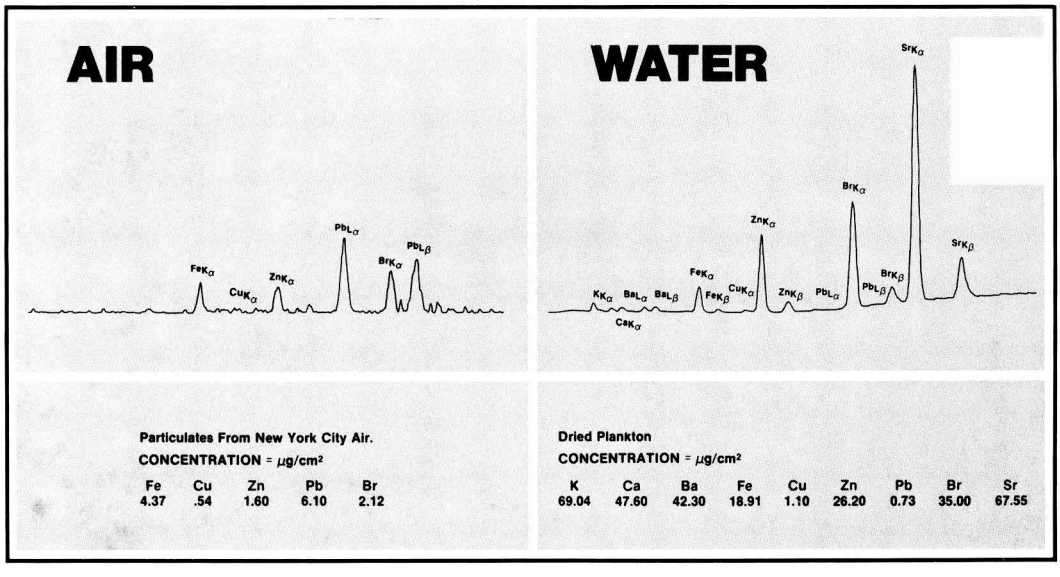

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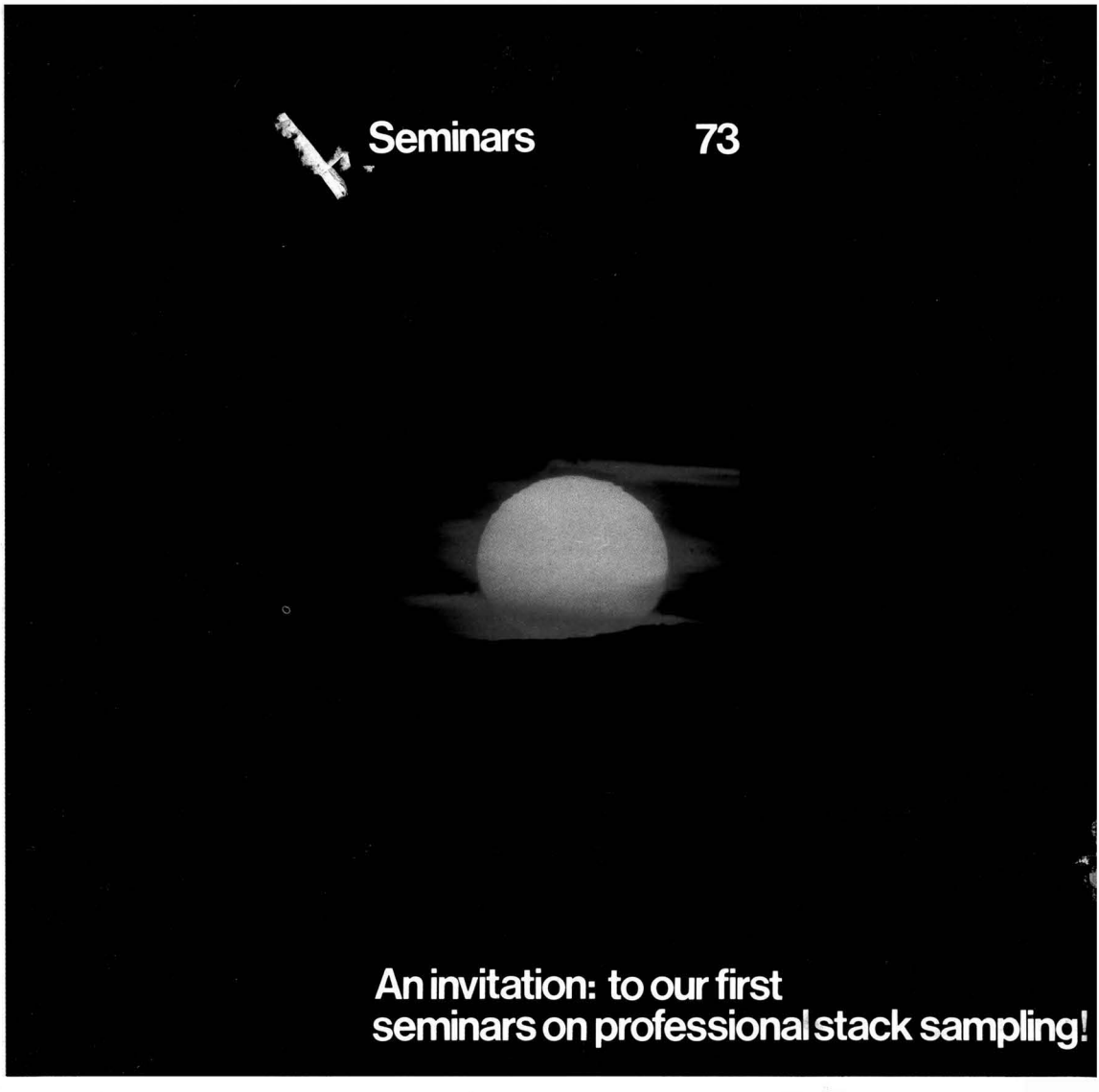

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